formed a double complex Bz·Py·I_2 of donor–acceptor character (thus, for example, the Py·I_2 complex, with charge distribution $Py^+I_2^-$, might perhaps act at its Py end as an acceptor toward Bz as a donor, or at its I_2 end as a donor toward Bz as an acceptor); or perhaps the shift may be due to a "contact" donor–acceptor interaction with the Bz molecules which surround it.

If we nevertheless treat the peaks as due to PyI_2 and assume that the equilibrium constant K_c is the same (200) in benzene as in *n*-heptane, and neglect any loss of activity of the I_2 due to its interaction with the benzene (allowance for this would probably not make a great difference), we compute that 97% of the Py should be complexed for curve A and 87% for curve B. This gives peak molar extinction coefficients for PyI_2 in benzene solution which agree well with those obtained in *n*-heptane (see Table I, last column). However, in view of the doubled peak widths, the total intensities are about double those in heptane.

Returning to a consideration of the 204 cm.$^{-1}$ Bz·I_2 peak in Fig. 2, and noting in the case of curves A and B that about 0.01 mole/*l.* of I_2 is used up in forming Py.I_2 with the 0.01 mole/*l.* of Py present, the available concentrations of I_2 free to interact with Bz are 0.29 *M*, 0.091 *M* and 0.40 *M* for curves A, B, and C, respectively. Based on the heights of the (absorption coefficient) peaks in Fig. 2, the peak extinction coefficients ϵ_{max} at 204 cm.$^{-1}$ in terms of total available I_2 are then 1.59, 2.41, 2.40 for curves A, B and C, respectively. If one now supposes (but *cf.* ref. 4) that there exists in I_2 solutions in Bz an equilibrium $Bz + I_2 \leftrightarrows Bz \cdot I_2$ with a definite Bz·I_2 complex, then for this complex, according to Cromwell and Scott, $K_x = 2.3$.[11] With this value of K_x, one finds for ϵ_{max} for the Bz·I_2 *complex* the values 2.26, 2.57, 3.47 from curves A, B and C, respectively, or an average of 2.77.

Turning now to Fig. 3, we see the characteristic peak of the Py·I_2 complex or BzPyI_2 double complex, again in a solution which is mainly benzene, but this time with a small iodine concentration (0.01 *M*) and large Py concentrations, instead of *vice versa.* As expected, the Bz·I_2 peak is missing (the small peak at 212 cm.$^{-1}$ in curve B may be ignored); it should be too weak to detect at 0.01 *M* I_2 concentration. Assuming again that the equilibrium constant K_c for PyI_2 is the same in benzene as in heptane, we compute that 97% of the I_2 should be complexed in the case of the 0.5 *M* and 87% in that of the 0.1 *M* Py solution. The computed ϵ_{max} values based on PyI_2 are now found in good agreement with those from Figs. 1 and 2 (*cf.* Table I). Notably, the *half-intensity widths* are now about the same as in heptane solutions, which indicates that the excess iodine, rather than the benzene, is responsible for the increased widths in the curves of Fig. 2 discussed above.

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[11] T. M. Cromwell and R. L. Scott, This Journal, **72**, 3825 (1950). $K_x = (Bz \cdot I_2)/(I_2)[Bz]$, where [Bz] is the mole fraction of Bz (very nearly 1 here).

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Dimorphic Modifications of Dibasic Strontium Phosphate, $SrHPO_4$

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Received July 1, 1958

A study of the strontium phosphates has disclosed the existence of two crystalline modifications of dibasic strontium phosphate. These modifications behave similarly in the presence of water; but on firing to convert to the pyrophosphates, they follow separate reaction paths dependent upon the original crystal structure Analogies to the crystal structures of other phosphates are given.

Introduction

References to detailed studies of the calcium phosphates are easily found,[1–3] and many of these papers contain information on the chemistry of dibasic calcium phosphate, $CaHPO_4$ and its hydrate $CaHPO_4 \cdot 2H_2O$. In contrast, with the exception of a phase rule study of the system $SrO–P_2O_5–H_2O$ at 25° by Tartar and Lorah,[4] there has been little work on the chemistry of dibasic strontium phosphate.

Knowledge of the crystal structures of the dibasic phosphates of calcium and strontium is in a similar state. Thus, single-crystal diffraction techniques have shown that $CaHPO_4$ is triclinic[5] with space group $P\bar{1}$, and $CaHPO_4 \cdot 2H_2O$ is monoclinic[6] with space group I 2/a. However, structure data on $SrHPO_4$ are both scarce and contradictory. For instance, de Schulten[7] claimed orthorhombic symmetry for $SrHPO_4$ while Bengtsson[8] in a more recent X-ray diffraction study of the monetites, found that $SrHPO_4$ was either monoclinic or triclinic.

We have discovered that $SrHPO_4$ may be precipitated from solution in two different crystalline modifications similar to the formation of the calcite and aragonite polymorphs of $CaCO_3$,[9] and we have designated these polymorphs as α-$SrHPO_4$ and β-$SrHPO_4$. In agreement with Ranby, *et al.*,[10] it has been shown that α-$SrHPO_4$ converts to β-

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[1] H. Bassett, *Z. anorg. Chem.*, **53**, 34, 49 (1907); **59**, 1 (1908); *J. Soc. Chem. Ind. (London)*, **28**, 722 (1910); *J. Chem. Soc.*, **111**, 620 (1917).

[2] J. d'Ans and R. Knütter, *Angew. Chem.*, **65**, 578 (1953).

[3] W. F. Neuman and M. W. Neuman, *Chem. Revs.*, **53**, 1 (1953).

[4] H. V. Tartar and J. R. Lorah, This Journal, **51**, 1091 (1929).

[5] G. MacLennan and C. A. Beevers, *Acta Cryst.*, **8**, 579 (1955).

[6] C. A. Beevers, *ibid.*, **11**, 273 (1958).

[7] A. de Schulten, *Bull. Soc. Franc. Mineral.*, **27**, 109 (1904).

[8] E. Bengtsson, *Arkiv Kemi Mineral. Geol.*, **15B**, 1 (1941).

[9] J. L. Wray and F. Daniels, This Journal, **79**, 2031 (1957).

[10] P. W. Ranby, D. H. Mash and S. T. Henderson, *Brit. J. App. Phys.*, Supplement #4, S18 (1955).

$Sr_2P_2O_7$ and finally to α-$Sr_2P_2O_7$ upon firing. However, the behavior of β-$SrHPO_4$ on pyrolysis is erratic and remarkable, since it yields a material satisfying the formula $Sr_2P_2O_7 \cdot {}^1/_2H_2O$ which, at higher temperatures, is converted to β-$Sr_2P_2O_7$ and α-$Sr_2P_2O_7$. The dissolution of both α- and β-$SrHPO_4$ in water yields crystals of $Sr_3(PO_4)_2$ as well as strontium hydroxyl apatite.

Experimental

A. **Preparation of α-$SrHPO_4$.**—This material was precipitated by two slightly different procedures. The first procedure followed the method given by Tartar and Lorah,[4] in which SrO, or $Sr(OH)_2$, was added slowly to dilute H_3PO_4 until there was a slight excess of undissolved SrO. The excess SrO was filtered out and the filtrate heated slowly with stirring. Precipitation of α-$SrHPO_4$ began at about 60° and was complete between 75 to 80°.

Anal. Calcd. for $SrHPO_4$: Sr, 47.7; P, 16.9. Found: Sr, 46.7; P, 16.8.

α-$SrHPO_4$ was also prepared by the addition of $(NH_4)_2HPO_4$ to a soluble strontium salt such as $SrCl_2$ or $Sr(NO_3)_2$ keeping the solution temperature at 50° or above. The reaction was allowed to proceed until there was a calculated excess of $(NH_4)_2HPO_4$ as indicated by a sharp rise in the *p*H of the solution. The precipitate was washed free of soluble anions with hot water.

Anal. Calcd. for $SrHPO_4$: Sr, 47.7; P, 16.9. Found: for precipitation temperature of 50°; Sr, 47.6; P, 16.0. For precipitation temperature of 80°: Sr, 47.6; P, 16.3.

The absolute density of α-$SrHPO_4$ based on 5 determinations using conventional pycnometer techniques was 3.54 ± 0.02.

B. **Preparation of β-$SrHPO_4$.**—Two preparations were also used for β-$SrHPO_4$. In the first method, NH_4OH was added very slowly to a dilute solution (0.03 molar) of monobasic strontium phosphate, $Sr(H_2PO_4)_2$, at room temperature, until the solution was slightly basic. The precipitate so formed was washed with alcohol and acetone. NaOH was used in place of NH_4OH with similar results.

Anal. Calcd. for $SrHPO_4$: Sr, 47.7; P, 16.9. Found: using NH_4OH, Sr, 48.2; P, 15.6. Using NaOH, Sr, 47.8; P, 16.0.

The second method of preparing β-$SrHPO_4$ is similar to the second method of preparing α-$SrHPO_4$ in that $(NH_4)_2HPO_4$ is added to a soluble strontium salt until there is a slight excess of $(NH_4)_2HPO_4$. However, for the formation of β-$SrHPO_4$, the temperature of precipitation was maintained between 1 and 25°. The precipitate was washed free of soluble anions with cold water.

Anal. Calcd. for $SrHPO_4$: Sr, 47.7; P, 16.9. Found: Sr, 47.3; P, 16.3.

The absolute density of β-$SrHPO_4$ based on 29 determinations using conventional pycnometer techniques was 3.46 ± 0.02.

C. **Pyrolysis Experiments and Preparation of $Sr_2P_2O_7 \cdot {}^1/_2H_2O$.**—Samples of both α- and β-$SrHPO_4$ were placed in uncovered silica crucibles and maintained at constant temperature (±20°) overnight in an electric furnace. The temperature range covered 180 to 1300° at arbitrary intervals depending upon the location of the phase transition temperatures. The temperature was measured by Pt–Rh thermocouple buried in the sample.

$Sr_2P_2O_7 \cdot {}^1/_2H_2O$ was prepared by maintaining β-$SrHPO_4$ at a temperature between 320 and 480° for about 16 hr.

Anal. Calcd. for $Sr_2P_2O_7 \cdot {}^1/_2H_2O$: Sr, 48.9; P, 17.3. Found: at 320°; Sr, 49.3; P, 16.8. At 430°; Sr, 49.4; P, 16.9. At 480°; Sr, 49.5; P, 16.8.

D. **Reactions of $SrHPO_4$ with H_2O.**—The reactions of α- and β-$SrHPO_4$ with H_2O were studied by continued exposure of the samples to hot distilled water in a conventional Soxhlet apparatus. Small samples were removed every few days for inspection and X-ray diffraction identification.

E. **X-Ray Diffraction, Differential Thermal and Thermogravimetric Analyses.**—All X-ray diffraction patterns were taken on a Philips Norelco unit. A copper tube, with nickel filter, operated at 35 Kv. and 15 ma. was utilized throughout. Debye–Scherrer powder patterns were taken with large diameter (114.6 mm.) cameras for most of the initial patterns and many later ones on mixed samples. No correction was made for film shrinkage since calibration measurements showed the correction to be negligible over the region reported. More reliable intensity information and 2Θ values were taken from diffractometer tracings taken at a scanning speed of ${}^1/_4$° per minute on a Norelco wide-range goniometer. The apparatus used in the differential thermal analysis was a modification of that described by Stone.[11] The thermogravimetric analysis was performed on a Stanton thermogravimetric balance having a continuous recorder. Heating rates were 10° per minute for both methods.

Results

Table I contains *d*-spacings and relative intensity values out to 2Θ equal to 36° for the compounds: α-$SrHPO_4$, β-$SrHPO_4$ and $Sr_2P_2O_7 \cdot {}^1/_2H_2O$. These data include the strongest lines for all compounds and make possible a definite identification when compared to other strontium phosphates. Calculated *d*-spacings from diffractometer tracings and films were in good agreement.

TABLE I

α-$SrHPO_4$		β-$SrHPO_4$		$Sr_2P_2O_8 . {}^1/_2H_2O$		
d	*I*	*d*	*I*	*d*	*I*	
6.9	15	9.2	12	8.9	12	
5.05	9	5.76	18	5.57	15	
4.84	6	4.65	13	4.67	6	
4.68	6	4.57	23	4.47	25	
4.50	6	4.15	6	4.14	13	
4.38	4	4.01	20	3.99	22	
4.23	4	3.65	55	3.67	20	D
3.76	9	3.59	100	3.55	45	
3.49	100	3.26	70	3.44	20	
3.46	90	3.13	83	3.24	100	
3.38	7	3.02	70	3.00	30	D
3.21	5	2.87	42	2.86	19	
3.14	7	2.60	37	2.77	8	
3.08	8	2.53	17	2.62	12	
3.04	75					
3.00	34					
2.86	45					
2.83	42					
2.62	15					
2.53	22					

Materials precipitated at intermediate temperatures, 30° for example, gave patterns indicating the presence of both α- and β-$SrHPO_4$, and the analytical data agreed with the $SrHPO_4$ stoichiometry. However, additional diffraction lines at d = 3.71, 3.34 and 2.69 Å. were observed. These additional lines were also found in a mixed α- and β-$SrHPO_3$ prepared by the addition of $SrCO_3$ to dilute H_3PO_4. At present, we are unable to account for these lines.

The transformation of α-$SrHPO_4$ to β-$Sr_2P_2O_7$ and finally to α-$Sr_2P_2O_7$ is straightforward. X-ray identification of the products of thermal treatment showed that α-$SrHPO_4$ was stable up to 300°, but that at 370° the structure had changed to β-$Sr_2P_2O_7$ with a diffraction pattern equivalent to that found by Ranby, *et al.*[10] The β-$Sr_2P_2O_7$ structure was itself stable up to about 800° where a second phase change occurred with the formation of the α-$Sr_2P_2O_7$ structure, in fair agreement with Ranby's results. The high temperature, or α-

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[11] R. L. Stone, Ohio State Univ. Studies Engineering Series, Bulletin No. 146, 1951.

form of $Sr_2P_2O_7$, was found at temperatures as high as 1300°.

The corresponding study of the products formed by firing β-$SrHPO_4$ gave surprisingly different results. The β-$SrHPO_4$ structure was found up to 300°, but from 320–480° a material having a unique X-ray diffraction pattern was formed. The analytical and thermogravimetric data on this compound were in agreement with the formula $Sr_2P_2O_7 \cdot {}^1/_2 H_2O$. The X-ray patterns were essentially identical for materials fired for long periods at 350 and 450° and the pattern was distinct from other strontium phosphates. At 500°, this material was transformed into the β-$Sr_2P_2O_7$ structure, which in turn changed to the α-$Sr_2P_2O_7$ structure between 760 and 870°. β-$Sr_2P_2O_7$ never converted to α-$Sr_2P_2O_7$ below 750°. However, in a few cases, β-$SrHPO_4$ converted to α-$Sr_2P_2O_7$ (or an α-, β-$Sr_2P_2O_7$ mixture) at temperatures considerably below 750°. Available data indicate that this transformation arises from the $Sr_2P_2O_7 \cdot {}^1/_2H_2O$ form, since in one case pyrolysis of $Sr_2P_2O_7 \cdot {}^1/_2 H_2O$ also gave α-$Sr_2P_2O_7$ below 750°.

The difference in behavior between α- and β-$SrHPO_4$ on heating was corroborated by differential thermal analysis. Thus, α-$SrHPO_4$ exhibited one endothermic peak beginning at 370° and reaching a maximum at 475°; whereas β-$SrHPO_4$ gave two endothermic peaks: the first started at 320° and reached a maximum at 410° and, the second started at 560° and was complete by 575°. A much smaller but sharp endothermic peak was also observed between 760 and 775°.

An even clearer proof of the difference between α- and β-$SrHPO_4$ was obtained by thermogravimetric experiments. The loss of weight for α-$SrHPO_4$ started at 375° and continued without interruption to about 500°, corresponding to a weight loss of close to one mole water per mole of $Sr_2P_2O_7$. In contrast, the loss of weight of the β-$SrHPO_4$ sample started about 300° and continued at a rapid rate to 475° where it leveled out for about 100°. At about 575°, a second loss in weight occurred which continued until 650°. The weight loss corresponded to 0.48 mole water per mole $Sr_2P_2O_7$ for the first transition and 0.52 mole water for the second, correcting for the weight loss due to adsorbed water. The choice of the assigned chemical formula, $Sr_2P_2O_7 \cdot {}^1/_2H_2O$, was largely dependent upon these values. A comparison of the temperature values for the overnight heating experiments and those for the differential thermal and thermogravimetric analyses will show considerable discrepancies due to the inherent differences between pseudo-equilibrium measurements and those dependent upon the selection of an arbitrary heating rate.

Table II shows the X-ray identification of the reaction products of α- and β-$SrHPO_4$ with water.

The lines associated with the $Sr_3(PO_4)_2$ diffraction pattern were always "spotty" indicating the presence of large single crystals, whereas the lines due to strontium hydroxyl apatite were normal as would be expected from a powder with very small particle size. After washing for 9 days, both the α- and the β-$SrHPO_4$ samples contained many flat hexagonally shaped plates of $Sr_3(PO_4)_2$ mixed with material of lesser crystallinity. As additional confirmation that these crystals were indeed $Sr_3(PO_4)_2$, an X-ray powder pattern was taken of screened material and identified as tribasic strontium phosphate.

TABLE II

X-RAY IDENTIFICATION OF $SrHPO_4$ WASHED IN SOXHLET

Starting material	No. of days washed	X-Ray identification			
		β-$SrHPO_4$	α-$SrHPO_4$	$Sr_3(PO_4)_2$[12]	Strontium hydroxyl apatite[13]
β-$SrHPO_4$	4	Strong	None	None	Trace
	8	Strong	None	Weak	Weak
	11	Strong	None	Medium	Medium
	20	Medium	None	Medium	Medium
α-$SrHPO_4$	9	None	Strong	Medium	Trace
	26	None	Medium	Medium	Medium

Discussion

It is evident from this study that dibasic strontium phosphate may be precipitated in two different crystalline modifications depending upon the conditions of precipitation. As in the case of the calcite–aragonite transition,[9] the most critical preparation parameter is temperature. Thus, virtually pure α-$SrHPO_4$ is formed if the precipitation temperature is 40° or above and β-$SrHPO_4$ is formed if the precipitation temperature is 25° or below. At intermediate temperatures, mixtures of α- and β-$SrHPO_4$ are precipitated.

The precipitation of β-$SrHPO_4$ by the neutralization of a dilute solution of $Sr(H_2PO_4)_2$ seems at first inspection to conflict with the work of Lorah, *et al.*,[14] who used this method to prepare $Sr_3(PO_4)_2$. However, since in the present work the precipitate was simply washed with solvent, whereas in the work of Lorah, *et al.*, the precipitate was washed "until the phosphate-ion content of the water had decreased to a minimum," the following series of reactions could explain the difference in results.

$$Sr(H_2PO_4)_2 \xrightarrow{H_2O} \beta\text{-}SrHPO_4 + H_3PO_4 \qquad (1)$$

$$3(\beta\text{-}SrHPO_4) \xrightarrow{H_2O} Sr_3(PO_4)_2 + H_3PO_4 \qquad (2)$$

$$5Sr_3(PO_4)_2 + 3H_2O \longrightarrow 3Sr_5(OH)(PO_4)_3 + H_3PO_4 \quad (3)$$

This explanation is corroborated by the washing experiments listed in Table II in which both α- and β-$SrHPO_4$ are converted to $Sr_3(PO_4)_2$ plus strontium hydroxyl apatite and by the experiments of Lorah, *et al.*,[14] in which $Sr_3(PO_4)_2$ is converted to strontium hydroxyl apatite on long exposure (one-half complete after 46 days). Equations 2 and 3 also provide an explanation of the results of the Soxhlet experiments.

It is interesting that crystals of $Sr_3(PO_4)_2$ are easily formed by treating $SrHPO_4$ with water, whereas $MgHPO_4$ is converted to hydroxyl-bobbierite and finally to hydrated magnesium oxide,[15] while $CaHPO_4$ yields only calcium hydroxyl apatite[1,2] and $BaHPO_4$ undergoes no change at all even in boiling water.[16] The effect of cationic

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(12) W. H. Zachariasen, *Acta Cryst.*, **1**, 263 (1948).

(13) R. Klement, *Z. anorg. allgem. Chem.*, **242**, 215 (1939).

(14) J. R. Lorah, H. V. Tartar and L. Wood, THIS JOURNAL, **51**, 1097 (1929).

(15) R. Klement, *Z. anorg. allgem. Chem.*, **228**, 232 (1936).

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radius is evident from the trend toward decreased hydrolysis and degree of hydration with increasing size of the alkaline-earth ion. This tendency toward hydration of the magnesium and calcium phosphates over that of the strontium and barium phosphates is also shown by the existence of the trihydrate, $MgHPO_4 \cdot 3H_2O$[17] and the dihydrate, $CaHPO_4 \cdot 2H_2O$,[18] whereas in this work no evidence of a corresponding dihydrate of dibasic strontium phosphate was found nor has any similar compound been reported for barium.

Obviously after dissolution in water, there is no difference in behavior between the α- and β-$SrHPO_4$ phases. However, it is evident that their solid-state high-temperature reactions are different. Thus, α-$SrHPO_4$ loses water to go directly to the β-pyrophosphate, *i.e.*

$$2(\alpha\text{-}SrHPO_4) \xrightarrow{300\text{–}370°} \beta\text{-}Sr_2P_2O_7 + H_2O \quad (4)$$

This reaction is confirmed by differential thermal analyses which show one endothermic peak and is further corroborated by thermogravimetric data. In contrast, β-$SrHPO_4$ goes through an intermediate state before converting to the pyrophosphate, *i.e.*

$$2(\beta\text{-}SrHPO_4) \xrightarrow{300\text{–}320°} Sr_2P_2O_7 \cdot {}^1/_2H_2O + {}^1/_2H_2O \quad (5)$$

$$Sr_2P_2O_7 \cdot {}^1/_2H_2O \xrightarrow{480\text{–}500°} Sr_2P_2O_7 + {}^1/_2H_2O \quad (6)$$

Again the differential thermal analysis results are in qualitative agreement with this mechanism showing two endothermic peaks and thermogravimetric data also support this interpretation. The third endothermic peak obtained between 760 and 775° on heating β-$SrHPO_4$ is undoubtedly due to the β-$Sr_2P_2O_7$ to α-$Sr_2P_2O_7$ transition, in good agreement with the transition temperature of 750° given by Ranby.[10]

The possibility exists that $Sr_2P_2O_7 \cdot {}^1/_2H_2O$ may not be a distinct chemical specie, but instead may be a mixture of strontium ortho- and pyrophosphates with considerable amorphous material of a type similar to that obtained by Edwards and Herzog[19] in their dehydration experiments on sodium orthophosphate. Indeed the presence of amorphous material at temperatures corresponding to the formation of $Sr_2P_2O_7 \cdot {}^1/_2H_2O$ was indicated by the high background shown on the diffractometer patterns. However, since the stability of this material over a considerable temperature range has been demonstrated, the intermediate has been assigned the formula $Sr_2P_2O_7 \cdot {}^1/_2H_2O$ corresponding to its analytical composition. More detailed studies of thermal transitions would be required to completely determine the species present.

The X-ray diffraction pattern for β-$SrHPO_4$ given in Table I compares favorably with the pattern for $SrHPO_4$ listed by Hannewalt, *et al.*,[20] but there is no comparable published data on α-$SrHPO_4$. In the absence of single-crystal diffraction data on these dimorphs of $SrHPO_4$, it is very difficult to determine their crystal structure. Yet it is possible to make some interesting analogies to known structures. For instance, Pauling[21] has shown the importance of the radius ratio for various cations relative to oxygen in determining the choice of possible structures. Carbonates of divalent metals whose radius ratio is less than 0.67 crystallize in the calcite structure, whereas those which have a radius ratio greater than 0.67 crystallize in the aragonite structure. The same relationship seems to hold to some extent for the nitrates of the alkali metals and the borates of Sc, In, Y and La.

The critical radius ratio for the phosphates appears to be somewhat greater than 0.67 since the trivalent orthophosphates ($M^{III}PO_4$) of Nd, Ce and La with radius ratios between 0.87 and 0.92 have been shown to crystallize in two modifications—one monoclinic and one hexagonal.[22] The occurrence of dimorphs of $SrHPO_4$ instead of $CaHPO_4$ might then have been predicted since the radius ratio of strontium to oxygen having a value of 0.96 is closer to the range found in the $M^{III}PO_4$ compounds than is the radius ratio of 0.78 for calcium to oxygen.

The available published data on the crystal structures of the monetites ($M^{II}HPO_4$) are given in Table III.

TABLE III

CRYSTAL STRUCTURES OF THE MONETITES ($M^{II}HPO_4$)

Compound	Radius ratio	Crystal class	Space group
$CaHPO_4$	0.78	Triclinic	$P\bar{1}$
$SrHPO_4$	0.96	.....	..
$PbHPO_4$	1.00	Monoclinic	P2/b
$BaHPO_4$	1.05	Orthorhombic	Pmn

The structures of $CaHPO_4$ and $BaHPO_4$ have been fully described in recent publications,[5,23] but the structure of $PbHPO_4$[8] is open to question since only the positions of the heavy metal ions were determined and the identity of the space group was not definitely established. A comparison of the X-ray diffraction patterns for $CaHPO_4$ and α-$SrHPO_4$ shows marked similarities indicating that these two compounds may be isomorphous. If so, α-$SrHPO_4$ is triclinic with space group $P\bar{1}$. Without single crystal diffraction data, one cannot propose with any rigor the space group or crystal structure of β-$SrHPO_4$.

Acknowledgments.—The authors wish to thank Mr. G. J. Meisenhelter for the analytical determinations of strontium and phosphorus, Dr. W. S. Hummers for the differential thermal analyses, and Mr. T. J. Veleker for his help with some of the X-ray measurements.

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