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The synthesis of apatites with an organophosphate and in nonaqueous media

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ABSTRACT

The syntheses of barium, cadmium, calcium, lead, and strontium apatites were performed in anhydrous polar organic solvents such as DMSO, anisole, pyridine, glacial acetic acid, ethanol, methanol, and DMF. Reactions took place under anhydrous conditions at temperatures ranging from 80 to 120 °C and for durations of 1–6 days. Ten apatites were synthesized in nonaqueous solvents and three (PbApF, PbApCl, SrApCl) were obtained using trimethylphosphate as the phosphate source. The use of nonaqueous solvents alleviates the formation of hydrogen phosphates which occurs in aqueous solution for some divalent cations. The limited solubility of even alkali metal salts in many of the solvents also produces nonapatitic double salts such as $NaPb_4(PO_4)_3$, $NaPbPO_4$, $KPb_4(PO_4)_3$, $Cd(OH)NO_3$, and $NaBaPO_4$.

1. Introduction

The biologically, geologically, and environmentally important apatites $M_5(PO_4)_3X$, where M is a divalent cation such as Ca, Pb, Ba, Sr, and Cd, and X is a halide or hydroxide, are synthesized either by addition of the appropriate metal salt to a phosphate or hydrogen phosphate in water, frequently with the addition of ammonia to adjust pH, or by high temperature reaction of the salts [1]. The convenience of the aqueous method is moderated somewhat by the formation of hydrogen phosphates or ammonia complexes rather than the desired product for some metal ions [2]. The reaction of a phosphate with a metal salt in nonaqueous solvent holds promise as a means of avoiding formation of these undesirable products. Of course, reactions of salts in nonaqueous media can be problematic because of the low solubility of starting materials in the solvents employed.

Organic molecules, such as amides and alkyl phosphates, have been used to modify the particle or surface characteristics of calcium hydroxyl apatite [3–7], cadmium hydroxyl apatite [8], and lead hydroxyl apatites [9], but to our knowledge there has been no study of the effect of nonaqueous solvents on the synthesis of apatites.

The present investigation reports on our study of the synthesis of apatites in a variety of organic solvents, including DMSO, anisole, DMF, pyridine, acetic acid, phenol, methanol, and ethanol, which were selected because of the relatively greater solubility of the starting materials in these solvents. The crown ethers 18-crown-6 and 15-crown-5 were utilized as solubilizing agents in some cases.

Incorporation of the phosphate source in a nonaqueous solvent could be particularly advantageous. Trimethylphosphate could react with metal halides, presumably according to the following reaction:

$$5MX_2 + 3(CH_3O)_3PO \rightarrow M_5(PO_4)_3X + 9CH_3X.$$

This reaction was also explored with a variety of metal halides.

2. Experimental

All glassware was dried for at least 45 min in a 120 °C oven and stored under dry conditions. All reagents were reagent grade; absolute alcohols were dried over molecular sieves and all other solvents had a water content of less than 0.005% and were stored and used from their 100 mL bottles. Both anhydrous and hydrated salts were used as obtained commercially. Experiments with trimethylphosphate were performed in the hood, using double gloves, and washing all equipment with acetone before removal.

2.1. Synthesis

Syntheses were attempted using one of the reaction routes A–F given in Section 3. The quantities of reagents were calculated for the preparation of 0.50 g of product assuming 100% yield. The reagents were placed into a two-neck 50-mL round bottom flask containing a thermometer and condenser fitted with a Drierite-filled drying tube. Solvent (25–30 mL) was added to the flask and the mixture was heated and stirred magnetically.

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The product was filtered by aspiration and was washed thrice, alternating methanol and acetone. Water was also used as a wash only if preliminary XRD analysis indicated a water-soluble phase. The product was dried for at least 20 min by aspiration and placed in a 120 °C oven overnight. Cadmium containing compounds were dried in a Drierite-filled desiccator.

2.2. Analysis

Constituent ions were analyzed qualitatively by first dissolving the compound in 3 M nitric acid. Phosphate was identified qualitatively using 0.5 M ammonium molybdate reagent. Chloride, bromide, and iodide were identified qualitatively with 0.1 M silver nitrate. The cations were identified qualitatively by standard methods.

The identities of the products were determined by XRD using a Philips 3520 XRD system with a monochrometer and a copper X-ray tube. Phase identity was established using figure of merit (FOM) values as well as careful visual matching of peaks with those in the International Center for Diffraction Data (ICDD) PDF-2 Sets 1–44 Inorganics (includes zeolites and minerals) (1994) database. The presence of fluoride was confirmed by dissolving the sample in 3 M HNO_3, followed by a search for an ^{19}F resonance on a Varian INOVA 500 MHz NMR spectrometer at 470.12 MHz.

3. Results and discussion

3.1. Nonaqueous syntheses

Apatites of barium, calcium, cadmium, lead, and strontium were successfully prepared by the reaction routes shown below, where M and X are the cation and anion incorporated into $M_5(PO_4)_3X$ (MApX):

(A) $5MX_2 + 3Na_3PO_4 \rightarrow M_5(PO_4)_3X + 9NaX$
(B) $5MX_2 + 3Na_3PO_4 \cdot 12H_2O \rightarrow M_5(PO_4)_3X + 9NaX + 12H_2O$
(C) $5MX_2 + 3K_3PO_4 \rightarrow M_5(PO_4)_3X + 9KX$
(D) $5MX_2 + 3(NH_4)_2HPO_4 \rightarrow M_5(PO_4)_3X + 6NH_4X$
(E) $5M(NO_3)_2 + 3Na_3PO_4 + NaX \rightarrow M_5(PO_4)_3X + 10NaNO_3$
(F) $5M(NO_3)_2 + 3Na_3PO_4 + NH_4X \rightarrow M_5(PO_4)_3X + 9NaNO_3 + NH_4NO_3$
(G) $5MX_2 + 3(CH_3O)_3PO \rightarrow M_5(PO_4)_3X + 9CH_3X.$

The solvents differed depending on M and X and no single route was found to be superior for the preparation of all apatite products. In addition, product formation could not be predicted solely from the solubility of the starting materials. Most reactions were run at 80–120 °C for at least 1 day to increase the dissolution of the starting materials and the yield of product. Yields ranged from 50% to 70% with no apparent relationship to route or solvent. As evidenced in a PbApCl synthesis in DMSO, increased temperature seemed to improve the purity as indicated by a decrease in the XRD figure of merit values. In many cases, the powder diffraction pattern contained sharper lines than are routinely obtained using aqueous methods. The routes and conditions for successful preparations are summarized in Table 1. The xrd line patterns for PbApF, prepared using TMP in DMSO, and for BaApCl, prepared in anisole, are shown in Figs. 1 and 2.

3.2. Barium apatites

The syntheses of barium apatites in DMSO generally require the absence of sodium ion because of preferential formation of $NaBaPO_4$. For example, attempted preparation of BaApF in anisole and 18-crown-6 using route B produced a precipitate identified as $NaBaPO_4$. The insolubility of BaF_2 in all solvents probably contributed to the difficulty in obtaining the apatite.

Barium chloroapatite was obtained in anisole using routes B and C, and in anisole with 18-crown-6 by routes B and C.

The attempted preparation of BaApCl in DMSO, routes A, B, C, and D yielded Na_3PO_4, $NaBaPO_4$, an amorphous product, and $BaHPO_4$, respectively. In phenol, route C produced $BaHPO_4$. The formation of barium hydrogen phosphate may be due to the protic nature of phenol and ammonium hydrogen phosphate. Barium bromoapatite was not prepared successfully in anisole with 18-crown-6 using routes B and C which yielded barium phosphate. The preparation of barium hydroxyapatite was unsuccessful in anisole with 18-crown-6 by route B and in pyridine by route D.

3.3. Cadmium apatites

Cadmium fluoroapatite was obtained using route F in anisole with 2 mL of glacial acetic acid presumably because cadmium nitrate tetrahydrate and sodium phosphate were soluble in anisole and ammonium fluoride was moderately soluble in glacial acetic acid. It was identified by ^{19}F NMR and XRD. Cadmium chloroapatite was successfully prepared by route A in a 1:1 anisole and ethanol mixture. The purity of the product improved with repeated washings with distilled water due primarily to the removal of the NaCl byproduct. The reactions were done in mixed solvents because sodium phosphate showed the highest solubility in anisole while cadmium chloride was most soluble in DMSO or ethanol.

The synthesis of cadmium fluoroapatite was attempted in DMSO using route A, but resulted in CdF_2. Attempts to prepare CdApCl using route B in anisole with 18-crown-6 ether produced a mixture of NaCl and Na_3PO_4. An attempt using route A in DMSO produced sodium phosphate. Although $CdBr_2$ is soluble in DMSO, CdApBr could not be obtained by route A in a 1:1 DMSO and anisole mixture (sodium phosphate was obtained). An attempt at cadmium hydroxyapatite by route E in anisole produced sodium nitrate and $Cd(OH)NO_3$.

3.4. Calcium apatites

Calcium fluoroapatite was obtained using route F with anisole and 2 mL glacial acetic acid). Although the XRD of the product indicated a mixture of CaF_2 and either the fluoro or hydroxy apatite (the patterns for the hydroxy- and fluoroapatites are very similar), the acidic reaction mixture confirms the presence of the fluoroapatite. Calcium hydroxyapatite was produced with route E in anisole. Route E, using NaOH, was preferred to the use of calcium hydroxide for solubility reasons.

Attempts to prepare CaApF using route B in ethanol and route A in a 1:1 DMSO and anisole mixture resulted in calcium fluoride. Calcium chloroapatite could not be obtained using route A or B in ethanol, route A in 1:1 ethanol and anisole mixture, route A in 1:1 ethanol–anisole containing 15-crown-5 ether, and when a solution of calcium chloride in ethanol was titrated into anisole with sodium phosphate. In DMSO, route A resulted in sodium phosphate, route B produced sodium phosphate and sodium chloride, route D produced NH_4HPO_4, route A with 2:1 anisole and DMSO mixture and 18-crown-6 ether resulted in sodium phosphate. Route A with methanol and 15-crown-5 ether was attempted because of the solubility of starting materials in this mixture, but resulted in Na_2HPO_4. Attempts to prepare CaApOH using route B in anisole with 18-crown-6 ether and in ethanol produced calcium hydroxide, as did route A in TMP and DMSO.

Table 1
Summary of solvents and conditions for successful preparations of apatites.

Compound	Route	Solvent(s)	Reaction time (days)	Temperature (°C)
BaApCl	B	anisole	1	110
	C	anisole	1	123
	A	anisole + 18-crown-6	6	125
	B	anisole + 18-crown-6	2	125
	C	anisole + 18-crown-6	2	110
CaApF	F	anisole + glacial acetic acid	2	115
CaApOH	E	anisole	2	130
CdApF	F	anisole + glacial acetic acid	3	120
CdApCl	A	anisole + EtOH	2	81
PbApBr	D	DMSO	4	21
PbApCl	C	anisole + 18-crown-6	4	125
	D	DMSO	1	115
	C	phenol	4	110
	G	DMSO	2	150
PbApF	D	DMSO	2	114
	G	DMSO	4	150
PbApOH	D	pyridine	3	85
SrApCl	G	DMSO	3	130
SrApOH	A	anisole + 18-crown-6	4	115

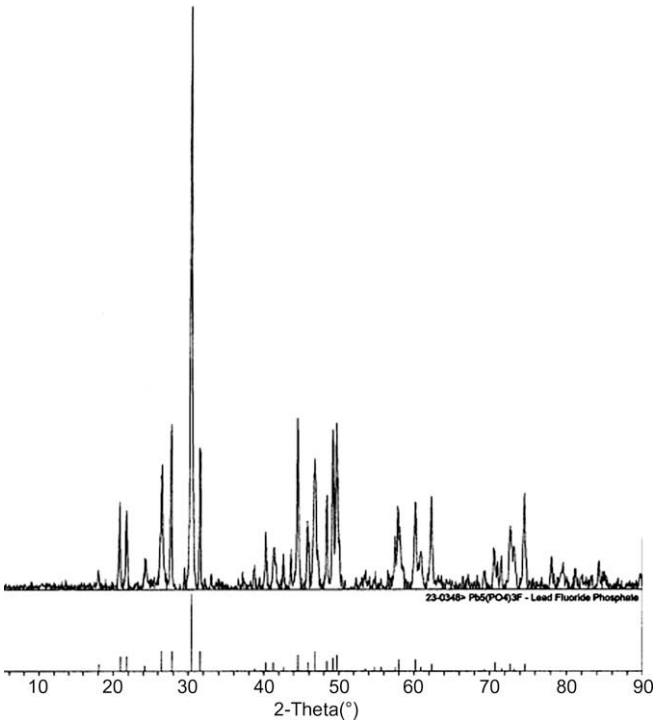

Fig. 1. The XRD line pattern, and its database comparison, for PbApF synthesized with TMP in DMSO.

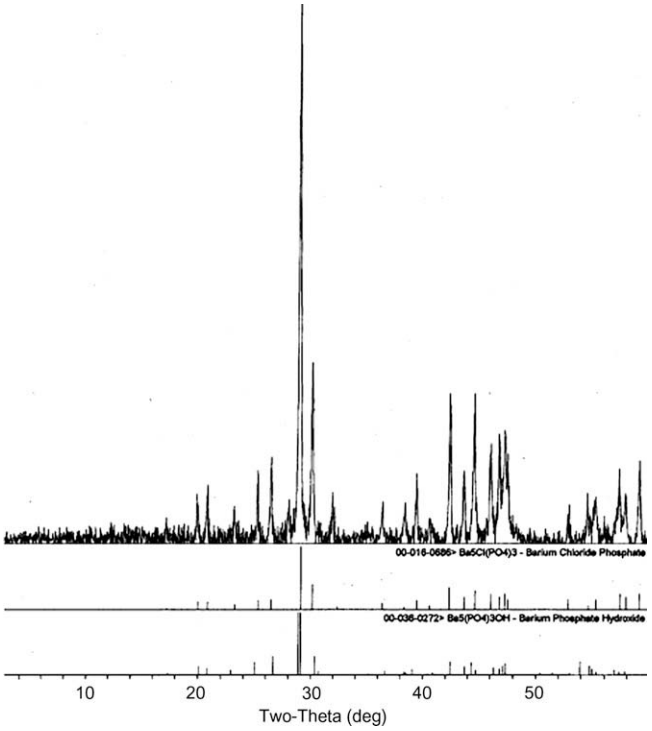

Fig. 2. The XRD line pattern, along with the database comparison, for BaApCl, prepared in anisole.

3.5. Lead apatites

In most of the solvents used, the formation of sodium lead phosphate double salts $NaPb_4(PO_4)_3$ or $NaPbPO_4$ were obtained as the main product. The presence of potassium ion (route C) resulted in the formation of $KPb_4(PO_4)_3$ in DMSO and the apatite in anisole with 18-crown-6 ether as well as in phenol. Most successful lead apatite syntheses utilized route D.

Lead fluoroapatite was successfully prepared by route D in DMSO. It was identified by both XRD and ^{19}F NMR spectroscopy. Lead chloroapatite was obtained with route C in anisole with 18-crown-6 for 4 days (heating for 2 days produced lead chloride) and in phenol. It was also successfully prepared by route D in DMSO at room temperature or with heating. The purity of the product increased with heating as indicated by XRD figure of merit values. Lead bromoapatite was obtained with route D in DMSO at room temperature. The preparation of lead hydroxyapatite was successful using route D in pyridine (chosen because of the solubility of lead hydroxide and NH_4HPO_4 and its basicity), as well as with a 1:1 mixture of pyridine and DMSO.

Attempts to prepare PbApF using route B in anisole with 18-crown-6 ether produced $NaPb_4(PO_4)_3$. The chloroapatite could not be obtained with anisole and DMSO; all attempts using route B in DMSO or anisole with 18-crown-6 gave $NaPb_4(PO_4)_3$. Due to its insolubility only the starting lead chloride was isolated in route A in anisole with 18-crown-6 ether. Attempts to prepare PbApOH using route E with 1:1 anisole and DMSO resulted in $NaPb_4(PO_4)_3$.

Table 2
Comparison of aqueous and nonaqueous syntheses [1,2][a].

Compound	Synthesis in aqueous solution	Synthesis in nonaqueous solvent
BaApBr	no	no
BaApCl	yes	yes
BaApF	yes	no
BaApOH	yes	no
CaApBr	no	no
CaApCl	no	no
CaApF	yes	yes
CaApOH	yes	yes
CdApBr	no	no
CdApCl	yes	yes
CdApF	yes	yes
CdApOH	yes	no
PbApBr	yes	yes
PbApCl	yes	yes
PbApF	yes	yes
PbApOH	yes	yes
SrApBr	no	no
SrApCl	yes	yes
SrApF	yes	no
SrApOH	yes	yes

[a] Including syntheses with TMP.

3.6. Strontium apatites

Even under anhydrous conditions, strontium hydroxyl apatite forms preferentially to all other strontium apatites: SrApOH was formed in routes B and C in anisole with 18-crown-6 ether in syntheses for hydroxy-, chloro-, and bromoapatites.

Syntheses of SrApF were attempted by route D in DMSO, but only the starting material SrF_2 was isolated. Attempts to prepare SrApF produced the hydroxyapatite. Sodium phosphate was formed when preparations were attempted in DMSO by routes A and B and in anisole by route A.

3.7. Trimethylphosphate as a phosphate source and solvent

Trimethylphosphate (TMP) was used as a phosphate source in the reaction with the following metal salts: $BaCl_2$, BaF_2, $SrCl_2$, SrF_2, $SrBr_2$, $CaCl_2$, $Ca(OH)_2$, CaF_2, $CdCl_2$, $PbCl_2$, $Pb(OH)_2$, and PbF_2. Lead fluoroapatite, lead chloroapatite, and strontium chloroapatite were formed with TMP in DMSO.

4. Conclusions

Of the 20 apatites listed in Table 2, 15 have been prepared in aqueous solution and 10 have now been prepared in nonaqueous solvents. In general, the solubilities of the starting materials in the solvents studied were very limited and the reactions required heating from 1 to 6 days. Because some hydrated salts are more soluble in these solvents, the hydrates were utilized in some reactions. The formation of hydrogen phosphates of the divalent cation, which hinders formation of CaApCl, CaApBr, and PbApOH in aqueous solution [1], was alleviated in routes A through F. The formation of nonapatitic double salts, such as $NaPb_4(PO_4)_3$, $NaPbPO_4$, $KPb_4(PO_4)_3$, $Cd(OH)NO_3$, and $NaBaPO_4$ occurred with some regularity due to the limited solubility of these salts in the solvents used. Although the use of the crown ether did improve the solubility of some salts, it was not helpful in all solvents. It was used with anisole because of its effect on the solubility of the hydrated sodium phosphate and barium salts, and with methanol to dissolve anhydrous sodium phosphate and calcium chloride.

Understandably, there was no single route or solvent that could be employed for all preparations. Moreover, the solubilities of the starting materials was not always an indication of the success of the synthesis. It was often the case that the complete dissolution of the simple salts was not necessary. For example, the starting materials in the preparation of CdApCl using route A in EtOH and anisole formed a white slurry but the reaction successfully produced the chloroapatite. However, anisole was used more frequently than the other solvents in the successful preparations (Table 1).

The reaction of metal salts with trimethyl phosphate was of interest because of the easy formation of the lead apatites in the reaction:

$$3(CH_3)_3PO_4 + 5PbX_2 \rightarrow Pb_5(PO_4)_3X + 9CH_3X.$$

This method produced PbApCl, PbApF, and SrApCl in TMP/DMSO mixtures. However, numerous attempts to prepare other apatites, including BaApF, BaApCl, CaApCl, CaApBr, SrApF, and SrApBr, using this method were unsuccessful. The reaction as written above for the formation of PbApCl, for example, is thermodynamically favorable and is easily accomplished with due caution for the toxicity of TMP. Reaction with TMP produces SrApCl, which could not be obtained using inorganic phosphates in nonaqueous solvents.

A combination of nonaqueous and TMP methods, therefore, can be used to prepare most apatites that have previously been prepared in aqueous solution. The nonaqueous conditions also produce double salts that may be of interest for other reasons. These include $NaPb_4(PO_4)_3$, $NaPbPO_4$, $KPb_4(PO_4)_3$, $Cd(OH)NO_3$, and $NaBaPO_4$.

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