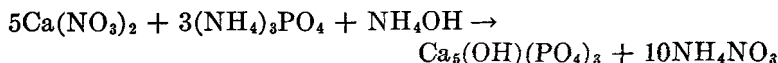


17. PENTACALCIUM MONOHYDROXYORTHOPHOSPHATE

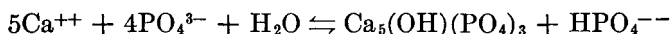
(Hydroxylapatite)



SUBMITTED BY ERICH HAYEK* AND HEINRICH NEWSELY*

CHECKED BY MAX L. RUMPEL†

Hydroxylapatite is the stable orthophosphate of calcium in neutral and alkaline media. Its preparation in pure form is difficult, since with the customary precipitation reaction the monohydrogen phosphate ion always forms according to the reaction:



Therefore, tetracalcium monohydrogen triphosphate ("octaphosphate"), $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$, which displays a structure similar to apatite, readily forms, solely or at least partially, in the place of hydroxylapatite.¹ Such precipitates change to the β -tricalcium phosphate upon calcination. In the preparation of a uniformly crystalline product one must perform a tedious boiling-out process² or the hydrothermal synthesis;³ either of these methods, however, accommodates only a small lot (*ca.* 70 mg., crystal size 0.3 mm.) or else the preparation has a small sodium content⁴ (0.5% from 2 g. of material and up to 2-mm. crystal size). In either case, considerable apparatus and expenditure of time are required.

These difficulties can be overcome, for example, by carrying out the precipitation at normal temperature in a medium of sufficiently high pH so that the PO_4^{3-} concentration is not exceeded by that of HPO_4^{--} and, moreover, by

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employing the easily volatilized ammonia in the precipitation.⁵ It is necessary both to bring the reaction medium to a high pH value and to allow the phosphate solution to flow into that of the calcium salt to obtain a homogeneous product. Furthermore, it is important to employ a nitrate solution instead of a chloride; otherwise, during calcination of the voluminous precipitate, some ammonium chloride and chlorapatite may be formed through metathesis.

Procedure

Seventy-eight and seven-tenths grams (0.33 mol) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 300 ml. of water in a 2-l. flask. The solution is adjusted to a pH of 12 by the addition of concentrated ammonia (CO_2 -free) and is then diluted to 600 ml. Into this solution is dropped slowly, with vigorous stirring, a solution of 26.4 g. (0.2 mol) of diammonium hydrogen phosphate in 500 ml. water, which similarly has been brought to pH 12 with ammonia and thereafter diluted to 800 ml. A voluminous precipitate forms. The filtering properties of the reaction mixture may be improved by gently boiling it for 10 minutes. The precipitate is allowed to settle and the supernatant solution is separated from the precipitate by decantation and by use of a suction filter, with application of a weak vacuum.

The filter cake is washed with 100 ml. of hot water, dried at 150° , and heated for an hour at 240° to remove the ammonium nitrate. By strong heating at 800° for an hour, the product becomes largely anhydrous and considerably hardened. This hardening is of importance when the solid is to be ground to a predetermined particle size.

The yield, theoretically 33.5 g., amounts to 30 to 32 g. because of mechanical losses which are difficult to avoid.

Properties

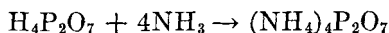
The hydroxylapatite obtained by this method is in the form of white fragments which appear highly porous.

Under the electron microscope the material shows a structure corresponding to hexagonal prisms which terminate in pyramids, length about 30 to 60 $m\mu$, width 10 to 20 $m\mu$. By the use of analytically pure starting materials in the indicated proportions, the atomic ratio Ca/P corresponds within a deviation of less than 1% of the theoretical value 1.67. Even by using less pure starting materials important amounts of the impurities iron, aluminum, and manganese, as well as in part magnesium, are removed by filtration of the ammoniacal solution. Owing to the great surface area, a little water content (<1%) is retained even after heating at red heat according to the above procedure; it can be removed only by long heating at 900°. Hydroxylapatite begins to decompose above 1100°.

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18. TETRAAMMONIUM PYROPHOSPHATE



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Tetraammonium pyrophosphate has been prepared by bubbling ammonia into an ice-water solution of pyrophos-

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