dried over anhydrous sodium sulfate, filtered and the filtrate evaporated to dryness *in vacuo*, the residual crystals were collected and recrystallized from boiling ethylene dichloride. The colorless crystals so obtained melted at 109–110°. A mixed melting point with an authentic sample of the nitrobase of the *erythro* series gave no depression.

Calcd. for $C_9H_{12}N_2O_4$: N, 13.20. Found: N, 13.28.

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Preparation of Macrocrystalline Fluorapatite Containing Radioactive Phosphorus

BY GLENN V. ELMORE AND E. O. HUFFMAN

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The properties of fluorapatite, $Ca_{10}(PO_4)_6F_2$, are important in the technology of phosphate fertilizers, a field with which the Tennessee Valley Authority is concerned. The thermodynamic properties of fluorapatite were evaluated recently,[1] and other properties of the compound are being studied.

Fluorapatite containing radioactive phosphorus was needed in a study of the kinetics of solution of the apatite. A product of high specific activity was wanted, and existing methods of preparation[2,3] were considered unsuitable because of the difficulty of conducting such operations as mixing, grinding and screening without undue hazard to the operator. A method devised for the preparation of macrocrystals of radioactive apatite in a high degree of purity is the subject of the present report.

Method of Crystallization.—Fluorapatite can be prepared from a melt of its components in a flux. Thus, when a melt of an orthophosphate of calcium or potassium in an excess of calcium fluoride was heated at 1400° in a vacuum, part of the solvent calcium fluoride was vaporized, and crystals of fluorapatite were formed. Removal of the excess calcium fluoride was incomplete, however, even after 24 hours of heating.

Substitution of alkali metal fluorides for the calcium fluoride resulted in melts from which the non-apatite fluoride could be evaporated completely at 1200° in a vacuum. Although good fluorapatite was obtained with either sodium fluoride or potassium fluoride, the sodium salt was preferred because it was less hygroscopic.

When the fluoride was evaporated from the melt in an externally heated porcelain tube, the vapor attacked the porcelain and caused contamination of the fluorapatite with silica. To avoid this contamination, the platinum crucible containing the charge was suspended in a vertical glass tube and heated by induction. The glass wall remained cool and did not contaminate the apatite. The fluoride vapor condensed on the glass.

The melt had a pronounced tendency to creep over the edge of the crucible during evaporation of the solvent. Crystals formed on the outside of the container, and the inside was essentially empty at the end of an experiment. This creeping of the melt removed part of the solvent from the hot interior of the crucible to the cooler exterior where its evaporation was incomplete. Complete evaporation of the solvent in 5 hours was effected by suspending the crucible and its contents inside a second platinum crucible of slightly larger diameter and heating the outer crucible at 1200° by induction. This arrangement provided an external source of heat for the crucible containing the charge. Good crystals of fluorapatite were deposited on the outside of the inner crucible.

The method finally developed for the crystallization of fluorapatite was shown to be equally suitable for the preparation of macrocrystalline chlorapatite from a solution of its components in sodium chloride or potassium chloride.

In subsequent application of the method to the growth of crystals of fluorapatite, a high-quality laboratory preparation of microcrystalline fluorapatite was the source of the apatite components. The microcrystalline material conveniently supplied the components in correct ratio and essentially free of impurities. The method of its preparation has been described.[1]

A spectrographic analysis of a typical macrocrystalline fluorapatite prepared from the smaller crystals showed the following percentages of impurities: Na_2O, 0.14; MgO, 0.1; SrO, 0.01; SiO_2, 0.05; Fe_2O_3, < 0.01; Al_2O_3, < 0.01; CuO, < 0.002. The preparation gave a strong apatite pattern[4] by X-ray diffraction. No other crystalline phase was detected in the X-ray analysis.

A microscopic examination showed that the colorless rod crystals of fluorapatite were optically clear and free of growth imperfections other than elongated air cavities. The crystals ranged from 1 to 5 mm. in length. The (0001) cleavage was prominent. The crystals were hexagonal and uniaxial (−) with $n_\epsilon = 1.627$ and $n_\omega = 1.631$. Traces of platinum, calcium oxide and α-tricalcium phosphate were detected as crystalline impurities. A 3-hour digestion of the apatite with a neutral solution of ammonium citrate at 60° removed all the calcium oxide and α-tricalcium phosphate except isolated fine-grained deep-seated inclusions.

Incorporation of P^{32}.—To prepare radioactive fluorapatite, 0.1 g. of the microcrystalline apatite was dissolved in several milliliters of concentrated nitric acid and mixed with 2 ml. of a solution containing 50 mc. of carrier-free P^{32} as phosphate in nitric acid.[5] The amount of P^{32} was minute in proportion to the phosphorus from the apatite but was enough to impart a high specific activity to the final product.

The solution was evaporated in a platinum crucible without boiling. The nitrate in the residue was decomposed at red heat. Sodium fluoride then was added, and fluorapatite was crystallized from the mixture in the manner described.

The radioactive crystals, upon microscopic examination, appeared to be of the same high quality as that reported for the non-radioactive preparations. The refractive indexes of the two types of preparations were identical.

Acknowledgment.—K. L. Elmore suggested the crystallization of fluorapatite from an alkali fluoride as a solvent. J. R. Lehr made the microscopic examinations, J. P. Smith the X-ray examinations and Frances M. Youngblood the spectrographic analyses.

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(1) E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **73**, 5581 (1951).

(2) G. Chaudron and R. Wallaeys, *Bull. soc. chim. France*, D132 (1949).

(3) R. Wallaeys and G. Chaudron, *Compt. rend.*, **230**, 1867 (1950).

(4) St. Náray-Szabó, *Z. Krist.*, **75**, 387 (1930).

(5) Supplied by Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tenn.

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Bromination, Iodination and Phenylation of Thianaphthenes

BY RUSSELL GAERTNER

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In continuation of studies of the effect of a "blocking" group in the ortho position on abnormal reactions of arylmethyl Grignard reagents,[1] 2-bromo-3-(bromomethyl)-thianaphthene (I) was obtained by the action of N-bromosuccinimide on 2-bromo-3-methylthianaphthene. I appeared to react normally in the cyclic Grignard reactor, but only polymers and traces of impure products could be isolated from the reactions with ethyl chlorocarbonate and formaldehyde. The presence of a trace of a coupling product, presumably 1,2-bis-(2-

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(1) R. Gaertner, THIS JOURNAL, **74**, 2991 (1952).