Synthesis of Carbonato-apatite[1]

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A considerable amount of work has been done on the synthesis of hydroxy- and fluoro-apatites both in dry systems at high temperature[3-5] and by precipitation reactions.[6] More recently, the synthesis of carbonato apatites by solid state reactions at high temperature has been reported.[3]

Carbonato-apatite is structurally an apatite which has ($CO_3^=$) groups substituted for (OH^-) groups in the crystal lattice.

The occurrence of carbonato-apatite as a constituent of bones has been previously suggested by Prien.[7] However, the investigations of Dallemagne, *et al.*,[8] indicate that this compound is not a constituent of bones. They found that acids attack the carbonate leaving the phosphate intact. Also, it has been reported that carbonato-apatite is one of the forms of phosphates found in alkaline soils.[9,10]

In this paper are presented the results of an investigation carried out to synthesize a carbonato-apatite from suspension at relatively low temperature.

Synthesis.—The synthesis of carbonato-apatite was carried out in the presence of an excess of alkali according to the reaction

$$10CaCO_3 + 6KH_2PO_4 + 12OH^- \dashrightarrow Ca_{10}(PO_4)_6CO_3 + 6K^+ + 9CO_3^= + 12H_2O$$

The final procedure evolved from a series of investigations is as follows.

One gram of $CaCO_3$ C.P. grade is placed into a 250-ml. erlenmeyer flask which contains 10 ml. of water. After the addition of 60 ml. of 0.20 *M* KH_2PO_4 (which is about 50% in excess of the stoichiometric proportion) enough 2 *N* NaOH is added to make the suspension 0.50 *N* with respect to the concentration of NaOH. Then the flask is sealed with a rubber stopper provided with a glass tubing, shaken intermittently for 5 minutes and digested on the hot plate at 90° overnight. Following this, the solid phase is washed by centrifuging 5 times with distilled water and twice with ethyl alcohol. Tests for alkalinity failed to give a pink color with phenolphthalein indicating that all the excess of base has been removed. Finally, the alkali-free solid phase was dried at 110° and then heated for 2 hours at a temperature of 300°.

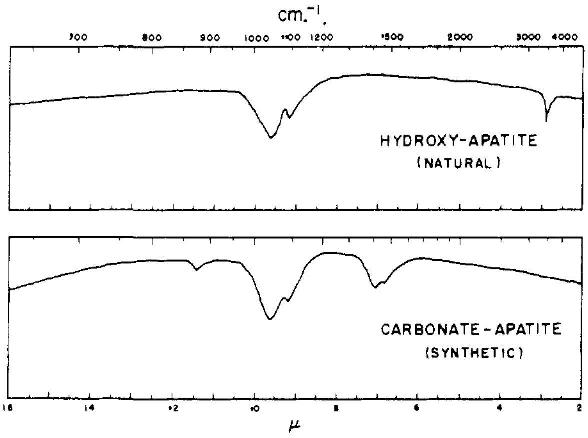

Fig. 1.—Infrared curves of apatites.

Characterization.—Firstly, an X-ray spectrogram of a finely powdered specimen of a natural apatite[11] was taken using the G.E. X-ray recording spectrometer with a Cu Kα target and a nickel filter. The d spacings were obtained from standard tables, and the intensities corrected for background (Table I). A spectrogram of the synthetic material showed d spacings similar to those obtained with the natural apatite. However, the intensities of the reflections varied considerably. Samples of the synthetic material heated at 300° for 2 hours gave patterns which had the same d spacings with the intensities of the reflections very similar to those obtained with the natural apatite (Table I).

Table I

Lattice Spacings and Estimated Intensities of Apatites[a]

Hydroxy-apatite

3.866(2.8), 3.426(4.3), 3.153(3.2), 3.058(2.0), 2.796(10.0)
2.771(6.5), 2.698(5.0), 2.614(3.0), 2.248(2.5), 2.141(1.0)
1.968(0.5), 1.941(3.8), 1.887(2.3), 1.830(3.4), 1.797(2.2)
1.772(1.4), 1.746(1.6), 1.718(1.3), 1.692(0.4), 1.639(0.8)
1.537(0.6), 1.501(1.0), 1.472(1.2), 1.454(1.0), 1.448(1.2)
1.426(0.8)

Carbonato-apatite

3.866(2.6), 3.418(4.0), 3.120(1.2), 3.048(2.0), 2.796(10.0)
2.771(7.4), 2.698(3.8), 2.629(2.2), 2.398(2.6), 2.250(1.8)
2.141(1.0), 1.956(0.6), 1.941(2.3), 1.887(1.4), 1.835(2.3)
1.797(1.4), 1.772(1.0), 1.742(0.5), 1.725(1.2), 1.698(1.6)
1.639(0.6), 1.527(1.4), 1.460(0.5), 1.454(1.0), 1.448(1.2)

[a] First figure represents d_{hkl} spacing and figure in brackets the corresponding estimated intensity.

The presence of $PO_4^{\equiv}$ and OH^- ions in the natural apatite and of $PO_4^{\equiv}$ and $CO_3^=$ ions in the carbonato-apatite was established by means of infrared spectroscopy. The absorption spectra were recorded using the Perkin–Elmer Model 21 recording infrared spectrometer. In fact, the absorption curves in Fig. 1 show the presence of ionic groups as follows: for $PO_4^{\equiv}$ at 1045 and 1095 cm.$^{-1}$; for $CO_3^=$ at 1418, 1460 and 875 cm.$^{-1}$ and for OH^- at 3600 cm.$^{-1}$, respectively. It is thus shown that carbonato-apatite does not contain OH^- groups and that they have been replaced by $CO_3^=$ ions.

Discussion

The experimental results presented in Table I show that carbonato-apatite is structurally like a hydroxy-apatite as is evidenced by the close agreement found in the d_{hkl} spacings and the intensities of the reflections. Brasseur and Dallemagne[3] showed previously that hydroxy-apatites and carbonato-apatites synthesized at high temperatures have the same b_0 and c_0 parameters but that the a_0 in carbonato-apatite is slightly smaller (d_{300} = 3.120 Å. in carbonato-apatite and 3.153 Å. in hydroxy-apatite, respectively). Although the effective radii of both the OH^- and the $CO_3^=$ are the same, they actually differ in shape. The hydroxyl is a sphere while the carbonate ion is a flat trigonal group, this being the reason for the small discrep-

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(1) Taken in part from a Ph.D. thesis submitted by Luis A. Romo to the Graduate Faculty of the University of Wisconsin, Fall, 1953.

(2) Research associate in Geochemistry at the Pennsylvania State University, State College, Pennsylvania.

(3) A. L. Brasseur and M. J. Dallemagne, "Reaction dans L'État Solide," Cent. Nat. Rech. Scient., Paris, 1948, pp. 107–108.

(4) G. Chaudron and R. Wallaeys, *ibid.*, pp. 103–105.

(5) S. B. Hendricks, W. L. Hill, K. D. Jakob and M. E. Jefferson, *Ind. Eng. Chem.*, **23**, 1413 (1941).

(6) P. W. Arnold, *Trans. Faraday Soc.*, **46**, 1061 (1950).

(7) E. L. Prien, *J. Urology*, **57**, 944 (1947).

(8) J. Dallemagne, H. Brasseur and J. Mellen, ref. 3, pp. 109–116.

(9) T. F. Buehrer, Ariz. Agr. Exp. Sta., Tech. Bull. 42 (1932).

(10) L. A. Romo, Ph.D. Thesis (Fall, 1953), Univ. Wisconsin, Madison, Wisconsin.

(11) The sample was obtained from a single crystal of hydroxy-apatite, Asparagus-stones, Durangon, Mexico, supplied by Wards Natural Science, Rochester, New York.

ancy recorded in one of the parameters. Moreover, the fact that carbonato-apatite differs from hydroxy-apatite because of the replacement of hydroxyls by carbonate ions is evidenced by the information obtained by means of infrared spectroscopy.

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Kinetics and Mechanism of the Pinacol Rearrangement. I. The Perchloric Acid-catalyzed Rearrangement of Benzopinacol and of Tetraphenylethylene Oxide in Acetic Acid Solution[1]

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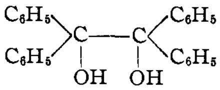
The perchloric acid-catalyzed rearrangement of benzopinacol (P) to β-benzopinacolone (K) in acetic acid occurs by two kinetically distinguishable routes, one of which involves direct rearrangement and the other involves intermediate formation of tetraphenylethylene oxide (E). At 75° approximately 80% of the ketone is formed by the latter route. Correlation of H_0 values of the medium with the rate constants of the reaction system

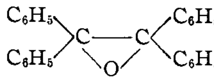
$$\begin{tikzcd} P \arrow[r] \arrow[rr, bend right] & E \arrow[r] & K \end{tikzcd}$$

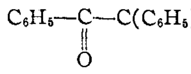
shows that for the three reactions a reversible proton transfer to P or E is followed by the rate-determining ionization of the oxonium complex. The large positive values of the entropy of activation for the rearrangement of E and for the composite reaction of P suggest that the classical carbonium ion is an intermediate in these processes.

Although the molecular rearrangements of tetraaryl pinacols to pinacolones have been studied extensively with respect to the relative migratory aptitudes of the aryl groups,[3] the kinetic characteristics of these reactions have received comparatively little attention. The rearrangement of $4,4',4'',4'''$-tetrachlorobenzopinacol and of the corresponding epoxide in acetyl chloride was studied kinetically by Meerburg[4] with the aid of an analytical method which involved measurement of the alcoholic alkali consumed by cleavage of the pinacolone. At 30° he observed fluctuations in the concentration, or apparent concentration, of the ketone for which he was unable to account. He concluded, however, that the epoxide could not be an intermediate in the rearrangement of the pinacol. The kinetics of the rearrangement of *cis*- and *trans*-1,2-diphenylacenaphthene-1,2-diol in acetic acid has been the subject of three investigations[5] in all of which the progress of reaction was followed by analysis for unchanged pinacol by oxidation with lead tetraacetate. The results of these investigations are not completely conclusive, particularly with respect to the ability of the *trans* isomer to undergo rearrangement.

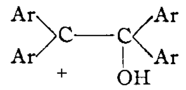
In its gross aspects the mechanism of the pinacol rearrangement is firmly established.[6] However, there are numerous detailed features of these reactions which have been inadequately investigated, particularly in the tetraaryl pinacols in which the shift is to a tertiary carbon atom. These include the stereochemical changes at the migration terminus, the effect of substituent groups upon energy and entropy of activation, and the relative importance in the transition state of the carbonium ion (IV) and the phenonium ion[7] (V). The tetraarylethylene oxides (II) have received only scant attention and there is inadequate experimental support for the commonly held opinion that the rearrangements of the epoxides and of the corresponding pinacols are completely analogous. Some of these problems are under investigation in this Laboratory. The present communication records the results of the kinetic study of the rearrangement of benzopinacol (I) and of tetraphenylethylene oxide (II) to β-benzopinacolone (III) in acetic acid with perchloric acid as the catalyst.

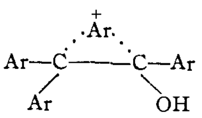

I (P)


II (E)


III (K)

$C_6H_5-C(=O)-C(C_6H_5)_3$


IV


V

Experimental Part

Materials.—Glacial acetic acid (Mallinckrodt Chemical Works, bichromate test grade) was further purified by the method of Orton and Bradfield[8] modified by omission of acetic anhydride. The acid was distilled through an 18-

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[1] Presented before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September, 1952; Abstracts of Papers 24 M.

[2] Shell Oil Co., Wood River, Ill. This paper is abstracted from the Ph.D. Thesis of Herbert J. Gebhart, Jr., St. Louis University, June, 1952.

[3] For an excellent review of the pinacol rearrangement see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 451–534.

[4] P. A. Meerburg, *Rec. trav. chim.*, **24**, 131 (1905); **28**, 267, 270 (1909).

[5] P. D. Bartlett and R. F. Brown, THIS JOURNAL, **62**, 2927 (1940); R. Criegee and K. H. Plate, *Ber.*, **72B**, 178 (1939); H. Sello, University Microfilms, Ann Arbor, Mich., Pub. No. 1286 (1949).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. IX.

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