December, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **56**, *3843—3844 (1983)* 3843

Succinate-complexed Octacalcium Phosphate

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(Received May 4, 1983)

Synopsis. A succinate-complexed calcium phosphate has been synthesized by conducting the hydrolysis of α-tricalcium bis(phosphate) in the presence of succinate ions. The organic substance is considered to be introduced into the structure of the hydrolysis product, *i.e.*, octacalcium bis(hydrogenphosphate) tetrakis(phosphate) pentahydrate, through the replacement of HPO_4^{2-} by $C_4H_4O_4^{2-}$.

Octacalcium bis(hydrogenphosphate) tetrakis(phosphate) pentahydrate (OCP), $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, is, structurally related to hydroxyapatite (HAp) and is a precursor in the formation of HAp in bones, teeth, and urinary calculi. The structure of OCP is composed of alternative stackings of an "apatitic layer" (A-layer) with the composition of $Ca_{12}(PO_4)_8 \cdot 2H_2O$ and a "hydrated layer" (B-layer) of $Ca_4(HPO_4)_4 \cdot 8H_2O$ which is compositionally the same as brushite ($CaHPO_4 \cdot 2H_2O$).[1] HAp and other calcium phosphates have been widely studied in interactions with organic compounds related to biological, biomaterial, and bio-chromatographic problems. According to these studies, various organic substances have been shown to be adsorbed or ion-exchanged on the surface of calcium phosphates, however in one instance there is a possibility that glycine might be introduced into the HAp structure.[2] Generally it would be reasonable to consider that organic molecules or ions are difficult to introduce into calcium phosphates, because of their large size and steric conformations. Here, although the OCP structure is not classified normally into so-called layered compounds consisting of layers bound to each other weakly by van der Waals force or hydrogen bonds, we would expect from structural considerations that OCP must behave more actively towards organic compounds than HAp and other calcium phosphates and might incorporate some organic substances into the B-layer. In this work, we present data supporting the idea that succinate ions can be introduced into the B-layer.

Experimental

Powdery α-tricalcium bis(phosphate) (α-TCP), α-$Ca_3(PO_4)_2$, was used for the synthesis of a reference OCP (ref-OCP) and a succinate-containing OCP (succinate-OCP). The α-TCP was prepared by heating an equimolar mixture of γ-$Ca_2P_2O_7$ and $CaCO_3$ at 1200 °C for 1 h.[3] The ref-OCP was prepared by the hydrolysis of α-TCP in a 0.5 M (1 M=1 mol dm^{-3}) sodium acetate solution of 50 °C at a pH of 5.4±0.1 for 3 h. This procedure was a modification of the method developed previously.[4] The succinate-OCP was prepared by conducting the hydrolysis in the presence of 0.25 M succinate ions at 40 °C and at an initial pH of 6.0±0.1 for 3 h. The resulting OCP samples were dried at 40 °C and their products calcined at several temperatures were examine by X-ray diffraction, heating weight loss and Ca/P ratio. The chemical analyses for CaO and P_2O_5 were performed by a chelatometric EDTA titration method and a spectrophotometric molybdovanadophosphate method, respectively. The basal spacing of the OCP structure was taken from the (100) reflection.

Results and Discussion

A change in the basal spacing was observed for the succinate-OCP, and this is the most direct and reliable indication of the introduction of succinate into the OCP structure. Table 1 lists the basal spacings, Ca/P ratios of the ref-OCP and succinate-OCP with some relevant data. The data about the ref-OCP were admitted within experimental errors as those of OCP having adsorbed water. The succinate-OCP showed an expansion in basal spacing and an increased in Ca/P ratio, compared with the ref-OCP. Such changes keeping the OCP structure suggested that the replacement of HPO_4^{2-} by $C_4H_4O_4^{2-}$ took place within the structure, not on the surface. From a structural point of view on the OCP unit-cell structure,[1] it was speculated that two of the four HPO_4^{2-} groups within the B-layer seemed more exchangable than the other two HPO_4^{2-} groups which were considered to be tightly bound by sharing one oxygen of HPO_4^{2-} in the A-layer. Therefore, the two HPO_4^{2-} groups would posses a comparatively high probability for the replacement. A general formula was established to be $Ca_8(HPO_4)_{2-z}(PO_4)_4(C_4H_4O_4)_z \cdot mH_2O$ z=0—1. The succinate-OCP had the composition $Ca_8(HPO_4)_{1.17}(PO_4)_4(C_4H_4O_4)_{0.83} \cdot 5.5H_2O$. Here, the value of z was determined from the Ca/P ratio (1.55), and m was estimated by distributing the residual amount (19.5%), except the analytical amounts of Ca (31.8%) and PO_4 (48.7%), among 1.17(H), 0.83 ($C_4H_4O_4$), and m(H_2O). Similarly, the ref-OCP was $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5.1H_2O$. Repeated runs with a little difference in initial pH seemed to cause sensitively variations within the ranges $0.7 \lesssim z < 1.0$ and $5 \lesssim m \lesssim 7$.

Table 1. Charactors of succinate-OCP in comparison with ref-OCP

Prepared OCP	Basal spacing d_{100}/Å	Ca/P (mole ratio)	Weight loss/%[a]			Calcination product by X-ray[a]		Composition[b]	
			400 °C	700 °C	900 °C	700 °C	900 °C	z	m
Ref-OCP	18.7	1.34	9.8	11.1	11.4	Ap	β-T, β-Py	0	5.1
Succinate-OCP	21.5	1.55	10.3	13.2	17.4	Ap	α-T, β-T, Ap	0.83	5.5

a) Heated up to each temperature at 10 °C min^{-1}. Ap: Apatitic phase, α- and β-T: α- and β-$Ca_3(PO_4)_2$, β-Py: β-$Ca_2P_2O_7$. b) A general formula was assumed as $Ca_8(HPO_4)_{2-z}(PO_4)_4 (C_4H_4O_4)_z \cdot mH_2O$. See in the text.

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