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Structure and Properties of the Condensed Phosphates. XIV. Calcium Polyphosphates

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The known crystalline calcium phosphates in the polyphosphate region of composition all exhibit straight-chain anions. Trömelite is a pentapolyphosphate whereas, α-, β-, γ- and δ-calcium metaphosphates are all long-chain phosphates. There is also a dicalcium tripolyphosphate. Vitreous calcium phosphates consist of a bell-shaped distribution of various sized chain anions. The sodium calcium salt having the formula $Na_4CaP_6O_{18}$ is a trimetaphosphate.

In the polyphosphate region of composition[2] there are a number of calcium phosphates. The $CaO-P_2O_5$ phase diagram[3] covering this region shows two pyrophosphates [α- and β- $Ca_2P_2O_7$], a crystalline species called trömelite, and two metaphosphates [α- and β-$Ca(PO_3)_2$]. All of these crystalline materials exhibit considerable regions of solid solution, so that a specific empirical composition cannot be assigned to a given crystal X-ray diffraction pattern. Several other crystalline calcium phosphates also have been produced in the thermal decomposition of monocalcium phosphate.[4] Two of these compounds exhibit a $(CaO+H_2O)/P_2O_5$ mole ratio a little greater than unity. They have been called γ- and δ-calcium metaphosphate. Another crystalline compound having the empirical composition $4CaO{\cdot}H_2O_3P_2O_5$ has been called "tetracalcium dihydrogen hexaphosphate." Glasses can readily be made throughout the entire polyphosphate region of the $CaO-P_2O_5$ system. The molecular constitutions of several typical glasses as well as of the crystalline compounds described above are reported in this paper. In addition, structural information is also given for the crystalline sodium calcium metaphosphate[5] exhibiting the empirical formula $Na_4Ca(PO_3)_6$.

Experimental

Samples Studied.—The β-, γ- and δ-calcium metaphosphates and the so-called "tetracalcium dihydrogen hexaphosphate" were obtained from Dr. W. L. Hill of the United States Department of Agriculture at Beltsville, Maryland. These are the same samples described in refs. 3 and 4. The sodium calcium metaphosphate came from Dr. G. W. Morey of the United States Department of the Interior, Geological Survey, Washington, D. C. The trömelite and α-calcium metaphosphate were made in this Laboratory, as were three vitreous calcium phosphates having CaO/P_2O_5 mole ratios of 7/5, 9/7 and 1/1. A number of different preparations of trömelite were made and found by X-ray to have varying amounts of meta- and pyrophosphate impurities. The preparation which was finally chosen for careful study was predominately trömelite with a small amount of β-calcium pyrophosphate, according to its X-ray diffraction powder pattern. The CaO/P_2O_5 mole ratio of this preparation was exactly 7/5.

All calcium phosphates made in our Laboratory were prepared by grinding together the proper ratio of mono- and dicalcium orthophosphates [reagent grade $Ca(H_2PO_4)_2{\cdot}H_2O$ and Monsanto pharmaceutical grade $CaHPO_4$] and heating the resulting uniform, finely divided mixture. The crystalline compounds were obtained by heating the proper orthophosphate mixture for several days at the correct temperature according to the phase diagrams.[3] The glasses resulted from quenching melts having the proper CaO/P_2O_5 ratios between heavy copper chill plates. The glasses were clear, and showed no signs of crystallinity.

Preparation of Solutions.—The calcium phosphates are all insoluble in water and must be dissolved by special means. A considerable amount of effort was spent on finding the optimum method of dissolving the substances being investigated in order that the molecular composition of the solutions would represent that of the respective solids. In a preliminary study, the sodium form of an ion-exchange resin was slurried with the finely powdered calcium phosphate. Under these conditions, the vitreous calcium phosphates were completely dissolved in three days but the trömelite proved too difficult to dissolve by this method.

The best solvent was found to be a 3% solution of disodium ethylenediaminetetraacetate dihydrate, $Na_2H_2[(CO_2CH_2)_2N(CH_2)_2N(CH_2CO_2)_2]{\cdot}2H_2O$, adjusted to a *p*H of 7.0–7.3 with sodium hydroxide. When lower concentrations of the ethylenediaminetetraacetate were used, the rate of dissolution became inordinately slow. Higher concentrations were not generally employed because of gel formation with some of the samples. Thus, when a 6% solution of the ethylenediaminetetraacetate was used on δ- and γ-calcium metaphosphates, the powdered samples gelatinized instead of dissolving. The *p*H was always kept in the neutral region so as to reduce hydrolysis of the condensed phosphates during dissolution.

The calcium phosphates could be divided into several groups on the basis of their rate of dissolution in the aqueous ethylenediaminetetraacetate solvent. In all cases, about 50 mg. of the finely-powdered calcium phosphate was put into 20 ml. of the ethylenediaminetetraacetate solution in a large test-tube agitated by a magnetic stirrer, at room temperature. The glasses were found to dissolve completely within an hour, whereas the α-calcium metaphosphate took three days to dissolve. The β-calcium metaphosphate, "tetracalcium dihydrogen hexaphosphate" and the sodium calcium metaphosphate were essentially all dissolved in six days. The δ- and γ-calcium metaphosphates were found to be more slowly soluble, with about 91 and 65%, respectively, dissolving in six days. The trömelite was the most slowly soluble, with about 40% dissolving in seven days.

Since the trömelite dissolves so slowly, it was necessary to make measurements on solutions resulting from only partial dissolution of a sample. Therefore, the dissolution of the trömelite was studied rather carefully to find out whether or not any fractionation of molecular species would be observed. The experiments indicated that the β-calcium metaphosphate, which often is found with trömelite, is extracted in the first few days but that the β-calcium pyrophosphate remains behind. On the basis of our experiments, we could not determine whether β-calcium pyrophosphate dissolved much more slowly or nearly as fast as the trömelite. Both X-ray data on leached samples and multiple extractions of a given sample indicated that the trömelite did not correspond to two or more major molecular species, which were separated by the partial dissolution of the sample.

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(2) The polyphosphate region lies between $M_2O{\cdot}P_2O_5$ and $2M_2O{\cdot}P_2O_5$, where M stands for one equivalent of a cationic substance (*e.g*, a metal or hydrogen) or the organic radical of an alcohol or phenol esterified by the phosphate. The polyphosphate generic formula is $M_{n+2}P_nO_{3n+1}$. In accordance with common usage, the prefix *poly-* is used instead of the correct term *ina-* to denote a chain phosphate. Thus the chain based on three phosphorus atoms is called tripolyphosphate. The metaphosphate composition, $M_2O{\cdot}P_2O_5$, may correspond either to rings (the so-called "true" metaphosphates) or to the longer chains.

(3) W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 457, 542 (1944).

(4) W. L. Hill, S. B. Hendricks, E. J. Fox and J. G. Cady, *Ind. Eng. Chem.*, **39**, 1667 (1947).

(5) G. W. Morey, THIS JOURNAL, **74**, 5783 (1952).

TABLE I

PAPER CHROMATOGRAPHY[6] OF CALCIUM POLYPHOSPHATES

	% of total phosphorus as the following phosphate									
Phosphate	Ortho	Pyro	Tripoly	Tetra-poly	Penta-poly	Hexa-poly to ennea-poly	Non-moving	Tri-meta	Tetra-meta	Higher rings
Trömelite	1.5	9.9	5.5	0	83.1	0	0	0	0	0
"Tetracalcium dihydrogen hexaphosphate"	7.1	10.8	82.1	0	0	0	0	0	0	0
	4.2	7.3	88.5	0	0	0	0	0	0	0
α-Calcium metaphosphate	1.5	0	0	0	0	0	98.5	0	0	0
β-Calcium metaphosphate	0.3	0	0	0	0	0	99.7	0	0	0
γ-Calcium metaphosphate	7.7	3.5	30.3	0	0	0	58.8	0	0	0
δ-Calcium metaphosphate	14.9	11.3	5.8	0	0	0	68.0			
Sodium calcium trimetaphosphate	0	0	0	0	0	0	0	0	100	0

Evaluation Methods.—Both one-dimensional and two-dimensional paper chromatography were carried out according to the procedures[6] developed in this Laboratory. In addition, dilute-solvent chromatography[7] was employed on the crystalline calcium metaphosphates and the vitreous calcium phosphates to estimate the molecular weight. When the acid chromatographic solvent is diluted with approximately an equal part of water, the long chain phosphates move from the origin of the chromatogram and form a band extending in the direction of the solvent flow. From the size and placement of this band, an estimate can be made of the average chain length and distribution of chain lengths in a sample. Since calcium was found to affect the rate of motion of the long chain phosphates on such a dilute-solvent chromatogram, the calcium phosphates studied by dilute-solvent chromatography were dissolved in a solution containing 3% of the disodium ethylenediaminetetraacetate dihydrate, with *p*H adjusted to 7.3 and the concentrations of phosphorus, calcium, sodium and potassium all adjusted to 17 meq./l., and chloride to 34 meq./l.

The average molecular weight and distribution of molecular sizes in the shorter-chain vitreous calcium phosphates were also determined by a modification of Westman's chromatographic procedure.[8] In this case, the relatively readily soluble glasses were put into solution by use of the sodium form of finely divided Amberlite-120 ion-exchange resin (< 100 mesh particles).

The light scattering technique[9] also was employed to determine the molecular weight of the vitreous and crystalline calcium metaphosphates. For the α- and β-crystalline varieties, as well as for the glasses, a 6% ethylenediaminetetraacetate solution was employed as solvent. Sodium bromide was not used because it caused gel formation. The usual 3% solution of ethylenediaminetetraacetate was employed with the δ- and γ calcium metaphosphates, since higher concentrations caused salting out. The only other deviation from the published procedure[9] was the use of a cellulose ester filter with an average pore radius of 0.5 μ to clean up the solutions. This was an H. A. white, plain filter from the Millipore Filter Corp. of Watertown, Massachusetts.

Results and Conclusions

Calcium Pentapolyphosphate, $Ca_7(P_5O_{16})_2$.—As shown by the example given in Table I, paper chromatography indicates that trömelite is a pentapolyphosphate. The presence of ortho-, pyro- and tripolyphosphate in the solution is mainly attributable to partial hydrolysis during the period of a week taken to dissolve the sample. In addition, some of the pyrophosphate came from the small amount of β-pyrophosphate accompanying the trömelite.

The fact that trömelite corresponds to an area of solid solution as do the calcium metaphosphates and calcium pyrophosphates indicates that a small amount of different sized chains can be incorporated into the crystal without disturbing the lattice. Be this as it may, trömelite must be considered as a calcium pentapolyphosphate[10] just as the pyrophosphate is a dipolyphosphate.

Dicalcium Tripolyphosphate, $Ca_2HP_3O_{10}$.—The crystalline compound previously called[4] "tetracalcium dihydrogen hexaphosphate" is a tripolyphosphate, as indicated by the results shown in Table I for solutions of two different samples. It should be noted that, although a normal salt of the tripolyphosphate anion does not appear in the $CaO-P_2O_5$ phase diagram, at least one crystalline acid tripolyphosphate can be made.

Crystalline Calcium Metaphosphates, $Ca_{(n+2)/2}P_nO_{3n+1}$ for Large Values of n.—The data in Table I indicate that α-, β-, γ- and δ-calcium metaphosphates are all long-chain compounds, since rings were not detected in two-dimensional paper chromatography. The light-scattering measurements show that the α and β modifications are chains having a weight-average number of phosphorus atoms equal to *ca.* 10,000. On the other hand, the δ and γ modifications correspond to much smaller chain lengths, the weight average being about 200–600. In a less quantitative fashion, the dilute-solvent chromatography agrees with these degrees of polymerization. Furthermore, it shows that there is a distribution of molecular weights in all of the solutions. This means that the crystalline calcium metaphosphates are similar to the Kurrol's salts, and to crystalline organic high polymers, in that there is a distribution of various length chains in a given crystal. Although it was not investigated, the average chain length can presumably vary from one preparation to another of the calcium metaphosphates. According to the analyses presented by Hill *et al.*,[4] the γ- and δ-metaphosphates contain some water. This accounts for the relatively short chain lengths observed in these preparations. The structural similarity between δ-calcium metaphosphate and the anhydrite form of calcium sulfate is interesting in view of the chain structure of the phosphate anions. It would be desirable to have a detailed

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(6) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

(7) S. Ohashi and J. R. Van Wazer, manuscript being prepared for publication.

(8) M. J. Smith, Ontario Research Foundation Report 5703, Separation and Colorimetric Determination of Phosphate Mixtures and Glasses (August 8, 1957). Also see J. P. Crowther, *Anal. Chem.*, **26**, 1383 (1954); and A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 758 (1956).

(9) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).

(10) J. R. Van Wazer and S. Ohashi, *ibid.*, **80**, 1010 (1958).

crystal structure analysis of δ-calcium metaphosphate.

Calcium Phosphate Glasses, $Ca_{(n+2)/2}P_nO_{3n+1}$ for n = 5, 7 and *ca.* 20.—The molecular weight of the calcium phosphate glass made by heating monocalcium orthophosphate to 1400° for 2 hr. and quenching the melt was determined by means of light scattering. It was found to correspond to a weight average of *ca.* 20 phosphorus atoms per chain, on the assumption of a straight-chain structure. The dilute-solvent paper chromatography gives rough agreement with this value and a distribution of sizes in qualitative agreement with the size distributions observed for similar sodium phosphate glasses having about the same degree of polymerization.

Application of the Westman paper chromatographic procedure to the glasses having number average chain lengths of 5 and 7 gave the results shown in Table II, where the experimental data is compared with the theoretical[11] distribution for rigid-rod molecule ions. Like all of the other phosphate glasses which have been studied,[12,13] there is no detectable orthophosphate in fresh solutions of the calcium phosphate glasses exhibiting a CaO/P_2O_5 mole ratio less than unity. It should also be noted that the experimentally observed distribution function is sharper than that theoretically calculated.[13] This is true also in the region of intermediate average chain lengths for the lithium, sodium and potassium phosphate glasses.[14] The fact that the three alkali metal ions and the calcium ion each led to a unique set of size-distribution curves in the vitreous phosphates shows that second-order parameters, at least those involving packing of the atoms, must be taken into account to obtain exact size-distribution curves.[11]

The inordinately large amount of pentapolyphosphate found in both glasses described in Table II indicates that pentapolyphosphate and calcium ions fit together especially well, even in an amorphous structure made up of various sized anions. Obviously, the presence of some undetected crystalline trömelite in the glasses would invalidate this idea.

The findings presented here on calcium phosphate glasses lead to the conclusion that they—like the sodium phosphate glasses—are a mixture of chain phosphates. Obviously, the data presented for the calcium phosphates are not as conclusive as the great bulk of evidence[13] which has been amassed to show that the vitreous sodium phosphates consist of a mixture of chain homologs, with a small percentage of rings building up as the average chain length increases. However, it is reasonable to believe that this is also the case for the vitreous calcium phosphates.

TABLE II

DISTRIBUTION OF CHAIN LENGTHS IN CALCIUM PHOSPHATE GLASSES

% of total phosphorus as the following Phosphate	Pentapolyphosphate glass			Heptapolyphosphate glass		
	experiment A	B	rigid rod theory[11]	experiment A	B	rigid rod theory[11]
Ortho	0	0	0.0	0	0	0.0
Pyro	2	2	6.2	3	2	3.1
Tripoly	6	7	10.1	4	4	4.8
Tetrapoly	13	14	13.1	7	7	6.3
Pentapoly	20	19	14.6	14	14	7.5
Hexapoly	9	10	14.3	7	9	8.3
Heptapoly	9	8	12.5	7	8	8.9
Octapoly	8	8	10.0	8	8	8.6
Higher homologs	34	30	19.2	51	47	52.5

Sodium Calcium Trimetaphosphate, $Na_4Ca(P_3O_9)_2$.—The mixed sodium calcium metaphosphate discovered by Morey, according to the chromatographic data presented in Table I, is a trimetaphosphate. This means that it must exhibit the formula $Na_4Ca(P_3O_9)_2$, where the $P_3O_9^{3-}$ ion is based on a six-membered ring of alternating phosphorus and oxygen atoms. The formula of this salt is quite different from that of the alkaline earth metal trimetaphosphates precipitated from aqueous solution by the early investigators.[15] These precipitated double salts exhibited 1:1 ratios of alkali metal to alkaline earth metal so that they fortuitously could be used to "prove" the trimeric structure of the metaphosphate, which we still recognize as a trimetaphosphate today on the basis of other more trustworthy evidence.[16]

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(11) J. R. Parks and J. R. Van Wazer, THIS JOURNAL, **79**, 4890 (1957).

(12) A. E. R. Westman and P. A. Gartagenis, *J. Am. Ceramic Soc.*, **40**, 293 (1957).

(13) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Chemistry, Interscience Publishing Co., New York, N. Y., 1958, Chapter 12.

(14) See pages 764–765 of ref. 13.

(15) T. Fleitmann and W. Henneberg, *Ann. Chem.*, **65**, 304 (1848); C. J. Lindbom, *Ber.*, **8**, 122 (1875); G. von Knorre, *Z. anorg. Chem.*, **24**, 381 (1900).

(16) See Chapter 11 of ref. 13.