Studies of Inorganic Ion Exchangers. VI.[1] The Formation Region and Dehydration Behavior of Various Titanium(IV) Bis(hydrogenorthophosphate) Hydrates

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The formation region, dehydration behavior, and lattice constants of various types of titanium(IV) bis(hydrogenorthophosphate) hydrates were investigated. α-$Ti(HPO_4)_2\cdot H_2O$ was formed by refluxing an amorphous titanium phosphate (ATP) with H_3PO_4 at 110—165 °C or by treating it with H_3PO_4 (up to 11.5 mol dm^{-3}) under hydrothermal conditions at temperatures up to 250 °C. (β-γ)-$Ti(HPO_4)_2\cdot xH_2O$ was obtained by refluxing ATP with H_3PO_4 (15—16 mol dm^{-3}) above 165 °C. γ-$Ti(HPO_4)_2\cdot 2H_2O$ was formed by a hydrothermal reaction of ATP and H_3PO_4 (10—16 mol dm^{-3}) at 200—300 °C. In the thermal analysis of $Ti(HPO_4)_2$, no difference in weight loss was found at temperatures up to 920 °C of α-form irrespective of the drying conditions of the samples. The (β-γ)-form dried under reduced pressure over P_2O_5 had a composition corresponding to that of a 1/2 hydrate. The γ-form dried at a relative humidity of 75% had a composition identical to that of the dihydrate. In view of the X-ray diffraction, it seemed that the (β-γ)-form (11.6 and 9.2 Å) was changed by drying under reduced pressure over P_2O_5 to the β-form (9.2 Å) as anhydride. The γ-form (11.6 Å) was dehydrated to the β-form by heating. The change in the inter-layer distance upon dehydration was also confirmed by means of a that of the electron diffraction. Thus, it was considered that the (β-γ)-form was a mixture as a quasi stable form.

Various types of titanium(IV) bis(hydrogenorthophosphate) hydrates have been synthesized by refluxing amorophous titanium phosphate with phosphoric acid, and their peculiar ion-exchangeability has been investigated.[1-5] α-$Ti(HPO_4)_2\cdot H_2O$[6] was formed at phosphoric acid concentrations of 13—62%, while $Ti(HPO_4)_2\cdot 0$—1/2 H_2O was obtained at 64% or higher.[2,3] Alluli *et al.*[7] synthesized $Ti(HPO_4)_2\cdot 2H_2O$ by heating amorphous titanium phosphate with 10 mol dm^{-3} of phosphoric acid at temperatures of 200 °C or higher in a sealed tube. They suggested that the crystal structure of this compound was not identical with that of α-$Ti(HPO_4)_2\cdot H_2O$, but similar to that of γ-$Zr(HPO_4)_2\cdot 2H_2O$.

In the present study, crystalline titanium phosphates are synthesized by refluxing and by hydrothermal reactions, and the formation regions of the individual modifications are determined.

Experimental

Preparation of Crystalline Titanium(IV) Bis(hydrogenorthophosphate). Refluxing Method: The preparation of $Ti(HPO_4)_2\cdot xH_2O$ by refluxing phosphoric acid with amorphous titanium phosphate was carried out by the method previously reported.[2,3] The products were dried by storing them in a desiccator charged with a saturated aqueous solution of urea (75—78% in relative humidity at room temperature).

Hydrothermal Reaction Method: One gram of amorphous titanium phosphate was sealed with 10 cm^3 of phosphoric acid (10—16 mol dm^{-3}) in a 20-cm^3 hard glass tube, after the tube was placed in a 200-cm^3 stainless steel autoclave with 80 cm^3 of water to prevent its rupture. The autoclave was then heated at 140—300 °C. The products in the tubes were separated from the mother liquors, washed with water, and then dried at a relative humidity of 75—78%.

Analyses: The chemical analyses of the product were carried out by the method previously reported.[2] The X-ray diffraction was performed with Ni-filtered Cu *Ka* radiation (30 kV P, 20 mA). The thermal analysis was carried out with a microthermal analyzer at a heating rate of 10 °C/min.

Electron Diffraction: The electron diffraction was performed with the aid of a Hitachi HU-12A electron microscope equipped with a standard cooling holder, HC-4. Selected area diffraction patterns were measured at 100 kV.

Results and Discussion

Formation of Various Titanium(IV) Bis(hydrogenorthophosphate). The conditions for the synthesis of $Ti(HPO_4)_2\cdot xH_2O$ by the reaction of amorphous titanium phosphate with phosphoric acid and the analytical data of the products are shown in Table 1.

Chemical Analysis and X-Ray Diffraction: In No. 1 of Table 1, α-titanium(IV) bis(hydrogenorthophosphate) monohydrate was produced by refluxing amorphous titanium phosphate with phosphoric acid at 140°C. This product was already known to have an interlayer distance of 7.6 Å[7] (Å=10^{-10} m). In Nos. 2—4, the drying conditions for the products obtained by refluxing amorphous titanium phosphate with phosphoric acid of high concentrations were different from that established hitherto, so the products gave analytical data corresponding to those of the 1/2—1 hydrate. In the X-ray diffraction diagram, the products are shown to have interlayer distances of 11.6 and 9.2 Å. When we prepared this product for the first time, we gave it the chemical formulas of $Ti(HPO_4)_2\cdot 1/2\,H_2O$[2] and also $Ti(HPO_4)_2\cdot 0$—$1/2H_2O$.[3] In the present study, however, this product gave, as has been described above, values of 1/2—1 hydrate. Accordingly, we will now designate as (β-γ)-$Ti(HPO_4)_2\cdot xH_2O$ the product shown in the past as $Ti(HPO_4)_2\cdot 0$—$1/2H_2O$.

In Nos. 5—7, hydrothermal reactions between amorphous titanium phosphate and phosphoric acid having various concentrations were carried out at 175 °C. α-$Ti(HPO_4)_2\cdot H_2O$ was formed at H_3PO_4 concentrations of 10 and 14.4 mol dm^{-3}. However, a mixture of the α- and γ-forms was formed at a H_3PO_4 concentration of 16 mol dm^{-3}.

In Nos. 8—10, when the hydrothermal reaction was

Table 1. Synthesis and analysis of titanium(IV) bis(hydrogenorthophosphate)

	Reaction conditions						Reaction products[c)]				
No.	Raw material[a)] ATP (g)	Mother liquor H_3PO_4 (mol dm^{-3})	Mother liquor Volume (cm^3)	Method[b)]	Temp °C	Time h	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	Estimated formula	X-Ray diagram (form)
1	7.0	12.8	250	REF	140	30	31.8	55.4	14.3	$Ti(HPO_4)_2 \cdot 0.9H_2O$	α
2	5.0	15.9	200	REF	170	100	32.0	56.8	11.2	$Ti(HPO_4)_2 \cdot 0.5H_2O$	$(\beta$-$\gamma)$
3	9.0	16.5	275	REF	175	50	31.6	55.9	12.5	$Ti(HPO_4)_2 \cdot 0.8H_2O$	$(\beta$-$\gamma)$
4	5.0	15.8	205	REF	170	50	31.0	55.0	14.0	$Ti(HPO_4)_2 \cdot 1.0H_2O$	$(\beta$-$\gamma)$
5	1.0	10.0	10	HTR	175	72	31.1	55.2	13.7	$Ti(HPO_4)_2 \cdot 1.0H_2O$	α
6	1.0	14.4	10	HTR	175	72	31.1	55.1	13.8	$Ti(HPO_4)_2 \cdot 1.0H_2O$	α
7	1.0	15.9	10	HTR	175	72	30.0	53.3	16.7	$Ti(HPO_4)_2 \cdot 1.5H_2O$	$\alpha+\gamma$
8	1.0	10.0	10	HTR	200	144	31.0	55.1	13.9	$Ti(HPO_4)_2 \cdot 1.0H_2O$	α
9	1.0	14.4	10	HTR	200	144	29.8	52.0	18.2	$Ti(HPO_4)_2 \cdot 1.8H_2O$	$\alpha+\gamma$
10	1.0	15.9	10	HTR	200	144	29.1	51.5	19.4	$Ti(HPO_4)_2 \cdot 2.0H_2O$	γ
11	1.0	10.0	10	HTR	250	72	31.0	54.9	14.1	$Ti(HPO_4)_2 \cdot 1.0H_2O$	α
12	1.0	14.4	10	HTR	250	72	28.6	50.8	20.6	$Ti(HPO_4)_2 \cdot 2.2H_2O$	γ
13	1.0	15.9	10	HTR	250	72	29.4	52.5	18.1	$Ti(HPO_4)_2 \cdot 1.7H_2O$	γ
14	3.0	10.0	35	HTR	280	18	29.1	51.5	19.4	$Ti(HPO_4)_2 \cdot 2.0H_2O$	γ
15	1.0	10.0	10	HTR	300	30	29.3	51.9	18.8	$Ti(HPO_4)_2 \cdot 1.9H_2O$	γ
16	1.0	12.2	10	HTR	300	30	28.9	51.4	19.7	$Ti(HPO_4)_2 \cdot 2.0H_2O$	γ
17	1.0	15.9	10	HTR	300	30	29.0	51.4	19.6	$Ti(HPO_4)_2 \cdot 2.0H_2O$	γ

a) ATP: Amorphous titanium phosphate. b) REF: Refluxing method, HTR: hydrothermal reaction method. c) The products are stored for one week in a desiccator with a relative humidity of 75% and then analyzed.

carried out at 200 °C, the product was gradually converted from the α-form to the γ-form *via* a mixture of the α- and γ-forms due to the increasing concentration of H_3PO_4. In Nos. 11—13, the hydrothermal reaction was carried out at 250 °C. The α-form was formed at a H_3PO_4 concentration of 10 mol dm^{-3}, but the γ-form was formed at 14.4 mol dm^{-3}. The hydrothermal reaction was carried out at 280 °C in No. 14 and at 300 °C in Nos. 15—17. At such an elevated temperature, γ-$Ti(HPO_4)_2 \cdot 2H_2O$ was formed at a H_3PO_4 concentration of 10 mol dm^{-3} or higher.

The Formation Regions of Various Titanium(IV) Bis(hydrogenorthophosphate) Hydrates: The formation regions of various titanium(IV) bis(hydrogenorthophosphate) are shown in Fig. 1.

The curve AB shows the relation between the temperature of phosphoric acid and its concentration. The solid phase formed under the reaction conditions on the curve AB was α-$Ti(HPO_4)_2 \cdot H_2O$. At higher phosphoric acid concentrations, $(\beta$-$\gamma)$-$Ti(HPO_4)_2 \cdot xH_2O$ was formed as the solid phase at a refluxing temperature of 165 °C or higher. The conditions for forming this product are shown by a dotted line (BC) as an extension of the solid line (AB). The regions of the formation of the α- and γ-forms by the hydrothermal reaction are separated by a curve MN. A mixture of the α- and γ-forms was formed in the vicinity of the curve.

Water of Crystallization of Various Titanium(IV) Bis(hydrogenorthophosphate) Hydrates: Table 1 shows the percentages of H_2O calculated from the weight loss at 700 °C of the reaction product stored in a desiccator at a relative humidity of 75—78%. As the water content varies according to the degree of drying, the DTA and TG of α-, $(\beta$-$\gamma)$-, and γ-titanium(IV) bis(hydrogenorthophosphate) differed in drying conditions, as Figs. 2, 3, and 4 show.

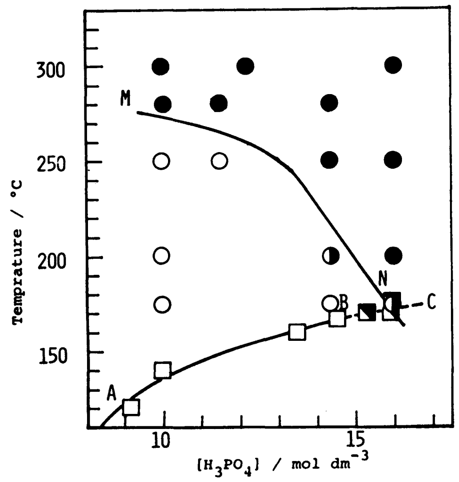

Fig. 1. Formation region of titanium(IV) bis(hydrogenorthorhosphate).
○, ◩: α-$Ti(HPO_4)_2 \cdot H_2O$, □ $(\beta$-$\gamma)$ $Ti(HPO_4)_2 \cdot xH_2O$, ◑: $\alpha+\gamma$-$Ti(HPO_4)_2 \cdot 1$—$2\ H_2O$, ●: γ-$Ti(HPO_4)_2 \cdot 2H_2O$. Reflux is indicated with square signs. Hydrothermal reaction is indicated with circular signs.

α-$Ti(HPO_4)_2 \cdot H_2O$: In the DTA curve of Fig. 2, the broad endothermic peak appearing at temperatures below 100 °C is caused by the dehydration of free water attached to the sample. The endothermic peaks at 260 and 510 °C are due to the liberation of the water of crystallization and condensation. The weight losses at 200 °C of the samples dried at relative humidities of 100 and 75% and under reduced pressure over P_2O_5 were as small as 2.0, 0.9, and 0.8% respectively, thus

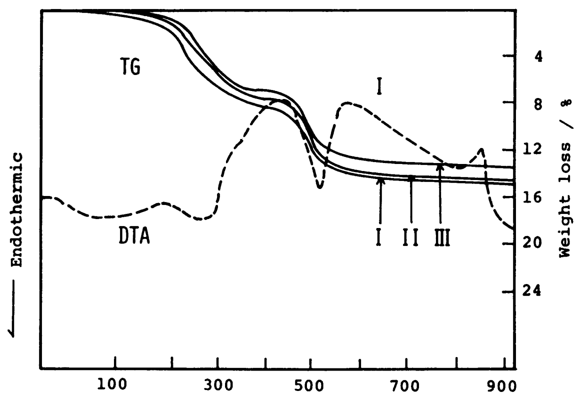

Fig. 2. DTA and TG curves for α-titanium(IV) bis(hydrogenorthophosphate). I: Product stored in relative humidity 100%. II: Product stored in relative humidity 75%. III: Product vacuum-dried over P_2O_5.

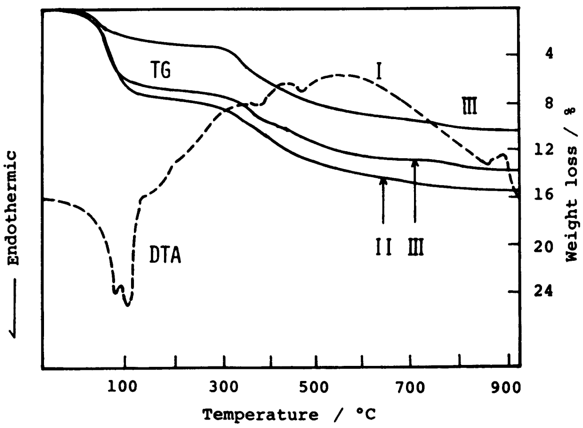

Fig. 3. DTA and TG curves for (β-γ)-titanium(IV) bis(hydrogenorthophosphate).
I: Product stored in relative humidity 100%. II: Product stored in relative humidity 75%. III: Product vacuum-dried over P_2O_5.

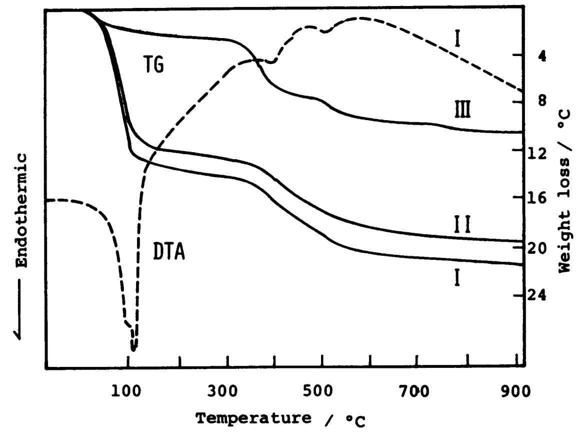

Fig. 4. DTA and TG curves for γ-titanium(IV) bis(hydrogenorthophosphate).
I: Product stored in relation humidity 100%. II: Product stored in relative humidity 75%. III: Product vacuum-dried over P_2O_5.

permitting the assumption that the water of crystallization of α-$Ti(HPO_4)_2 \cdot H_2O$ is strongly combined with the salt. The weight losses of the individual samples by heating up to 900 °C were 15.0, 14.2, and 13.3% respectively. These values approximately equal a theoretical value of 13.9 (%) ($2H_2O$/α-$Ti(HPO_4)_2 \cdot H_2O \times 100$).

(β-γ)-$Ti(HPO_4)_2 \cdot xH_2O$: In the DTA curve of Fig. 3, a big endothermic peak resulting from dehydration appears at about 100 °C. Two small endothermic peaks resulting from condensation appear at 370 and 464 °C. In the TG curve of Fig. 3, the weight losses at 200 °C of the samples dried at relative humidities of 100 and 75% and under reduced pressure over P_2O_5 were 8.5, 7.0, and 3.0% respectively. These values were extremely large as compared with those of the above described α-$Ti(HPO_4)_2 \cdot H_2O$. In the case of (β-γ)-$Ti(HPO_4)_2 \cdot xH_2O$, the interlayer distance was so great that the water contained therein was easily eliminated by heating at a relatively low temperature. The weight losses at 920 °C of (β-γ)-$Ti(HPO_4)_2 \cdot xH_2O$ dried at relative humidities of 100 and 75% and under reduced pressure over P_2O_5 were 15.5, 12.5, and 10.4% respectively. Only the weight loss of the sample which had been dried under reduced pressure over P_2O_5 agreed with the calculated value of 10.86 (%) ($1.5\,H_2O/Ti(HPO_4)_2$-$1/2\,H_2O \times 100$).

γ-$Ti(HPO_4)_2 \cdot 2H_2O$: Allulli *et al.*[7] measured the TG of titanium(IV) bis(hydrogenorthophosphate), which was regarded identical with the γ-form, and gave this compound the chemical formula of $Ti(HPO_4)_2 \cdot 2H_2O$. In the DTA curve of Fig. 4, a slightly branched endothermic peak by dehydration appears at about 100 °C, while endothermic peaks by condensation appear at 390 and 498 °C, in a tendency similar to that of the DTA curve of the (β-γ)-form. In the TG curve of Fig. 4, the weight losses at 200 °C of the samples dried at relative humidities of 100 and 75% and under reduced pressure over P_2O_5 were 13.6, 12.0, and 2.4% respectively. A substantial part of the water of crystallization in each sample was released up to the above temperature. The weight loss at 920 °C of only the sample dried at a relative humidity of 75% was in agreement with the calculated value of 19.6 (%) ($3H_2O/Ti(HPO_4)_2 \cdot 2H_2O \times 100$).

Change in the Interlayer Distance of (β-γ)- and γ-Titanium(IV) Bis(hydrogenorthophosphate). Clearfield *et al.*,[8] who first synthesized γ-$Zr(HPO_4)_2 \cdot 2H_2O$ with an interlayer distance of 12.2 Å, obtained β-$Zr(HPO_4)_2$ with an interlayer distance of 9.4 Å by drying the γ-form under reduced pressure over anhydrous calcium sulfate for several weeks at room temperature. In the present studies, we have confirmed whether or not the interlayer distance of titanium(IV) bis(hydrogenorthophosphate) is also changed by drying.

In the case of α-$Ti(HPO_4)_2 \cdot H_2O$, the interlayer distance (7.6 Å) of the samples was not changed by the drying conditions.

(β-γ)-$Ti(HPO_4)_2 \cdot xH_2O$ synthesized by the refluxing method had a composition of approximately 0.7 hydrate at a relative humidity of 75%, and it showed X-ray diffraction peaks at 11.6 and 9.2 Å. The occurrence

TABLE 2. SPACINGS OF VARIOUS TITANIUM (IV) BIS(HYDROGENORTHOPHOSPHATE) HYDRATES DETERMINED BY MEANS OF THE ELECTRON-DIFFRACTION PATTERNS

			α-Ti(HPO$_4$)$_2$·H$_2$O			β-Ti(HPO$_4$)$_2$				γ-Ti(HPO$_4$)$_2$·2H$_2$O		
h	(1) k	l	(2) d_{obsd}/Å	(3) $d/_{calcd}$/Å	(4) d_x/Å	(5) d_{obsd}/Å	(6) d_{calcd}/Å	(7) d_x/Å	(8) d_{obsd}/Å	(9) d_{obsd}/Å	(10) d_{calcd}/Å	(11) d_x/Å
0	0	2	7.52	7.618	7.62	9.34	9.211	9.21	9.32	11.26	11.62	11.62
0	1	1	5.03	4.955		6.07	6.037		6.06	6.21	6.026	
0	1	2	4.34	4.317		5.25	5.250	5.21	5.22	5.63	5.633	5.57
1	0	$\bar{1}$		8.634		5.18	5.183			5.29	5.289	
0	1	3	3.59	3.647	3.68		4.428	4.48	4.57	5.00	4.953	
1	0	1		6.647		4.71	4.727				4.778	
1	0	$\bar{3}$	5.12	5.083		4.35	4.332				4.850	
1	0	2	5.03	4.989		4.16	4.176		4.14		4.328	4.28
1	$\bar{1}$	$\bar{1}$	4.53	4.480		4.04	4.025			4.09	4.087	
1	1	0	4.43	4.466		4.01	3.999		4.01	4.00	4.015	
1	$\bar{1}$	$\bar{2}$	4.11	4.147	4.02	3.94	3.869			4.05	4.036	
1	$\bar{1}$	2	3.55	3.613			3.496		3.52		3.592	
1	0	$\bar{5}$	3.09	3.188		3.29	3.281			3.96	3.950	
1	0	3	3.88	3.883			3.631	3.64			3.873	
0	2	0	2.62	2.620	2.61	3.21	3.195		3.18	3.21	3.220	
1	0	4	3.12	3.145	3.15	3.16	3.159			3.45	3.458	3.45
0	2	$\bar{1}$	2.54	2.582	2.53	3.15	3.148			3.19	3.190	
1	0	$\bar{7}$	2.26	2.279	2.24		2.531			3.16	3.155	3.16
0	$\bar{2}$	2	2.34	2.478	2.49	3.03	3.018		3.06		3.103	
1	0	5	2.33	2.328	2.38	2.78	2.768			3.10	3.096	3.02
0	2	4	2.16	2.159	2.24	2.62	2.625		2.63		2.816	
2	0	$\bar{1}$	4.49	4.474			2.603		2.61	2.61	2.622	
1	2	1	2.37	2.437	2.38		2.647			2.67	2.670	
2	0	0	4.27	4.269	4.27	2.56	2.564			2.57	2.567	2.57
2	0	$\bar{2}$	4.34	4.317		2.59	2.591				2.644	
2	$\bar{1}$	$\bar{1}$	3.47	3.403	3.45	2.40	2.411			2.42	2.428	
1	1	6	2.06	2.072			2.287			2.55	2.558	
1	$\bar{2}$	$\bar{5}$	2.05	2.024	2.02		2.289			2.50	2.496	
2	0	2	3.29	3.323		2.36	2.364				2.389	
0	3	2	1.70	1.702		2.08	2.075			2.12	2.111	

Lattice constant		Lattice constant		Lattice constant	
Measured by means of the electron-diffraction patterns	Value calculated by the least-squares method from the face indices and peak values in X-ray diffraction	Measured by means of the electron-diffraction patterns	Value calculated by the least-squares method from the face indices and peak values in X-ray diffraction	Measured by means of the electron-diffraction patterns	Value calculated by the least-squares method from the face indices and peak values in X-ray diffraction
a=8.95 Å	a=9.06 Å	a=5.21 Å	a=5.22 Å	a=5.29 Å	a=5.27 Å
b=5.24 Å	b=5.17 Å	b=6.39 Å	b=6.40 Å	b=6.44 Å	b=6.42 Å
c=15.97 Å	c=16.05 Å	c=18.72 Å	c=18.72 Å	c=23.94 Å	c=24.29 Å
β=107.4°	β=110.93°	β=100.2°	β=100.3°	β=103.9°	β=102.5°

of these two peaks is suggestive of the coexistence of the γ-form with an interlayer distance of 11.6 Å and the β-form with that of 9.2 Å. It is of interest that, when this sample was dried under reduced pressure over P$_2$O$_5$, the diffraction peak of the γ-form entirely disappeared, while the diffraction peak of the β-form alone appeaed. This compound can be converted reversible into, the γ-form by the absorption of water and into the β-form by releasing the water.

γ-Ti(HPO$_4$)$_2$·2H$_2$O synthesized by the hydrothermal reaction method had a composition corresponding exactly to that of the dihydrate at a relative humidity of 75%, and it showed an intensive diffraction peak at 11.6 Å. When the sample was dried under reduced pressure over P$_2$O$_5$, this peak was reduced in intensity, but a diffraction peak at 9.2 Å which characterized the β-form as anhydrous salt did not appear. When the water of crystallization was entirely eliminated from the sample by drying it further under heating (120 °C), the γ-form was converted into the β-form; the latter, however, tended to be converted reversibly into the γ-form by absorption of moisture in the air.

Lattice Constants. *α-Ti(HPO$_4$)$_2$·H$_2$O*: The indices of each lattice of α-Ti(HPO$_4$)·$_2$H$_2$O and the calculated values of the corresponding spacing are shown in (1) and (3) of Table 2. The patterns of this crystal may be indexed by assuming an monoclinic unit cell with dimensions of a=8.95 Å, b=5.24 Å, c=15.97

Å, and β=107.45°. The calculated spacings, "d_{calcd}" were almost entirely consistent with those measured by the selected-area electron diffraction. The results of the calculation are shown in Table 2.

γ-$Ti(HPO_4)_2 \cdot 2H_2O$: When the crystals of γ-Ti(HPO_4)$_2 \cdot 2H_2O$ under cooling below −150 °C with liquid nitrogen, were subjected to selected-area electron diffraction, interlayer water was not released; the crystal structure of the γ-form was also retained.

The values of spacing obtained from the electron-diffraction patterns are shown in Table 2(9). The index of the crystal face and the spacing of γ-Ti(HPO_4)$_2 \cdot 2H_2O$ were calculated using the lattice constants estimated from the peak values in powder X-ray diffraction and from electron-diffraction net patterns. The values of the spacing are shown in Table 2(10). These values (10) are in agreement with the values (9) obtained from the electron-diffraction patterns, if the axes a, b, and c are 5.29, 6.44, and 23.94 Å, and if the angle β is 103.9°.

β-$Ti(HPO_4)_2$: When γ-Ti(HPO_4)$_2 \cdot 2H_2O$ was irradiated with an electron beam under a high vacuum in the column of an electron microscope, the water of crystallization between the layers was released; the γ-form (dihydrate) was, therefore, converted into the β-form (anhydrate). The values of the lattice constant and of the face index, as determined by the electron-diffraction net patterns are shown in Table 2.

In comparing the lattice constants of β-Ti(HPO_4)$_2$ with these of γ-Ti(HPO_4)$_2 \cdot 2H_2O$, the a and b axes were found to be almost equal in length in the two forms, while the c axis was 23.9 Å in the γ-form, but as short as 18.7 Å in the β-form. In view of this fact, the β-form was converted from the γ-form when the interlayer water of the γ-form was eliminated from the crystal.

Electron Diffraction of (β-γ)-$Ti(HPO_4)_2 \cdot xH_2O$: To confirm (β-γ)-Ti(HPO_4)$_2 \cdot xH_2O$ as a mixture of the β- and γ-form in a quasi-stable form, we observed the electron-diffraction patterns of this compound when the water of crystallization had been eliminated by elevating the temperature by means of irradiation with an electron beam. Table 2(8) shows the measured values of the spacing obtained from the electron-diffraction patterns of the (β-γ)-from. These values were in good agreement with the values of the electron diffraction of the β-form alone, as is shown in Table 2(5). This result apparently shows that a mixture of β-Ti(HPO_4)$_2$ and γ-Ti(HPO_4)$_2 \cdot 2H_2O$ crystals was dehydrated and converted to the β-form.

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