Intercalation of Quaternary Ammonium Ions into γ-Titanium Phosphate

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The intercalation of alkyltrimethylammonium ions into γ-titanium phosphate, $\mathrm{Ti(HPO_4)_2 \cdot 2H_2O}$ (γ-TiP), was investigated to clarify the mechanism of intercalation of quaternary ammonium ions into the layered phosphate. Alkyltrimethylammonium ions with short alkyl chains (the number of carbon atoms, n=6 to 10) were scarcely intercalated into γ-TiP, while those with long alkyl chains (n=12 to 18) were easily intercalated and formed a monolayer in the interlayer region, in which the alkyl chains inclined at 57.4° to the γ-TiP layers. The increase of the number of carbon atoms in alkyl chains and the volume of the solvent in the reaction solution led to the increase of the uptakes of quaternary ammonium ions. Based on these results, some bactericides with quaternary ammonium ion structure were then intercalated into γ-TiP, and the products obtained were stable to heat.

Layered phosphates of tetravalent metals such as Ti and Zr are insoluble acid salts and known to be typical inorganic ion exchangers.[1—3] Layered phosphates can readily intercalate various organic bases such as amines[4] and exchange protonated alcohols.[5] Extensive studies on the intercalation of alkylamines into layered phosphates clearly demonstrate the formation of a bilayer in the interlayer region, in which the carbon chains incline at roughly 60° to the zirconium or titanium phosphate layers.[6—9] Recently, the intercalation of phospholipid with quaternary ammonium ion structure in γ-TiP has been reported.[10] However, the intercalation of quaternary ammonium ions has scarcely been investigated and the detailed mechanism has not yet been described.[11,12]

Quaternary ammonium salts are very useful materials as bactericides, dyes, and medicines in both industrial and pharmaceutical fields. For example, benzalkonium chloride (alkylbenzyldimethylammonium chloride) has been used as an antibacterial agent and thiamine hydrochloride (vitamin $\mathrm{B_1}$), which is closely related to metabolism of saccharide, is a very effective drug for vitamin $\mathrm{B_1}$ deficiency symptoms such as beriberi and neuritis. Intercalation of quaternary ammonium ion may lead to new functional materials that are characterized by controlling the release of quaternary ammonium ion, maximum duration of effectiveness, and good thermal stability. To produce well-designed functional materials using intercalation compounds, it is necessary to understand the mechanism of intercalation of quaternary ammonium ion especially regarding the arrangement between the sheets of layered phosphate.

Therefore, we have undertaken a fundamental study of the intercalation of quaternary ammonium ions including some bactericides into γ-TiP. The uptakes of guest molecules and the interlayer distances between the sheets of layered phosphate were measured. Based on these results and the structures of quaternary ammonium ions, the mechanism of the intercalation of quaternary ammonium ions into γ-TiP will be discussed. Also the intercalation of bactericides is presented.

Experimental

Chemicals. γ-TiP was prepared according to the procedure described in a previous paper.[13] Reagent-grade quaternary ammonium salts were used without further purification. These structural formulas are shown in Fig. 1. Unless otherwise stated, guaranteed grade reagents from Wako Chemical Industries Ltd., were used.

Intercalation Procedures. In order to investigate the effects of the number of carbon atoms (n) in alkyl chains of alkyltrimethylammonium ions on the interlayer distances of obtained intercalation compounds and their uptakes into phosphate, we first tried the following. γ-TiP (1.0 g) was suspended in 0.5 $\mathrm{dm^3}$ of 0.02 $\mathrm{mol\,dm^{-3}}$ aqueous alkyltri-

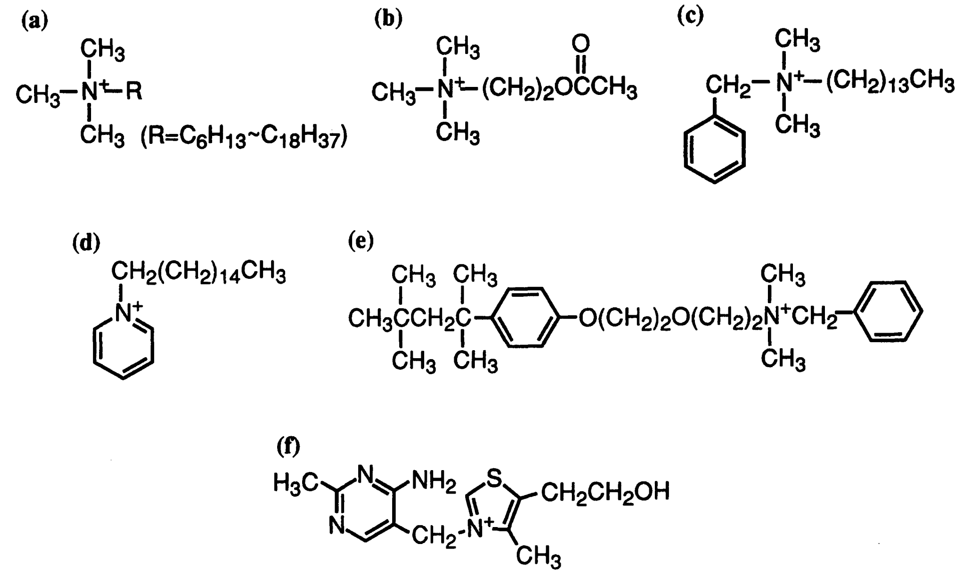

Fig. 1. Quaternary ammonium ions used in the present study. (a) alkyltrimethylammonium ion, (b) acetylcholinium ion, (c) benzalkonium ion, (d) cetylpyridinium ion, (e) benzethonium ion, (f) thiaminium ion.

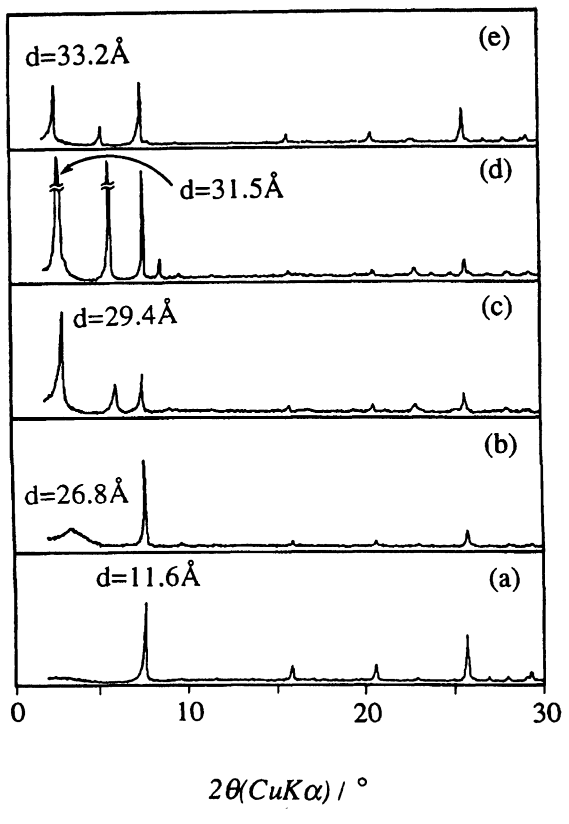

Fig. 2. X-Ray diffraction patterns of the alkyltrimethylammonium ion intercalation compounds of γ-TiP. (a) γ-TiP, (b) dodecyltrimethylammonium ion, (c) tetradecyltrimethylammonium ion, (d) hexadecyltrimethylammonium ion, (e) octadecyltrimethylammonium ion.

methylammonium bromide solution in an Erlenmeyer flask and the suspension was stirred at 40 °C for 5 h. Next, to investigate the effects of the volume of solvent on uptakes of quaternary ammonium ions, γ-TiP (1.0 g) was suspended in various volumes of aqueous solution containing 0.01 mol tetradecyltrimethylammonium bromide and the suspension was stirred at room temperature for 5 h.

Bactericide and medicine intercalation compounds were obtained by suspending γ-TiP (1.0 g) in 2 dm^3 of 0.005 $mol\,dm^{-3}$ aqueous solution of a guest compound and stirring at room temperature for 5 h. The resultant products were filtered, washed with distilled water, and dried in air.

Analytical Procedures. The X-ray diffraction patterns were measured with a Rigaku Geigerflex 2011 using Ni-filtered Cu *Kα* radiation to monitor all new phases and measure these interlayer distances. A Rigaku Denki differential thermogravimetric analyzer, TG 8110, was used with a platinum–rhodium pan in an air flow for the DTA and TG. Elemental analyses of C and N were done with a Sumigraph NC-90A.

Results and Discussion

Intercalation of Alkyltrimethylammonium Ions. Intercalation of alkyltrimethylammonium ions (the number of carbon atoms, $n=6$ to 18) into γ-TiP was examined to clarify their arrangements between the sheets of layered phosphate. Alkyltrimethylammonium ions ($n=12$ to 18) were intercalated into γ-TiP as proved by the X-ray diffraction patterns in Fig. 2. Figure 2b—e illustrates that new diffraction peaks corresponding to the intercalation compounds of alkyltrimethylammonium ions ($n=12$ to 18) appeared at a lower angle than that ($d=11.6$ Å) of host γ-TiP (Fig. 2a). Such a low angle shift in the diffraction peak clearly demonstrates that these ammonium ions are intercalated into γ-TiP with the expansion of the interlayer distances, which are estimated from the lowest angle reflection peak and specified in Fig. 2. The interlayer distance increased with the increase of alkyl chain length ($n=12$ to 18) of ammonium ions. Alkyltrimethylammonium ions of

n=6 to 10, however, were not intercalated into γ-TiP, because the X-ray diffraction patterns of the products obtained from the reaction of γ-TiP with these ammonium ions were completely the same as that of the host compound (Fig. 2a).

The interlayer distances (d) of the alkyltrimethylammonium ion (n=12 to 18) intercalation compounds of γ-TiP were plotted as a function of the number of carbon atoms (n) in the alkyl chain as shown in Fig. 3. The plot gives a straight line, suggesting that the alkyltrimethylammonium ion intercalated is regularly oriented in the interlayer region of γ-TiP and the angle to the layer is constant. The slope of the straight line is calculated to be 1.07. The length of alkyl chain increases by 1.27 Å for each additional carbon atom, assuming that the conformation of alkyl chain is all *trans* without kink and *gauche* blocks. Therefore, alkyltrimethylammonium ion forms a bilayer in layered phosphate when the slope of the straight line is higher than 1.27 and a monolayer when the value is lower than 1.27. Consequently, it is concluded that alkyltrimethylammonium ions form a monolayer in the interlayer region of γ-TiP.

The interlayer distances (d) of alkyltrimethylammonium ion intercalation compounds are expressed as the following equation,[14]

$$d\ (\text{Å}) = 14.3 + 1.27n \sin\alpha = 14.3 + 1.07n,$$

where n is the number of carbon atoms in the alkyl chain, and α is the angle of orientation of the alkyl chain to the layer. The value of 14.3 Å is the intercept of the straight line in Fig. 3. Consequently, the angle (α) of orientation of the alkyl chain to the layer calculated from this equation is $\alpha = \sin^{-1}(1.07/1.27) = 57.4°$. In intercalation of normal alkylamines into γ-TiP, it has been reported that the alkyl chains in alkylamines incline at roughly 60° to the phosphate layers.[7,9] The value of α for alkyltrimethylammonium ions is nearly equal to those for normal alkylamines. A schematic structural model of the dodecyltrimethylammonium ion intercalated into γ-TiP is shown in Fig. 4. The alkyltrimethylammonium ions form a monolayer in the interlayer region, in which the alkyl chains incline at 57.4° to the γ-TiP layers.

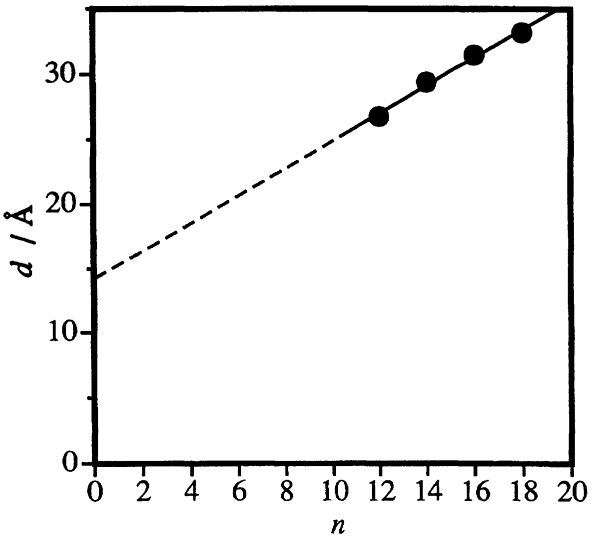

Fig. 3. Interlayer distances (d) of the alkyltrimethylammonium ion intercalation compounds of γ-TiP as a function of the number of carbon atoms (n) in the alkyl chain.

Factors Influencing the Intercalation of Quaternary Ammonium Ion. To examine the effects of the number of carbon atoms upon the facility of intercalation of quaternary ammonium ion, uptakes of alkyltrimethylammonium ions (n=6 to 18) into γ-TiP were measured by elemental analyses of C and N. Figure 5 shows the relationship between uptakes of alkyltrimethylammonium ions into γ-TiP and the number of carbon atoms (n) in the alkyl chain. The intercalations of alkyltrimethylammonium ions (n=12 to 18) into γ-TiP were confirmed also by these results, but the uptakes for n=6 to 10 were close to zero. It can be seen from Fig. 5 that increasing the number of carbon atoms up to n=16 in the alkyl chain leads to increasing the uptake.

These results are contrary to that expected from steric requirements by the ion sizes of alkyltrimethylammonium ions, and imply that the intercalation is based on both an ion-exchange reaction between host and guest and the van der Waals force between alkyl chains. The intercalation of ammonium ion must occur from electrical attraction between the O_3PO^- moiety in the layered phosphate and the N^+R_4 moiety in the ammonium ion. Only this electrical attraction is too weak to lead to the intercalation of ammonium ion. In the case of quaternary ammonium ions, particularly, because steric hindrance around N^+ may contribute to weakening the attraction, the intercalation requires the van der Waals force by which ammonium ions are tightly held in the interlayer region. Hence, alkyltri-

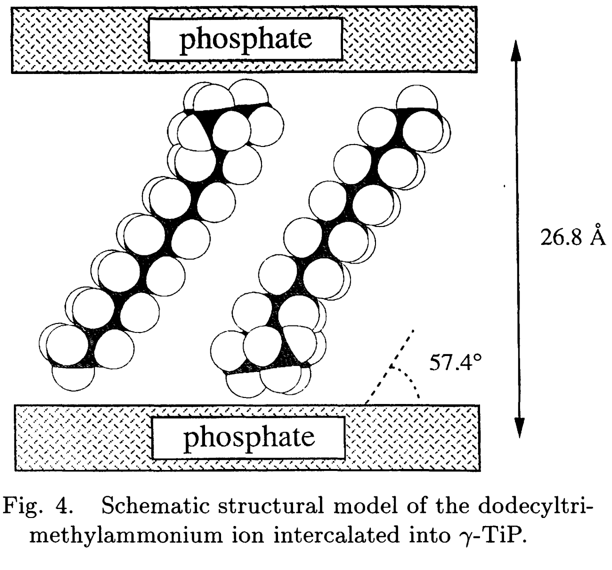

Fig. 4. Schematic structural model of the dodecyltrimethylammonium ion intercalated into γ-TiP.

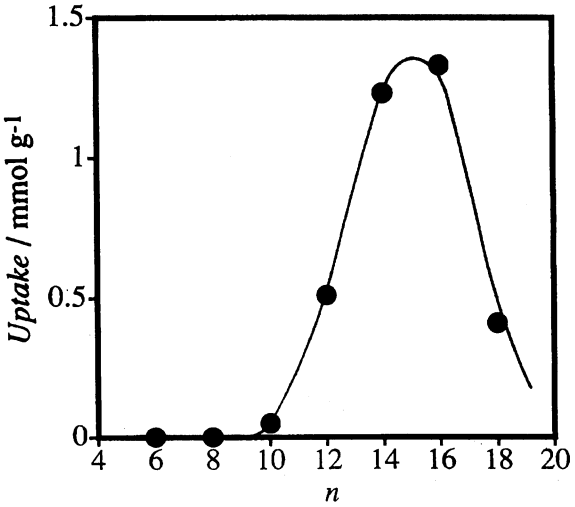

Fig. 5. Relationship between uptakes of alkyltrimethylammonium ions into γ-TiP and the number of carbon atoms (n) in the alkyl chain.

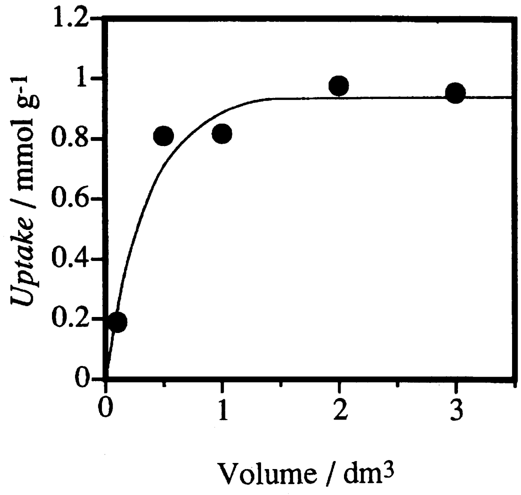

Fig. 6. Relationship between uptakes of tetradecyltrimethylammonium ions into γ-TiP and volume of solvent.

methylammonium ions with long alkyl chains, which were expected to have a strong van der Waals force between alkyl chains, can be readily intercalated into γ-TiP, but those with short alkyl chains are difficult to intercalate. On the other hand, for alkyltrimethylammonium ions with too-long chains, the influence of the molecule size of the guest should not be ignored. The fact that the uptake for $n=18$ decreased is because the ammonium ion is so large that it is difficult to insert into the interlayer region of γ-TiP. Thus, the facility of intercalation of quaternary ammonium ion is strongly influenced by the alkyl chain length of ammonium ion, and the optimum number of carbon atoms was 14 to 16.

To investigate the effects of the volume of solvent upon uptake of quaternary ammonium ion, the uptakes of the products obtained by suspending γ-TiP in various volumes of aqueous solution containing constant (0.01 mol) tetradecyltrimethylammonium ion were measured. Figure 6 shows the relationship between uptake of tetradecyltrimethylammonium ion into γ-TiP and the volume of solvent. As can be seen, for less volume of solvent, that is, in more concentrated solution, the uptake of ammonium ion was very low. However, the uptake increased with increasing the volume of solvent up to ca. 1.0 dm^3 and was approximately constant above this volume.

It is known that alkyltrimethylammonium ions with long alkyl chains form micelles over the critical micelle concentration (cmc). The size and shape of the micelles are different depending on the kind and the concentration of the surfactant. Small micelles are formed in diluted solution, and the size of the micelles increases up to an inherent size for the surfactant with increasing concentration of the solution. The formation of large micelles inhibits intercalation of alkyltrimethylammonium ions into layered phosphate.

At 40 °C, the cmc for tetradecyltrimethylammonium chloride is 4 mmol dm^{-3},[15] which corresponds to 0.01 mol in 2.5 dm^3. Above this concentration, that is, below the volume of 2.5 dm^3 in Fig. 6, tetradecyltrimethylammonium ion forms micelles in the solution assuming the cmc for tetradecyltrimethylammonium bromide at room temperature is equal to that for chloride. Alkyltrimethylammonium ions are, therefore, easy to be inserted into γ-TiP because they are in the form of a monomer or form small micelles in the solution above the volume of 1.0 dm^3 in Fig. 6, but decreasing the volume of solvent leads to decreasing the uptake owing to the increase of micelle size below 1.0 dm^3. Thus the uptakes of quaternary ammonium ions are influenced by the volume of solvent. The concentration of reaction solution should be taken into consideration when ammonium ions with long alkyl chain are intercalated.

Quaternary ammonium ions are inserted into the interlayer region of layered phosphate as a monomer or a small micelle by the electrical interaction between the O_3PO^- moiety in phosphate and the N^+R_4 moiety in ammonium ion, and then those inserted are tightly held in the interlayer region by the van der Waals force.

Intercalation of Bactericide and Medicine with Quaternary Ammonium Ion Structure. The intercalations of compounds shown in Fig. 1b—f were attempted. New diffraction peaks for intercalation compounds appeared in the X-ray diffraction patterns for benzalkonium, cetylpyridinium (N-hexadecylpyridinium), and benzethonium ions. As an example, Fig. 7 shows the X-ray diffraction pattern of the benzalkonium ion intercalation compound of γ-TiP. As can be seen, a new phase with interlayer distance 29.4 Å was formed.

The interlayer distances (d) of the other quaternary ammonium ion intercalation compounds are shown in Table 1. It is noteworthy that the interlayer distances

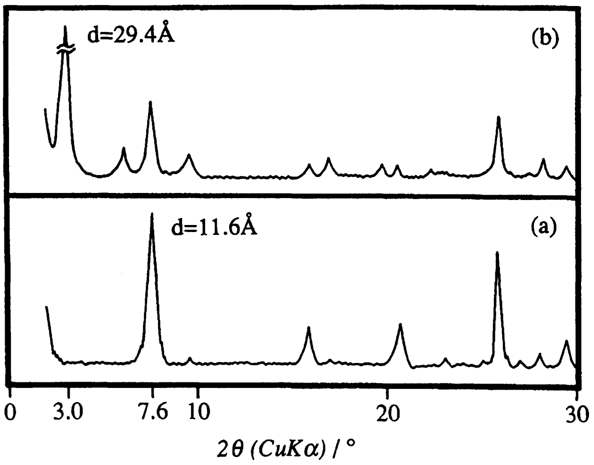

Fig. 7. X-Ray diffraction pattern of the benzalkonium ion intercalation compound of γ-TiP. (a) γ-TiP, (b) benzalkonium ion.

Table 1. Interlayer Distances (*d*) and Uptakes of Quaternary Ammonium Ions into γ-TiP

Quaternary ammonium ion	*d* / Å	Uptake / mmol/g of γ-TiP
Benzalkonium ion	29.4	1.23
Cetylpyridinium ion	32.7	1.61
Benzethonium ion	31.5	0.04
Acetylcholinium ion	11.6[a)]	0.01
Thiaminium ion	11.6[a)]	0.03

a) The same interlayer distance with γ-TiP.

for benzalkonium (n=14) and cetylpyridinium ions (n=16) were equal to those of the alkyltrimethylammonium ions having the alkyl chain of equal length (n=14 and n=16). Thus, benzalkonium and cetylpyridinium ions may form a monolayer in the interlayer region of γ-TiP. As the X-ray diffraction patterns of acetylcholinium and thiaminium ions were completely the same as that of the host compound.

As shown in Table 1, the uptakes of benzalkonium and cetylpyridinium ions with long alkyl chains were comparatively high, while those of acetylcholinium and thiaminium ions were very low. The intercalation of quaternary ammonium ion requires the van der Waals force among guest molecules as stated above. In the case of acetylcholinium and thiaminium ions, the lengths of the alkyl chains in these molecules are so short that the van der Waals force cannot act sufficiently. The lengths of alkyl chains in benzalkonium and cetylpyridinium ions are sufficiently long to make the van der Waals force act. However, the van der Waals force of benzethonium ion, with a branching chain, is weaker than those of benzalkonium and cetylpyridinium ions with long alkyl chains. Consequently, benzalkonium and cetylpyridinium ions are readily intercalated but other quaternary ammonium ions are intercalated with difficulty.

The uptake of cetylpyridinium ion was higher than that of benzalkonium ion. This is because the length (n=16) of the alkyl chain in cetylpyridinium ion is longer than that (n=14) in benzalkonium ion, that is, the van der Waals force of cetylpyridinium ion is stronger than that of benzalkonium ion. The uptake of alkyltrimethylammonium ion of n=16 was also higher than that of n=14 (Fig. 5). In addition, steric hindrance around N^+ in the cetylpyridinium ion is smaller than that in the benzalkonium ion because the reaction position of cetylpyridinium ion is N^+ in the aromatic ring. Therefore, N^+ in cetylpyridinium ion can more easily approach the P–OH group in layered phosphate than that in benzalkonium ion.

Thermal Stability of Intercalation Compound. Although the above bactericides and medicines have been extensively applied in both industrial and pharmaceutical fields, one of their defects is that such organic compounds cannot be used at high temperatures owing to their thermolability. For example, because heating at about 200 °C is necessary for the production of synthetic fiber and plastic, those including bactericides and medicines are impossible to produce. Since bactericides and medicines are expected to be rendered more stable by being held in the interlayer region of layered phosphate, we examined the thermostabilities of quaternary ammonium ions intercalated into γ-TiP. Figure 8 shows DTA and TG curves for γ-TiP, benzalkonium chloride, and the benzalkonium ion intercalation compound of γ-TiP. In the DTA curve of γ-TiP (Fig. 8a), two endothermic peaks from the dehydration of water of crystallization appeared at about

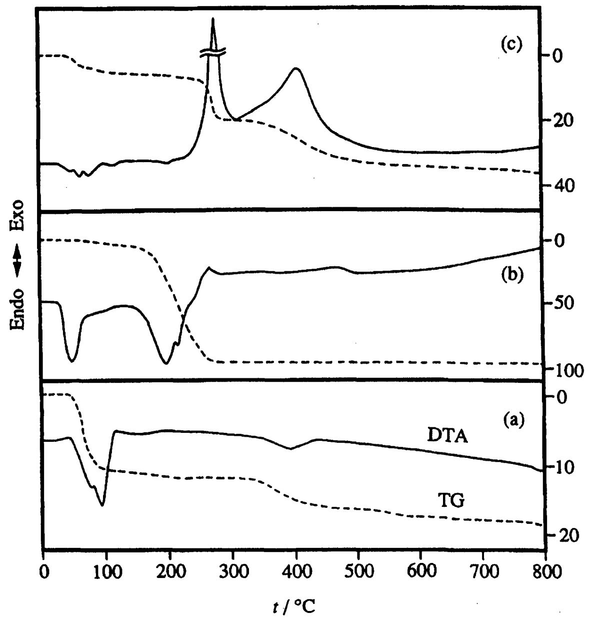

Fig. 8. DTA and TG curves of the benzalkonium ion intercalation compound of γ-TiP. (a) γ-TiP, (b) benzalkonium chloride, (c) benzalkonium ion intercalation compound.

100 °C, and an endothermic peak from the dehydration of structural water appeared at 390 °C.[16)]

As can be seen from the endothermic peak at 200 °C in Fig. 8b, benzalkonium chloride is completely vaporized at this temperature. On the other hand, in the benzalkonium ion intercalation compound (Fig. 8c), two large exothermic peaks appeared at about 280 and 410 °C with the weight losses of 13.9 and 14.8%, respectively. A part of benzalkonium ion intercalated into γ-TiP was found to be carbonized because the sample became partially gray after calcination at 800 °C. Also, the results of DTA and TG indicated that benzalkonium ion intercalated into γ-TiP is kept in the interlayer region up to 280 °C without vaporization. It was thus proved that thermal stable materials with antibacterial action were produced by intercalating bactericides into layered phosphate. The thermostable intercalation compounds obtained are expected to be applicable to developments of new fibers and plastics with antibacterial action.

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