

Intercalation of Cyclic Amines into α -Titanium Phosphate

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Abstract. The intercalation of some amines (aniline, benzylamine, cyclohexylamine, piperidine, pyridine, pyrazine and piperazine) into α -titanium phosphate, $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, has been investigated by the batch method and/or by exposing the host to the vapour of the amines. The changes in the interlayer distance of the solid during the intercalation process was followed by X-ray powder diffraction. The new intercalates were characterised by chemical and thermal analysis. Materials with a monolaminar and/or bilaminar arrangement of amine molecules in the phosphate interlayer region are obtained depending on the nature of the amine. Due to steric hindrance, saturated phases are not obtained for all amines studied. The thermal decomposition of the intercalates (nitrogen atmosphere), takes place in three stages: dehydration, removal of amines and condensation of the hydrogenphosphate to pyrophosphate groups.

Key words: α -titanium phosphate, intercalation, amines.

1. Introduction

Layered titanium phosphates are versatile materials, amenable to structural design by modulation of both their ionic frameworks and organic constituents [1]. Studied for many years as ion exchangers [2, 3], these solids now show promise of a much wider range of reactivity and applications, which derive from their chemical and thermal stability, and structural tunability [4].

α -Titanium bis(monohydrogenophosphate) monohydrate, conventionally denoted as α -titanium phosphate (α -TiP), shows resemblances with clay minerals [5] specially with those of the montmorillonite type. The crystals are monoclinic with space group $\text{P}2_1/\text{n}$ [6, 7]. The size of the entranceways into the cavities is ~ 2.5 Å and the interlayer distance is 7.6 Å. The unit-cell dimensions are $a = 8.6403(2)$, $b = 5.0093(1)$, $c = 15.5097(4)$ Å, $\beta = 101.324(2)^\circ$ [7].

Many studies have been carried out on the intercalation of *n*-alkylamines into compounds such as α -ZrP [8, 9], α -SnP [10, 11] and α -TiP [12, 13]. However, few studies on the intercalation of other amines (secondary, tertiary, cyclic or arylc amines) are reported in the literature, apart from intercalates of pyridine, bipyridine and phenanthroline as intermediates in exchange processes into zirconium

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phosphates [14–18], studies on the intercalation of aniline, benzylamine, pyridine, piperidine and pyrazine in α -ZrP [19–24], and aniline in α -TiP [22].

In this work the intercalation of primary (cyclohexylamine, aniline and benzylamine), secondary (piperidine and piperazine) and tertiary (pyridine and pyrazine) amines into α -TiP have been studied.

2. Experimental

2.1. MATERIALS

All chemicals were of reagent grade (Aldrich) and used without further purification. α -TiP was prepared as previously reported [25]. The crystalline solid obtained was washed with water until all chloride was eliminated (AgNO_3 test), dried at 50 °C and ground to a particle size of less than 0.03 mm [26].

2.2. INTERCALATION PROCEDURE

Vapour phase. Intercalation compounds with amines were obtained by placing α -TiP in an atmosphere saturated with amine vapour at room temperature for 1–100 days. The intercalated samples were air dried at 50 °C and stored in a desiccator over a solution of 50% H_2SO_4 .

Aqueous phase. 0.5 g of α -TiP was equilibrated with 50 mL aqueous solutions of amine (for concentrations see Table I) at 25 °C following the batch method during 48 hours. The solids obtained were separated by centrifugation, washed with deionized water, dried and stored as above.

2.3. ANALYTICAL PROCEDURES

The diffractometer used was a Philips PW 1729/1720 model with $\text{CuK}\alpha$ radiation. Thermal analysis was performed with a Mettler TA 4000 (TG 50, DSC 30, under nitrogen, heating rate 5 °C min^{-1}) instrument. Phosphorus and titanium content in the solids was determined by using a SpectraSpec DCP-AEC Spectrometer after dissolving a weighed amount of sample in $\text{HF}(\text{aq})$. Microanalytical data (C, N) were obtained with a Perkin–Elmer 240B elemental analyser. The infrared spectrometer used was a Perkin Elmer 1000 FT-IR spectrophotometer.

3. Results

3.1. THE α -TiP/ANILINE SYSTEM

The intercalation of aniline vapours into α -TiP develops very slowly. After 40 days of contact time, the XRD pattern only shows signals for the host material (Figure 1a), hence, only a superficial process takes place. Nevertheless, after 70 days, a new signal in the XRD curve can be seen (Figure 1b), together with

Table I. Interlayer distance, microanalytical data (C and N), experimental weight loss at 800 °C and proposed composition of the intercalation compounds obtained by solid-vapour contact.

Amine	Contact time (d)	d_{002} (Å)	Experimental			Composition	Calculated		
			%C	%N	% w.l.		%C	%N	% w.l.
Aniline	70	7.6 + 18.2	5.15	0.99	19.74	90% α -TiP + 10% $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{O}$	5.15	0.99	22.58
Benzylamine	70	7.6 + 19.0	31.79	5.09	48.95	20% α -TiP + 80% $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{H}_2\text{O}$	31.32	5.22	48.29
Cyclohexylamine	60	7.6 + 9.7	5.74	1.28	20.15	50% α -TiP + 50% $\text{Ti}(\text{HPO}_4)_2 \cdot 0.4\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$	5.18	1.00	20.09
	180	7.6 + 9.7	6.15	1.37	22.30	40% α -TiP + 60% $\text{Ti}(\text{HPO}_4)_2 \cdot 0.4\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2$	6.13	1.19	21.22
Piperidine	70	7.6 + 13.6	17.45	3.93	37.23	50% α -TiP + 50% $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_5\text{H}_{10}\text{NH} \cdot 2\text{H}_2\text{O}$	17.05	3.97	36.94
	100	7.6 + 13.6	23.11	5.76	45.50	25% α -TiP + 75% $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_5\text{H}_{10}\text{NH} \cdot 2\text{H}_2\text{O}$	22.56	5.26	44.37
Pyridine	8	7.6 + 11.1	11.85	2.97	27.56	40% α -TiP + 60% $\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$	11.79	2.75	24.96
	60	7.6 + 11.1	14.33	2.93	31.86	25% α -TiP + 75% $\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$	14.19	3.31	30.03

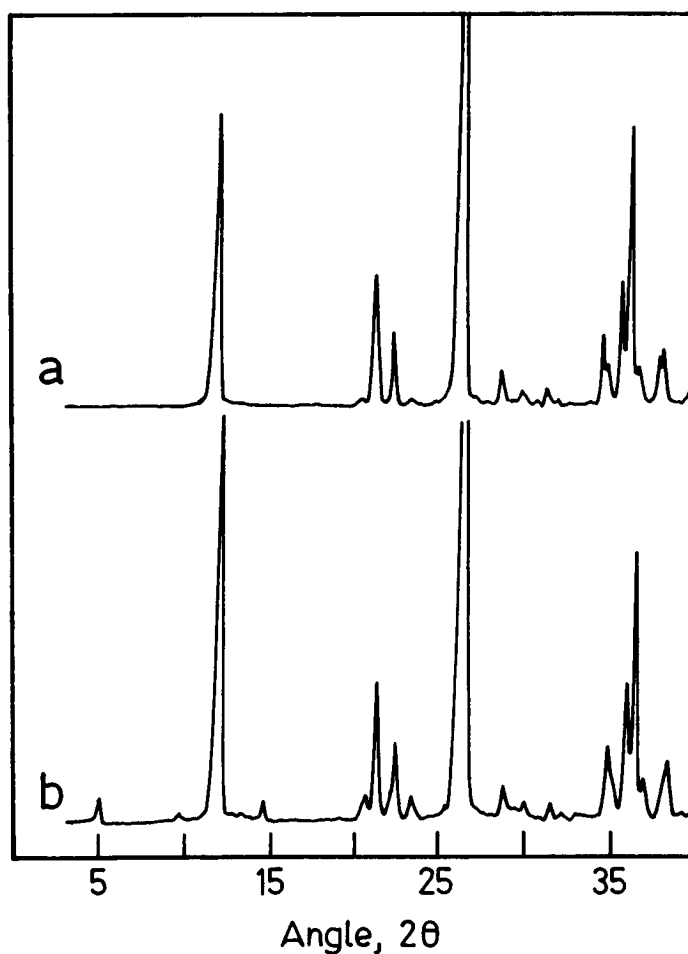


Figure 1. XRD patterns of the samples obtained by contact of α -TiP with aniline vapour: (a) 40 days, (b) 80 days.

peaks for non-intercalated α -TiP. This new phase shows an interlayer distance of 18.2 Å, the intensity of this signal increases as a function of the contact time. Taking into account that the recorded interlaminar value is similar to that shown by the saturated intercalate of aniline in α -ZrP [24], the intercalation into α -TiP also provides a saturated solid formulated as $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{O}$. From the elemental microanalysis (C, N) and thermal analysis (TG) (Table I) it can be deduced that only 10% of the host layers have been intercalated.

Due to the low water solubility of aniline the solution intercalation studies for this amine were performed in organic solvents (acetone, hexane and isopropyl ether). In all cases, an amine/ α -TiP ratio equal to 200 mmol/g was used. When the solvent was isopropyl ether or hexane, the XRD pattern shows a peak at 18.2 Å and

the typical reflections of α -TiP. The reaction, as in the vapour phase, takes place with a low yield, most of the α -TiP not being intercalated. Table II lists the solid compositions obtained from elemental microanalysis and TG. When the solvent was acetone intercalation does not occur.

3.2. THE α -TiP/BENZYLAMINE SYSTEM

Figures 2a and 2b show the XRD patterns of the benzylamine intercalates in α -TiP as a function of the contact time. Two crystalline phases are present: the host, and an intercalate with an interlayer distance of 19.0 Å. Experimental data (Table I) show that after 70 days of contact time 80% of α -TiP has been intercalated with the amine, and as with aniline, full intercalation is not possible.

The intercalation in aqueous media gives intercalates with an interlayer distance (XRD, Figures 2c and 2d) of 15.4 Å, signals for α -TiP are not present. A broad, low intensity band appears at lower angle, which corresponds to an interlayer distance of 19.0 Å (the same value was obtained in the vapour phase). In both media, the benzylamine molecules react with all acid centres of α -TiP, yielding solids with a composition: $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{H}_2\text{O}$ (Table II).

3.3. THE α -TiP/CYCLOHEXYLAMINE SYSTEM

The intercalation of cyclohexylamine in the vapour phase is a very slow process, for even after 180 days of contact time the XRD pattern of the solid obtained still shows the presence of α -TiP (Figure 3a). A new phase ($d = 9.7$ Å) corresponding to the cyclohexylamine intercalate can also be seen. Analytical data confirm partial intercalation (Table I).

Nevertheless, in the aqueous phase layered solids showing a 14.4 Å interlayer distance, have been obtained, and no signals of α -TiP are present (Figure 3b). By means of microelemental analysis and TG data (Table II) a formulation $\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$ can be proposed.

3.4. THE α -TiP/PIPERIDINE SYSTEM

The intercalation of piperidine vapour into α -TiP layers gives a solid showing an interlayer distance of 13.6 Å (Figures 4a and 4b). The intensity of this signal increases as a function of the reaction time, and simultaneously, the crystallinity of the solid obtained decreases. After 100 days of contact time the material is amorphous to X-rays. The results obtained by elemental microanalysis and TG (Table I) are compatible with the formation of a saturated phase. The intercalation process in the aqueous phase provides similar solids to the ones obtained in the vapour phase (Figures 4c and 4d, Table II).

Table II. Interlayer distances, microanalytical data (C and N), experimental weight loss at 800 °C and proposed composition of the intercalation compounds obtained by solid-liquid contact.

Amine	Solvent	Concn. (mmol/g)	d_{002} (Å)	Experimental			Calculated			
				% C	% N	% w.l.	Composition	% C	% N	% w.l.
Aniline	Acetone	200	7.6	–	–	14.09	100% α -TIP	–	–	13.96
	Hexane	200	7.6 + 18.2	9.96	1.95	24.02	80% α -TIP + 20% Ti(HPO ₄) ₂ ·2C ₆ H ₅ NH ₂ ·H ₂ O	9.76	1.89	24.81
Benzylamine	Isopropylether	200	7.6 + 18.2	7.62	1.36	22.85	85% α -TIP + 15% Ti(HPO ₄) ₂ ·2C ₆ H ₅ NH ₂ ·H ₂ O	7.55	1.47	22.36
	Water	50	15.4	35.54	5.84	52.44	Ti(HPO ₄) ₂ ·2C ₇ H ₇ NH ₂ ·H ₂ O	35.60	5.93	52.98
Cyclohexylamine	Water	100	15.4 + 19.0	35.48	5.16	52.55	Ti(HPO ₄) ₂ ·2C ₇ H ₇ NH ₂ ·H ₂ O	35.60	5.93	52.98
	Water	50	14.4	32.04	6.18	51.40	Ti(HPO ₄) ₂ ·2C ₆ H ₁₁ NH ₂ ·H ₂ O	31.59	6.14	51.33
Piperidine	Water	100	14.4	31.72	6.36	52.30	Ti(HPO ₄) ₂ ·2C ₆ H ₁₁ NH ₂ ·H ₂ O	31.59	6.14	51.33
	Water	2	7.6 + 13.6	6.35	1.34	23.84	85% α -TIP + 15% Ti(HPO ₄) ₂ ·2C ₅ H ₁₀ NH ₂ ·H ₂ O	6.29	1.46	22.44
Pyridine	Water	5	7.6 + 13.6	19.88	4.94	39.87	40% α -TIP + 60% Ti(HPO ₄) ₂ ·2C ₅ H ₁₀ NH ₂ ·H ₂ O	19.42	4.53	40.14
	Water	90	7.6 + 11.1	3.36	0.87	17.86	85% α -TIP + 15% Ti(HPO ₄) ₂ ·C ₅ H ₅ N·H ₂ O	3.33	0.77	17.74
Piperazine	Water	100	7.6 + 11.1	5.04	1.16	20.95	75% α -TIP + 25% Ti(HPO ₄) ₂ ·C ₅ H ₅ N·H ₂ O	5.40	1.26	20.08
	Water	10	Amorphous	12.34	7.74	45.53	Ti(HPO ₄) ₂ ·C ₄ H ₈ (NH) ₂ ·4H ₂ O	12.06	7.03	44.23
Pyrazine	Water	5	Amorphous	11.54	7.22	46.39	Ti(HPO ₄) ₂ ·C ₄ H ₄ N ₂ ·5H ₂ O	11.71	6.83	45.87

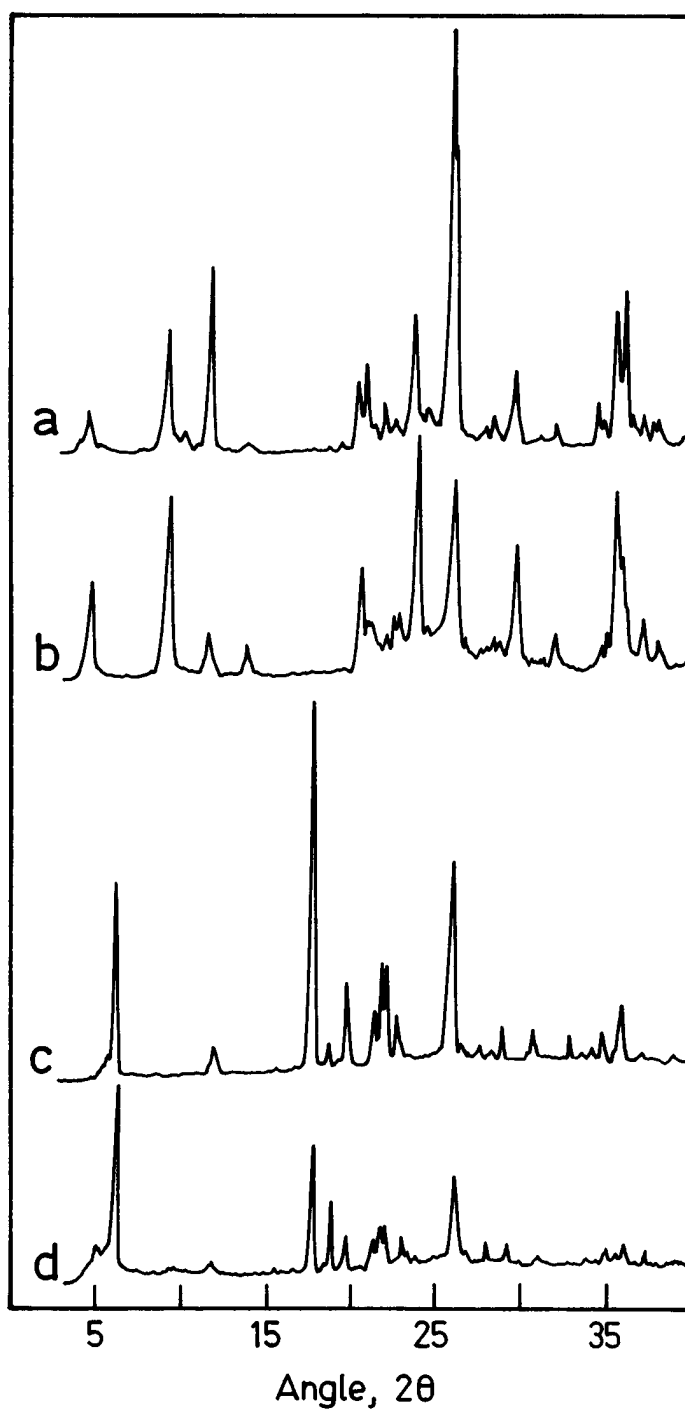


Figure 2. XRD patterns of the samples obtained by contact of α -TiP with benzylamine vapour: (a) 40 days, (b) 70 days and aqueous solutions of benzylamine: (c) 50 mmol/g, (d) 100 mmol/g.

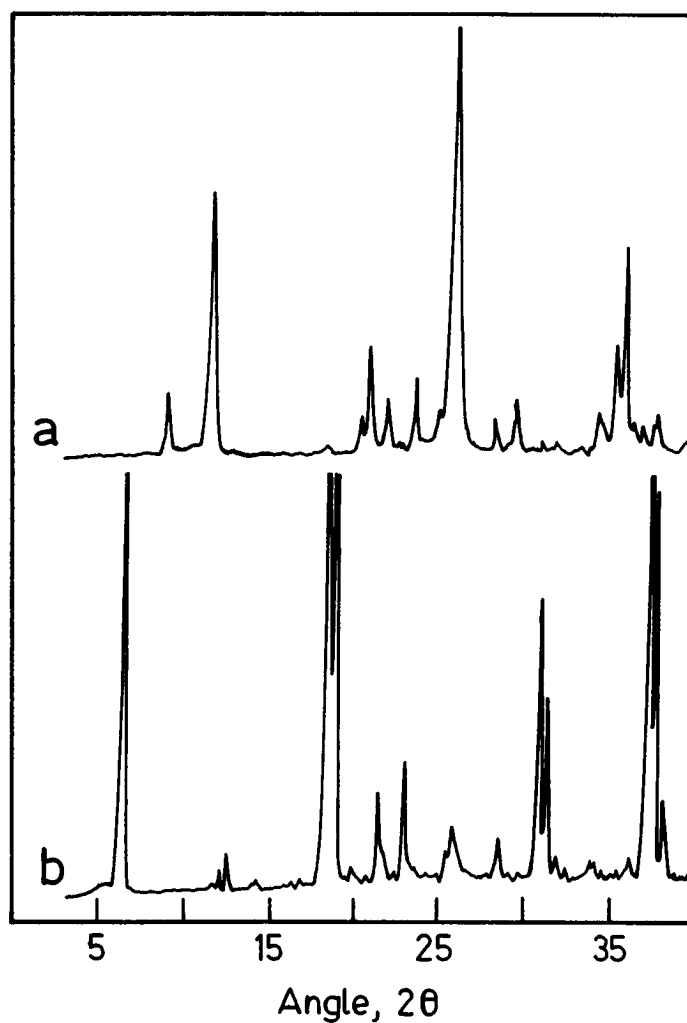


Figure 3. XRD patterns of the samples obtained by contact of α -TiP with: (a) cyclohexylamine vapour (180 days), and (b) aqueous solutions of cyclohexylamine (100 mmol/g).

3.5. THE α -TiP/PYRIDINE SYSTEM

After 8 days of contact time a new phase with of a 11.1 Å interlayer distance was obtained although α -TiP can also be seen in the XRD pattern. The extent of intercalation increases slowly as a function of the contact time (Figures 5a and 5b). Table I lists analytical results which prove that the intercalation takes place partially. The intercalation process in the aqueous phase provides similar solids to the ones prepared in the vapour phase (Table II).

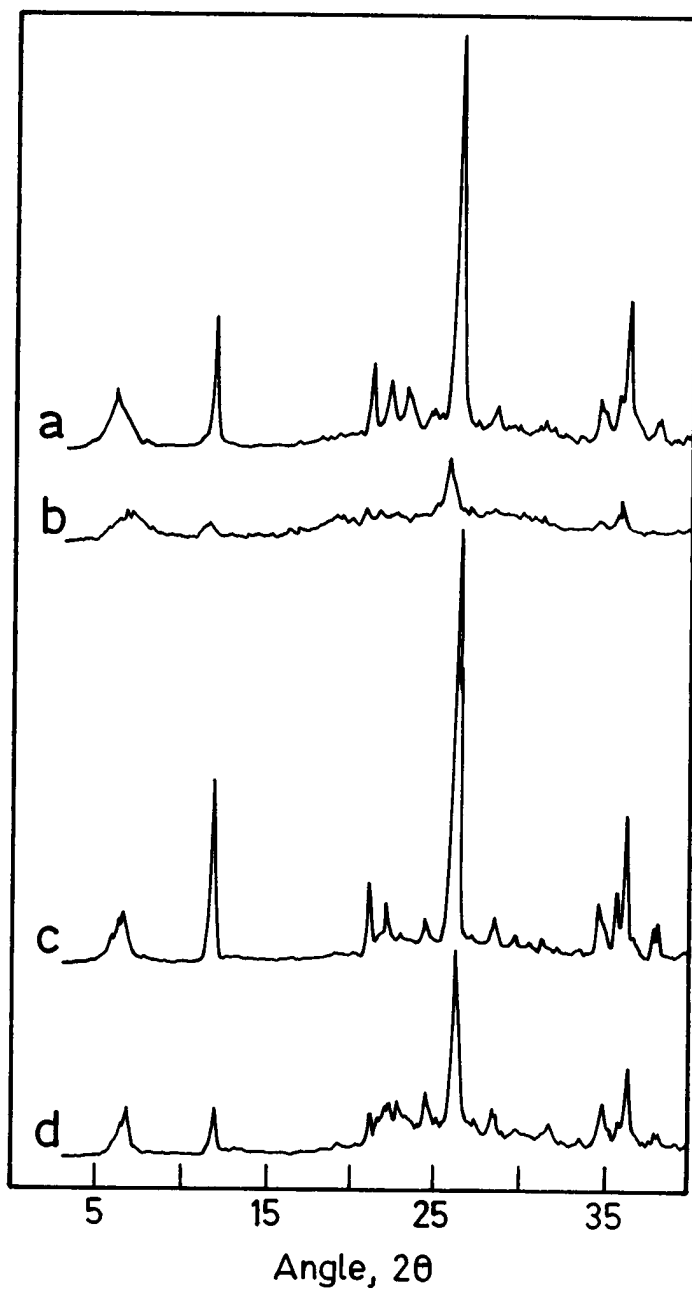


Figure 4. XRD patterns of the samples obtained by contact of α -TiP with piperidine vapour: (a) 40 days, (b) 100 days and aqueous solutions of piperidine, (c) 2 mmol/g, (d) 5 mmol/g.

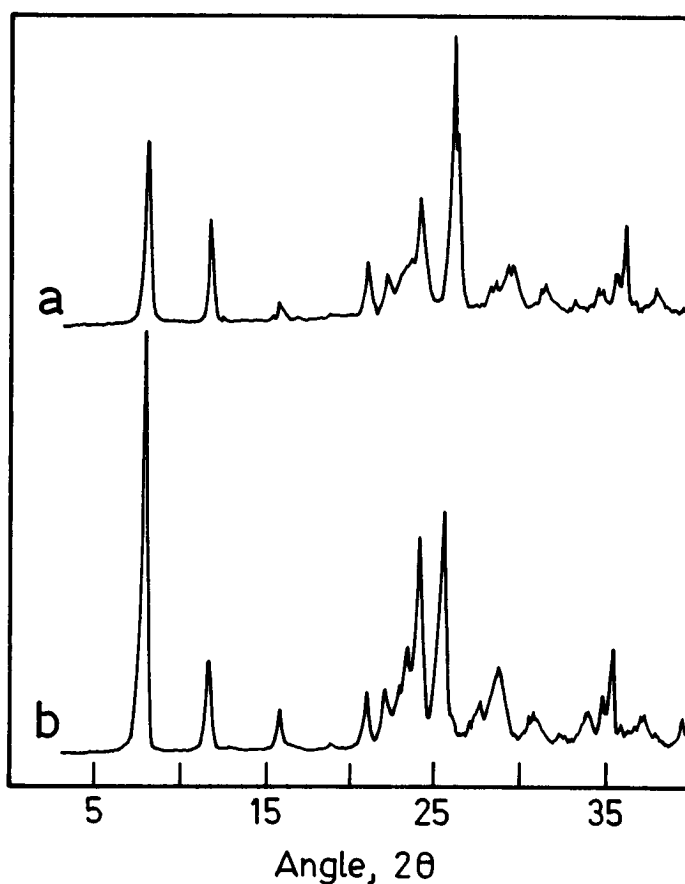


Figure 5. XRD patterns of the samples obtained by contact of α -TiP with pyridine vapour: (a) 8 days, (b) 63 days.

3.6. THE α -TiP/PIPERAZINE AND α -TiP/PYRAZINE SYSTEMS

Both reagents are solid at room temperature, therefore the intercalation process has been studied in aqueous solution. In both cases, the reaction breaks the lamellar structure of the solid resulting in poor crystalline materials. All acid centres of α -TiP are saturated with amine molecules (Table II).

4. Discussion

4.1. GUEST-HOST INTERACTION

The absorption of amines by layered phosphates gives rise to intercalation compounds stable in air. The reaction may be considered as an acid base topotactic solid state reaction between a layered acid host and a Brönsted-base guest. The protonation of amines must be demonstrated by applying spectroscopic techniques.

Figure 6 shows the infrared spectra of α -TiP and the intercalation compounds. In α -TiP/amine intercalates, the spectra were mostly composites of those of α -TiP and the respective amine, except for the absorption bands around the region 1700–1300 cm^{-1} . For primary amines, the —NH_3^+ deformation band should appear near 1600 cm^{-1} . As the host α -TiP has a band at 1620 cm^{-1} due to the bending vibration of water, we consider that the more intense absorptions are due to the superposition of absorption of water and the protonated amine (Figures 6b–6d). In the secondary amines case, protonation should be seen in the region 1620 to 1560 cm^{-1} . Figures 6e and 6f show bands at *ca.* 1560 cm^{-1} . IR spectra of α -TiP/pyridine and α -TiP/pyrazine (Figures 6g and 6h) do not show typical —NH^+ group bands (2500–2325 and 2200–1800 cm^{-1}) indicating an ineffective amine protonation process.

4.2. ARRANGEMENT OF THE AMINES IN THE SOLID PHASE

At full intercalation, the *n*-alkylmonoamines give rise to compounds containing two moles of amine per mole of Ti and form a bilayer of extended alkyl chains in the interlayer region, tilted at an angle of 57.9° to the phosphate layer [12].

The arrangement of the amine molecules in the α -TiP layers is described on the basis of the previously reported studies on the intercalation of linear amines into α -TiP. In the *n*-alkylamines case, the interlayer distance of the intercalates is a linear function of the number of carbon atoms in the alkyl chain [12]. The theoretical interlaminar distance showed for a hypothetical intercalation compound with a hypothetical *n*-alkylamine without carbon atoms ($n_c = 0$), $d = 10.1 \text{ \AA}$, might be related to the region occupied by the α -layer and the terminal —NH_3^+ groups in a bilayer arrangement. Therefore, assuming that the interpenetration of the —NH_3^+ groups within the surface layers is independent of the organic chain the inclination angle of the amine molecule to the phosphate layer can be obtained from Equation 1:

$$\alpha = \sin^{-1}[(d_{002} - 10.1)/(2 \times L)], \quad (1)$$

where L will be defined for each amine.

The distance between the N and the C4 in the aniline molecule is 4.2 \AA [27], a bilayer arrangement perpendicular to the layer aniline molecules should give a basal spacing of 18.5 \AA ($10.1 + 2 \times 4.2$), which is very close to the experimental value (18.2 \AA). From Equation 1 it can be deduced that the aromatic ring is tilted at an angle of 74° to the α -layers.

It is possible to determine the tilted angle of benzylamine bilayers to the phosphate layer in the intercalate obtained in the vapour phase ($d = 19.0 \text{ \AA}$). Taking into account that the Csp^3 -Caromatic bond length is 1.5 \AA [27], and that in a *trans-trans* conformation of extended alkyl chains the length increase per carbon atom is 0.7 \AA [12], the N-C4 distance must be $L = 4.8 \text{ \AA}$, thus from Equation 1, the average

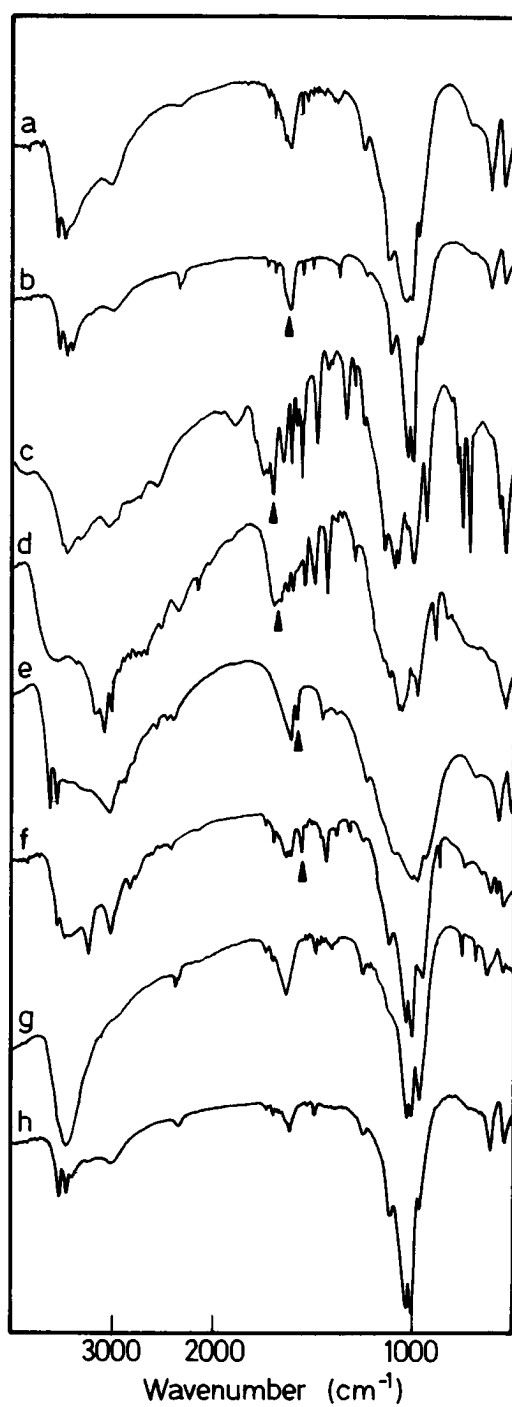


Figure 6. Infrared spectra of: (a) α -TiP, (b) α -TiP/aniline, (c) α -TiP/benzylamine, (d) α -TiP/cyclohexylamine, (e) α -TiP/piperidine, (f) α -TiP/piperazine, (g) α -TiP/pyridine, (h) α -TiP/pyrazine.

inclination angle of the benzylamine molecules with respect to the phosphate layer is 68° .

The benzylamine intercalate prepared in the aqueous phase presents two crystalline phases; the same phase as that obtained in the vapour phase ($d = 19.0 \text{ \AA}$) and a new phase in a higher proportion ($d = 15.4 \text{ \AA}$). The phase ratio is a function of both the amine concentration in the starting solution and the reaction time. The final situation is not a true equilibrium state, hence, a metastable phase is obtained, which slowly moves to the stable thermodynamic phase. The fact that both phases (15.4 and 19.0 \AA) share the same chemical composition (with saturation of all acid centres of α -TiP) must be explained considering structural factors. It is possible to assume two different ideal arrangements of the benzylamine molecules in the interlaminar space. In the first, the phenyl group is perpendicular to the layer, explaining the higher interlayer distance phase. In the second arrangement, the C—N bonding is perpendicular to the phosphate layer, giving a lower interlayer spacing, due to the oblique orientation of the phenyl group. For the intercalate at 15.4 \AA , the phenyl ring must be tilted at an angle of 33° to the phosphate plane, instead of 19.5° , which should be expected if the C—N bonding is perpendicular to the α -layer.

The intercalation of cyclohexylamine in the vapour phase gives a solid with an interlayer distance of 9.7 \AA . Due to the cyclohexylamine molecular size, such small interlayer spacing can be only understandable if the amine molecules are in a parallel arrangement to the phosphate layers, the same happens in the earlier stage of n -alkylamines intercalation into layered phosphates (13). Provided that the surface area associated with each acid centre in the α -TiP structure is 21.6 \AA^2 , and the cyclohexylamine molecule size can be assumed as $8.4 \times 6.1 \text{ \AA}^2$, the maximum amount of intercalated amine, in this arrangement, can be 0.4 mol per mol of titanium(IV). The formulation $\text{Ti}(\text{HPO}_4)_2 \cdot 0.4\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$ should agree with a maximum space occupation.

When the intercalation of cyclohexylamine is carried out in aqueous solution, saturated intercalates formulated as $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$ ($d = 14.4 \text{ \AA}$) are obtained. The length of each intercalated cyclohexylamine molecule should be similar to that of each intercalated n -butylamine molecule in a *trans-trans* conformation (18.8 \AA) [12]. Assuming that both the cyclohexylamine molecules are placed in a bilayered arrangement in the interlayer region in a chair conformation and the C2-C3 bonding is perpendicular to the phosphate layer. Nevertheless, the cyclohexylamine intercalate shows a shorter interlayer distance which must be associated with a tilted orientation of the amine molecules to the titanium phosphate layer ($d = 14.4 \text{ \AA}$). An average inclination angle of 33° can be calculated from Equation 1.

The intercalation of piperidine both in vapour and solution phases gives rise to intercalates showing a 13.6 \AA interlayer distance. As this value is slightly smaller than that observed for the bilaminar arrangement of cyclohexylamine molecules into α -TiP layers (above), it can be assumed that the piperidine intercalate also

has a bilaminar arrangement of amine molecules. A perpendicular arrangement of piperidine molecules should increase the interlayer spacing by 5.12 Å [$L = 2(1.54 + 2 \times 0.51)$]. Thus, the average inclination angle can be calculated from Equation 1: $\alpha = 43^\circ$.

The pyridine intercalation yields intercalates of 11.1 Å interlayer distance in both vapour and solution phases. Such a low basal spacing cannot be associated with a bilayered arrangement of amine molecules, since in that case, the intercalate interlayer distance should be greater than 15 Å. The α -phenylphosphonate of titanium(IV) shows an interlayer distance of 15.2 Å [28] and the interlaminar distance of α -TiP is 7.6 Å. In a monolaminar arrangement of pyridine molecules the interlaminar distance of the intercalate should be close to the average distance of α -phenylphosphonate and α -TiP. The calculated (11.4 Å) and the experimental (11.1 Å) values are in good agreement. Thus, as a conclusion, the pyridine intercalate has a monolaminar arrangement of amine molecules and a composition $\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot n\text{H}_2\text{O}$ can be proposed.

For a monolaminar arrangement of amino groups into the α -TiP layer Equation 1 must be modified. In this case, the theoretical interlaminar distance shown by a hypothetical intercalation compound with a supposed n -alkylamine without carbon atoms, might be related to the region occupied by the α -layer and the terminal $-\text{NH}_3^+$ groups in a monolayer arrangement, gives an interlayer distance of 7.8 Å (13), hence Equation 1 changes to Equation 2 for a monolaminar arrangement:

$$\alpha = \sin^{-1}[(d_{002} - 7.8)/L], \quad (2)$$

where L will be defined for each amine.

The distance N-C3 of the pyridine molecule can be accepted as 2.8 Å. Assuming that the amine molecule is placed perpendicular to the phosphate layer, an interlayer distance of 10.6 Å should be expected. The difference with the experimental value (11.1 Å) can be explained taking into account that a different interaction exists between the α -layer and the $-\text{CH}_3$ group, in the n -alkylamines case, or between the α -layer and the aromatic ring, in the pyridine case.

The intercalation of piperazine or pyrazine yields materials amorphous to X-rays. In both cases, the diamine molecule could be anchored to two acid centres from different phosphate layers, giving a crystallinity loss with formation of highly disordered solids, which probably keeps their layered nature in short distance interactions.

Table III lists the chemical composition for the intercalates obtained, indicating the arrangement of the amine molecules in the interlayer region as well as the calculated average inclination angle of the amine molecules to the phosphate layer.

4.3. THERMAL DECOMPOSITION

$\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{H}_2\text{O}$ (15.4 Å). The TG pattern (Figure 7a) for the benzylamine intercalate shows three main mass losses. The first one ($T \leq 100^\circ\text{C}$)

Table III. Interlayer distances, monolamellar (M) or bilamellar (B) disposition of the amines and average inclination angle for the $\text{Ti}(\text{HPO}_4)_2 \cdot x(\text{amine})n\text{H}_2\text{O}$ intercalation compounds.

Amine	d_{002} (Å)	x	n	Disposition	α (deg)
Aniline	18.2	2	1	B	74°
Benzylamine	19.0	2	1	B	68°
	15.4	2	1	B	33°
Cyclohexylamine	9.7	0.4	1	M	0°
	14.4	2	1	B	33°
Piperidine	13.6	2	2	B	43°
Pyridine	11.1	1	1	M	90°

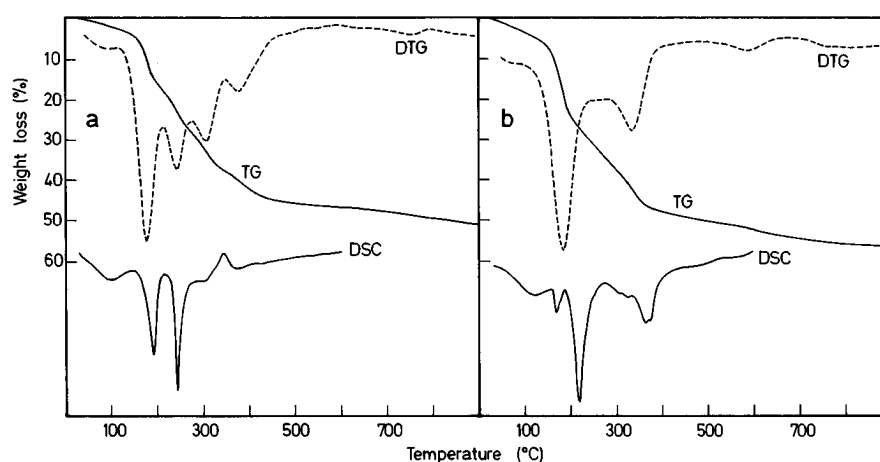


Figure 7. TG, DTG and DSC curves of: (a) $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{H}_2\text{O}$, and (b) $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$.

corresponds to the loss of crystallization water. Later, different amine decomposition processes take place in the temperature range 125 to 500 °C. A later mass loss can be seen (500 to 650 °C), associated with elimination of constitutional water (transformation of the hydrogenophosphate groups into pyrophosphate). It can be seen from Table IV that the mass losses associated with each step are quite similar. The DTG curve shows that the process rate is not constant and relative minima in the mass loss are detected at 175, 240, 305 and 375 °C. The DSC curve shows an earlier band related to the dehydration process followed by two endothermic bands at 180 and 240 °C, which are related to the first two stages in the amine desorption process. Two more, less well-defined bands, can be seen according to minima in the DTG curve.

Attempts to isolate the intermediate phases have been undertaken by placing the intercalate in an oven at selected temperatures. The intercalate treatment at

Table IV. Thermal decomposition process of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{H}_2\text{O}$: interlayer distances, microanalytical data (C and N), experimental weight loss (TG data), proposed composition of the intermediate compounds and enthalpy variation referred to one mole of starting material.

Product of reaction	d_{002} (Å)	Experimental			Calculated			ΔH° (kJ mol ⁻¹)
		% C	% N	% weight loss	% C	% N	% weight loss	
$\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_7\text{H}_7\text{NH}_2$	15.4	37.78	6.63	3.7	37.01	6.17	3.81	26.3
$\text{Ti}(\text{HPO}_4)_2 \cdot 1.5\text{C}_7\text{H}_7\text{NH}_2$	–	–	–	13.2	31.47	5.24	11.34	49.9
$\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_7\text{H}_7\text{NH}_2$	–	24.76	4.05	10.1	24.25	4.04	11.34	50.9
$\text{Ti}(\text{HPO}_4)_2 \cdot 0.5\text{C}_7\text{H}_7\text{NH}_2$	–	14.61	2.58	11.7	14.31	2.39	11.34	–
$\text{Ti}(\text{HPO}_4)_2$	–	–	–	10.3	–	–	11.34	–
$\text{Ti}_2\text{P}_2\text{O}_7$	–	–	–	3.5	–	–	3.81	–

100 °C allows for the isolation of anhydrous solid, which presents a similar XRD pattern to the hydrated phase. Heating the sample at $T > 100$ °C yields a solid amorphous to X-rays. The intercalate thermal decomposition process is described in Table IV, the experimental and theoretical values for the formation of 75, 50 and 25% intercalation phases are in good agreement.

Enthalpy variation values of $26.3 \text{ kJ mol}^{-1} \text{ H}_2\text{O}$ and $\sim 100 \text{ kJ mol}^{-1}$ benzylamine have been calculated for the dehydration and amine desorption processes respectively.

$\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$ (14.4 Å). Figure 7b show TG, DTG and DSC curves obtained from the thermal treatment of cyclohexylamine intercalated into α -TiP. The TG curve shows that the mass loss follows several stages. Firstly the loss of crystallization water occurs to obtain anhydrous intercalated solid at 100 °C. Later, the loss of intercalated cyclohexylamine takes place in two steps (100 to 275 °C and 300 to 650 °C) of 1 mol of amine per mol of titanium each. At 800 °C the material obtained has the TiP_2O_7 composition. DTG and DCS curves show that the thermal desorption process is complicated since five or six bands are observed. The first takes place at $T \leq 100$ °C, and corresponds to an endothermic process associated with the solid dehydration. At 170 °C a peak related to a phase transition of the anhydrous intercalate takes place, probably due to a chair to boat solid state conformational change of the cyclohexylamine molecule. At 220 °C and 360 °C two endothermic bands can be related with the two stages of the amine desorption process. A later band can be seen ($T = 600$ °C) associated with the loss of structural water originated from the decomposition of hydrogenphosphate groups.

As in the benzylamine case, the XRD pattern for the cyclohexylamine intercalate heated at 100 °C (anhydrous material) shows the same interlayer distance as the hydrated solid. The material obtained after treatment at 370 °C present a basal spacing (XRD) of 7.4 Å, typical of the α -TiP anhydrous phase [29], although the elemental microanalysis gives a carbon content (Table V) which indicates that the desorption process is not complete at that temperature. The experimental data listed in Table V are in good agreement with the proposed mass loss sequence.

Enthalpy variations have been calculated for the dehydration process ($20.1 \text{ kJ mol}^{-1} \text{ H}_2\text{O}$), phase transition (8.5 kJ mol^{-1} intercalate) and amine desorption ($\sim 80 \text{ kJ mol}^{-1}$ cyclohexylamine).

The enthalpy variation associated with the dehydration process seems to be independent of the intercalated amine. The basicity of cyclohexylamine, in aqueous solution, is higher than that of benzylamine ($\text{pK}_b = 3.4$ and 4.7 , respectively) due to the positive charge of an ammonium ion being better dispersed by having alkyl groups instead of hydrogen substituents on nitrogen. Nevertheless, the host-guest interaction is stronger in the benzylamine case, thus, organic hydrophobic interactions and steric hindrance seems to be the most important factor in this case.

Table V. Thermal decomposition process of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_{11}\text{NH}_2 \cdot \text{H}_2\text{O}$: interlayer distances, microanalytical data (C and N), experimental weight loss (TG data), proposed composition of the intermediate compounds and enthalpy variation referred to one mole of starting material.

Product of reaction	d_{002} (Å)	Experimental			Calculated			ΔH° (kJ mol ⁻¹)
		% C	% N	% weight loss	% C	% N	% weight loss	
$\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_6\text{H}_{11}\text{NH}_2$	14.4	32.97	6.49	3.5	32.88	6.39	3.95	20.1
$\text{Ti}(\text{HPO}_4)_2 \cdot \text{C}_6\text{H}_{11}\text{NH}_2$	—	—	—	23.6	21.25	4.13	21.71	84.3
$\text{Ti}(\text{HPO}_4)_2 \cdot 0.1\text{C}_6\text{H}_{11}\text{NH}_2$	7.4	2.30	0.54	17.2	2.88	0.56	19.54	73.7
$\text{Ti}(\text{HPO}_4)_2$	7.4	—	—	3.1	—	—	2.17	—
TiP_2O_7	—	—	—	4.8	—	—	3.95	—

5. Conclusions

The behaviour of α -titanium phosphate towards aniline, benzylamine, cyclohexylamine, piperidine, pyridine, pirazine and piperazine cannot be systematized. Due to steric hindrance saturated intercalates cannot be obtained from these amines. The interlayer distance shown by the intercalation compounds is dependent on the nature and arrangement of the amine molecule (mono or bilaminar) and the synthetic method (solution or vapour). The weight loss by thermal decomposition of α -titanium phosphate/benzylamine and α -titanium phosphate/cyclohexylamine intercalation compounds consists of the following stages: a) loss of the crystal water, b) loss of the organic molecules and c) loss of the structural water.

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