

## A study of the thermal behaviour of $\alpha$ -layered tin(IV) phosphonate $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$

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### Abstract

The thermal behaviour of tin(IV) 2-carboxyethylphosphonate was studied by TGA and DSC techniques under oxygen and nitrogen atmospheres. The decomposition stages are more defined in nitrogen than in oxygen, but in both cases the layered compound is stable up to around 300°C. Samples treated thermally at temperatures ranging from 100 to 900°C for 1 h at atmospheric pressure exhibit XRD and FTIR data suggesting the formation of  $\text{Sn}(\text{HPO}_4)_2$  as intermediate and the cubic pyrophosphate as the final product of the decomposition.

### INTRODUCTION

Layered phosphonates and phosphates of tetravalent metals are becoming increasingly important because of their potential applications in catalysis and separation science [1–6]. Recently, some authors pointed out the possibility of growing these compounds as thin films on a suitable surface, with the prospect of obtaining supramolecular ordered materials [7]. In an earlier study, we reported the formation of new tin(IV) layered compounds, described by the formula  $\text{Sn}(\text{RPO}_3)_2$  (R is phenyl, 2-carboxyethyl) and  $\text{Sn}(\text{ROPO}_3)_2$  (R is dodecyl), from the reaction of  $\text{SnCl}_4$  with phosphonic acids and phosphoric esters in aqueous acidic medium [8]. The temperature ranges of the thermal stability, the decomposition steps and the final products after heating these compounds constitute important data for the evaluation of their applications.

In this paper we investigate the thermal behaviour of tin(IV) 2-carboxyethylphosphonate by TGA and DSC techniques. In addition, the samples were heat treated at different temperatures and their evolution monitored by infrared and X-ray powder diffraction measurements in order

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to correlate the chemical and structural changes taking place at each heating step. The data obtained represent the first results for post-transitional layered phosphonates reported in the literature.

## EXPERIMENTAL

The sample used in this work was prepared by the reaction of a nitric acid solution of  $\text{SnCl}_4$  with 2-carboxyethylphosphonic acid (CEPA), as previously described in ref. 8.

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) curves were obtained with a Du Pont model 1090 DSC/TGA system at a heating rate of  $5^\circ\text{C min}^{-1}$  under nitrogen and oxygen atmospheres with a flux of  $30\text{ cm}^3\text{ min}^{-1}$ .

Infrared (IR) spectra of samples were recorded in Nujol and Fluorolube dispersions between KBr windows on a Nicolet 60SX-B Fourier transform spectrometer.

X-ray diffraction (XRD) patterns were measured with a Shimadzu XD-3A diffractometer using  $\text{Cu K}\alpha$  1.5418 Å Ni-filtered radiation (30 kV and 20 mA) at a scan rate of  $2\text{ deg min}^{-1}$ .

The infrared and X-ray measurements are performed for samples treated thermally in the  $100\text{--}900^\circ\text{C}$  range for 1 hour.

## RESULTS AND DISCUSSION

### *TGA and DSC measurements*

The results of the thermogravimetric analysis obtained under nitrogen and oxygen are presented in Fig. 1.

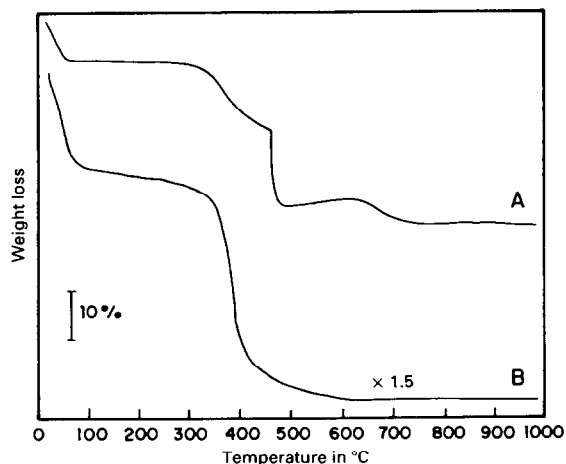


Fig. 1. TGA curves for  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$  in: A, nitrogen; B, oxygen atmospheres.

The TGA curve of the sample heated under nitrogen shows a first peak in the region of 40–70°C, which corresponds to water loss and establishes a value of 2.4 for the water/phosphonate ratio. A more complex thermal event occurs between 340 and 485°C, where a slow loss was observed by 480°C, followed by an abrupt loss starting near 485°C. TGA results performed under an atmosphere of oxygen (Fig. 1, curve B) are basically similar, except that the most prominent weight loss occurs in the range 340–590°C in a single step. The value of about 30% weight loss in this step in both experiments is very close to the amount for the organic moiety, as determined by elemental analysis [8]. In this manner the decomposition of the phosphonate begins near 340°C and continues up to 600°C, depending on the atmosphere. The TGA curve under nitrogen also shows a small mass gain (<2%) between 550 and 640°C, with a mass loss from 650 to 730°C (<4%).

It is important to note that the thermal decomposition of free 2-carboxyethylphosphonic acid starts at least 120°C lower in comparison to the layered tin(IV) derivative [9]. The presence of Sn–O–P–R bonds leads to a substantial increase in the thermal stability of this system.

As pointed out by DiGiacomo and Dines [10], this stability depends on the organic radical being attached to the phosphorus atom. Similar compounds involving other tetravalent metals exhibit very high decomposition temperatures, e.g.  $Zr(O_3PCH=CH_2)_2$ , which loses only one third of its organic content up to 650°C [10].

The DSC curves are illustrated in Fig. 2 for experiments performed under nitrogen and oxygen atmospheres. These curves are in agreement with the TGA results with respect to the stages observed. The peak appearing in both measurements below 100°C can be attributed to the release of loosely bound water.

The curve recorded in nitrogen atmosphere in the range 100–450°C shows an endothermic peak with a minimum close to 330°C. It seems, however, that this thermal event occurs over a large range (200–450°C) including regions where the TGA curve presents no weight losses (200–350°C). These results indicate that this thermal exchange can probably be related to a concomitant process involving reorganization of the solid structure, followed by decomposition of the layered compound. This feature is not so apparent in the experiment carried out under oxygen atmosphere.

The main differences in the DSC curves as a result of changing the atmosphere are observed for temperatures around 400–500°C. A sharp endothermic peak at 485°C and a large exothermic peak at 460°C are observed under nitrogen and oxygen atmospheres, respectively. These results could be taken as an indication that different mechanisms are taking place. It is important to note that the sharpness of the peak in the nitrogen experiment characterizes a well-defined product and also is evidence that this step is not controlled by a diffusive mechanism. It is probable that in

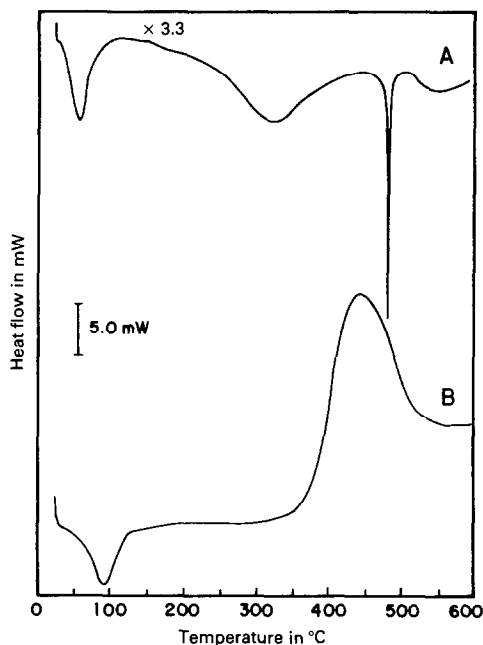


Fig. 2. DSC curves for  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$  in: A, nitrogen; B, oxygen atmospheres.

this step there is a combination of some of the fragments that resulted from the initial decomposition. The abrupt weight loss observed in the TGA curve (Fig. 1) near  $480^\circ\text{C}$  has a parallel with this sharp peak.

However, for the DSC curve recorded under oxygen atmosphere, the large exothermic peak can be associated with a sequence of thermal events, starting from decomposition of the organic moiety by rupture of phosphorus–carbon bonds, followed by reactions and decomposition of the newly formed species. These results correlate well with those obtained from TGA, considering the range of heat change temperatures.

### *XRD measurements*

The effect of thermal treatment under atmospheric pressure monitored by XRD is shown in Fig. 3 and the data are summarized in Table 1.

The first reflection (Fig. 3) assigned to the 002 family of planes and related to the interlayer distance of  $13.87 \text{ \AA}$  [8] is practically constant up to  $250^\circ\text{C}$ . The water release occurring in this temperature range does not cause significant structural change or long-range order modifications. This is understandable if one considers that, in this case, the presence of water is not so important to the cohesion of the layered structure.

For the sample heated at  $300^\circ\text{C}$ , it was observed that the well-defined reflections at  $2\theta = 6.37$  ( $d = 13.87 \text{ \AA}$ ) and  $12.41$  ( $d = 7.13 \text{ \AA}$ ) have disap-

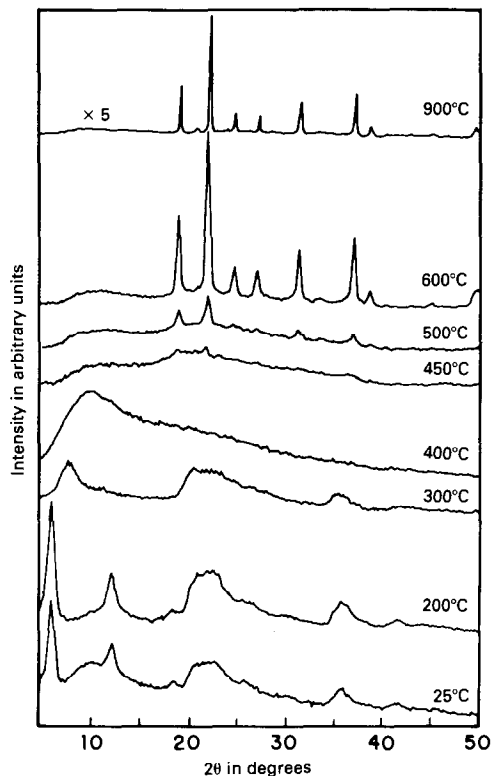


Fig. 3. X-ray diffraction patterns of  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$  samples treated thermally at the temperature indicated for 1 h.

peared, and a new peak appears at  $2\theta = 8.07$  ( $d = 10.95 \text{ \AA}$ ) with large FWDH, indicating the formation of a poorly ordered phase. Other poorly resolved reflections at  $2\theta = 19.73$  ( $d = 4.50 \text{ \AA}$ ) and  $2\theta = 35.92$  ( $d = 2.50 \text{ \AA}$ ) are also observed. This phase evolves to a pattern containing a single large peak situated near  $2\theta = 10.53$  ( $d = 8.4 \text{ \AA}$ ) for the sample heated at  $400^\circ\text{C}$ . It is difficult to identify by XRD the phase appearing in the  $300\text{--}400^\circ\text{C}$  temperature range, but the possibility of these phases arising from the reaction of the remaining phosphorous moiety with other substances, especially water from the decomposition of the organic radical, is not discarded.

As can be seen, for the sample treated thermally at  $450^\circ\text{C}$  (Fig. 3) a new phase begins to crystallize with weak reflections near  $2\theta = 19.17$  ( $d = 4.63 \text{ \AA}$ ) and  $2\theta = 23.10$  ( $d = 3.85 \text{ \AA}$ ). At this point the reflections at  $d = 8.40 \text{ \AA}$  are not clearly observed. The crystallinity of this phase increases with increase in temperature and can be indexed with good agreement to cubic  $\text{SnP}_2\text{O}_7$  [11]. Similar results are obtained for the decomposition of  $\alpha\text{-Sn}(\text{HPO}_4)_2$ , although for the organic derivative studied here, the cubic pyrophosphate phase was formed at lower temperatures than for the hydrogen phosphate.

TABLE 1

Interplanar distance and intensity for  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$  samples treated thermally at different temperatures

25°C	200°C	300°C	400°C	450°C	500°C	600°C	900°C
13.87s	13.87s						
		10.95m					
8.78w	8.78w		8.40b				
7.13m	7.13m						
4.74w	4.74w						
		4.50m		4.63vw	4.60w	4.60s	4.60s
							4.23vw
4.04b	4.04b						
					3.99vs	3.99vs	3.99vs
				3.85vw			
							3.71vw
						3.56m	3.56m
						3.25m	3.25m
					2.82vw	2.82m	2.82m
2.49w	2.49w	2.50w					
					2.40vw	2.40vw	2.40vw
						2.29w	2.30w
						1.99vw	1.99vw
						1.85w	1.83w

Key: b, broad; m, medium; s, strong; vs, very strong; vw, very weak; w, weak.

### FTIR spectra

Figures 4 and 5 show the FTIR spectra of solids as a function of heat treatment temperatures in the ranges  $4000\text{--}1300\text{ cm}^{-1}$  and  $1400\text{--}400\text{ cm}^{-1}$ , respectively. We note that the spectra remain virtually unchanged for temperatures below  $300^\circ\text{C}$  in the region between  $4000$  and  $1300\text{ cm}^{-1}$  (Fig. 4).

The main modifications occur in the case of samples treated at  $300^\circ\text{C}$  (Fig. 4) and are (i) a strong decrease in intensity for the bands situated near  $1700\text{ cm}^{-1}$  and at  $1434$  and  $1409\text{ cm}^{-1}$  assigned to  $\nu(\text{C}=\text{O})$  and  $\delta(\text{P}-\text{CH}_2)$  [12], respectively; (ii) disappearance of the bands at  $1293$ ,  $1260$ ,  $815$ , and  $766\text{ cm}^{-1}$ , associated with P–C bonds; (iii) a decrease in intensity and an increase in the absorption attributed to  $\nu(\text{P}=\text{O})$  of the  $\text{PO}_3$  group near  $1080\text{ cm}^{-1}$ ; (iv) two new bands at  $614$  and  $511\text{ cm}^{-1}$ .

From these results it is reasonable to assume that the decomposition of the layered compound occurs in two overlapping stages: breaking of the P–C bonds, and decomposition of the organic moiety in carbon dioxide and water. The data presented here confirm the scheme proposed by DiGiacomo and Dines in which the decomposition of similar phosphonates starts with

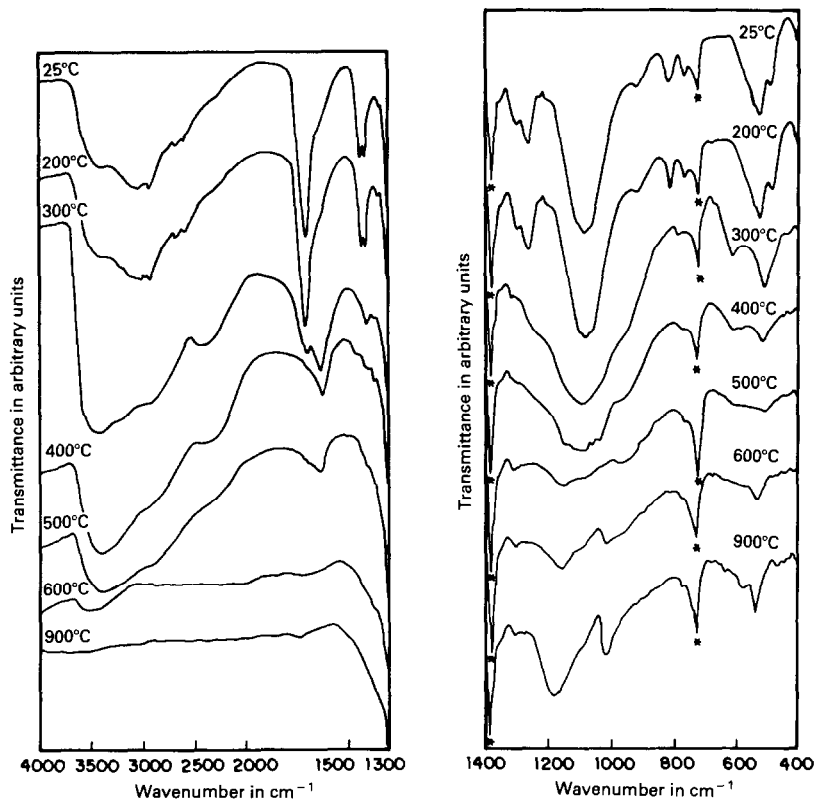


Fig. 4. Infrared spectra ( $4000\text{--}1300\text{ cm}^{-1}$ ) of  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{PO}_3)_2$  samples treated thermally at the temperatures indicated for 1 h.

Fig. 5. Infrared spectra ( $1400\text{--}400\text{ cm}^{-1}$ ) of  $\text{Sn}(\text{C}_3\text{H}_5\text{O}_2\text{CO}_3)_2$  samples treated thermally at the temperatures indicated for 1 h (\* denotes Nujol bands).

homolytic scission of the phosphorus-carbon bond [10]. In our case, formation of the 2-carboxyethyl radical is expected.

For the sample heated at  $400^\circ\text{C}$ , the spectra showed no absorptions that can be ascribed to the presence of carbon-carbon bonds (Figs. 4 and 5). In the  $4000\text{--}1300\text{ cm}^{-1}$  region the only bands observed are a strong-broad band at  $3375\text{ cm}^{-1}$ , a weak-medium band at  $1627\text{ cm}^{-1}$ , and a weak band at  $2322\text{ cm}^{-1}$ . In the region of lower wavenumbers, a strong-broad band, with some shoulders, centred at  $1082\text{ cm}^{-1}$  and two other weak bands at  $609$  and  $518\text{ cm}^{-1}$  (Fig. 5) are observed. The position and shape of these bands strongly suggest the formation of poorly crystallized tin(IV) hydrogen-phosphate phase,  $\text{Sn}(\text{HPO}_4)_2$ . This phase is probably hydrated if we consider the presence of the  $1627\text{ cm}^{-1}$  absorption, attributable to the water deformation band  $\delta(\text{OH}_2)$  and the  $3375\text{ cm}^{-1}$  band, assigned to an OH absorption  $\nu(\text{OH})$  of water and to the P-OH group. In this sense, the bands at  $1082$ ,  $609$  and  $518\text{ cm}^{-1}$  are due to stretching of the P-O bonds  $\nu(\text{PO})$

and  $\text{PO}_3$  deformations, respectively. A similar spectral picture was observed for  $\text{Zr}(\text{HPO}_4)_2$  gel [13]. We note in Fig. 5 that even at  $300^\circ\text{C}$  some of the bands described are present, indicating that small amounts of the phosphate phase is formed.

For temperatures higher than  $400^\circ\text{C}$ , the more important spectral features are (i) a gradual decrease in intensity of the bands assigned to OH absorption, which are no longer observed at  $900^\circ\text{C}$ ; (ii) a shift of the P–O stretching to higher wavenumbers (by approx.  $100\text{ cm}^{-1}$ ) and the disappearance of the absorptions associated with  $\text{PO}_3$  deformations; and finally, (iii) the presence of a new absorption at  $1019\text{ cm}^{-1}$ . These results suggest that a dehydration process occurs above  $400^\circ\text{C}$  leading to the formation of a pyrophosphate phase as the final product, thus confirming the XRD data. This dehydration process suggests the condensation of P–OH groups to form P–O–P, and is evidenced by the band at  $1019\text{ cm}^{-1}$ . A similar scheme was proposed by other authors [14] and has been accepted as typical for the thermal decomposition of tetravalent metal hydrogenphosphates.

## CONCLUSIONS

TGA and DSC techniques have demonstrated that the decomposition of tin(IV) carboxyethylphosphonate is dependent on the atmosphere used and starts at about  $300^\circ\text{C}$ . The XRD and FTIR data for the samples treated thermally at atmospheric pressure indicate that above  $300^\circ\text{C}$  the decomposition starts with the scission of P–C bonds, concomitantly with the decomposition of the organic radical formed. The formation of the well-crystallized cubic tin(IV) pyrophosphate,  $\text{SnP}_2\text{O}_7$ , as a final product ( $900^\circ\text{C}$ ) can be understood as a consequence of the formation of tin(IV) hydrogenphosphate intermediate, followed by its condensation.

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