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THERMAL STUDIES OF TIN(II) AND TIN(IV) DIHYDROXYPHENOLATES

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ABSTRACT

The thermal behaviour of tin(II) and tin(IV) compounds with 2,3-dihydroxynaphthalene and pyrogallol was studied by thermogravimetry (TG) and differential thermal analysis (DTA).

All the compounds decompose in several steps, with partial elimination of ligand, elimination of the remaining ligand and SnO_2 residue formation.

INTRODUCTION

Our previous works [1–3] studied the complex formation of tin(II) and tin(IV) with 2,3-dihydroxynaphthalene (H_2DN) and pyrogallol (H_2Pg).

Here we report a TG and DTA thermal study of the complexes synthesized in our previous works.

EXPERIMENTAL

Methods

Thermal analyses, by means TG and DTA, were carried out on a Setaram thermobalance, in dry nitrogen and dynamic oxygen atmospheres using samples of ~ 30 mg and a heating rate of 4°C min^{-1}. Al_2O_3 was used as a reference material.

X-ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using Cu-K_α radiation.

Samples

The compounds studied, whose syntheses and characterization have been described previously [1–3], are the following: SnDN, $(PyH)_2Sn(Pg)_3$, $(N(But)_4)_2Sn(DN)_3$ and $Sn(DN)_2$.

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RESULTS AND DISCUSSION

The TG and DTA curves for SnDN, obtained under oxygen, are shown in Fig. 1.

The TG curve shows that the decomposition of the Sn(II) compound takes place in two overlapping steps. The first process consists of a weight increase, probably due to O_2 absorption corresponding to oxidation of Sn(II) to Sn(IV), in the 240–260°C temperature range. The second process corresponds to a weight loss at 305–416°C. In the DTA curve, these processes appear as exotherms at 305, 387 and 416°C which indicates that these processes correspond to the pyrolytic decomposition of the compound. At this point, a residue of SnO_2 is obtained as revealed by the X-ray diffraction pattern. The weight percentage of the residue (46%) corresponds to SnO_2.

Figure 2 shows the TG and DTA plots of Sn(IV) compounds.

The TG curve of $(PyH)_2Sn(Pg)_3$ shows that this compound is stable in the 50–210°C temperature range. The pyrolytic decomposition of the compound takes place between 220 and 453°C. At this point, the residual weight loss is 74.4% of the original weight, in good agreement with the theoretical value expected for the formation of SnO_2, the final product of the pyrolytic process. The DTA curve shows two exothermic effects, at 248–285 and 368°C, which correspond to the combustion of the ligands.

Anhydrous $(N(But)_4)_2Sn(DN)_3$ is stable below 260°C. The TG curve shows a fast decomposition in two steps: (1) elimination of 1 mol But_3N per mole of compound at 308°C, with a weight loss of 35.3% which corresponds to the theoretical value required (34.2%); (2) elimination of the remaining ligand and formation of SnO_2 as revealed by X-ray patterns. The total weight loss (84.2%) corresponds to the theoretical value required (86.1%).

The DTA curve shows endothermic and exothermic processes at 275 and

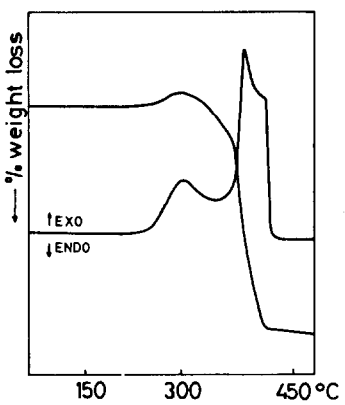

Fig. 1. TG and DTA curves of SnDN.

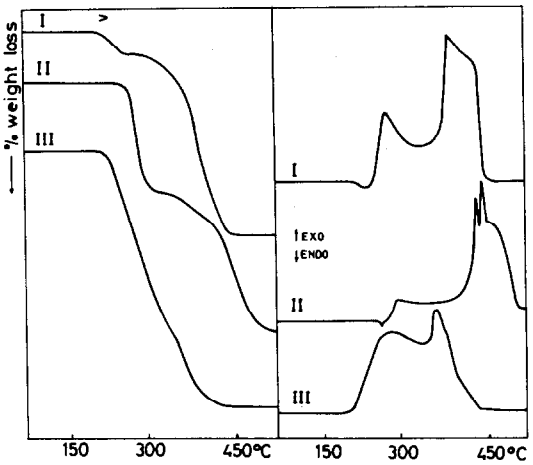

Fig. 2. TG and DTA curves of (I) $Sn(DN)_2$; (II) $(N(But)_4)_2Sn(DN)_3$; and (III) $(PyH)_2Sn(Pg)_3$ under dynamic oxygen atmosphere.

308°C overlapping with each other. The second step occurs with an exothermic effect at 440 and 450°C.

The TG curve of $Sn(DN)_2$ shows that the decomposition takes place in two differentiated steps: (1) partial elimination of the ligand (7.1% weight loss); (2) elimination of the remaining ligand and SnO_2 formation as revealed by X-ray patterns. The calculated total weight loss for the pyrolytic process (65.6%) is in good agreement with the observed value (65.6%). The DTA curve shows, at 254°C, an endothermic peak associated with the first weight loss. An exothermic peak at 278°C occurs without weight loss partially overlapping with the other exothermic process (393–450°C), and is associated with the total elimination of the ligand and SnO_2 residue formation.

Figure 3 shows the TG–DTA curves of $Sn(DN)_2$ in dry nitrogen and dynamic oxygen atmospheres. The DTA curve under dry nitrogen at 254°C

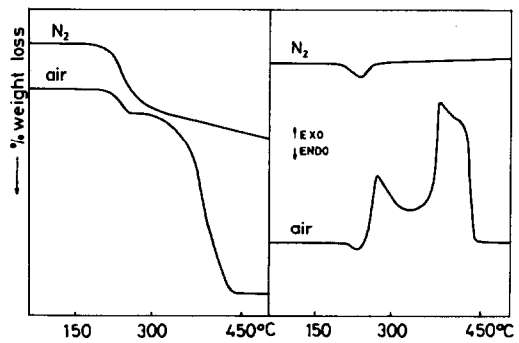

Fig. 3. TG and DTA curves of $Sn(DN)_2$ in dry nitrogen and dynamic oxygen atmospheres.

shows an endothermic peak associated with a weight loss (17.3%) in the TG curve, which is different to that observed in the TG–DTA of the same compound in O_2 atmosphere. This fact suggests that in the latter process there are two overlapping steps: (1) partial elimination of the ligand associated with the endothermic process; (2) O_2 absorption associated with an exothermic process.

In the dry nitrogen process, above 300°C the decomposition is extended to 700°C with slow weight loss.

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