Journal of Thermal Analysis, Vol. 53 (1998) 241-246

THERMAL STUDIES OF DI- AND TRIPHENYLTIN(IV) COMPLEXES OF SALICYLHYDROXAMIC ACID

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(Received September 23, 1996; in revised form July 16, 1997)

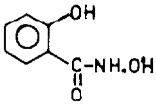
Abstract

Thermal decomposition of di- and triphenyltin(IV) complexes derived from potassium salicylhydroxamate (KSHA) of compositions $Ph_2SnCl(SHA)$, $Ph_2Sn(SHA)_2$ and $Ph_3Sn(SHA)$ has been studied by TG, DTG and DTA. Based upon thermal mass losses the transitory formation of diphenyltin oxide, Ph_2SnO as the possible intermediate from the decomposition pattern of all the three complexes has been proposed. Both DTG and DTA give well-defined peaks in the appropriate regions. These studies reveal the formation of SnO_2 as the ultimate product.

Keywords: complexes, organotin moiety, salicylhydroxamate ion

Introduction

In recent years, the ligating ability of hydroxamic acids with metal ions [1, 2] has attracted increasing interest because of their relevance in a wide variety of chemical, biological and applied problems [3–6]. However, there are only a few scattered reports [7–12] which describe the thermal behaviour and stability of such complexing agents and their complexes in the solid state. Amongst organotin compounds with such ligands, to our knowledge, there has only been one report [13], on the thermal behaviour of di- and triorganotin(IV) derivatives of N,N-disubstituted hydroxylamines. In continuation of our recent efforts to understand the coordinative and biological properties of hydroxamic acids bound to organotin moiety [14], we present here the results of thermal studies of organotin salicylhydroxamates with an aim that they may provide an information regarding the strength of metal-ligand bond. Structural representation of the parent ligand is given below:



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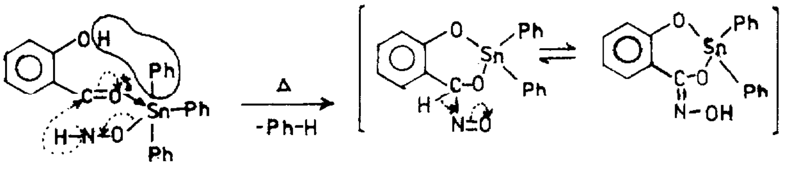
Experimental

Complexes of composition $Ph_3Sn(SHA)$, $Ph_2SnCl(SHA)$ and $Ph_2Sn(SHA)_2$ have been synthesized by reacting Ph_3SnCl and Ph_2SnCl_2 with appropriate amounts of potassium salicylhydroxamate, KSHA in THF+MeOH mixture. The TG, DTG and DTA curves were recorded on Perkin Elmer TGS-2 thermogravimetric analyzer along with TADS computer system at Regional Sophisticated Instrumentation Centre, Nagpur University. The thermocouple used was Pt/Pt-Rh with a temperature range of 20–1000°C. The thermal investigations were carried out by heating the sample in Pt crucible in air atmosphere and a heating rate of 10°C min^{-1} was employed.

Results and discussion

$Ph_3Sn(SHA)$

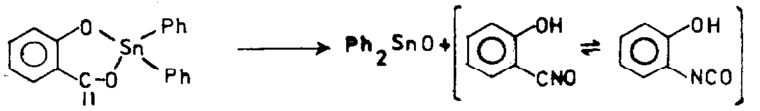
A careful examination of the thermal decomposition curves of triphenyltin salicylhydroxamate in Fig. 1 reveal that the decomposition proceeds mainly through three distinct steps. The complex does not seem to be very stable as indicated by its early decomposition at ~40°C. An initial abrupt mass loss amounting to 13.45% in the temperature range 40–78°C has been attributed to the removal of benzene occurring due to the rupture of Sn–C bond from the complex and not the tin-ligand coordinate bond at this temperature as follows:



$Ph_3Sn(C_7H_6NO_3)$ $Ph_2Sn(C_7H_5NO_3)$ ......(1)

The DTG peak corresponding to this escape of benzene is observed at 65°C.

A subsequent mass loss of 25.75% in the second step in the temperature range 80–170°C is rationalised in terms of the loss of a possible another organic moiety, *o*-hydroxyphenyl-cyanate or isocyanate ($C_7H_5NO_2$) which results into the formation of Ph_2SnO as the probable intermediate given below:



$Ph_2Sn(C_7H_5NO_3)$ $(C_7H_5NO_2)$ ......(2)

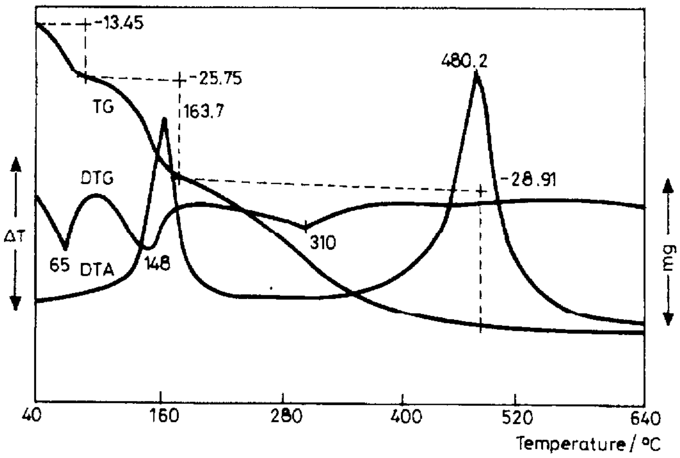


Fig. 1 TG, DTG and DTA curves of $Ph_3Sn(SHA)$

This is also supplemented by the appearance of an exothermic peak at 163.7°C in DTA curve accompanied by DTG peak at 148°C.

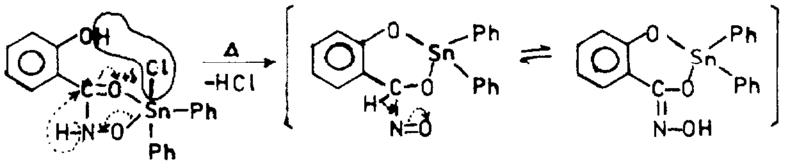
The final mass loss of 28.91% in the temperature range 170–490°C has been attributed to the oxidative decomposition of Ph_2SnO in the form of biphenyl, diphenyl ether, diphenylene oxide, etc. leaving behind final residue, SnO_2 as shown below:

$$Ph_2SnO \xrightarrow[\text{decomposition}]{\text{oxidative}} SnO_2 + \begin{array}{l}\text{biphenyl or}\\ \text{diphenyl ether or}\\ \text{diphenylene oxide}\end{array} \qquad (3)$$

Similar organic matter is reported to have been lost from metal phenoxides also in literature [15]. The oxidative decomposition is reflected in the exothermic peak in DTA at 480.2°C. Only a feeble and broad DTG peak at 310°C has been observed for this decomposition. The overall loss of mass from the curve is 68.11% while the theoretical loss in mass for the conversion of $Ph_3Sn(SHA)$ to SnO_2 is 73.0%.

$Ph_2SnCl(SHA)$

Thermal mode of decomposition of the complex monochlorodiphenyltin(IV) salicylhydroxamate shown as thermogravimetric curve in Fig. 2 indicates that the complex is stable upto 40°C and after that it begins to decompose. The thermal decomposition seems to take place in two steps with one significant break ~170°C. However, initially a small mass loss (6.8%) in temperature range 40–60°C indicated by an inflection in the TG curve ~60°C corresponds well with the loss of hydrogen chloride gas as



$Ph_2SnCl(C_7H_6NO_3)$ $Ph_2Sn(C_7H_5NO_3)$

The DTG with a peak at 52°C has also supported this decomposition.

The major decomposition is observed in the temperature range 60–170°C which amounts to a loss of 35.5% and is well represented by DTG and DTA peaks at 158 and 162.1°C respectively. This is in conformity with the loss of the bound ligand in the complex, thereby leading to a tentative formation of Ph_2SnO (e.g. 2).

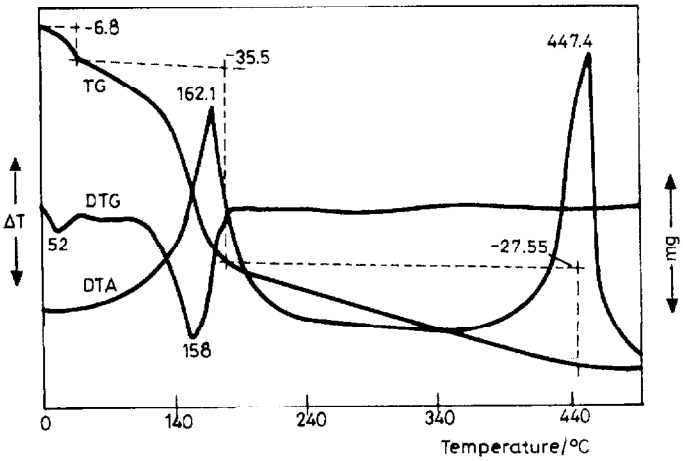


Fig. 2 TG, DTG and DTA curves of $Ph_2SnCl(SHA)$

The final mass loss of 27.55% in the temperature range 170–450°C attributed to the oxidative decomposition of intermediate is consistent with the formation of SnO_2 as the terminal product (e.g. 3). The corresponding DTA shows heat liberation symbolised by an exothermic peak at 447.4°C. No peak in DTG has however been observed for this mass loss.

$Ph_2Sn(SHA)_2$

A perusal of the TG/DTG/DTA curves of the complex $Ph_2Sn(SHA)_2$ in Fig. 3 reveal that it begins to decompose ~50°C and the decomposition apparently occurs in two steps. The major mass loss of 46.89% in the temperature range 40–170°C accounts for the loss of two ligand molecules in a single step. This de-

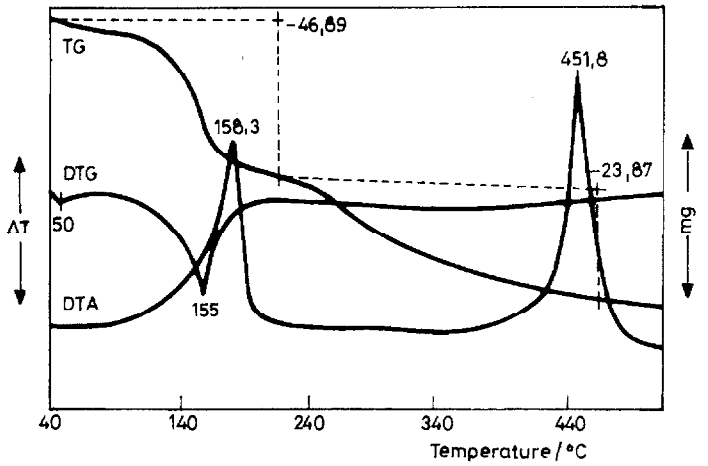


Fig. 3 TG, DTG and DTA curves of $Ph_2Sn(SHA)_2$

composition, however, is indicated by two peaks in DTG and one peak at 158.3°C in DTA. It may be mentioned here that corresponding to mass loss upto 60°C and an insignificant DTG peak at 50°C, no intermediate of definite stoichiometry could be proposed. The decomposition upto 170°C however fits well with the proposition of Ph_2SnO as the probable intermediate, though it appears unstable in the absence of any plateau observed in TG around this temperature.

A continued mass loss of 23.87% in the temperature range 170–475°C in the second step has been proposed to be due to the oxidative decomposition of Ph_2SnO to yield SnO_2 as the ultimate product. It is also supplemented by DTA peak at 451.8°C.

Nevertheless, since no analytical evidence of composition of the intermediates proposed in different complexes could be obtained because of their unstable nature, the possibility of some other types of intermediates cannot be ruled out.

Some useful conclusions drawn from the present study are:

1) The decomposition more or less is a continuous process. No plateau are observed in the decomposition patterns which are indicative of the non-formation of any stable intermediate. The TG curve however reveals that for all the complexes an inflexion at 170°C may account for the proposition of Ph_2SnO as a probable intermediate.

2) It is of interest to note that the final step of decomposition is not projected in DTG curve.

3) The measured percentages of the residual masses (SnO_2) are in good agreement with calculated values and are also consistent with the proposed stoichiometry of the complexes.

4) The final mass loss terminates ~500°C.

Thus based upon modes of thermal decomposition in each of the organotin hydroxamate complexes, it is apparent that Sn–O bond is comparatively more stable than Sn–Cl and Sn–C bonds. These decompositions should therefore be helpful in understanding the mechanism of biodegradation of hydroxamates in biological systems.

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