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A THERMOGRAVIMETRY/DIFFERENTIAL THERMAL ANALYSIS AND PYROLYSIS/GAS CHROMATOGRAPHY–MASS SPECTROMETRY STUDY OF SEVERAL TIN(IV) DITHIOCARBAMATE COMPLEXES IN AN AIR ATMOSPHERE

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ABSTRACT

Our P/GC–MS system has been modified such that pyrolysis can be performed in an air atmosphere. Several tin(IV) dithiocarbamate complexes have been pyrolysed in air in order to rationalise the precise role of oxygen in the decomposition process. Further, the effectiveness of the P/GC–MS technique in separating pyrolysis products from individual decomposition stages was investigated using tetrakis(diethyldithiocarbamato)tin(IV) which, from standard TG studies, is known to decompose in air in two stages. It is doubtful, whether complete separation was achieved due to the similarity of products obtained from each stage of decomposition, however, the general method has potential.

INTRODUCTION

TG/DTA studies may be carried out in vacuum, in an inert atmosphere or in air. Frequently, the derivatograms obtained in air and in an inert atmosphere are different, which is usually a direct consequence of the involvement of oxygen in the decomposition process. A TG/DTA study of tetrakis(diethyldithiocarbamato)tin(IV) provides an example of the general phenomenon[1]. In air, the thermogram (Fig. 1) indicates the presence of two separated stages of decomposition involving relatively large losses of mass, whereas the thermogram in nitrogen (Fig. 2) indicates only one combined stage of decomposition which is associated with a number of overlapping consecutive steps. It is of interest to study further the decomposition of this complex in air using a modified P/GC–MS technique which provides an opportunity to test whether the decomposition products of each stage of decomposition can be separated and identified. Our modified technique also enables the investigation of the effects of oxygen on the mechanisms of decomposition of the substituted tin(IV) dithiocarbamate complexes previously studied[1–3]

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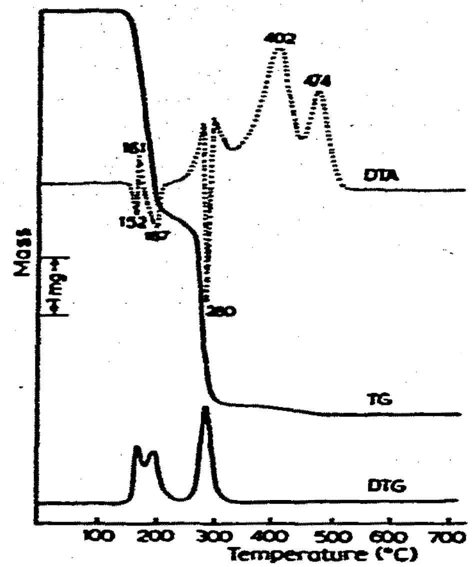


Fig. 1. TG/DTA of tetrakis(diethyldithiocarbamato)tin(IV) in air.

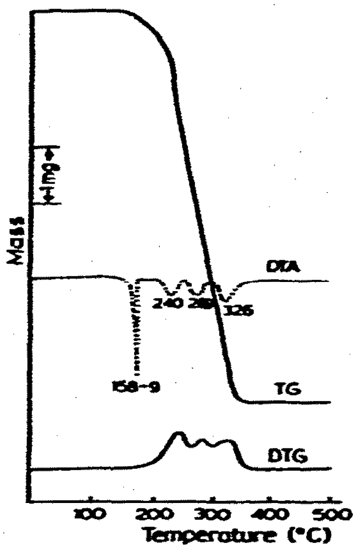


Fig. 2. TG/DTA of tetrakis(diethyldithiocarbamato) (tinIV) in nitrogen.

EXPERIMENTAL

The P/GC–MS technique

In our standard P/GC–MS technique described previously[2,4], helium is used as the carrier gas and it is, therefore, convenient to use helium as the inert atmosphere for pyrolysis. Briefly the method involves heating the sample in a furnace and passing the products of decomposition into the GC column which is interfaced to a mass spectrometer/computer system. In order to allow the pyrolysis to be carried out in air rather than helium, a valve system was devised which replaces the helium flow with an air flow. The air flow was taken from the supply for the flame ionization detector—not normally used in GC–MS work. Air is caused to flow through the carrier gas flow controller, the pyrolysis unit and the column, for a time sufficient to flush the system and to perform the pyrolysis. As the air flows through the column, which is held at room temperature for this process, the dump valve at the end of the column (normally used to prevent large amounts of solvent entering the mass spectrometer) diverts most of the flow to atmosphere. At the end of the heating period, the air is replaced with helium by the operation of a valve, the dump valve is closed and the pyrolysis unit is removed in the usual way[2]. In all other respects the procedure is the same as previously reported[2]. The final furnace temperature is that appropriate for the particular sample under study.

RESULTS AND DISCUSSION

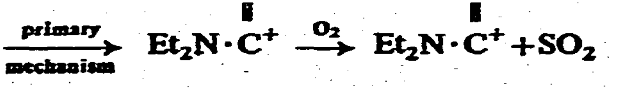
TG—disubstituted tin(IV)dithiocarbamates

The thermograms of disubstituted tin(IV) dithiocarbamates differ in air and nitrogen in that, although the procedural decomposition temperature for each complex is approximately the same in both atmospheres, the remaining decomposition occurs at a much faster rate in air. This is probably caused by the oxidation reactions which liberate energy in addition to that supplied by the furnace, thus causing the increased rate of decomposition.

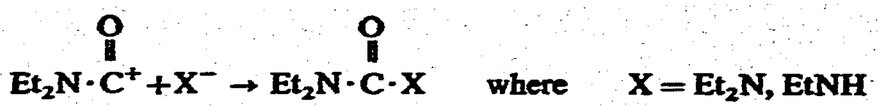
P/GC–MS—air atmosphere—disubstituted tin(IV)dithiocarbamates

As previously reported, pyrolysis of these complexes in helium[1-3] yields, among other compounds, N,N,N',N'-tetraethylurea and N,N-diethylformamide in trace amounts. However, the relative proportions of these compounds increase significantly with respect to the main decomposition product, carbon disulphide, when the pyrolysis is performed in air. The compound N,N,N'-triethylurea was not observed in helium pyrolysis but was detected as a minor decomposition product in air pyrolysis. However, N,N-diethylthioformamide, which was previously observed in helium pyrolysis, was obtained in negligible yield relative to carbon disulphide in air pyrolysis. These specific differences between yields of minor decomposition products from air and helium pyrolyses are common to all the tin dithiocarbamate complexes studied in the present work.

It is proposed that the presence of oxygen does not influence the primary mechanism of decomposition but reacts with one of the unstable intermediates produced in the primary decomposition. A possible reaction is:



$$\xrightarrow[\text{mechanism}]{\text{primary}} Et_2N\cdot\overset{\overset{S}{\|}}{C^+} \xrightarrow{O_2} Et_2N\cdot\overset{\overset{O}{\|}}{C^+} + SO_2$$



$$\mathrm{Et_2N}\cdot\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{+}+\mathrm{X}^{-}\rightarrow \mathrm{Et_2N}\cdot\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot\mathrm{X}\qquad\text{where}\qquad \mathrm{X}=\mathrm{Et_2N},\ \mathrm{EtNH}$$

A number of other compounds containing the $Et_2N \cdot C = O$ group were detected. These will be discussed later since they were not common to all air pyrolysis of the tin(IV) dithiocarbamates studied.

Highly volatile compounds which have very short retention times such as carbonyl sulphide and ethylmercaptan cannot be detected by this modified P/GC–MS technique since, during the 3-min heating period when air is flowing through the pyrolysis unit and the GC column, the effluent gas is diverted to atmosphere.

Thermal decomposition of bis(diethylydithiocarbamato)diphenyltin(IV) in air

Apart from the species mentioned earlier, the only other species which was not present in helium pyrolysis was S-phenyl N,N-diethylmonocarbamate. It is postulated that this compound is the result of the reaction of the Ph radical with the $Et_2N \cdot C = O$ radical. The derivatograms of this complex in air and nitrogen are shown in Figs. 3 and 4, respectively.

Thermal decomposition of bis(diethyldithiocarbamato)tin(IV) dihalide complexes in air

The three complexes $(Et_2NCS_2)_2SnX_2$ (X = Cl, Br, I) were pyrolysed in air. The derivatograms of these complexes (Cl, Br, I) in air and nitrogen are shown in Figs. 5 and 6, 7 and 8, and 9 and 10, respectively. The decompo-

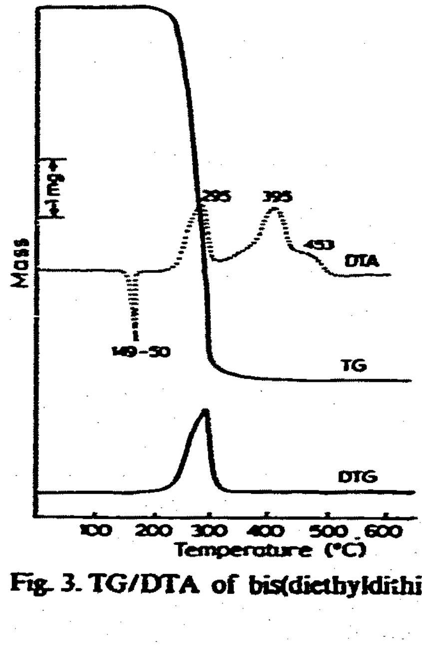


Fig. 3. TG/DTA of bis(diethyldithiocarbamato)diphenyltin(IV) in air.

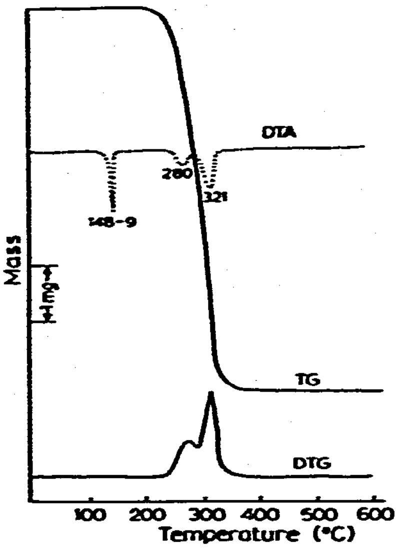


Fig. 4. TG/DTA of bis(diethyldithiocarbamato)diphenyltin(IV) in nitrogen.

sition products were similar to those obtained from helium pyrolysis as indicated by the computer total ion monitor (CTIM) which operates by reconstructing a chromatogram from the sum of the peaks in the mass spectrum. Our system is also equipped with a source total ion monitor (STIM) which measures the ion output at the source. Both systems have advantages and disadvantages but our normal practice has been to use only the CTIM. The sensitivity of this indicator depends upon the ion multiplier gain setting. Where a large dynamic range of sample concentration is encountered it is common practice to increase gain and hence the CTIM output for trace peaks. The STIM output remains unaffected.

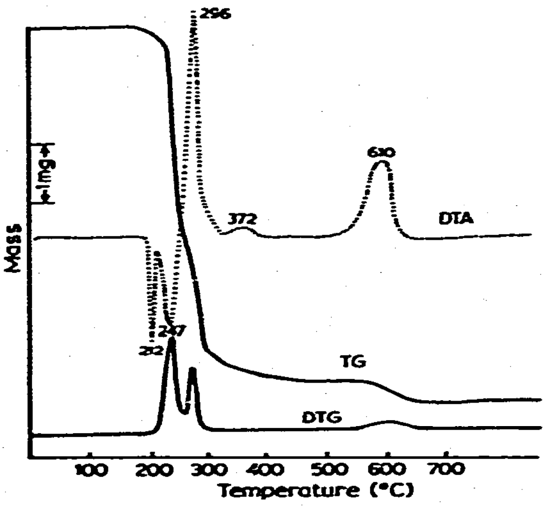


Fig. 5. TG/DTA of dichlorotin(IV)bisdiethyldithiocarbamate in air.

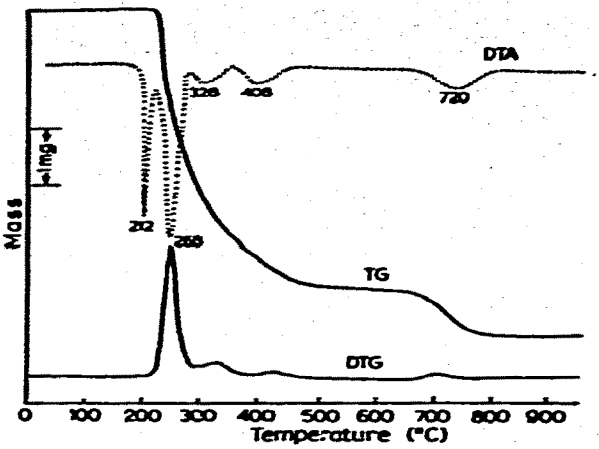


Fig. 6. TG/DTA of dichlorotin(IV)bisdiethyldithiocarbamate in nitrogen.

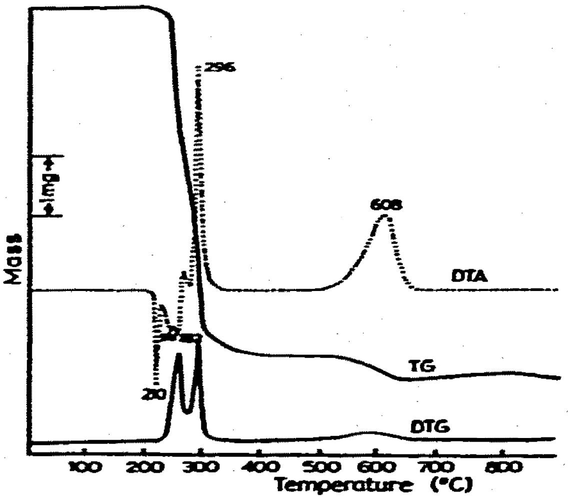


Fig. 7. TG/DTA of dibromotin(IV)bisdiethyldithiocarbamate in air.

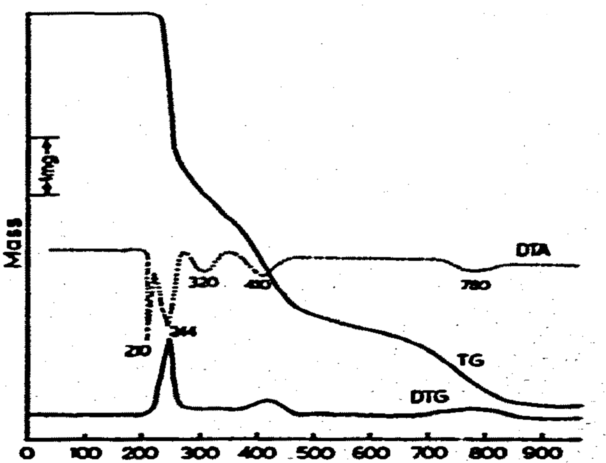


Fig. 8. TG/DTA of dibromotin(IV)bisdiethyldithiocarbamate in nitrogen.

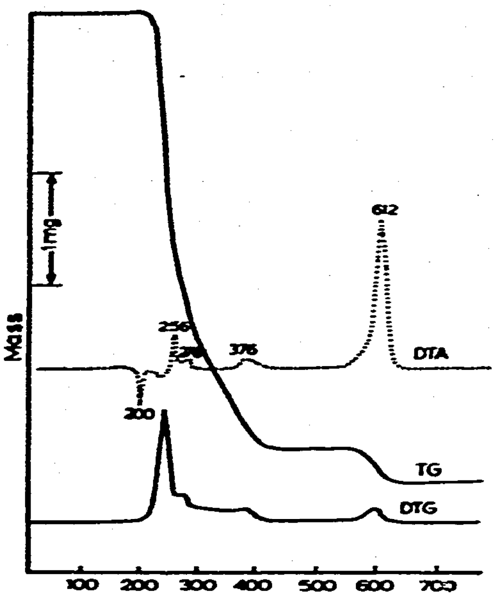


Fig. 9. TG/DTA of bisdiethyldithiocarbamatotin(IV)diiodide in air.

In order to obtain information about relative amounts of individual compounds in these experiments both systems were used. This immediately revealed an interesting trend in that the relative yields of S-ethyl N,N-diethyldithiocarbamate to N,N,N′,N′-tetraethylthiourea and ethylisothiocyanate to carbon disulphide increased as X was changed from chlorine to iodine.

In the original experiments on these compounds using helium[1-3] the STIM was not used and this trend was not observed. Because of this, it was concluded that the halogen ligands had no significant influence on the mechanism of decomposition of the dithiocarbamate ligands, a finding now shown to be only qualitatively true.

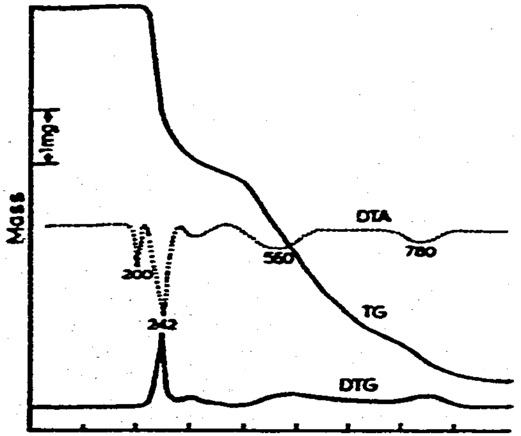
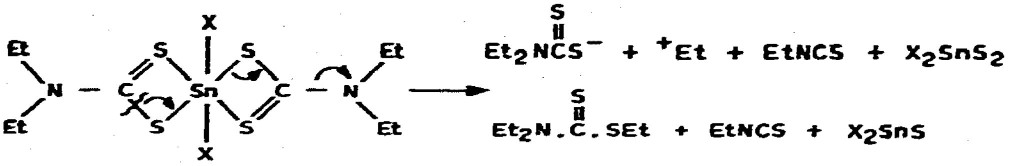


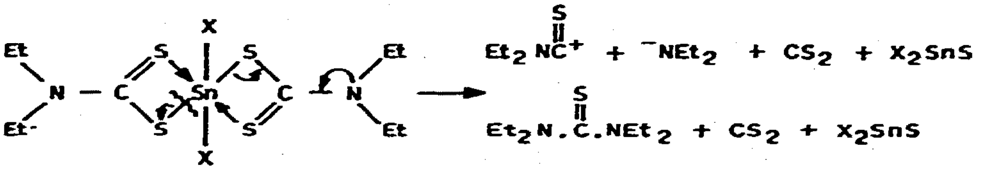
Fig. 10. TG/DTA of bisdiethyldithiocarbamatotin(IV)diiodide in nitrogen.

The trend may be rationized as follows, Mechanism I, given in the original paper[2], competes with an alternative mechanism, II.

Mechanism I



Mechanism II



Although mechanism II increases in importance as X is changed from chlorine to iodine, mechanism II remains of minor significance overall.

Mechanism I appears to be the normal mode of decomposition of bidentate ligands, while Mechanism II yields the same products as the decomposition of two monodentate ligands. This may be explained as the consequence of the increasing distortion in the axial plane of the dithiocarbamate ligands as X changes from chlorine to iodine resulting in the lengthening of the tin–sulphur bonds. The increasing size of the halogen atom weakens the tin–sulphur bonds, thus favouring Mechanism II.

Thermal decomposition of tetrakis(diethyldithiocarbamato)tin(IV) in air

A previous TG/DTA study of tetrakis(diethyldithiocarbamato)tin(IV) has shown that thermal decomposition in air proceeds in two stages both of which involve relatively large losses of mass. This behaviour is best explained by the formation of relatively stable solid intermediate products of decomposition which are produced as a result of oxidation of $L_2Sn = S$ and SnL_2*. These species were proposed as intermediates resulting from decomposition of the complex in an inert atmosphere in a previous paper[1]. Oxidation of either the sulphur atom attached to the tin atom in $S = SnL_2$ or the tin atom in SnL_2 can occur. The oxidation of Sn(II) to Sn(IV) is known to occur, since bis(diethyldithiocarbamato)tin(IV) is unstable in air at room temperature[5]. The thermal stability of the oxidized intermediate products is due to the stronger bonding of the remaining ligands which is caused by several factors. The electron withdrawing capacity of the oxygen atoms causes an increase in the Sn–S bond strength due to the electrons of the Sn–S bonds being bound more strongly to the tin atom. Also the loss of either the major portion of two ligands or

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*L represents the diethyldithiocarbamate ligand.

two complete ligands, in the initial decomposition, removes some steric strain previously associated with the metal–ligand bonds. The probability of two separated stages of decomposition is further enhanced by the relatively low temperature at which the primary decomposition occurs and insufficient heat is available to break the Sn–S bonds in L_2SnS and SnL_2 which subsequently decompose at a higher temperature.

The feasibility of effecting complete separation of the pyrolysis products of each stage of thermal decomposition was examined in the present work. Stepwise heating was employed: the sample was heated to a temperature corresponding to completion of the first stage of decomposition and the products collected. The sample was then allowed to cool prior to reheating to obtain the products of the second decomposition stage. The two upper temperature limits involved were derived from conventional TG profiles. The small sample size (1 mg) and rapid, variable heating rate together produce minor detrimental effects on the separation of the two stages of decomposition[6] but the rapid heating rate does effect the completeness of either or both decomposition stages.

The pyrolysis products obtained from each stage of decomposition were similar. This is not an unexpected result because of the similarity of the ligands. However, such similarity of products makes it impossible to determine whether complete separation of both stages has occurred. If the first decomposition stage is only partially complete, then some of the products of this stage will be collected, together with those of the second stage, after the reheating procedure has been carried out. This may occur for several reasons. Insufficient time at the required temperature (i.e., insufficient heat) will cause only partial initial decomposition. It is well known that decomposition does not occur uniformly throughout a sample[6] especially when the material is heaped or in the form of crystals. The wide range of volatility of the pyrolysis products can cause problems in separation of the products of two stages of decomposition. The highly volatile compounds such as carbon disulphide can easily escape the sample region whereas less volatile compounds such as tetraethylthiourea have an increased possibility that incomplete volitization can occur. Also there is the possibility of adsorption of such involatile compounds on the remaining solid intermediate products. For these reasons the possibility exists that complete separation of the pyrolysis products of each stage was not achieved. However, the similarity of the pyrolysis products of each stage suggests that similar mechanisms of decomposition are associated with both stages.

CONCLUSION

The modified P/GC–MS technique for thermal decomposition studies in an air atmosphere is of considerable value in rationalizing the precise role of oxygen in the decomposition process. Also our modified technique offers the possibility of using gases other than inert gases for pyrolysis studies.

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