

A THERMOGRAVIMETRY/DIFFERENTIAL THERMAL ANALYSIS, EVOLVED GAS ANALYSIS AND PYROLYSIS/GAS CHROMATOGRAPHY-MASS SPECTROMETRY STUDY OF DIHALOTIN(IV)BISDIETHYLDITHIOCARBAMATES

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ABSTRACT

Three dihalotin(IV)bisdiethyldithiocarbamates have been subjected to controlled pyrolysis/GC-MS analysis and the major products of the first stage of decomposition identified. These data, in addition to those obtained from TG/DTA analysis are used to determine the decomposition mechanism of the complexes. In an inert atmosphere dihalotin(IV)bisdiethyldithiocarbamate pyrolyses to yield carbon disulphide and tetraethylthiourea as the major volatile products and dihalotinsulphide as the major solid phase intermediate, which subsequently decomposes to yield tin sulphide. It has been conclusively shown that the nature of the halogen ligands has no influence on the mode of thermal decomposition of these complexes. The proposed thermal decomposition mechanism correlates well with the known structure of the complexes.

INTRODUCTION

The thermochemistry of the metal complexes of dialkyldithiocarbamic acids has been extensively studied in recent years following the observation by D'Ascenzo and Wendlandt¹ in 1969, that a large number of metal diethyldithiocarbamate complexes are volatile in an inert atmosphere. Subsequent thermogravimetric analyses of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Hg(II) complexes showed that thermal degradation occurred in several well-defined steps. The DTA profiles revealed the following progressive behaviour, dehydration, fusion, volatilisation and multi-step decomposition. However, intermediates from the thermal decomposition were not deduced nor were the thermal decomposition mechanisms reported.

The volatile nature of the complexes is of intrinsic interest from the viewpoint of GC separation of a mixture of dithiocarbamate complexes. The formulation of a thermal decomposition mechanism for such complexes affords valuable evidence as to the nature of the metal-sulphur bond. However, the TG/DTA technique alone does not usually provide sufficient information to deduce an unambiguous thermal decomposition mechanism since, even

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when the thermal decomposition occurs in well-defined stages, a mixture of products is evolved in unknown relative proportions. Thus, it appears that previous TG data on metal dithiocarbamates have only qualitative significance.

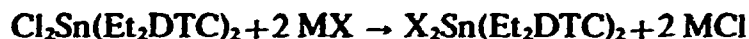
The pyrolysis/gas chromatography/mass spectrometry technique (P/GC-MS) developed by the authors facilitates the identification of the products of a thermal degradation. In an early study of copper dithiocarbamates², the decomposition occurred as a single step³ and this made the experimental procedures relatively simple. It was only necessary to heat the sample to a temperature above that required for decomposition to obtain all the products, which were then injected onto the GC column simultaneously. Separation and identification of the products led to the deduction of an unambiguous decomposition mechanism. This study indicated that, although a thermal degradation may occur as a clearly defined step, the products may be a complex mixture. Thus, in a case where the decomposition is more complicated, it is advantageous to control the pyrolysis, so as to collect and identify the products of each stage. A necessary prerequisite for this method is a knowledge of the temperatures at which the various stages of decomposition occur. An experimental procedure can be envisaged, in which the sample may be heated to a temperature just above the end of the primary decomposition and, with the sample remaining at this temperature, the GC-MS analysis may be carried out. Further stepwise heating would allow the products of subsequent steps to be analysed.

In view of the report by D'Ascenzo et al.⁴ that dichlorotin(IV)bisdiethyl-dithiocarbamate decomposed in a well-defined two step manner, this compound was selected in order to test the above procedure. However, our data (Figs. 1 and 4) indicated that a well-defined two step decomposition does not occur and it was therefore apparent that a further investigation of the thermal behaviour of this compound was necessary. Furthermore, in order to investigate the influence of halogen ligands on the thermal decomposition mechanism of this class of complexes, the thermal decomposition behaviour of the dibromotin(IV)diethyldithiocarbamate and diiodotin(IV)bisdiethyldithiocarbamate was examined. No thermal data on the latter compounds could be found in the literature.

EXPERIMENTAL

Synthesis of complexes

For TG/DTA and P/GC-MS studies of these complexes, high purity is essential. The syntheses described by Bonati et al.⁵ for the dihalotin(IV)bisdiethyldithiocarbamate complexes were found to be unsatisfactory due to incomplete replacement of the chloro ligand by bromine or iodine. The following reaction represents the method used in the synthesis of the dibromo and diiodo complex



where $\text{MX} = \text{NaBr}$ and KI .

The dichloro complex was prepared by reaction of anhydrous tin tetrachloride with the sodium salt of diethyldithiocarbamic acid in warm acetone. The solid product formed was obtained by decanting the supernatant solution. The solid product was then allowed to dry in air and the melting point determined. This method was repeated using the decanted material until the M.P. of the product did not change. Microanalysis (Table 1) and mass spectral data indicated a low (<2%) level of impurity—mainly ligand and solvent.

The dibromo complex was prepared by the general method of Bonati et al.⁵ using warm acetone as solvent. The product was contaminated by a chlorotin(VI)dithiocarbamate complex as indicated by mass spectrometry and it was apparent that the exchange of the halogen atoms had not proceeded to completion. This was overcome by decanting the supernatant liquid and reacting it with excess NaBr and additional acetone. This procedure was repeated until only a very small amount of the chloro-containing complex remained, as indicated by the mass spectrum of the solid product. However, excessive repetition of this procedure resulted in the production of tin tetrabromide and it was necessary to maintain a balance between these two impurities. It was interesting to note a slight colour change, from pale yellow to yellow, as the purity of the required dibromo complex improved.

In the case of the diiodo complex, the halogen exchange occurred very readily, even in cold solution. However, the tin tetraiodide was also easily formed and it was necessary to maintain strict control over the quantity of KI with a resulting increase in unexchanged product. The colour change was much more noticeable, from pale yellow to bright yellow. An orange tint indicated formation of tin tetraiodide. The addition of excess diethyldithiocarbamate ligand failed to reconvert the tin tetraiodide to the diiodo complex.

Impurities in the latter compounds, i.e., the dichloro, the mixed halogen compounds or the tetrahalides are at low levels as indicated by microanalysis data (Table 1).

TABLE 1

MICROANALYSIS DATA

Microanalysis carried out by Microanalysis Service, Melbourne University

Complex	M.P. (°C)	M.P. (°C) (Lit.)	C	H	N	S	X	
$\text{Cl}_2\text{Sn}(\text{Et}_2\text{DTC})_2$	212	220–221 ⁵ , 200–201 ⁶ , 219 ⁷	24.8	4.0	5.9	26.2	14.9	Found
Pale yellow			24.8	4.1	5.8	26.6	14.6	Calculated
$\text{Br}_2\text{Sn}(\text{Et}_2\text{DTC})_2$	210	220 ⁵ , 203 ⁷	21.2	3.8	4.7	22.4	26.0	Found
Yellow			20.9	3.5	4.9	22.3	27.8	Calculated
$\text{I}_2\text{Sn}(\text{Et}_2\text{DTC})_2$	198–199	202 ⁵ , 200 ⁷	20.0	3.0	3.9	18.8	37.5	Found
Bright yellow			20.0	3.0	4.2	19.2	37.9	Calculated

Mass spectra of the complexes were recorded using a JEOL JMS-D100 mass spectrometer at an electron ionising energy of 75 eV.

TG/DTG and DTA data were obtained using a Rigaku-Denki thermal analysis system. Samples were heated in atmospheres of dry air and oxygen-free nitrogen. The sample mass range was 5–12 mg and the furnace heating rate was 10 °C min⁻¹.

Thermal decomposition products were determined using the pyrolysis/GC-MS technique previously described². The only difference between our technique and that reported previously was in the design of the sample holder. The holder consists of a stainless steel tube, silver soldered to a stainless steel syringe needle in which a small glass tube containing the sample is inserted. The glass tube is sealed at one end with a small hole in the wall, to allow the carrier gas to pass to the GC column. The technique involves heating the sample in the holder surrounded by a small furnace. A comparison of results of P/GC-MS analyses of the dichloro complex using the original glass system and modified stainless steel system indicated that the stainless steel had no effect on the relative yields and the chemical classes of decomposition products. The stainless steel holder is far more robust. The products are transported onto the GC column by the carrier gas (helium) which flows through the holder during the heating period. After the heating ceases, the helium is switched to bypass the sample holder which may then be removed for cleaning. The GC column was 12 × 1/8 in. O.D. glass column packed with 3% DC550 on 60/80 Chromosorb G. The helium flow-rate was 10 cm³ min⁻¹ and the oven temperature was programmed at 12 °C min⁻¹ up to 200 °C, after an initial hold-period at room temperature of 3 min. The sample was heated for 3 min. The complete GC-MS-computer system has been described elsewhere³. The system is equipped with two total ion monitors. One continuously senses the output of the mass spectrometer ion source and thus produces a record similar to that of the gas chromatograph detector. The other is a computer reconstruction of this obtained by summation of the mass spectral peak intensities in each spectrum. With due regard for instrumental effects, both produce an output proportional to the amount of sample present in the source at any given time.

An evolved gas analysis (EGA) was carried out in order to detect the highly volatile gases of decomposition which are not sufficiently well-resolved on the GC column. This was done using the same mass spectrometer, by heating the sample in an all-glass gas inlet system.

RESULTS AND DISCUSSION

Mass spectral data

The mass spectra of the dihalotin(IV)bisdiethyldithiocarbamate complexes are complicated by the presence of the isotopes of chlorine, bromine

and tin. In all cases the probe temperature required to obtain the spectra is in the temperature range in which decomposition occurs. Thus the possibility exists that the spectra include those of intermediates in the decomposition process. However, all ions observed are related to the parent complex, independent of which process leads to their formation. These considerations are not material to these studies since the spectra were obtained to ascertain the nature and extent of impurities. In any case the existence of a parent molecular ion for the dichloro compound indicates that at least some of this material exists in the ion source in the gas phase. The other two complexes do not exhibit molecular ions; a not entirely unexpected results in view of the increased lability of the tin-halogen bonds and it is, therefore, possible that these compounds can also exist in the gas phase.

With due regard to the above considerations the mass spectra obtained are consistent with the correct molar masses and structures of these complexes. The main feature of all the spectra is the fragmentation of the diethyldithiocarbamate ligand. Ions formed as a result of the rupture of the metal-ligand bonds are also observed. The spectra exhibit peaks corresponding to the ions $X_2SnL_2^+$, $XSnL_2^+$, SnL_2^+ , X_2SnL^+ , SnL^+ , XSn^+ , Sn^+ and X^+ . Further fragmentation of the ligand results in ions $SSCNEt_2^+$, $SCNEt_2^+$, $SCNHEt^+$, $SCNH_2^+$, CS_2^+ , NEt_2^+ , Et^+ and a doublet corresponding to $HNEt^+$ and SC^+ (weak). L and X represent the diethyldithiocarbamate ligand and the halogen atom, respectively. As previously stated, the mass spectra of dibromo and diiodo complexes show the presence of small quantities of impurities. Both the bromo and iodo samples contain a chloro complex as indicated by the $ClSnL_2^+$, Cl_2SnL^+ , $ClSnL^+$ and $ClSn^+$ ions found in the mass spectra. Also a series of groups corresponding to SnX_4^+ , SnX_3^+ and SnX_2^+ ions were observed in the mass spectrum of both bromo and iodo complexes resulting from the fragmentation of the tin tetrahalide impurity.

TG/DTA analysis of dihalotin(IV)bisdiethyldithiocarbamates

All thermograms of the three complexes (Figs. 1 to 6) in both air and nitrogen show that decomposition begins just after the melting point. There are three decomposition steps. In air, the first two steps are immediately consecutive and involve sudden losses of mass. In nitrogen, the mass loss at the first step is sudden but the loss of mass in the second step is more gradual. In both air and nitrogen, an almost constant relative loss of molar mass occurs in the first step and it is clear that most of the diethyldithiocarbamate ligands are lost. In the second step, the increasing molar mass lost in the progression from the chloro to the iodo complex indicates that the halogen ligands are lost during this step. The temperature ranges and percentage mass losses in the

*The ion ($SCNEt_2^+$) is the base peak in all spectra.

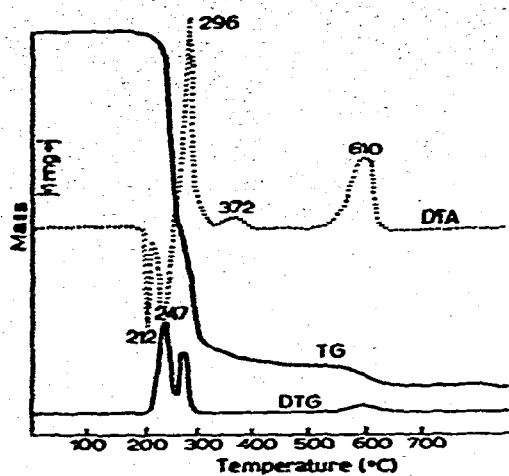


Fig. 1. TG/DTA of dichlorotin(IV)bisdiethyldithiocarbamate in air.

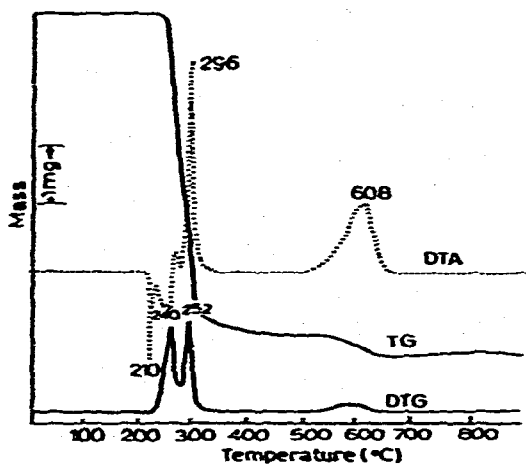


Fig. 2. TG/DTA of dibromotin(IV)bisdiethyldithiocarbamate in air.

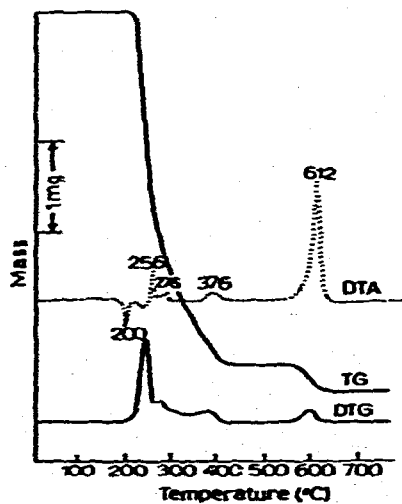


Fig. 3. TG/DTA of bisdiethyldithiocarbamatotin(IV)diiodide in air.

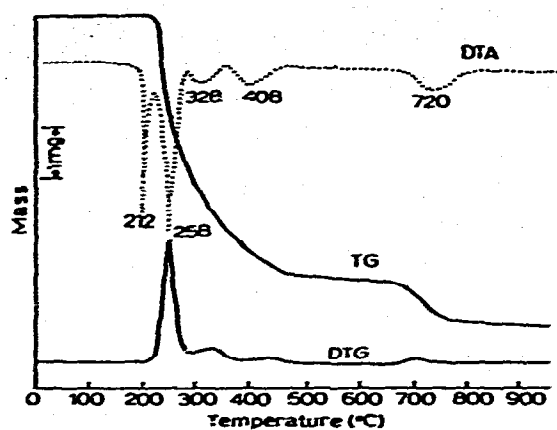


Fig. 4. TG/DTA of dichlorotin(IV)bisdiethyldithiocarbamate in nitrogen.

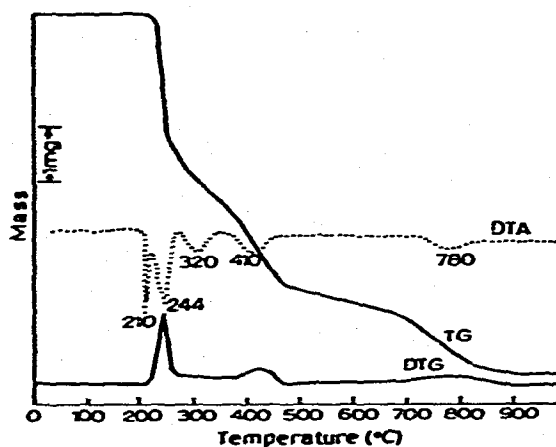


Fig. 5. TG/DTA of dibromotin(IV)bisdiethyldithiocarbamate in nitrogen.

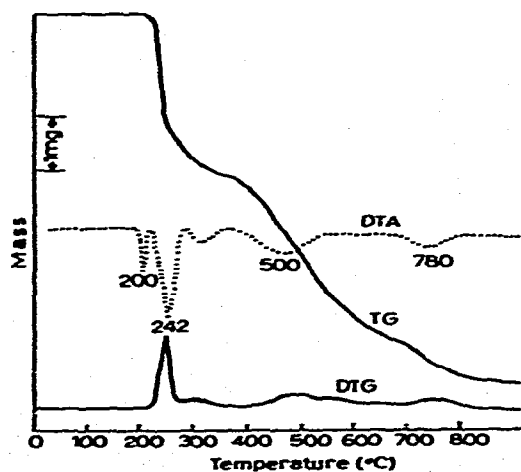


Fig. 6. TG/DTA of bisdiethyldithiocarbamatotin(IV)diiodide in nitrogen.

decomposition are given in Table 2. The theoretical percentage mass losses corresponding to the proposed mechanism of thermal decomposition are also given.

TABLE 2

SUMMARY OF TG DATA FOR DIHALOTIN(IV)BISDIETHYLDITHIOCARBAMATE COMPLEXES

	<i>First step</i>	<i>Second step</i>
<i>Atmosphere, air</i>		
$\text{Cl}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	212–260	260–320
Percentage mass loss	45.8	18.5
$\text{Br}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	210–260	260–330
Percentage mass loss	40.9	29.1
$\text{I}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	200–260	260–400
Percentage mass loss	38.9	32.5
<i>Atmosphere, nitrogen</i>		
$\text{Cl}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	212–320	320–460
Percentage mass loss	51.7 (54.4)*	14.9 (14.6)
$\text{Br}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	210–340	340–600
Percentage mass loss	45.6 (46.0)	24.0 (27.8)
$\text{I}_2\text{Sn}(\text{Et}_2\text{DTC})_2$		
Temperature range (°C)	198–330	330–640
Percentage mass loss	39.9 (39.5)	39.9 (37.9)

*The percentage mass loss in brackets represents the percentage mass loss as calculated from the proposed mechanism of thermal decomposition.

In all cases the third step is clearly separated from the second. In air, the third step involves the gradual conversion of the remaining tin sulphide to tin(IV) oxide. The gradual formation of tin(IV) oxide possibly proceeds via the formation of a number of tin sulphides and mixed sulphur oxide species^{9,10}. The TG/DTA profile for the third step in air indicates a slight loss of mass coupled with a large exothermic change possibly indicating the formation of some of these species. In nitrogen, the third step involves the decomposition of tin(II) sulphide to metallic tin and sulphur at a high temperature (above 750 °C).

The DTA peaks correspond exactly with the greatest rate of mass loss in the TG in all steps, in both atmospheres, except for the first endothermic DTA peak which corresponds to the melting point of the complex. The DTA data indicate that, in nitrogen, the first and second steps are endothermic due to the breakage of bonds and the formation of stable products via reactive in-

intermediates. In air, the first step is endothermic but the second is markedly exothermic; probably a reaction between air and the residual tin sulphide is occurring.

EGA data for dihalotin(IV)bisdiethyldithiocarbamates

For the identification of the volatile compounds evolved upon heating the sample in the glass inlet system to the GC/MS, the process of successive subtraction of reference mass spectra was used. Upon identification of a volatile component by comparison with reference mass spectra^{11,12}, the corresponding mass spectrum was subtracted from the total EGA mass spectrum with the appropriate adjustment of *m/e* peak intensities. By this method minor amounts of ethylisothiocyanate and diethylamine were identified in the presence of extremely large amounts of carbon disulphide. For each complex studied, ethyl halide was detected. Tetraethylthiourea was not detected in the

TABLE 3

IDENTIFICATION TABLE OF PYROLYSIS PRODUCTS FROM GC-MS ANALYSIS

No.	Name	Identification Ref.
1.	Carbonyl sulphide	11
2.	Ethyl mercaptan	11
3.	Acetone (solvent)	11
4.	Carbon disulphide	11
5.	Diethylamine	11
6.	Triethylamine	11
7.	1-Ethyl pyrrole	11
8.	Ethylisothiocyanate	11
9.	1-Ethylthiaziridine-3-thione*	
10.	Diethyl disulphide	11
11.	Diethylnitrosamine	12
12.	Unknown	
13.	Unknown (MW = 98)	
14.	N,N-diethylformamide	12
15.	Unknown	
16.	Unknown	
17.	Unknown	
18.	Unknown	
19.	N,N,N',N'-tetraethylurea	12
20.	N,N-diethylthioformamide*	
21.	Unknown (MW 156)	
22.	Unknown (MW 170)	
23.	S-Methyl N,N-diethyldithiocarbamate*	
24.	N,N,N',N'-tetraethylthiourea	12
25.	S-Ethyl N,N-diethyldithiocarbamate*	
26.	Chloroethane	11
27.	Bromoethane	11
28.	Iodoethane	11

*Proposed structure.

EGA since it is involatile at a pressure of about 0.5 Torr at room temperature. The B.P. of this compound is 93–95 °C under a reduced pressure of 0.8 mm of Hg (0.8 Torr)¹⁴.

The EGA data are in good agreement with the P/GC–MS data, even though the heating rate of 40 °C min⁻¹ is much slower than the furnace (>200 °C min⁻¹) in the P/GC–MS experiments.

The GC–MS analysis of the decomposition products of dihalotin(IV)bisdiethyldithiocarbamates

Only the first stage of thermal decomposition (in inert atmosphere-helium) of the three complexes results in compounds which can be detected by our technique. The main halogen product (halogen gas) is too reactive with the GC column to pass through it and the temperature of the third step of decomposition is too high for our technique to be applicable.

Most of the main decomposition products were identified by comparison with reference mass spectra^{11,12}. Other compounds were identified by deducing their molecular structure from their mass spectra and from the known structure of the complexes. In Figs. 7–9, the output of the source total ion monitor (STIM) is shown for the pyrolysis of each complex. The major products, carbon disulphide and tetraethylthiourea, were the same for each complex. The main difference between the decomposition products of each complex is the ethyl halides. There are also differences in the yields of minor products compared with the major products.

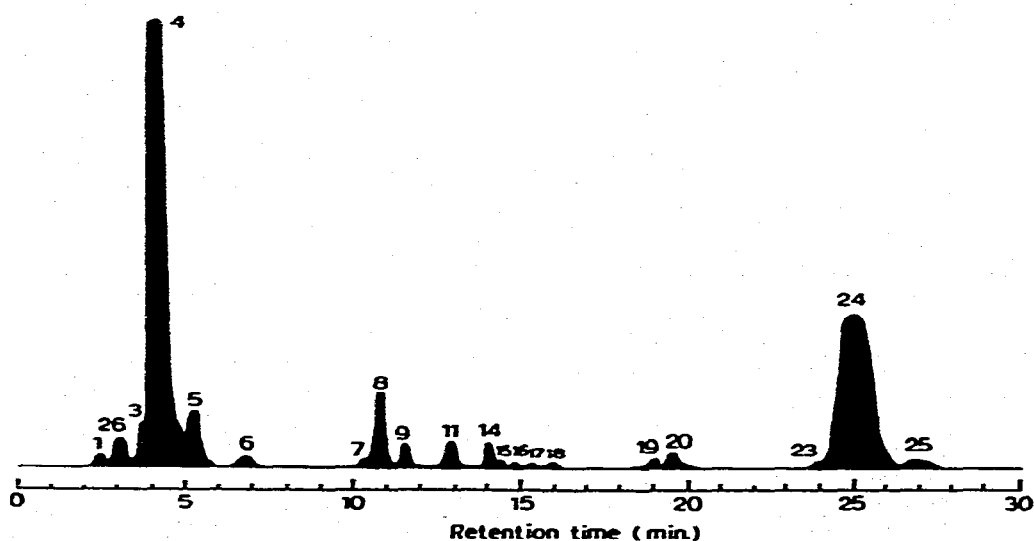


Fig. 7. STIM of P/GC–MS of dichlorotin(IV)bisdiethyldithiocarbamate.

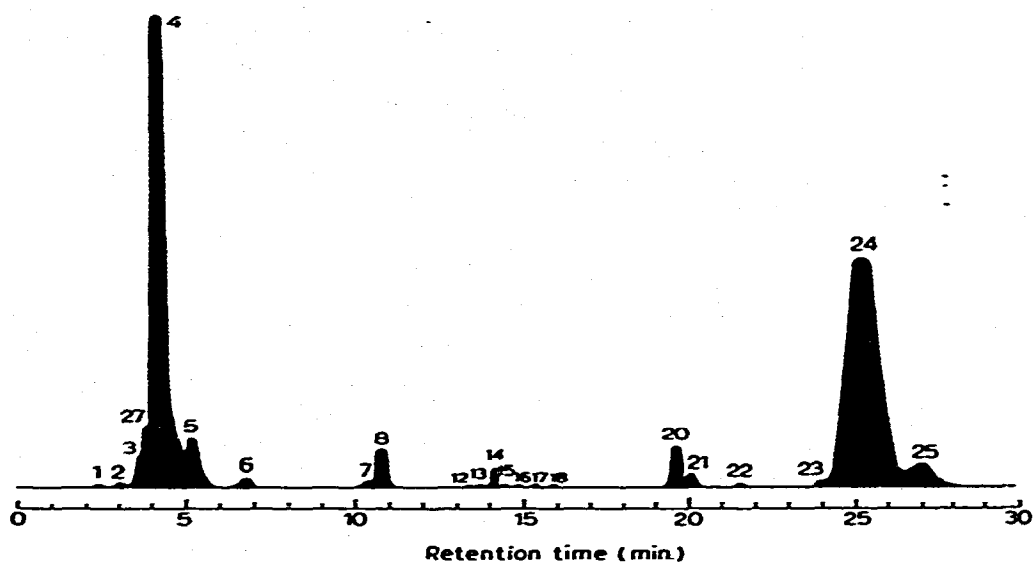


Fig. 8. STIM of P/GC-MS of dibromotin(IV) bisdiethyldithiocarbamate.

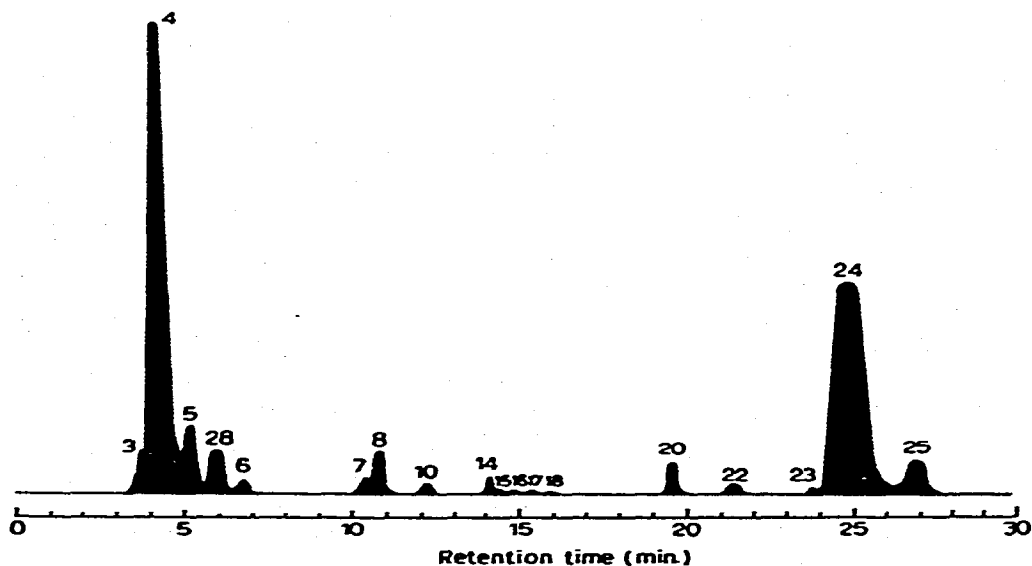


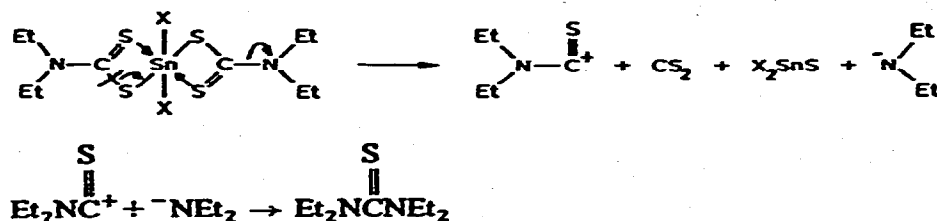
Fig. 9. STIM of P/GC-MS of bisdiethyldithiocarbamatotin(IV) diiodide.

CONCLUSION

The effectiveness of our technique, in separating the thermal decomposition products of each step, has not been proved, since only the products of the first step passed through the GC column. However, our technique has

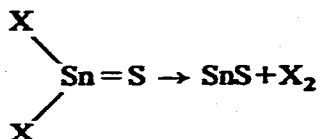
proved very valuable in elucidating the thermal decomposition mechanism for the dihalotin(IV)bisdiethylthiocarbamate complexes.

The major products of the first stage of decomposition in nitrogen were carbon disulphide and tetraethylthiourea. These products are very similar to the major products of decomposition of bisdiethylthiocarbamate copper(II) and hence the mechanism is probably very similar to that proposed by Sceney et al.² The mechanism for the first stage is envisaged as:



X represents the halogen ligand.

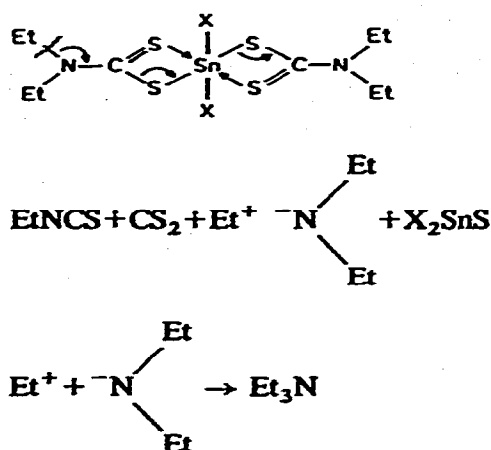
The second decomposition stage in nitrogen involves the decomposition of dihalotin(IV)sulphide possibly by the loss of the halogen gas. The ethyl halides are present in amounts too small to be considered as the major mode for the loss of halide ligands from the parent complexes. Their formation may be due to a minor reaction of the ethyl species with the halogen species. The proposed mechanism for the second stage is envisaged as:



This reaction probably involves interaction between molecules of X_2SnS leading to the formation of halogen gas.

The third decomposition stage in nitrogen involves the loss of sulphur from tin sulphide to yield metallic tin. The resulting concentrations of carbon disulphide and tetraethylthiourea should be equal in order to fit the postulated mechanism of thermal decomposition. Source total ion monitor runs indicated that the yield of tetraethylthiourea was less than that of carbon disulphide. This could be the result of secondary minor modes of decomposition which can also produce carbon disulphide but without the formation of tetraethylthiourea. Another possibility is that the ions postulated for the formation of tetraethylthiourea can react with impurities and with the halogen species to form other compounds. Earlier P/GC-MS runs on the impure dichloro complex have shown that the formation of tetraethylthiourea is dependent on the purity of the sample and with increasing purity, the yield relative to carbon disulphide increases.

Some of the minor decomposition products can be explained by slight alterations to the mechanism of thermal breakdown such as follows:



The triethylamine could possibly dehydrogenate to form 1-ethyl pyrrol thus supplying the hydrogen atoms for the formation of diethylamine (Et_2NH) and N,N -diethylthioformamide ($\text{Et}_2\text{N} \cdot \text{CS} \cdot \text{H}$). These products can easily form since both $\text{Et}_2\text{N} \cdot \text{CS}^+$ and $^-\text{NEt}_2$ ions are postulated in the thermal decomposition mechanism.

The GC-MS results indicate that small amounts of oxygen-containing molecules are present as products of decomposition. This is probably due to the presence of acetone (solvent), oxygen-containing impurities and water vapour. The pyrolysis of acetone does not occur readily at temperatures below 400°C ¹⁴. Unless one or more of the products acts as catalyst, the effect of acetone on the products of decomposition is expected to be negligible. The presence of impurities containing oxygen is the probable cause of some of the oxygenated species produced. However, the presence of water results in the formation of hydrogenated and oxygenated species via hydrogen abstraction and hydroxyl radical reactions.

It is interesting to note that the nature of the halogen ligand attached to the tin atom does not modify the thermal decomposition mechanism of the complex. X-ray structural data on the dihalotin(IV)bisdiethylthiocarbamate complexes are not available and Mössbauer spectral data¹⁵ for these compounds cannot differentiate between a tetrahedral and octahedral structure. However, infrared data obtained by Zaidi et al.⁷ indicate a *trans*-orientation of the halogen ligands in an octohedral structure. Our thermal data are consistent with an octahedral structure for the dihalotin(IV)bisdiethylthiocarbamates and the diethylthiocarbamate acting as a bidentate ligand.

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