A THERMOGRAVIMETRY/DIFFERENTIAL THERMAL ANALYSIS, EVOLVED GAS ANALYSIS AND PYROLYSIS/GAS CHROMATOGRAPHY–MASS SPECTROMETRY STUDY OF TETRAKIS (DIETHYLDITHIOCARBAMATO)TIN(IV)

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ABSTRACT

The thermal decomposition of tetrakis(diethyldithiocarbamato)tin(IV) has been studied by TG/DTA, EGA and P/GC–MS techniques. From the P/GC–MS analysis, it is apparent that the denticity of the dithiocarbamate ligand influences the mechanism of decomposition. Initially, the monodentate ligands decompose by a radical mechanism to form tetraethylthiuramdisulphide which decomposes further into carbon disulphide and diethylamine. The intermediate formed, bis(diethyldithiocarbamato)tin(II), decomposes in two different ways. The bidentate ligands decompose with the liberation of carbon disulphide and tetraethylthiourea, whereas the monodentate ligands, formed as a result of the high temperatures, decompose to produce S-ethyl N,N-diethyldithiocarbamate and ethylisothiocyanate. The overall thermal decomposition mechanism of tetrakis(diethyldithiocarbamato)tin(IV) is complex and the primary decomposition involves both ionic and radical recombination reactions.

INTRODUCTION

Previous studies by the authors on the thermal decomposition of disubstituted tin(IV)bisdiethyldithiocarbamates[1,2] have shown that both the denticity of the dithiocarbamate ligand and the nature of the other ligands attached to the central tin atom affect the thermal decomposition mechanism of these complexes. In order to study the influence of the denticity of the dithiocarbamate ligand on the thermal decomposition of these complexes in isolation, a neutral tin(IV) dithiocarbamate complex is required. X-ray diffraction studies on tetrakis(diethyldithiocarbamato)tin(IV)[3], show that both mono- and bidentate ligands are present. It is thus expected that the thermal decomposition of this complex will be affected by the mixed denticity of the ligands.

In this paper a mechanism of thermal decomposition of tetrakis(diethyldithiocarbamato)tin(IV) is proposed in which the initial decomposition takes place in the monodentate ligands to yield bis(diethyldithiocarbamato)tin(II) as an inter-

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mediate, which further decomposes to the tin(II)sulphide. This latter decomposition takes place in a manner not expected from a complex shown to possess only bidentate ligands[13,14].

EXPERIMENTAL

Synthesis

Tetrakis(diethyldithiocarbamato)tin(IV) was synthesized by the reaction of a slight excess of the stoichiometric amounts of the sodium salt of diethyldithiocarbamic acid with tetrachlorotin(IV) in acetone. This procedure is similar to those described in previous publications[4,5]. The resulting precipitate was filtered. Partial vaporization of the filtrate yielded more precipitate of the required product which was subsequently washed with water to remove residual sodium chloride. Microanalysis data are shown in Table 1.

TABLE 1

MICROANALYTICAL DATA (Microanalysis Service, Melbourne University)

$Sn(S_2CNEt_2)_4$	% C	% H	% N	% S	
M.P. = 158–159 °C	33.59	5.60	7.67	35.70	Found
	33.75	5.66	7.87	36.04	Calculated
Literature value of M.P. = 154–156 °C[4], 162°C[5]					
Final residue (TG analysis under nitrogen)	% S				
	19.8	Found			
	21.3	Calculated for tin(II)sulphide			

Mass spectra

Mass spectra were recorded on a JEOL JMS D-100 mass spectrometer using an electron ionizing energy of 75 eV.

TG/DTA

TG/DTA was carried out in air and nitrogen atmospheres using a Rigaku-Denki thermal analysis system at a heating rate of 10 °C min⁻¹ using sample sizes in the 7–12 mg range.

P/GC–MS technique

The technique has been described in detail previously[1,6]. Briefly, the method involves heating the sample in a furnace and passing the products of thermal decomposition into a GC column interfaced to a mass spectrometer/computer system. The temperature of the furnace was raised to 400 °C so that the sample was completely decomposed down to the final residue. A number of P/GC–MS analysis were carried with the GC column operating un-

der isothermal conditions at 200 °C in order to detect the less volatile sub-stances (high molar mass compounds).

Pyrolysis–gas chromatography technique

This technique is very similar to the P/GC–MS technique described above. A Pye 104 gas chromatograph was used in conjunction with a flame ionization detector (FID). The only difference between this technique and that described previously is that the decomposition products pass through the GC column to the FID instead of passing to the mass spectrometer. The same experimental conditions are used in both techniques.

EGA

The EGA was carried out on the tetrakis(diethyldithiocarbamato)tin(IV) by heating a sample in a glass tube surrounded by a furnace. The glass tube was attached to the gas inlet of the JEOL JMS D-100 mass spectrometer during the heating and analysis was carried out under vacuum.

RESULTS AND DISCUSSION

Mass spectral data

Mass spectrometry is routinely used to confirm molecular structure and stoichiometry and to detect the presence of impurities. However, the mass spectrum of tetrakis(diethyldithiocarbamato)tin(IV) was inconclusive since the only ions observed were those corresponding to SnL_2^+, SnL^+ and Sn^+ and frag-mentation products of the ligand (L). In a previous publication[1] the authors mentioned the possibility of the existence of intermediates formed as a result of thermal decomposition in the probe. The spectrum of the tin complex was obtained at a temperature of 180 to 200 °C at which decomposition certainly occurred and thus the spectrum is that of intermediate products [e.g., bis(die-thyldithiocarbamato)tin(II)]. However, the possibility that bis(diethyldithiocar-bamato)tin(II) exists as an impurity in the sample is extremely unlikely since the reduction of Sn(IV) to Sn(II) is unfavourable in the absence of a reducing agent in the synthesis. The mass spectrum indicated a very low level of dis-similar impurities (less than 1% by mass).

TG/DTA data

Decomposition of the complex in air (Fig. 1) occurs just after melting, with two major steps involving considerable losses of mass. The first step involves two processes, clearly indicated by the DTG and DTA with the first processes being exothermic and the second endothermic. Previous work by the authors has shown that all decomposition reactions of disubstituted tin(IV)di-thiocarbamates are endothermic in both air and nitrogen. The exception to this behaviour is the exothermic reaction of oxygen with the tin(II)sulphide resi-

due. It is postulated that the first process involves the partial decomposition of the tetrakis(diethyldithiocarbamato)tin(IV) and as a result of the exothermic reaction between the tin intermediate and oxygen contributes largely to the exothermic nature of the first process. The possibility exists that oxygen may react with the products of decomposition but an investigation of the decomposition of the complex in air[7] by the P/GC–MS technique has shown that only minor amounts of oxygenated species are produced and hence oxygen is bound to the residue rather than to the volatile species. However, this only explains the exothermic nature of the DTA but not the nett mass loss.
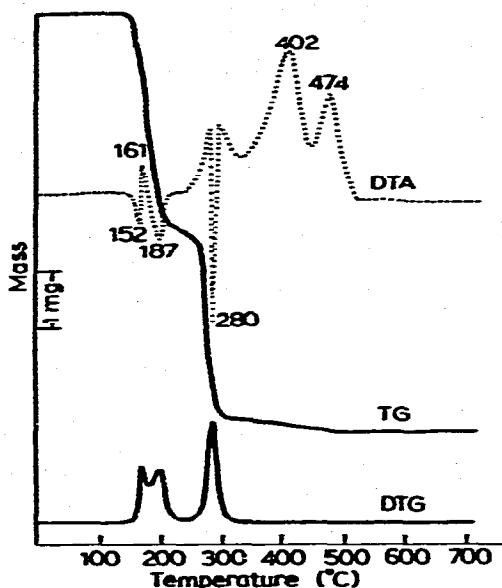

Fig. 1. TG/DTA of tetrakis(diethyldithiocarbamato)tin(IV) in air.

Therefore, it is postulated that the first process involves the formation of the decomposition products of the entire first step but with the immediate loss of the highly volatile compounds, such as carbon disulphide. The much less volatile compounds such as tetraethylthiourea and S-ethyl N,N-diethyldithiocarbamate are vaporized subsequently in the second process which immediately follows the first. This behaviour of the rate of mass loss in a single step of the thermal breakdown of the dithiocarbamate ligands is unusual. In the disubstituted tin(IV)dithiocarbamates previously studied by the authors[1,2], the DTG only indicated a single process of decomposition and loss of mass. The explanation of the unusual behaviour of the tetrakis(diethyldithiocarbamato)tin(IV) is the much lower temperature at which decomposition occurs which causes the volatilities of the decomposition products to become the predominating factor in determining the rate of mass loss, instead of the rate of formation of decomposition products. At higher temperatures (greater than

280 °C) the temperature is the predominating factor in determining the rate of mass loss.

The second step is clearly separated from the first and consists of two processes occurring simultaneously as shown by the DTA which indicates an endothermic peak superimposed on an exothermic peak. The exothermic process involves further oxidation of the tin residue. The endothermic process is due to the vaporization of the decomposition products. However, due to the higher temperature of decomposition the difference in the rate of mass loss of the various products is not apparent even though the same products of decomposition, with minor exceptions, are produced in each step[7].

The DTA indicates that two further exothermic reactions occur with small mass changes which are probably due to further oxidation of the mixed sulphur oxide tin residue. The final residue at 950 °C is tin(IV)oxide[8,9].

In nitrogen (Fig. 2), the decomposition process is much simpler and decomposition occurs shortly after melting with the TG profile showing only one step of decomposition. However, the DTG and DTA indicate that this
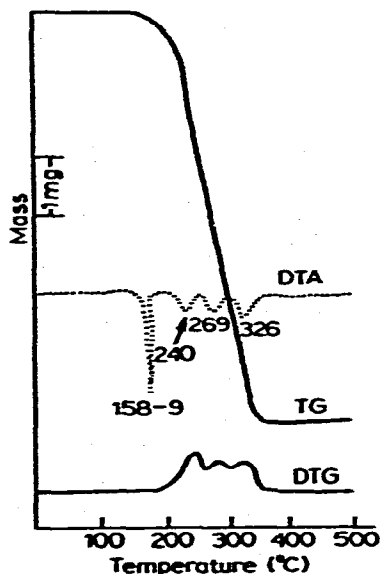

Fig. 2. TG/DTA of tetrakis(diethyldithiocarbamato)tin(IV) in nitrogen.

step is a combination of three immediately consecutive endothermic processes involving the loss of the dithiocarbamate ligands leaving tin(II) sulphide. The composition of the residue was confirmed by microanalysis of the sulphur content (Table 1). The endothermic nature of these processes indicates that the heat of vaporization of the decomposition products exceeds the energy required for their formation.

TABLE 2

PERCENTAGE MASS LOSS IN TG ANALYSIS OF
TETRAKIS(DIETHYLDITHIOCARBAMATO)TIN(IV)

	Nitrogen		Air	
Combined stages	82.0	(78.8)[a]	First stage	39.1
Residue	18.0	(21.2)	Second stage	33.3
			Residue	27.6

[a] Theoretical mass loss leaving tin(II) sulphide as residue.

P/GC–MS analysis of tetrakis(diethyldithiocarbamato)tin(IV)

The pyrolysis of the tin complex was carried out in an inert atmosphere (helium). Decomposition occurred progressively to the final residue of tin(II)sulphide. Separating the steps of decomposition was not possible.

Most of the decomposition products (Table 3) have been identified previously[1,2]; either by comparison with reference mass spectra[10,11] or by deducing a structure from a mass spectrum and the known structure of the dithiocarbamate ligands. The relative amounts of the products of decomposition are derived from the source total ion monitor (STIM) (Fig. 3). The STIM has been described previously[1].

In the GC–MS analysis carried out under the changed conditions described previously, two high mass species were detected. Due to their in-

TABLE 3

GC–MS ANALYSIS OF THE PYROLYSIS PRODUCTS OF
TETRAKIS(DIETHYLDITHIOCARBAMATO)TIN(IV)

No.	Name
1	Ethylmercaptan[a]
2	Carbonyl sulphide[a]
3	Carbon disulphide[a]
4	Diethylamine[a]
5	1-Ethylpyrrol[a]
6	Ethylisothiocyanate[a]
7	Diethyldisulphide[a]
8	N,N-diethylformamide[a]
9	N,N,N',N'-tetraethylurea[a]
10	N,N-diethylthioformamide[b]
11	Unknown MW = 156
12	N,N,N',N'-tetraethylthiourea[a]
13	S-Ethyl N,N-diethyldithiocarbamate[b]
14	N,N-diethylthiopropionamide[c]

[a] Identified previously from standard mass spectral data. [b] Identified by comparison of its mass spectrum with that of a structure proposed previously. [c] Structure proposed from mass spectral data.
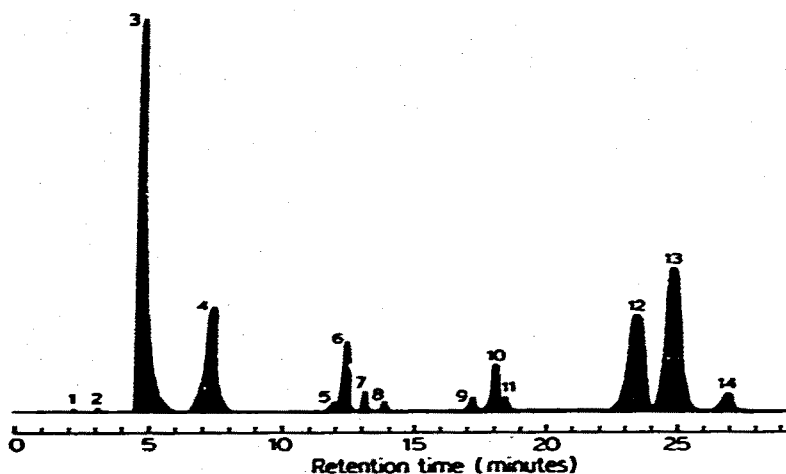
Fig. 3. STIM of P/GC–MS of tetrakis(diethyldithiocarbamato)tin(IV).

volatility these compounds are not readily swept out of the furnace and hence suffer further decomposition depending upon the experimental conditions. Thus these species were observed only occasionally. The mass spectra obtained for both compounds were very similar to each other. Both mass spectra contained peaks at m/e 116, 88, 60 and 29 only. Hence, the spectral data indicate the presence of the $Et_2N \cdot C = S$ group. The long retention times of the compounds[*] indicate that these species are of high molar mass. Unfortunately, at present the GC–MS computer system is limited to scanning up to an m/e value of 250 and hence a molecular ion, if present, might not have been detected. Compounds having a similar structure (e.g., tetraethylthiourea and S-ethyl N,N-diethyldithiocarbamate) posess relatively strong molecular ions (i.e., 40 and 80% of base peak, respectively). Since the mass spectrum indicates the presence of the $Et_2N \cdot C = S$ groups and no other peaks were observed, it is likely that these species have two $Et_2N \cdot = S$ groups in the molecular structure. The possible structures are discussed in the EGA section of this paper.
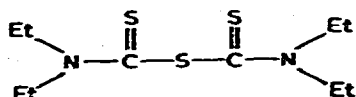
The evolved gas analysis

From the EGA data the previously identified products (carbon disulphide, diethylamine and ethylisothiocyanate) were detected. The mass spectrum of carbon disulphide dominated that of the other two decomposition products. However, an examination of the B[**] values tabulated in Cornu and Mas-

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[*]Retention times were 22 and 29 min with the GC column at 200 °C with a flow-rate of helium of 10 cm^3 min^{-1}. Under the same conditions S-ethyl N,N-diethyldithiocarbamate had a retention time of 7 min.
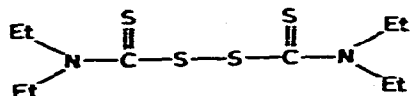
[**]The B value is the ratio of the base peak in the mass spectrum of the compound to the base peak in the mass spectrum of n-butane with both at the same pressure.

sot[10] clearly indicated that the amounts of the two compounds relative to carbon disulphide were greater than expected from examination of the mass spectrum of the evolved gases. The amount of carbon disulphide is slightly more than that of diethylamine whereas the amount of ethyl isothiocyanate is about two-thirds of that of carbon disulphide.

During the EGA, an involatile compound was deposited on the glass wall of the tube above the furnace. In the mass spectrum of this material, major peaks occurred at m/e values of 264, 149, 148, 147, 116, 88, 76, 72, 60, 44 and 29. As discussed previously in the P/GC–MS analysis, two high molar mass species were detected, possibly containing two $Et_2N \cdot C = S$ groups. The 264 peak appears to be the parent ion and associated with it is a $(M+2)^+$ peak which indicated the presence of at least 3 sulphur atoms. The other peaks were similar to those observed in the P/GC–MS analysis of the high molar mass compounds. Hence, a structure for one of these compounds may be proposed as:

$$
\begin{array}{ccccc}
 & \overset{S}{\underset{\parallel}{}} & & \overset{S}{\underset{\parallel}{}} & \\
Et\diagdown & \parallel & & \parallel & \diagup Et \\
 \;\; N & - C - S - & C & - N & \\
Et\diagup & & & & \diagdown Et
\end{array}
$$

In the mass spectrum of the tetrakis(diethyldithiocarbamato)tin(IV) a peak at m/e of 296 was detected with a $(M+2)^+$ peak indicating at least 4 sulphur atoms. It is possible that this peak corresponds to the parent ion of the high molar mass species detected in the P/GC–MS analysis and the structure is envisaged as:

$$
\begin{array}{cccccc}
 & \overset{S}{\underset{\parallel}{}} & & & \overset{S}{\underset{\parallel}{}} & \\
Et\diagdown & \parallel & & & \parallel & \diagup Et \\
 \;\; N & - C - S - & S & - & C - N & \\
Et\diagup & & & & & \diagdown Et
\end{array}
$$

The 264 peak is not detected in the mass spectrum of tetrakis(diethyldithiocarbamato)tin(IV) because of the interference of an intense peak due to the $Sn(S_2CNEt_2)^+$ ion.

The pyrolysis/gas chromatography technique

The pyrolysis/gas chromatography (P/GC) technique indicated that the amount of diethylamine was much larger than the other decomposition products other than carbon disulphide which is not detected by the FID.

CONCLUSION

A determination of a stepwise mechanism of thermal decomposition of the tetrakis(diethyldithiocarbamato)tin(IV) in an inert atmosphere is difficult because of the overlap of the decomposition steps (Fig. 1). However, it appears tha there are at least two competing mechanisms of thermal decomposition involving the dithiocarbamate ligands. This situation arises from the mixed denticity of the ligands.

The mechanism of thermal decomposition of tetrakis(diethyldithiocarbamato)tin(II) proposed below, involves the decomposition of two dithiocarbamate ligands by a radical mechanism, to form tetraethylethiuramdisulphide, which decomposes further to yield carbon disulphide and diethylamine. The source of hydrogen for abstraction reactions has been discussed in a previous publication[2]. (In the various diagrams L represent diethyldithiocarbamate ligand.)
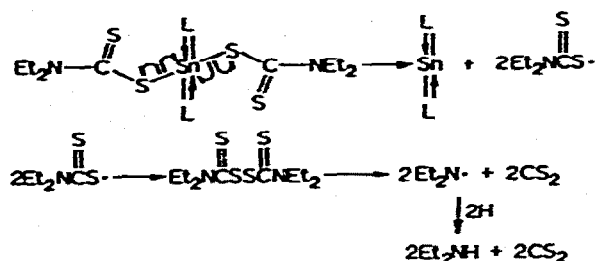
It was thought that the intermediate product, bis(diethyldithiocarbamato)tin(II) would have decomposed according to the following mechanism:
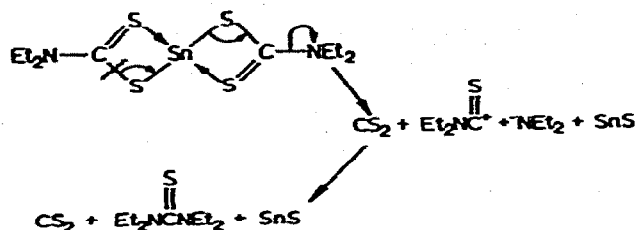
However, the presence of significant amounts of ethylisothiocyanate and S-ethyl N,N-diethyldithiocarbamate suggests that there is a competing mode of decomposition. It is postulated that monodentate ligands decompose to form the above-mentioned products according to a mechanism envisaged as:
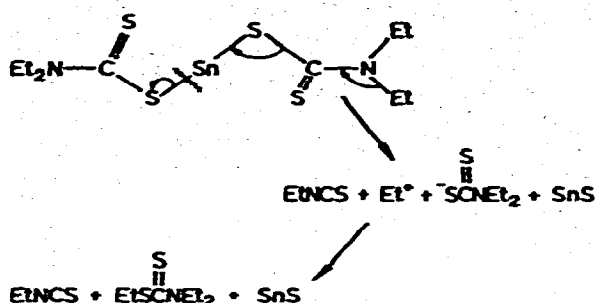
Furthermore, it is postulated that the bidentate ligands of bis(diethyldithiocarbamato)tin(II) are converted into pseudo-monodentate ligands by the increasing distortion of these ligands caused by the high temperatures[12] ($300°C^+$) at which the intermediate is formed.

The difference in the yields and types of decomposition products obtained by the EGA compared with those of the P/GC–MS technique can be explained by considering two factors. EGA was carried out under vacuum which allows the high molar mass compounds formed to escape from the furnace region, whereas under a pressure of one atmosphere as in the pyrolysis mode, extensive, if not total decomposition of such species occurs. The second factor is that the rate of heating in the P/GC–MS technique ($200°C\ min^{-1}$) is much faster than the rate of heating employed in EGA ($40°C\ min^{-1}$). If thermal conversion of bidentate ligands in bis(diethyldithiocarbamato)tin(II) to monodentate ligands does not attain equilibrium due to a fast rate of heating, then the yields of pyrolysis products belonging to bidentate ligands should be expected to be large. The slower rate of heating in EGA is more likely to allow equilibrium to be attained and hence the yields of pyrolysis products due to decomposition of monodentate ligands is greater. The data obtained in this study support such a conclusion.

ACKNOWLEDGEMENT

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