

THE THERMAL DECOMPOSITION OF BIS(DIETHYLDITHIOCARBAMATO)TIN(II)

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ABSTRACT

The thermal decomposition behaviour of bis(diethyldithiocarbamato)-tin(II) is reported. The compound is completely volatile under vacuum but decomposes in air and nitrogen. During heating in air, complex processes of oxidation and decomposition occur. Analysis of the decomposition products suggests that the two major modes of decomposition are competitive and temperature dependent.

INTRODUCTION

Our previous studies on tin dithiocarbamate complexes¹⁻⁵ have shown that the mechanisms of thermal decomposition are complex. Most of the complexes studied were of the "mixed ligand" variety, with halogen or phenyl groups bonded to tin in addition to monodentate or bidentate dithiocarbamate. Our accumulated thermal data on these complexes clearly show that halogen or phenyl ligands and the mode of binding of the dithiocarbamate ligand all influence the thermal decomposition mechanism of the complex. The logical extension of this work is to study the thermal decomposition of a tin dithiocarbamate complex in which only dithiocarbamate ligands in a known binding configuration are coordinated to tin. A suitable simple complex for such a study is bis(diethyldithiocarbamato)tin(II), $\text{Sn}(\text{Et}_2\text{dtc})_2$. We now report the results of a detailed investigation of the thermal decomposition of this compound. Our thermal data differ markedly from those previously reported by Perry and Geanangel⁶ and we conclude that in this previous work the compound reported as bis(diethyldithiocarbamato)tin(II) was a mixture of $\text{Sn}(\text{Et}_2\text{dtc})_2$ and tetrakis(diethyldithiocarbamato)tin(II), $\text{Sn}(\text{Et}_2\text{dtc})_4$.

INSTRUMENTAL

Melting points were determined using a Mettler FP-2 Hotstage Microscope unless otherwise stated. Mass Spectra were recorded on a JEOL JMS D-100 mass spectrometer using an ionizing energy of 75 eV. TG/DTG/DTA were carried out in

air, nitrogen and under vacuum using a Rigaku-Denki thermal analysis system, at a heating rate of 10°C per minute with samples of approximately 10 mg. The pyrolysis/gas chromatography-mass spectrometry (P/GC-MS) analyses were carried out using a GC-MS computer system described previously^{1, 4, 5}. The GC column used in these studies was a 6 ft. \times 1/8 in. o.d. glass column packed with 3% DC 550 on 60/80 Chromosorb G, AW-DMCS. All elemental analyses were performed by the CSIRO Microanalytical Service, Melbourne University, Melbourne, Australia. Infrared spectra were recorded by means of a Perkin Elmer 457 Grating Infrared Spectrophotometer using KBr pellets, and range 4000 to 250 cm^{-1} .

SYNTHESIS AND CHARACTERIZATION

Bis(diethyldithiocarbamato)tin(II) was synthesized using a modified procedure to one of those reviewed by Magee⁷. The diethylammonium salt of diethyldithiocarbamic acid (m.p. 81.0-81.5°C, cf. Lit. 81-82⁸ and 82-83°C⁹) was used instead of the sodium salt. An ethanolic solution of the salt was added to a similar solution of tin(II) chloride under a continuous stream of nitrogen. White crystals of $\text{Sn}(\text{Et}_2\text{dtc})_2$ are precipitated, even when the salt is added in less than stoichiometric quantity. The melting point, obtained from DTA data, 106-107°C, agrees with previously reported values (108-109°C¹⁰ and 112°C¹¹, (sealed tube)).

The elemental analysis data given in Table I, although limited, agree well with theoretical values.

TABLE I

ELEMENTAL ANALYSIS DATA FOR $\text{Sn}(\text{Et}_2\text{dtc})_2$

	%C	%H	%N
Calculated	28.92	4.85	6.75
Found	28.67	4.86	6.75

TABLE 2

THE MASS SPECTRUM OF $\text{Sn}(\text{Et}_2\text{dtc})_2$

<i>m/e</i>	Corresponding ion	<i>m/e</i>	Corresponding ion
416 ^a	$\text{Sn}(\text{S}_2\text{CNEt}_2)_2^+$ (molecular ion)	88	SCNHet^+
268	$\text{SnS}_2\text{CNEt}_2^+$	76	CS_2^+
208	$\text{Sn}(\text{S}_2\text{CNEt}_2)_2^{2+}$	72	NEt_2^+
148 ^a	$\text{S}_2\text{CNEt}_2^+$	60	H_2NCS^+
120	Sn^+	44	EtNH^+ and a weak CS^+
116	SCNEt_2^+ (base peak)	29	Et^+

^a *m/e* values incorrectly reported by Perry and Geanangel⁶.

Infrared spectroscopy and mass spectrometry were used to confirm the identity of the compound. Bonati and Ugo^{1,2} suggest that only the presence of highly asymmetric dithiocarbamate ligands can produce two absorption peaks in the C-S stretching region ($1050-950\text{ cm}^{-1}$)^{1,5}. For the complex studied, only one strong peak was observed in this region, at 992 cm^{-1} , indicating that the ligands are not greatly asymmetric. This agrees with X-ray studies^{1,2, 14}, where they were shown to be only slightly asymmetric.

The mass spectrum of $\text{Sn}(\text{Et}_2\text{dtc})_2$, obtained by direct insertion probe at 85°C , is given in Table 2. For clarity, only those ions containing the most abundant isotopes of the elements present are reported. A molecular ion is observed and other ions are easily rationalized from the postulated structure of the compound. The spectrum has been given previously by Perry and Geanangel⁶ but their data are limited and contain errors.

THE THERMAL DECOMPOSITION OF $\text{Sn}(\text{Et}_2\text{dtc})_2$

The thermal data obtained for decomposition in nitrogen, under vacuum and in air are given in Figs. 1-3. In a dynamic nitrogen atmosphere, the compound melts at $106-107^\circ\text{C}$, as shown by an endothermic DTA peak (Fig. 1). Decomposition occurs in the temperature range $210-360^\circ\text{C}$, with a residue. The relative mass loss

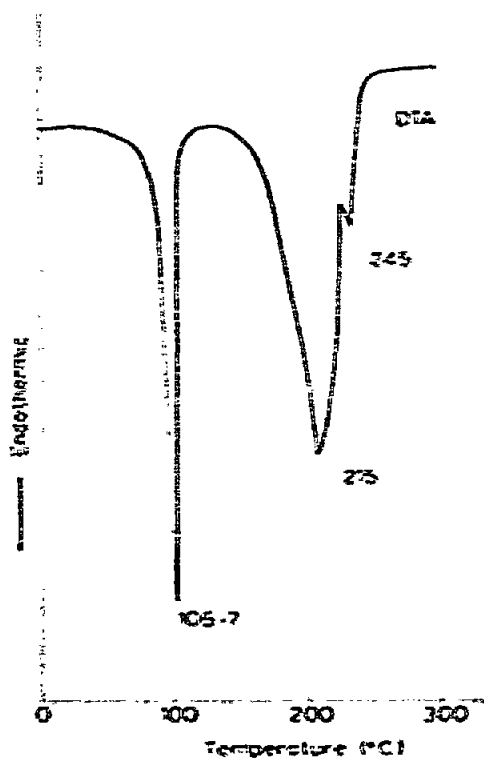
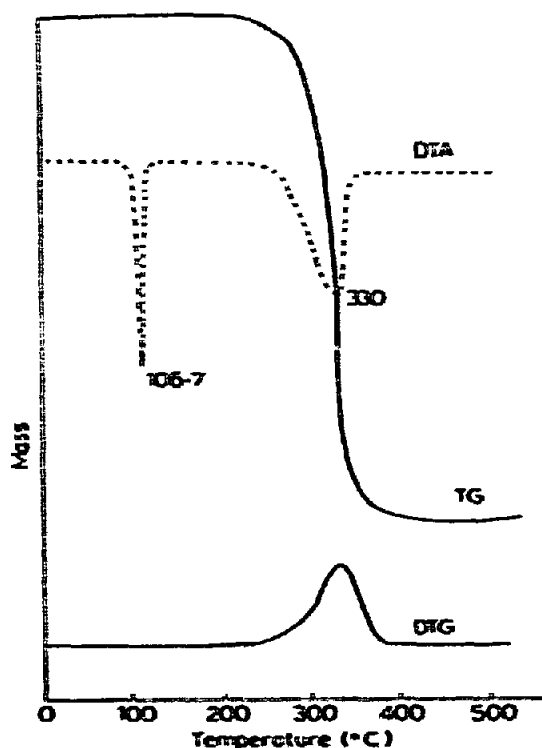


Fig. 1. A simultaneous TG/DTG/DTA of $\text{Sn}(\text{Et}_2\text{dtc})_2$ in a nitrogen atmosphere.

Fig. 2. A DTA of $\text{Sn}(\text{Et}_2\text{dtc})_2$ in a vacuum.

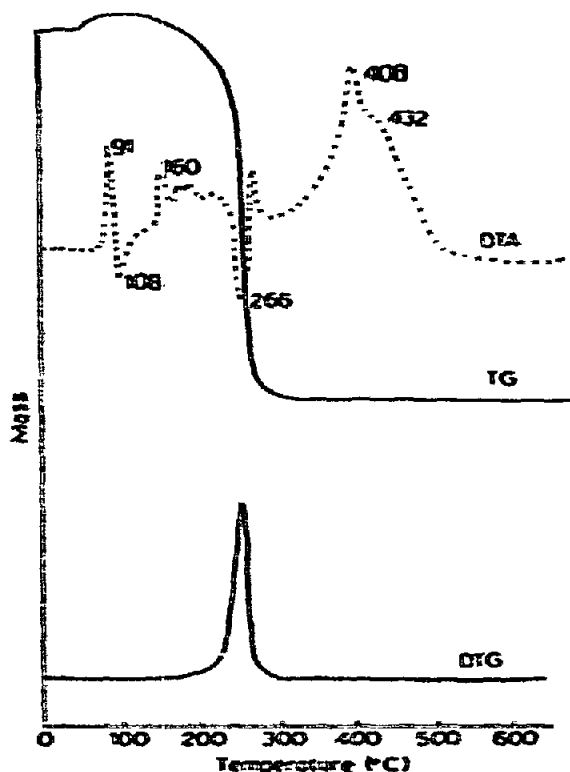


Fig. 3. A simultaneous TG/DTG/DTA of $\text{Sn}(\text{Et}_2\text{dtc})_2$ in an air atmosphere.

TABLE 3

PERCENTAGE MASS LOSSES OF $\text{Sn}(\text{Et}_2\text{dtc})_2$

Atmosphere	Decomposition Temp. ($^{\circ}\text{C}$)	% Mass loss found
Nitrogen	210-360	61.1 ^a
Air	200-310	59.2

^a cf. theoretical mass loss corresponding to a residue of tin(II) sulphide of 63.7%.

(Table 3) and the results of previous investigations¹⁻³ suggest that the residue is tin(II) sulphide. The suggestion by these authors¹, that tin(II) sulphide decomposes into metallic tin above 750 $^{\circ}\text{C}$, has been found to be incorrect. Tin(II) sulphide is stable at temperatures above 1000 $^{\circ}\text{C}$ ¹⁶. The data that gave rise to this supposition have been shown to be due to a systematic instrumental malfunction.

DTA data only were obtained for the analysis under vacuum ($< 10^{-2}$ torr) (Fig. 2). After melting, at 108 $^{\circ}\text{C}$, the compound vaporises in the range 150-250 $^{\circ}\text{C}$ with peak vaporisation at 215 $^{\circ}\text{C}$. Decomposition also probably occurs, as indicated by the small endothermic peak at 245 $^{\circ}\text{C}$, and a small residue (0.2 mg from a sample of 14.8 mg). Mass spectral studies, at a pressure less than 10^{-6} torr, indicate that the

compound is completely volatile at this pressure, as no residue was observed after analysis.

In a static air atmosphere (Fig. 3) the situation is more complex. An initial oxidation commences at 91 °C as indicated by the exothermic DTA peak and a small mass gain (approximately 2%). To confirm oxidation at this temperature a sample of the compound was maintained at 105 °C for one hour and the product submitted for microanalysis. The oxygen content found was 3.1%, which may be compared with the calculated value of 3.7% for the formula $\text{OSn}(\text{Et}_2\text{dte})_2$. The difference between these values suggests that the oxidation is incomplete. This is corroborated by the existence of a broad endothermic DTA peak at 108 °C. The latter is almost the same temperature as that observed for the melting point of pure $\text{Sn}(\text{Et}_2\text{dte})_2$ under nitrogen; the broadness of the peak suggests contamination, i.e., with the oxidised product. Finally, the exothermic DTA peaks commencing at 160 °C suggest further oxidation.

To supplement the thermoanalytical data, a sample of $\text{Sn}(\text{Et}_2\text{dte})_2$ was examined during heating in a melting point apparatus. A sharp colour change, from white to orange, occurs at 90–96 °C, soon after which the sample liquifies but then almost immediately solidifies again. The colour change is not reversed on cooling. The sample eventually turns yellow in the temperature range 150–180 °C. Between 190 and 200 °C, obvious signs of decomposition appear.

These observations, allied with the thermoanalytical data, may be explained as follows. The colour change, white to orange, is due to partial oxidation of the sample as a solid. As the temperature increases, phase changes occur during which the remaining unoxidised sample melts. Continuing oxidation causes the sample to solidify again, since the oxidised product is a solid at this temperature. The later colour change from orange to yellow suggests that oxidation may be complete when the temperature reaches 180 °C. However, the presence of an exothermic tail to the endothermic decomposition peak at 266 °C in the DTA, indicates that this may not always be the case for large samples such as are used for thermal analysis.

The decomposition of the oxidised products occurs within the range 190 to 310 °C with a residue, probably a mixture of SnO_2 and SnS_2 ^{17, 18}, which is eventually converted to SnO_2 ^{17, 18} when the temperature reaches 950 °C.

MECHANISMS OF THERMAL DECOMPOSITION

Samples of $\text{Sn}(\text{Et}_2\text{dte})_2$ were subjected to P/GC-MS analysis, initially at 400 °C. This is the temperature at which decomposition is substantially complete, as indicated by the thermoanalytical data. In order to study temperature effects, additional pyrolyses were carried out at three lower temperatures. The products of decomposition are listed in Table 4. The column used did not separate carbon disulphide and diethylamine effectively but analysis of the data indicates that carbon disulphide is the major product.

TABLE 4

PRODUCTS OF DECOMPOSITION OF Sn(II)diols IDENTIFIED BY THE P/OE-MS TECHNIQUE (SEE FIG. 4)

No.	Name	Formula	Relative amount of products		m/e values of important ions in mass spectrum
			Helium	Air	
1	Carbonyl sulphide ^a	COS	Trace	Trace	
2	Carbon disulphide ^a	CS ₂	Major	Major	
3	Diethylamine ^a	Et ₂ NH	Trace	Trace	
4	Pyridine ^a	C ₅ H ₅ N	Trace	Trace	
5	1-Ethylpyrrol ^a	C ₄ H ₇ N-C ₂ H ₅	Trace	Trace	
6	Ethylisothiocyanate ^a	Et-N=C=S	Minor	Minor	
7	1-Ethylthiazolidine-3-thione ^b	Et-N-C=S S	Trace	Trace	119(P), 104(BP) 90 and 76
8	Diethyl disulphide ^a	Et ₂ SSiEt	Trace	Trace	
9	Unknown MW = 127	O	Trace	Trace	
10	N,N Diethylformamide ^a	O Et ₂ NCH	Minor	Minor	
11	Unknown MW = 98	S	Trace	Trace	98(P), 83, 70, 69 and 55(BP)
12	N,N Diethylformamide ^b	S Et ₂ NCH	Minor	Minor	117(P and BP), 116, 88, 84, 72, 60, 44 and 29
13	N,N,N Triethylurea ^a	O Et ₃ CNH	Minor	Minor	
14	Unknown MW = 156	Et ₂ CNCHEt	Trace	Trace	156(P), 141, 128, 127, 113(BP), 99 and 83
15	Triethylthiourea	S Et ₃ CNH	Trace	Trace	

TABLE 4 (continued)

No.	Name	Formula	Relative amount of products		m/e values of important ions in mass spectrum
			Helium	Air	
16	Unknown MW ≈ 170		Trace	Trace	170(P), 155, 98(BP), 72 and 56
17	Unknown MW ≈ 166		Trace	Trace	
18	S-Methyl N,N diethylthiocarbamate ^a	S MeSCNEt ₂	Trace	Trace	163, 116, 91, 88, 72, 60, 44, 29 and 27
19	N',N',N,N Tetraethylthiourea ^a	S Et ₄ NCNEt ₂	Minor	Major	
20	S-Ethyl N,N diethylthiocarbamate ^b	S EtSCNEt ₂	Major	Major	177(P), 149, 148, 116(BP), 105, 88, 72, 60, 44 and 29
21	Unknown MW ≈ 175		Trace	Trace	175(P and BP), 174, 160, 146, 142, 103, 90 and 59
22	N,N Diethylthiopropionamide ^b	S Et ₂ CNEt ₂	Trace	Trace	145(P), 144, 117, 88, 60 and 44
23	Unknown		Trace	Trace	
24	Unknown MW ≈ 147		Trace	Trace	147(P and BP), 86, 60 and 44

^a Identified by comparison with standard mass spectra 19, 20.

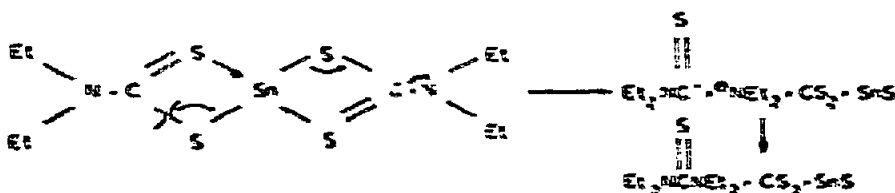
^b Proposed by comparison with the mass spectra of compounds, whose structures have been previously postulated by the authors.

P = Parent ion; BP = base peak of spectrum.

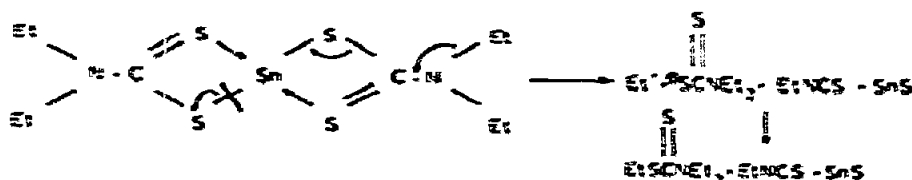
It should be pointed out that products in trace quantities are not necessarily due to decomposition of the pure complex. They may result from decomposition of impurities or reactions of impurities with true products or intermediates.

Relative yields depend mainly upon the final temperature reached during pyrolysis. From the results of analyses at different temperatures, it is clear that competing decomposition pathways are involved, similar to those proposed for other tin dithiocarbamates¹⁻⁵.

At low temperatures (200-300°C) the favoured mechanism appears to be Mechanism I



At higher temperatures, the following mechanism is favoured Mechanism II*



The increasing distortion of the metal-ligand bonds at higher temperatures causes the ligands to become increasingly isobidentate. This favours a mechanism of thermal decomposition initiated by the rupture of tin-sulphur bonds, i.e. mechanism II.

The two mechanisms only explain the presence of a few compounds. Other factors must be invoked to explain the remainder. Some products are the result of reactive intermediates postulated in the primary mechanisms, reacting with other substances to produce neutral hydrogenated species, e.g. N,N-diethylthioformamide and diethylamine. Others are clearly the result of cyclization and dehydrogenation, e.g. pyridine and 1-ethylpyrrol. The yields of these products increase with increasing temperature, indicating that they are formed by secondary decomposition reactions.

In general, the products obtained from pyrolysis in air are not markedly different from those obtained in helium, even when a previously oxidised sample is used for the pyrolysis. The major difference lies in the relative yields of some products. In both atmospheres, compounds containing oxygen are observed, whose yields, relative to the major products, are larger for pyrolysis in air. As previously discussed⁴,

* Both of these basic mechanisms have been previously proposed¹⁻⁵. The presence of other ligands may affect the relative importance of the two mechanisms, as described in refs. 2 and 3. Note, in ref. 4 the products have been inadvertently ascribed to the wrong mechanism, i.e., Mechanism I products to mechanism II and vice versa.

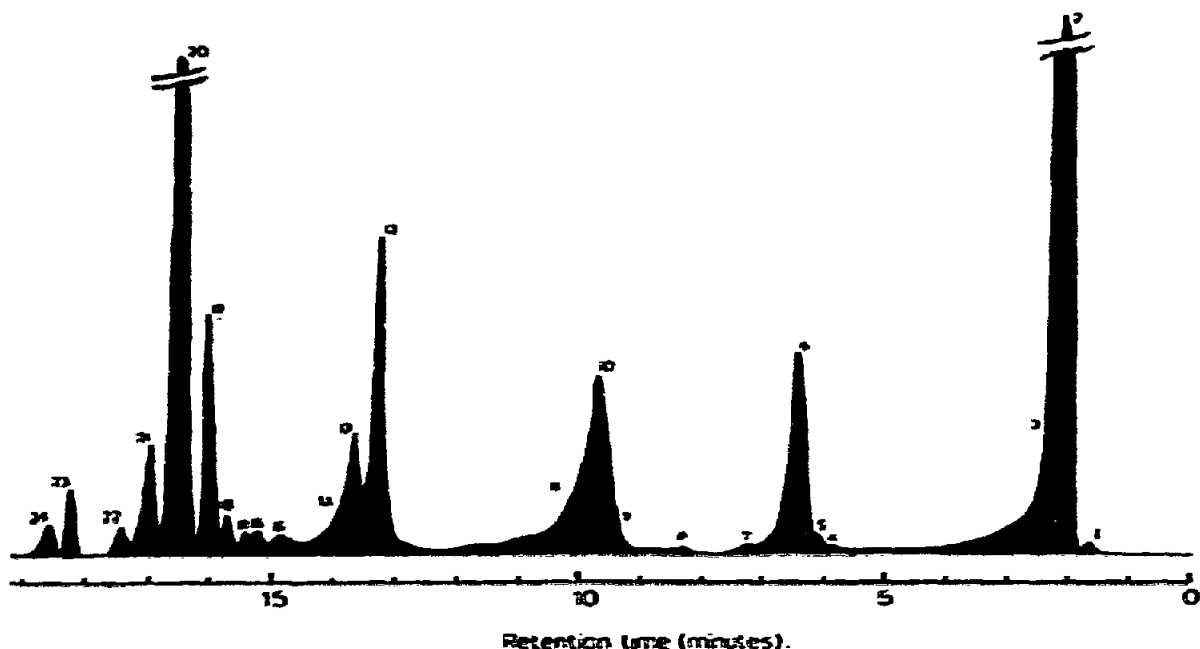


Fig. 4. A typical source total ion monitor output of a P/GC-MS analysis of $\text{Sn}(\text{Et}_2\text{dtc})_2$, carried out at 400°C in a helium atmosphere. For identification of compounds see Table 4.

the oxygen apparently reacts mainly with involatile residues, which leads eventually to complete oxidation¹⁷⁻¹⁹. The presence of oxygenated compounds after pyrolysis in helium has been previously observed^{1-3, 5} and ascribed to the presence of water or acetone trapped in the crystal structure.

Pyrolysis in air appears to favour mechanism I; also in the TG studies, a faster rate of decomposition is observed for pyrolysis in air. In a previous paper⁴, it was suggested that the increased decomposition rate is due to additional heat, produced by oxidation reactions, being gained by adjacent molecules, thus promoting the rate of decomposition. This accounts for the observed increase in the relative importance of mechanism I for air pyrolysis of $\text{Sn}(\text{Et}_2\text{dtc})_2$ since decomposition is promoted at a lower temperature than that expected to occur in the absence of the oxidation reactions.

COMPARISON WITH THE WORK OF PERRY AND GEANANGEL

The results given in this paper differ markedly from those reported by Perry and Geanangel⁶. We have studied this problem extensively and have concluded that the material studied by Perry and Geanangel was a mixture of $\text{Sn}(\text{Et}_2\text{dtc})_2$ and $\text{Sn}(\text{Et}_2\text{dtc})_4$; the latter predominating. A summary of the evidence supporting this conclusion is presented here.

Perry and Geanangel reported a synthesis of the bis-complex in which an "orange product" was obtained. We have repeated this synthesis and also obtained an orange product. However, authentic $\text{Sn}(\text{Et}_2\text{dtc})_2$ is white¹¹⁻¹³, and $\text{Sn}(\text{Et}_2\text{dtc})_4$

is orange. Thus it may be concluded that the product reported by Perry and Geanangel is certainly not the pure bis-complex.

The IR spectrum reported by Perry and Geanangel contains two strong peaks in the C-S stretching region, at about 1010 and 992 cm^{-1} . This is also the case for the tetrakis-complex³ and for the orange compound noted above. However we have shown that $\text{Sn}(\text{Et}_2\text{dtc})_2$ exhibits only one strong peak in this region, at 992 cm^{-1} .

Perry and Geanangel examined their material in a melting-point apparatus and reported a procedural decomposition temperature of 151°C, which is close to that reported for pure $\text{Sn}(\text{Et}_2\text{dtc})_4$, 160–162°C^{1,5}. When pure $\text{Sn}(\text{Et}_2\text{dtc})_2$ is examined by this procedure, phase changes and oxidation are observed at about 100°C.

Comprehensive thermal data obtained in this study do not agree with that given by Perry and Geanangel. Their TG data, obtained under nitrogen^{2,1}, show two stages, whereas our data indicate only one.

Though the mass spectra of all products are similar, the spectrum of $\text{Sn}(\text{Et}_2\text{dtc})_2$ appears at a much lower sample temperature (100°C) than either the orange product or $\text{Sn}(\text{Et}_2\text{dtc})_4$ (150°C). Small peaks due to the presence of relatively involatile decomposition intermediates are observed for the latter compounds but not for $\text{Sn}(\text{Et}_2\text{dtc})_2$.

The technique known in these laboratories as Programmed Probe Analysis (PPA)^{2,4}, produces very similar results for the orange compound and $\text{Sn}(\text{Et}_2\text{dtc})_4$, but results which are quite different from those produced by $\text{Sn}(\text{Et}_2\text{dtc})_2$. The results are currently being studied but they clearly indicate that the orange compound is not $\text{Sn}(\text{Et}_2\text{dtc})_2$.

Both the bis- and the tetrakis-complexes have been observed to be unstable in air at room temperature, the bis-complex oxidizes to form another orange compound. The remote possibility that the orange compound studied by Perry and Geanangel may have been an oxidised form of $\text{Sn}(\text{Et}_2\text{dtc})_2$ was eliminated by studying an oxidised sample under PPA conditions. These results are also under examination but there is no doubt that the orange product synthesised in these laboratories by the method of Perry and Geanangel and the orange-coloured oxidation product of $\text{Sn}(\text{Et}_2\text{dtc})_2$, are not the same compound.

CONCLUSION

As with other tin dithiocarbamates investigated¹⁻⁵, the decomposition of $\text{Sn}(\text{Et}_2\text{dtc})_2$ has been shown to be complex, involving two temperature-dependent and competitive mechanisms. Other secondary mechanisms are observed. However, since tin is in the oxidation state (II), the formation of radical species does not occur in the primary decomposition scheme, as in the case of the tin(IV) dithiocarbamates previously studied¹⁻⁵.

The thermal study of $\text{Sn}(\text{Et}_2\text{dtc})_2$ has shown that the previous suggestion by the authors concerning the isobidentate nature of the dithiocarbamate ligands in $\text{Ph}_2\text{Sn}(\text{Et}_2\text{dtc})_2$ ² is invalid at room temperature. The high temperatures used for

pyrolysis of $\text{Ph}_2\text{Sn}(\text{Et}_2\text{dte})_2$ (400°C), caused the formation of isobidentate ligands and, eventually, the formation of volatile products by way of Mechanism I. Naturally, the involatile products are different, due to the presence of the phenyl ligands. X-ray studies have shown that the ligands are bidentate at room temperature²³. The great complexity of the thermal decomposition of $\text{Ph}_2\text{Sn}(\text{Et}_2\text{dte})_2$ makes it extremely difficult to determine even semi-quantitatively, the volatile products of Mechanisms I and II, since they contribute to the total yield only to a minor extent.

The use of thermoanalytical data alone has been proved to be misleading in formulating decomposition mechanisms of even relatively simple coordination complexes²². In the case of tin dithiocarbamate complexes, it is only by identification of the products of thermal decomposition that the complicated mechanisms involved could be determined.

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