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

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ABSTRACT

The P/GC–MS and TG/DTA analysis, in an inert atmosphere, of bis(diethyldithiocarbamato)diphenyl tin (IV) indicates that the thermal decomposition proceeds in two consecutive stages. Loss of the dithiocarbamate ligands and the phenyl groups occurs within the temperature range of 210–380 °C leaving tin (II) sulphide as residue. The stability of the phenyl radical as a reactive intermediate, together with the unidentate bonding of the dithiocarbamate ligand, dramatically influence the major mode of thermal decomposition.

INTRODUCTION

In a previous publication[1] the pyrolysis/gas chromatography–mass spectrometry (P/GC–MS) technique developed by the authors was used to derive the mechanism of thermal decomposition of three of the dihalotinbisdiethyldithiocarbamates. It was found that the mechanism is independent of the nature of the halogen ligand attached to the tin atom. Thus, it is of interest to discover whether electron donating organic groups, such as phenyl, influence the mechanism of thermal decomposition of the dithiocarbamate ligand in $R_2Sn(dtc)_2$ complexes. The bis(diethyldithiocarbamato)-diphenyl tin (IV) (diphenyl complex) although difficult to obtain pure, is easily synthesised. The literature on this complex is sparse; the synthesis was first reported by Kupchik et al.[2]. The complex was characterised by infrared and UV-visible spectroscopy. F. Bonati et al.[3] reported infrared, NMR and dipole moment data and discussed the nature of the metal–sulphur bonds.

In recent years, several papers have been published on Mössbauer spectroscopy of the diphenyl complex[4–9], together with similar data for other tin dithiocarbamates. The Mössbauer spectrum of the diphenyl complex is some-

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what anomalous; the magnitude of the quadrupole splitting indicates *cis* orientation of the phenyl groups, but the sign of the splitting is typical of *trans* orientation. The apparent contradiction may be explained by the considerable distortion from regular octahedral symmetry.

The data presented in this paper lead to a determination of a mechanism of thermal decomposition for bis(diethyldithiocarbamato)diphenyl tin (IV) which differs markedly from that previously reported for dihalotin (IV) complexes. The phenyl and the diethyldithiocarbamate moieties react to form relatively stable intermediates, whereas in the dihalotin (IV) diehtyldithiocarbamates, the halogen ligand and the decomposition products of the dithiocarbamate ligand do not interact. Thus, for the general class of complexes $R_2Sn(dtc)_2$ the mechanism of thermal decomposition is dramatically influenced by the nature of the organic functional group bonded to the tin atom.

EXPERIMENTAL

Synthesis of the diphenyl complex

The synthesis of bis(diethyldithiocarbamato)diphenyl tin (IV) was achieved by reacting a 2:1 ratio of the sodium salt of diethyldithiocarbamic and dichlorodiphenyl tin in acetone. This synthesis is similar to a method described by Bonati et al.[3]. Sodium chloride was allowed to separate out and was removed by filtration. The filtrate was allowed to evaporate partially, causing precipitation of the product which was removed by filtration. The process was repeated several times. Thus a series of samples were obtained and the M.P. of each determined. The sample having the highest M.P. was presented for elemental microanalysis and the results are given in Table 1.

Mass spectrometry

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 on the diphenyl complex 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. The system could also be evacuated for studying the thermal behaviour of the complex in vacuum.

The P/GC–MS technique

The technique has been described in detail previously[1]. Briefly it 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 same heating procedure and GC conditions previously reported were used. However, some GC–MS runs were carried out with the GC column held at 200 °C using the same heating procedure for the furnace in order to detect the suspected higher molar mass species indicated by the mass spectra.

TABLE 1

MICROANALYSIS

	C	*H*	*N*	*S*	
Bis(diethyldithiocarbamato)diphenyl tin (IV)	46.65	5.44	5.06	22.5	found
Colour clear M.P. = 149–150					
(Lit. 152–154 °C[2], 146–147 °C[3])	46.40	5.31	4.92	22.52	calc.

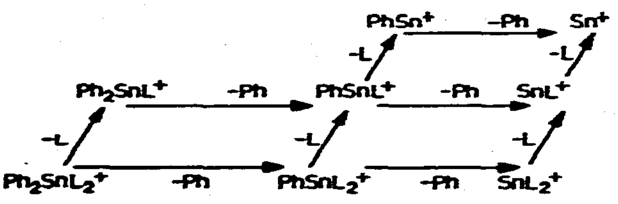
Microanalysis was carried out by the CSIRO Microanalysis Service, Melbourne University.

RESULTS AND DISCUSSION

Mass spectra of bis(diethyldithiocarbamato)diphenyl tin (IV)

Although elemental microanalysis indicated that the sample was relatively pure, a number of trace impurities were detected in the mass spectra. In earlier attempts to synthesize the product, these impurities were detected in larger amounts by mass spectrometry. The mass spectra are complicated by the presence of the isotopes of tin and chlorine. For clarity, only the mass spectral ions containing the ^{120}Sn or ^{35}Cl isotopes are discussed. Variation in the intensities of some groupes relative to other groups was evidently due to impurities having different volatilities from that of the diphenyl complex. With due regard for the presence of impurities, the mass spectrum of the bis(diethyldithiocarbamato)diphenyl tin (IV) is consistent with the assumed molar mass and molecular structure. The intensity of the parent molecular ion, *m/e* 570 (0.1 % of base peak, *m/e* 116) is very weak. Although the molecular ion was detected, there is a possibility of thermal decomposition in the probe as previously described[1]. The fragmentation mechanism is readily eludidated. Groups at *m/e* 570($Ph_2SnL_2^+$), 493($PhSnL_2^+$), 422(Ph_2SnL^+), 416(SnL_2^+), 345($PhSnL^+$), 268(SnL^+), 197($PhSn^+$) and 120(Sn^+) are observed, where Ph represents the phenyl and L the diethyldithiocarbamate ligands, respectively.

Fragmentation mechanism of bis(diethyldithiocarbamato)diphenyl tin (IV)



Groups of peaks at 454(Ph_2SnSL^+) and 300($SnLS^+$) in the diphenyl complex indicate that rupture of the sulphur–carbon bonds occurs. This did not occur in the dihalotin (IV) bisdiethyldithiocarbamates and indicates the monodentate nature of the dithiocarbamate ligand in the diphenyl complex. The fragmentation of the diethyldithiocarbamate ligand has been described previously[4].

Groups of peaks at *m/e* values of 612, 535, 503, 464, 457, 383, 351, 309, 229 and 155 are not associated with the diphenyl complex but with impurities. A very small amount of starting material (diphenyl tin (IV) dichloride) was detected by the groups at 344 ($Ph_2SnCl_2^+$) 309(Ph_2SnCl^+). A triphenyl tin impurity was detected by the groups at 351($SnPh_3^+$) and 383($SnPh_3S^+$) but the parent ion was not detected.

Two groups of impurity ions, a strong group at *m/e* 380 and a much weaker group at 457 were observed. Although the latter group suffered from interference from the group at 454 there was no doubt that the 380 group and the 457 group were associated since their relative intensity remained nearly constant whatever the conditions. The intensity pattern of the 380 group indicates the presence of one chlorine atom in the elemental composition. This ion is most probably formed from the 457 group by loss of phenyl. It is very likely that impurities in the sample are generated by incomplete replacement of chlorine ligand by the dithiocarbamate ligand. Hence, this impurity was assumed to be $ClPh_2Sn(SSCNEt_2)$ (MW = 457). The synthesis of this compound has been reported by Kupchick et al.[2].

The groups 612, 535 and 503 may be associated with some other very weak groups which occurred in the *m/e* range of 600–850. No definite structure can be proposed even though the presence of two tin atoms in the impurity were detected by the intensity pattern of peaks in the groups at 503, 535 and 612.

An earlier attempted preparation of the diphenyl complex yielded a compound of M.P. 146–147 °C. The mass spectrum indicated the presence of impurities of the order of 5–10% by mass. The preparation was repeated using a slight excess of the dithiocarbamate metal salt and the mass spectrum of the resulting complex indicated impurities present only to the extent of 1% by mass. Subsequent slow recrystallization in acetone produced clear crystals in contrast to the yellow material obtained by Bonati et al.[3]. Comparison between our data and that of Bonati et al.[3] indicates that the material studied by this group of workers was probably similar to our earlier preparation and hence the data reported for bis(diethyldithiocarbamato)diphenyl tin (IV) by Bonati et al.[3] may be suspect.

TG/DTA of the diphenyl complex

Decomposition of the complex did not occur immediately after the melting point (149–150 °C) as in the case of the dihalotin(IV)bisdiethyldithiocarbamate[1] but at a temperature of approximately 210 °C in both air and nitrogen.

In nitrogen, the DTA profile (Fig. 1) indicates that the two endothermic steps correspond precisely with the greatest rate of mass loss (peaks on DTG). Under the conditions employed, these steps are not completely separable. The resultant loss of mass and the colour of the product indicates that the final product was tin (II) sulphide.

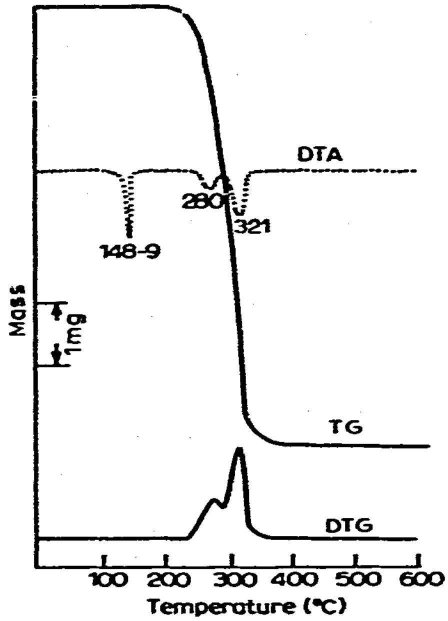


Fig. 1. TG/DTA of bis(diethyldithiocarbamato)diphenyltin(IV) in nitrogen.

In air, the DTG/DTA data (Fig. 2) indicate that the two decomposition steps are almost completely inseparable under the conditions used. Both decompositions are exothermic, indicating oxidation reactions of the products of decomposition with air.

A separate DTA run under vacuum (0.005 Torr) (Fig. 3) resulted in two endothermic peaks, the first, a narrow peak, corresponds to melting and the second broader peak corresponds to complete vaporization, which was confirmed by the entire loss of the complex in the sample pan.

The TG/DTA data in air and nitrogen are presented in Table 2.

P/GC–MS analysis of products of decomposition

P/GC–MS analysis of the complex was carried out using the method previously described[1]. Several analyses were performed under different conditions. From the results, it was apparent that the ratio of the high molar mass compounds to those of the low molar mass varied with the conditions of the experiment; longer heating periods yielding relatively greater amounts of the low molar mass compounds. From this, it appears that secondary decompositions

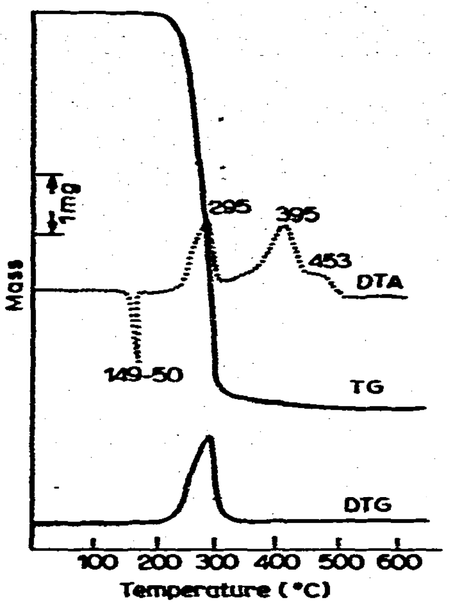


Fig. 2. TG/DTA of bis(diethyldithiocarbamato)diphenyltin(IV) in air.

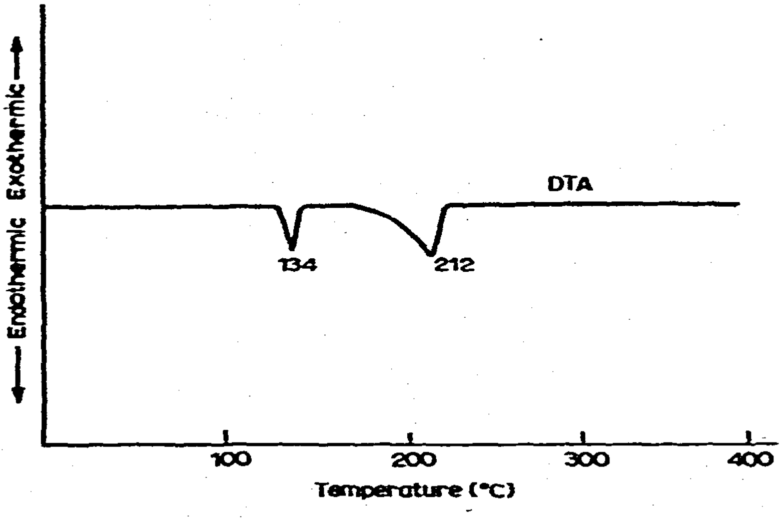


Fig. 3. Vacuum/DTA of bis(diethyldithiocarbamato)diphenyltin(IV).

occur. It is thus more difficult to clearly determine the mechanism of decomposition of the complex. However, it probably proceeds, at least partially, by way of the high molar mass intermediates.

This is further substantiated by the mass spectral analysis of a partially decomposed material obtained in an attempt to purify the complex by zone-refining in air. While most of this material was undecomposed complex, more volatile substances were detected. S-ethyl N,N-diethyldithiocarbamate and

TABLE 2

TG/DTA DATA OF THE DIPHENYL COMPLEX

	Atmosphere	
	Air	*Nitrogen*
Temperature range of decomposition	210–330 °C	215–380 °C
Temperature of DTG peaks	284, 288 °C	272, 316 °C
Percentage mass loss	68%	82% (78.8)[a]

[a] The figure in the brackets represents the theoretical mass loss leaving tin (II) sulphide as residue.

diphenyl sulphide were identified. Also, a substance having an apparent molar mass of 225 was observed. Changes in the intensity of this peak were accompanied by changes in the peaks at *m/e* 116, 88, and 60. Although these peaks appear in the spectrum of the complex and also in the sodium salt of the dithiocarbamate ligands which might be expected to be an impurity in the complex, it appears that they also occur in the spectrum of the MW 225 material. High resolution mass spectrometry indicated an elemental composition of $C_{11}H_{15}NS_2$ for this compound. This substance was not observed in any of the initial P/GC–MS analyses but the two other substances were detected. The relative amounts of the products of decomposition are shown in the source total ion monitor (STIM) in Fig. 4. The STIM has been described previously[1]. The significance of the production of these compounds will be discussed in the Conclusion.

The products of decomposition were identified from their mass spectra, either by comparison with reference spectra (10, 11) or by comparison with previous work[1] or by deduction from the mass spectrum and the known com-

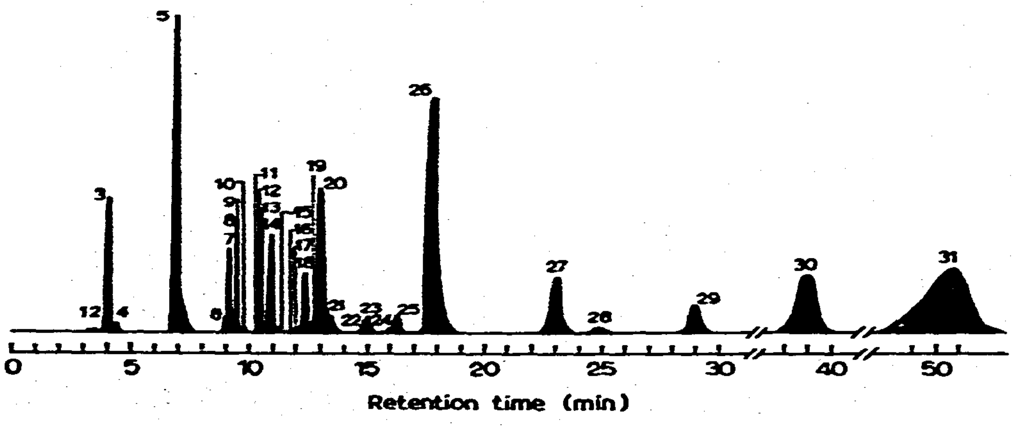


Fig. 4. STIM of P/GC–MS of bis(diethyldithiocarbamato)diphenyltin(IV).

position of the ligands. Compounds No. 5, 7, 14, 20 and 26 in Table 3 were the major products. No. 3, 18, 23, 25, 27, 29, 30 and 31 were minor products, the rest being present in trace quantities only.

TABLE 3

IDENTIFICATION TABLE OF PYROLYSIS PRODUCTS FROM GC–MS ANALYSIS

No.	*Pyrolysis product*
1	Ethyl mercaptan[a]
2	Carbonyl sulphide[a]
3	Carbon disulphide[a]
4	Diethyl amine[a]
5	Benzene[a]
6	1-Ethylpyrrol[a]
7	Ethylisothiocyanate[a]
8	Ethyl benzene[a]
9	1-Ethylthiaziridine-3-thione[b]
10	Styrene[a]
11	Diethyl disulphide[a]
12	Unknown MW = 98
13	N,N-diehtylformamide[a]
14	Phenyl mercaptan[a]
15	Cyanobenzene[a]
16	Benzothiazole[a]
17	1-Thia-(2,3 dihydroindene)[a]
18	Ethyl phenyl sulphide[a]
19	N,N,N',N'-tetraethylurea[a]
20	N,N-Diethylthioformamide
21	Unknown MW = 156
22	Unknown MW = 170
23	Biphenyl[a]
24	S-Methyl N,N-diethyldithiocarbamate[c]
25	N,N,N',N'-tetraethylthiourea[a]
26	S-Ethyl N,N-Diethyldithiocarbamate[b]
27	Diphenylsulphide[a]
28	Unknown MW = 147
29	N,N-Diethylthiophenylamide[b]
30	Diphenyl disulphide[a]
31	S-Phenyl N,N-diethyldithiocarbamate[b]

[a] Comparison with reference mass spectra data[10,11]. [b] Deduced structure. [c] Comparison with previous work[1].

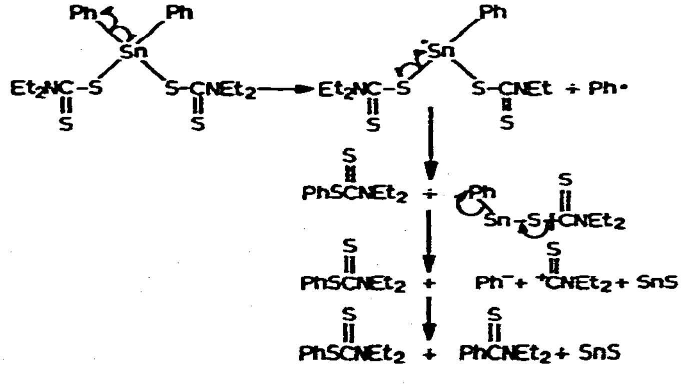
Later attempts to observe the $C_{11}H_{15}NS_2$ compound were made by using the changed GC conditions as described in the experimental section. In this way a good mass spectrum was obtained with major peaks at *m/e* 225, 116, 109, 88, 77, 60 and 29 leading to identification as compound 31 in Table 3. Further high molar mass compounds (28–30) were also detected and their identification was carried out on the basis of their mass spectra.

CONCLUSION

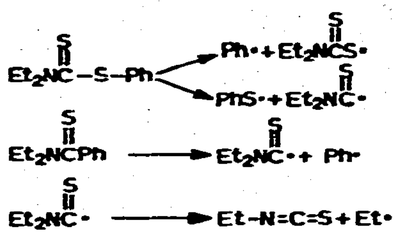
Due to the variety and amounts of the products resulting from thermal decomposition of bis(diethyldithiocarbamato)diphenyl tin (IV), it is difficult to propose a definite mechanism of decomposition. However, it is certain that there are several primary and secondary decompositions occurring as indicated by the decreasing ratio of higher molar mass compounds to lower molar mass compounds according to changes in experimental conditions.

The primary mechanisms of decomposition can be explained by a combination of ionic and radical reactions. However, the formation of some products of secondary decompositions are due only to radical reactions as discussed below. An additional problem associated with these mechanisms is the presence of hydrogenated species such as benzene. It is difficult to explain the formation of these species since stoichiometrically the amounts of hydrogenated and unhydrogenated species do not balance. The hydrogenated species are produced by abstraction of hydrogen radicals, but the source of this hydrogen is a matter of conjecture; it may be water or acetone of recrystallization.

The major mechanism of thermal decomposition of the bis(diethyldithiocarbamato)diphenyl tin (IV) involves the initial formation of the high molar mass compounds and their subsequent decomposition. The mechanism is envisaged as the homolytic dissociation of the tin–phenyl bond and the subsequent reaction of the radicals produced. This is followed by the heterolytic dissociation of the other tin–phenyl bond yielding the products indicated below including the tin (II) sulphide as residue.



The primary products of decomposition undergo further decomposition via the formation of radicals and their subsequent reactions and decomposition. The complete mass loss down to the tin sulphide does not occur during the primary decomposition because of the involatility of the products. Plausible decompositions of the primary products are given below.



A variety of radical recombination reactions can then occur as indicated by the products found in P/GC–MS analysis.

$$\mathrm{Et\cdot + \cdot S{-}\overset{\overset{\displaystyle S}{\|}}{C}NEt_2 \rightarrow Et S\overset{\overset{\displaystyle S}{\|}}{C}NEt_2}\ \text{(a major product)}$$

$\mathrm{PhS\cdot + Et\cdot \rightarrow PhSEt}$

$\mathrm{Ph\cdot + Et\cdot \rightarrow PhEt}$

$\mathrm{PhS\cdot + PhS\cdot \rightarrow PhS{-}SPh}$

$\mathrm{PhS\cdot + Ph\cdot \rightarrow Ph{-}S{-}Ph}$

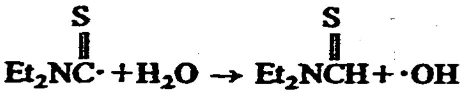
$\mathrm{Ph\cdot + Ph\cdot \rightarrow Ph{-}Ph}$

The possibility exists for the formation of small hydrocarbon species via the recombination of ethyl radicals. However, no such species were detected either by the FID detector or the P/GC–MS technique.

The radicals below may be involved in hydrogen abstraction reactions as indicated by the products found in GC–MS analysis. Possible reactions are

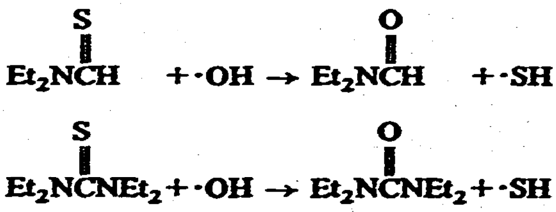
$\mathrm{Ph\cdot + H_2O \rightarrow PhH + \cdot OH}$ (benzene is a major product)

$\mathrm{PhS\cdot + H_2O \rightarrow PhSH + \cdot OH}$



$$\mathrm{Et_2N\overset{\overset{\displaystyle S}{\|}}{C}\cdot + H_2O \rightarrow Et_2N\overset{\overset{\displaystyle S}{\|}}{C}H + \cdot OH}$$

The hydroxyl radicals produced, possibly react further with the products of decomposition as indicated by oxygen containing species.



$$\mathrm{Et_2N\overset{\overset{\displaystyle S}{\|}}{C}H + \cdot OH \rightarrow Et_2N\overset{\overset{\displaystyle O}{\|}}{C}H + \cdot SH}$$

$$\mathrm{Et_2N\overset{\overset{\displaystyle S}{\|}}{C}NEt_2 + \cdot OH \rightarrow Et_2N\overset{\overset{\displaystyle O}{\|}}{C}NEt_2 + \cdot SH}$$

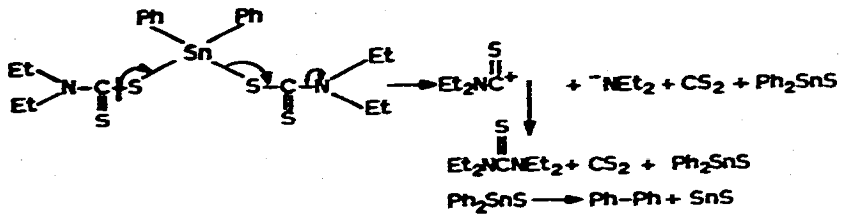
$\mathrm{CS_2 + \cdot OH \rightarrow COS + \cdot SH}$

Termination reactions

$HS\cdot + \cdot Ph \rightarrow PhSH$

$HS\cdot + \cdot Et \rightarrow EtSH$

A minor mechanism of thermal decomposition involves the formation of diphenyl, tetraethylthiourea and carbon disulphide and is envisaged as:



The mechanism of thermal decomposition of bis(diethyldithiocarbamato)diphenyl tin (IV) is greatly affected by both the nature of the groups directly bonded to the tin atom and the denticity of the dithiocarbamate ligands. In our studies of the thermal decomposition of tetrakisdiethyldithiocarbamatotin (IV)[12] the major decomposition products were carbon disulphide, tetraethylthiourea and S-ethyl N,N-diethyldithiocarbamate. X-ray diffraction studies[13] of the complex show that the dithiocarbamate ligands were both mono- and bidentate. The production of the S-ethyl N,N-diethyldithiocarbamate is strongly dependent on the dithiocarbamate ligand being monodentate in the original tin complex. Hence, the production of phenyl and ethyl substituted dithiocarbamates as decomposition products suggests that the dithiocarbamate ligands in the diphenyl complex are monodentate.

Thus, the products of thermal decomposition suggest that the structure of the complex involves a coordination number of four for tin and a tetrahedral symmetry. This is in agreement with Mössbauer spectroscopic data[8] for the complex.

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REFERENCES

1 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 335.
2 E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, 4 (1975) 973.
3 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 10 (1967) 257.
4 B. W. Fitzsimmons, *Chem. Commun.*, (1968) 1485.

5 B. W. Fitzsimmons, A. A. Owusu, N. J. Seeley and A. W. Smith, *J. Chem. Soc. A.*, (1970) 935.
6 R. V. Parish and C. G. Johnson, *J. Chem. Soc. A.*, (1971) 1906.
7 R. V. Parish, *Chem. Phys. Lett.*, 10 (1971) 224.
8 J. L. K. F. de Vries and R. H. Herber, *Inorg. Chem.*, 11 (1972) 2458.
9 R. Barbierie, L. Pelerito and C. Stocco, *Chim. Ind. (Milan)*, 56 (1974) 350.
10 Cornu and Massot, *Compilation of Mass Spectral Data*, Heyden & Son, U.K., 1966.
11 Stenhagen, Abrahamsson and McLafferty, *Registry of Mass Spectral Data*, John Wiley, New York, 1974.
12 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 361.
13 C. S. Marreld and E. O. Schlemper, *Acta Crystallogr.*, *B*, 27 (1971) 1964.