Thermochimica Acta, 133 (1988) 383–387
Elsevier Science Publishers B.V., Amsterdam

THE OXIDATION OF BIS(N,N-DIETHYLDITHIOCARBAMATO)TIN(II)

G.K. BRATSPIES, J.O. HILL and J.F. SMITH

Department of Chemistry, La Trobe University,
Bundoora, Victoria 3083, Australia.

ABSTRACT

The oxidation of bis(N,N-diethyldithiocarbamato)tin(II) has been studied by thermal degradation mass spectrometry. It is proposed that the oxidation of this complex in air is a complicated sequence of reactions involving structurally-related and possibly polymeric tin(IV) complexes.

INTRODUCTION

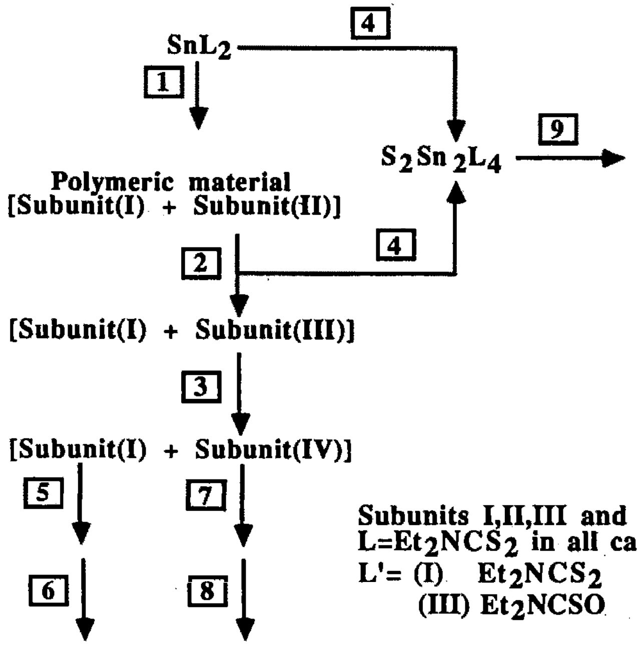
In a previous study [1], bis(N,N-diethyldithiocarbamato)tin(II) (abbreviated SnL_2), was shown to oxidise spontaneously, even at ambient temperature. In that study, we were able to distinguish between the complex and the decomposition of its oxidised products by using thermal degradation mass spectrometry (TDMS) [2] but were unable to interpret the results in detail.

Since this study [1], we have published further related work [3-5] and we have become aware of reports concerning the thermal rearrangement of the N.C=S.O functional group [6-14], particularly in thiocarbamates [8-14]. These studies [3-14] together with related papers [15-20, 22-24], mainly concerning the mass spectra of metal dithiocarbamates and related compounds [16-24], have allowed us to interpret the current TDMS results and we now propose a scheme for the oxidation of SnL_2 in air and the subsequent thermal decomposition of the oxidised products in vacuum.

EXPERIMENTAL

TDMS has been described previously [2]. The present application involves heating 10-100 µg of sample at a constant 12.5°C min^{-1} from ambient temperature to about 400°C in the direct insertion probe of a JEOL JMS D-100 mass spectrometer. As substances volatilise, ions are detected and the total ion intensity provides a record of the volatilisation. Mass spectra are recorded as appropriate throughout the analysis. The ionisation energy can be selected between 10-30 eV or set at 75 eV. Resolving power is set at about 1000.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50



Subunits I,II,III and IV are [OSnLL'}:
L=Et_2NCS_2 in all cases:
L'= (I) Et_2NCS_2 : (II) Et_2NCS_2O:
(III) Et_2NCSO : (IV) Et_2NCOS.

1 Oxidation of SnL_2, forming a polymer, consisting of subunits (I) and (II).
2 Sulfur expulsion from subunit (II) forming subunit (III).
3 Thermal rearrangement of subunit (III) into (IV).
4 Reaction of sulfur, from **2**, with unoxidised SnL_2 to form $S_2Sn_2L_4$.
5 Decomposition of subunit (I) into TETD and tin (II) oxide.
6 Decomposition of TETD into TETM and sulfur.
7 Decomposition of subunit (IV) into oxo-TETD and tin (II) oxide.
8 Decomposition of oxo-TETD into oxo-TETM and sulfur.
9 Decomposition of $S_2Sn_2L_4$ into SnL_2 and S_2.

FIG.1 Simplified scheme proposed for the oxidation of SnL_2 and the subsequent thermal decomposition of the oxidised products. Reactions **1-4** occur below 160°C in air; **5-8**, 180-240°C in vacuum and **9**, above 250°C in vacuum.

A procedure for the preparation of SnL_2 has been given previously [1]. The complex is volatile and has a characteristic mass spectrum. If small samples of freshly-prepared SnL_2 are subjected to TDMS as described above, ions appear at about 100°C and have disappeared when 180°C is reached. No further ions are observed and there is no residue.

This provides a convenient method of detecting unoxidised samples in oxidised samples since ions from the oxidation products are not observed below 180°C.

Finely-ground SnL_2 is heated in an oven at 160°C for 30 mins. After regrinding, a 50 μg sample is tested for unoxidised SnL_2. The procedure is repeated until no unoxidised SnL_2 remains. Fully oxidised material is then analysed by TDMS as described above.

RESULTS AND DISCUSSION

The results clearly show that decomposition of the oxidised products occurs with the evolution of a variety of compounds. A residue is also observed.

In analysing the overall results, it is first necessary to assign elemental compositions to each peak in the mass spectra. This is aided by previous assignments for metal dithiocarbamates as reported in the literature [1,3,5,16-18]. The next step is to establish possible molecular ions and thus, if possible, to identify the compounds present by comparison with mass spectra given in the literature [3,5]. If reference spectra are not available then spectra of closely related compounds [13,14,19-21] are used. In this way the behaviour of individual substances can be monitored and their relationships with other substances discerned.

The spectra are complicated by the presence of ions from extraneous Fe(III) and Ni(II) dithiocarbamate complexes. This phenomenon has been observed before [3,16,22-24] and is the result of thiuram disulphide, produced in the decomposition, reacting with the metal parts of the ion source [22,24] or residues deposited within it [3].

It is not possible within the scope of this paper to describe the detailed reasoning that led to our proposal of the scheme presented in Fig. 1. The general procedure is outlined above.

We propose that in the oxidation of SnL_2, structurally-related oxygenated, polymeric, tin(IV) complexes are involved which consist of subunits of the general type (OSnLL') in which L represents Et_2NCS_2 and where L' may be (I) Et_2NCS_2 (dithiocarbamate), (II) Et_2NCS_2O (dithioperoxycarbamate), (III) Et_2NCSO (thioncarbamate) or (IV) Et_2NCOS (monothiocarbamate).

Subunits I and IV predominate since II is thermally unstable under the imposed conditions and, with the expulsion of sulfur, forms III which in turn thermally rearranges into IV. The expelled sulfur reacts with unoxidised SnL_2 to form di-μ-sulfidobis[bis(N,N-diethyldithiocarbamato)tin(IV)], $S_2Sn_2L_4$, as previously reported by us [5].

The proposal of the structure of subunit II is based on a similar structure reported for a mixed ligand dithiocarbamate chromium(III) complex [15].

Thus the species generating the compounds observed in TDMS are derived from the thermal degradation of polymeric material consisting of subunits I and IV and from $S_2Sn_2L_4$. Under TDMS conditions the material decomposes to yield tetraethylthiuram disulfide (TETD) or oxo-TETD, from subunits I and IV respectively and these further decompose to yield tetraethylthiuram monosulfide (TETM) and oxo-TETM in a manner previously discussed for TETD [3]. We have previously reported [3,4] that decomposition of tin(IV) dithiocarbamate complexes in vacuum yields thiuram disulfide as a primary intermediate. Sulfur allotropes, including S_8 and S_6, are also evolved simultaneously with TETM and oxo-TETM.

Apart from the decomposition products already discussed, except for CS_2 and $(C_2H_5)_2NH$ the other products are present in relatively small yields and thus are of minor significance.

$S_2Sn_2L_4$ decomposes into SnL_2 and S_2 [5] with minor amounts of CS_2 and $(C_2H_5)_2NH$.

Without high resolution studies it is impossible to say if a dioxothiuram disulfide species is present. Its molecular ion is obscured by other ions.

CONCLUSION

The oxidation bis(N,N-diethyldithiocarbamato)tin(II) involves several sequential reactions which are incompletely understood in the absence of detailed structural data for the intermediate polymeric material.

REFERENCES

1. G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 27 (1978) 307.

2. J.F. Smith, Int. J. Mass. Spectrom. Ion. Phys., 26 (1978) 149.

3. G.K. Bratspies, J.F. Smith and J.O. Hill, J. Anal. Appl. Pyrolysis, 2 (1980) 35.

4. G.K. Bratspies, J.F. Smith and J.O. Hill, Thermal Analysis, Proceed. 6th ICTA Conf. Birhauser-Verlag, Basel, 2 (1980) 147.

5. G.K. Bratspies, J.F. Smith, J.O. Hill and P.J. Derrick, J. Thermal Anal., 16 (1979) 369.

6. M.S. Newman and H.A. Karnes, J. Org. Chem., 31 (1966) 3980.

7. A. Lanzani and G. Jacini, Riv. Ital. Soslanze Grasse, 48 (1971) 471: Chem. Abstr. 76: 1406092.

8. M.S. Newman and F.W. Hetzel, J. Org. Chem., 34 (1969) 3604.

9. K. Miyazaki, Tetrahedron Lett., (1968) 2793.

10. R.F. Hudson, A.J. Lawson and E.A.C. Lucken, J. Chem. Soc., Chem. Commun., (1971) 807.

11. J.D. Edwards and M. Pianka, J. Chem. Soc., (1965) 7338.

12. S. Braverman and B. Goldrath, Int. J. Sulfur Chem., 8 (1973) 55.

13. J.C. Tou and R.M. Rodia, Org. Mass Spectrom., 6 (1972) 493.

14. J.C. Tou, J. Phys. Chem., 75 (1971) 1903.

15. J.M. Hope, R.L. Martin, D. Taylor and A.H. White, J. Chem. Soc., Chem. Comm., (1977) 99.

16. K.W. Given, B.M. Mattson, G.L. Miesser and L.H. Pignolet, J. Inorg. Nucl. Chem., 39 (1977) 1309.

17. J. Krupcik, P.A. Lectercq, J. Garaj and J. Masaryk, J. Chromatogr., 171 (1979).

18. J.R. Dias, M. Zigon and S. Gomiscek, Org. Mass Spectrom., 16 (1981) 12.

19. W.R. Benson and J.N. Damico, J. Assoc. Off. Anal. Chem., 51 (1968) 347.

20. M. Lozynski, Org. Mass Spectrom., 17 (1982) 109.

21. G.K. Bratspies, Unpublished data.

22. J.K. Terlouw and J.J. De Ridder, Org. Mass Spectrom., 5 (1971) 1127.

23. B.C. Wood and R.K. Skogerboe, Appl. Spectrosc., 27 (1973) 10.

24. T. Tetsumi, M. Sumi, M. Tanaka and T. Shono, Polyhedron, 5 (1986) 703.