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THERMAL STUDIES ON TIN(IV) COMPLEXES OF *N*-ALKYLCYCLOHEXYL DITHIOCARBAMATES

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ABSTRACT

Tin(IV) complexes of *N*-alkylcyclohexyl dithiocarbamates of the type $Sn(RCyhxdtc)_nCl_{4-n}$ (Cyhx = Cyclohexyl, R = Me, $n = 2, 3$; R = Et, $n = 1, 2, 4$; R = i-Pr, $n = 1, 2$) have been synthesized. TG and DTA studies have been carried out for $Sn(MeCyhxdtc)_2Cl_2$, $Sn(EtCyhxdtc)Cl_3$, $Sn(EtCyhxdtc)_4$ and $Sn(i\text{-}PrCyhxdtc)Cl_3$ (in N_2). In addition, TG studies have been carried out for $Sn(MeCyhxdtc)_3Cl$, $Sn(EtCyhxdtc)_2Cl_2$ and $Sn(i\text{-}PrCyhxdtc)_2Cl_2$. Unless states, the studies have been carried out in air atmosphere.

INTRODUCTION

Dithiocarbamates form a class of sulphur–sulphur donor ligands, the metal complexes of which have been extensively studied for quite some years [1]. Interest in these complexes has been stimulated by their use in industry as vulcanization accelerators and as high pressure lubricants, whereas their use as fungicides and pesticides has induced a vast number of biological and biochemical studies [2]. A literature survey reveals that little work has been carried out on thermal studies of metal dithiocarbamato complexes [3–7]. In continuation of our previous work on metal dithiocarbamates [6,7] the present communication describes the preparation and thermal investigation of tin(IV) complexes of *N*-alkylcyclohexyl dithiocarbamates.

EXPERIMENTAL

Sodium salts of dithiocarbamic acid were prepared as reported in the literature [8]. Tin tetrachloride was prepared by the method given in Inorganic Laboratory Preparations [9].

Preparation of the complexes

These were prepared by the method reported by Zaidi et al. [10]. Stoichiometric proportions of tin tetrachloride and sodium dithiocarbamate were

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placed in a conical flask provided with a guard tube. About 100 ml anhydrous ethanol–chloroform mixture (1 : 1) was added. The contents were refluxed for 2 h. The solution was filtered to remove the precipitated sodium chloride. The filtrate was evaporated under vacuum until its volume was reduced to one half of the original. After the addition of pretroleum ether an oily product was obtained. In the case of *N*-methyl cyclohexyl and *N*-isopropyl cyclohexyl dithiocarbamate derivatives, it was thoroughly agitated in cold water until a solid crystalline product resulted. In the case of *N*-ethyl cyclohexyl dithiocarbamate compounds the oily product was refluxed for 15 min and a crystalline solid was isolated. It was filtered through G-4, sintered in a glass cruicible and dried under vacuum.

Physical measurements

TG data were recorded on a Stanton-Redcroft TG 750/770, G-70 thermoanalyser (Setaram, Lyon, France), a Du Pont instrument, and a Stanton-

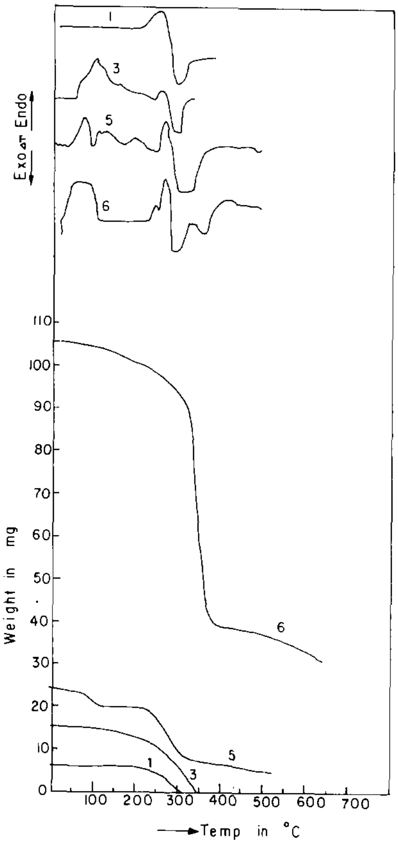

Fig. 1. TG and DTA curves of (1) $Sn(MeCyhxNCS_2)_2Cl_2$, (3) $Sn(EtCyhxNCS_2)Cl_3$, (5) $Sn(EtCyhxNCS_2)_4$, (6) $Sn(i\text{-}PrCyhxNCS_2)Cl_3$ (in N_2).

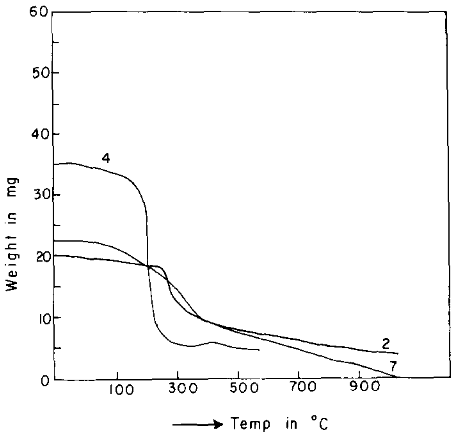

Fig. 2. TG curves of (2) $Sn(MeCyhxNCS_2)_3Cl$, (4) $Sn(EtCyhxNCS_2)_2Cl_2$, (7) Sn(i-$PrCyhxNCS_2)_2Cl_2$.

Redcroft thermobalance model TR-2. DTA curves were recorded on a Stanton-Redcroft RE 571.20 potentiometric recorder and on a Du Pont instrument. Simultaneous TG and DTA curves were recorded on a Stanton-Redcroft STA-780 series.

The heating rate for recording TG curves was 10°C min^{-1} in air atmosphere. In nitrogen atmosphere the heating rate was 4°C min^{-1} in a self-produced atmosphere using a silica crucible. In DTA the chart speed was 300 mm h^{-1} and the heating rate was 10°C min^{-1}. The reference material used was powdered α-alumina.

RESULTS

*(1) Dichlorobis(*N*-methylcyclohexyl dithiocarbamato) tin(IV)*

The TG curve for this complex shows that the complex is thermally stable up to 230°C, then decomposition sets in abruptly. Beyond this temperature the TG curve showed a weight loss up to 270°C. At this temperature the intermediate $Sn(SCN)_2Cl_2$ was probably formed (calc. wt. loss: 45.96%; found: 38.40%). This shows that the decomposition of $Sn(SCN)_2Cl_2$ is not complete and simultaneously decomposes to SnS_2 as far as 350°C, since it was not possible to raise the temperature above this, due to limitations of the instrument.

The decomposition of the complex at 230°C, as revealed by the TG trace, corresponds to an endothermic peak in the DTA profile. A subsequent broad exotherm covering a temperature range 250–270°C may be assigned to the reaction of air and residual tin sulphide.

(2) *Chlorotris(*N*-methylcyclohexyl dithiocarbamato) tin(IV)*

The TG curve reveals that the complex is thermally stable up to 235 °C. Thereafter, a deep-seated decomposition occurred giving a visible maximum around 370 °C. Here the organic matter decomposes linearly. From 370 °C onwards there is a slow loss in weight up to 520 °C but the curve is not perfectly horizontal. The intermediate $Sn(SCN)_4$ was probably formed during this step (calc. wt. loss: 51.80%; found: 60%) and simultaneously decomposes slowly. Beyond 520 °C the weight loss continues slowly above 800 °C and mixtures of sulphides and oxide of tin were formed.

(3) *Trichloro(*N*-ethylcyclohexyl dithiocarbamato) tin(IV)*

The TG curve for this complex shows a slow mass loss from 50 °C which is accelerated around 270 °C. In this temperature interval the organic matter decomposes, then from 270 °C onwards the intermediate $Sn(SCN)_2Cl_2$ was probably formed but the curve does not show any horizontal for the formation of this compound (calc. wt. loss: 28.4%; found: 23.4%). The decomposition probably proceeds beyond 350 °C and it could not be ascertained whether SnS_2 is the final product of thermal degradation, since it was not possible to raise the temperature above 350 °C due to limitations of the instrument.

The DTA curve shows well-defined peaks. The first endothermic peak at 90 °C is due to the melting of the complex. A good correlation is observed between endothermal peak temperature, due to the decomposition, and melting point obtained by the conventional capillary tube technique. A small endothermic peak is observed in the region 258–260 °C, immediately followed by a shallow exotherm (290–296 °C) which might be due to some intermediate which could not be isolated.

(4) *Dichlorobis(*N*-ethylcyclohexyl dithiocarbamato) tin(IV)*

The TG curve for this complex shows that there is little mass loss up to 160 °C. Beyond this temperature the decomposition sets in abruptly. The organic matter burns off linearly up to 200 °C after which there is a slow weight loss up to 380 °C. Between 200 and 380 °C the probable intermediate $Sn(SCN)_2Cl_2$ is formed (calc. wt. loss: 48.11%; found: 52.5%). From 380 °C onwards there is a slow weight loss up to 550 °C and the conversion to tin sulphide is not complete.

(5) *Tetrakis(*N*-ethylcyclohexyl dithiocarbamato) tin(IV)*

The TG curve shows that the complex was thermally stable up to 60 °C. Beyond this temperature the complex decomposes rapidly up to 170 °C followed by a slow mass loss up to 260 °C. Then there is a sharp drop in temperature up to 300 °C, probably since the intermediate $Sn(SCN)_4$ is formed (calc. wt. loss: 62.61%; found: 69%) after which there is a slow weight loss up to 500 °C due to the decomposition of thiocyanate to sulphide but this conversion to sulphide is not complete.

The DTA curve shows an endothermic peak at 64 °C which is due to the initial decomposition of the complex. This is followed by a exothermic peak at 83 °C, probably a reaction between air and the tin intermediate occurs in this process [11]. A sharp endothermic peak at 256 °C corresponds to the complete decomposition of the complex.

(6) Trichloro(N-isopropylcyclohexyl dithiocarbamato) tin(IV) (in N_2 atmosphere)

The TG curve for this complex shows a slow mass loss from ambient temperature and the decomposition sets in abruptly around 250 °C. Beyond this temperature the TG curve descended linearly up to 370 °C with the destruction of organic matter after which there is a slow decrease in weight up to 460 °C. This is probably due to the formation of the intermediate corresponding to the formula Cl_2SnS (Calc. wt. loss: 55.2%; found: 67.5%) which is simultaneously decomposed to tin sulphide (SnS). This decomposition is not complete even up to 650 °C.

The DTA curve shows a small endotherm at 231 °C followed by a sharp endotherm at 251 °C. This is due to the breakage of bonds and formation of stable products via a reactive intermediate as reported by Bratspies et al. [12]. A comparatively broad exotherm (339–340 °C) represents the organic matter omitted.

(7) Dichlorobis(N-isopropylcyclohexyl dithiocarbamato) tin(IV)

The TG curve shows that the decomposition begins around 70 °C. The decomposition is rapid up to 370 °C. In this temperature range (70–370 °C) the organic part of the complex has been burnt. This is followed by a slow weight loss up to 650 °C, probably due to the formation of the intermediate $Sn(SCN)_2Cl_2$ (calc. wt. loss: 57.8%; found: 60%) but the curve is far from horizontal. From 650 °C onwards the weight loss continues up to 900 °C due to the formation of sulphides, and simultaneous decomposition to oxide and pure oxide is not found even at 1000 °C.

DISCUSSION

The TG studies indicate that in air atmosphere, either $Sn(SCN)_2Cl_2$ or $Sn(SCN)_4$ is the intermediate product of the decomposition. It is revealed

TABLE 1

Thermal stability data, first decomposition range and activation energy values

Complex	Activation energy, E_a (kcal mol^{-1})	Decomp. range (K)
(1) $Sn(MeCyhxNCS_2)_2Cl_2$	4.87	503-553
(2) $Sn(MeCyhxNCS_2)_3Cl$	5.57	498-643
(3) $Sn(EtCyhxNCS_2)Cl_3$	18.80	323-543
(4) $Sn(EtCyhxNCS_2)_2Cl_2$	15.40	433-503
(5) $Sn(EtCyhxNCS_2)_4$	10.50	533-573
(6) $Sn(i\text{-}PrCyhxNCS_2)Cl_3$	24.56	523-643
(7) $Sn(i\text{-}PrCyhxNCS_2)_2Cl_2$	5.26	343-623

that these are subsequently transformed to SnS_2. The conformation of this latter step, however, could not be elucidated in some cases, since the conversion to SnS_2 is not complete at the final temperature of the TG curve.

The TG curve for $Sn(i\text{-}PrCyhxNCS_2)Cl_3$ in nitrogen atmosphere indicates that Cl_2SnS is initially formed, which may subsequently be transformed to

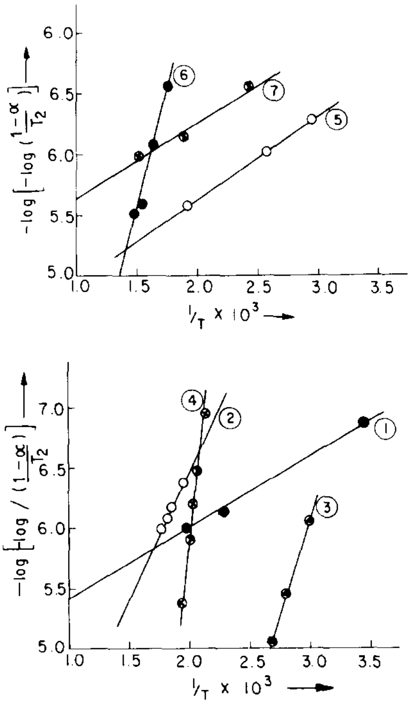

Fig. 3. Coats and Redfern linearisation curve of (1) $Sn(MeCyhxNCS_2)_2Cl_2$, (2) $Sn(MeCyhxNCS_2)_3Cl$, (3) $Sn(EtCyhxNCS_2)Cl_3$, (4) $Sn(EtCyhxNCS_2)_2Cl_2$, (5) $Sn(EtCyhxNCS_2)_4$, (6) $Sn(i\text{-}PrCyhxNCS_2)Cl_3$, (7) $Sn(i\text{-}PrCyhxNCS_2)_2Cl_2$.

SnS. In the case of $Sn(MeCyhxNCS_2)_3Cl$ and $Sn(i\text{-}PrCyhxNCS_2)_2Cl_2$ the TG curve in air atmosphere reveals that at 1000°C a mixture of tin sulphide and tin oxide is probably formed.

From the TG curves, the activation energy (Table 1) and the order of reaction for the first thermal decomposition step have been determined by the method of Coats and Redfern [13]. The order of reaction in each case is one.

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