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Coordination compounds

In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

THERMAL ANALYSIS STUDIES OF TIN DITHIOCARBAMATE COMPLEXES

A short review

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Abstract

A short review of the thermal analysis data available for dithiocarbamate complexes of tin(II) and tin(IV) is presented. Since the relevant thermal decomposition mechanisms are complicated, even for decompositions in inert atmospheres, mechanisms postulated on the basis of thermal analysis data alone are suspect. Realistic thermal decomposition mechanisms for these complexes can only be formulated when the relevant decomposition products are unambiguously identified. In this short review, an attempt is made to identify trends in these thermal analysis data, with particular reference to structural features of the corresponding complexes.

Keywords: complexes, decomposition mechanism, tin dithiocarbamate complexes

Introduction

The thermochemistry of the metal dithiocarbamate complexes has developed systematically and progressively over the last three decades. Major reviews of the field have been published by Hill and Magee [1] and by Sharma [2] which together, cover the relevant literature to 1985. The major thermal analysis techniques (TG, DTA, STA and DSC) have been applied to study the thermal characteristics of a very wide variety of metal dithiocarbamate complexes

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and it is now possible to classify the thermal properties of these complexes and to identify trends in such data, which have analytical and structural significance.

There has been some specific interest in tin dithiocarbamates, particularly over the last two decades. Thermal analysis studies of some of these complexes have been augmented by evolved gas analysis (EGA) studies, which have permitted the thermal decomposition pathways to be defined with some degree of confidence. Furthermore, trends in thermal decomposition behaviour have been rationalised in terms of the immediate environment of the coordinated metal and specific electronic effects associated with the dithiocarbamate ligand.

Since tin dithiocarbamate are important synthetic precursors of a wide variety of organometallic complexes, the thermal characteristics of this group of complexes are important in the design of organometallic synthetic procedures, especially those that involve ligand replacement sequences. Furthermore, tin organometallic complexes have important commercial application as active constituents of certain fungicides and pesticides. It is therefore appropriate that the thermal properties of the tin dithiocarbamate family of complexes are reviewed, with the specific aim of identification of trends in such data, such as the thermal decomposition behaviour of these complexes can be rationalised in terms of fundamental structural features.

Review

An early study of the thermal decomposition behaviour of tin dithiocarbamate complexes has been reported by Kupchik *et al.* [3]. A series of diphenyl- and dibenzyldithiocarbamato complexes of tin (IV) was heated in air and the solid residues formed were identified by conventional chemical analysis. The thermal stability limit of the diphenyl series of complexes ranges between 470 and 530 K, whereas that for the dibenzyl series is close to 400 K. Decomposition of the diphenyldithiocarbamato-tin(IV) complexes in air yields diphenylamine and the corresponding (bis(organotin)oxide or diphenyltin oxide. Decomposition of the dibenzyldithiocarbamato-tin(IV) complexes in air yields the corresponding bis(triphenyltin) sulphide trimer or diphenyl tin sulphide. Minor secondary products are also formed. This study indicates that the thermal decomposition pathways of tin dithiocarbamate complexes are complicated and certainly not predictable. Even for a series of structurally related complexes, it is difficult to decipher and rationalise trends in the thermal decomposition behaviour.

Perry and Geanangel [4] have reported TG data for bis(N,N-dimethyldithiocarbamato)tin(II) and bis(N,N-diethyldithiocarbamato)tin(II). The thermal decomposition of these complexes was conducted in a dynamic dry nitrogen atmosphere. A simple two-step decomposition mechanism for these complexes is proposed, involving the sequential liberation of the dithiocarbamato ligands and the final formation of tin metal as residue. This mechanism is stated to be supported by mass spectral data for the parent complexes. The volatile decomposition products are not identified and the purity of the original complexes is not stated.

Srivastava *et al.* [5] have investigated, by TG, the thermal decomposition behaviour in an inert atmosphere of a series of complexes of the type $Ph_2SnXdtc$, X = halogen or pseudohalogen. A two-step thermal decomposition mechanism is evident and, in all cases, the final residue is tin metal. However, neither the volatile decomposition products not any stable intermediates are stated. Srivastava and Bargava [6] have extended this study and have reported the thermal decomposition behaviour of tetrakis(morpholine-N-carbodithioato)tin(IV) and dichlorobis(morpholine-N-carbodithioato)tin(IV) in an inert atmosphere, using TG. A four-step thermal decomposition mechanism is evident for the former complex: three ligands are lost consecutively and the fourth step yields SnS_2 and hence tin metal at 573 K. However, for the latter complex, a two-step thermal decomposition mechanism applies with the intermediate formation of $Sn(CNS)_2Cl_2$ and the final formation of tin metal. Again, it is difficult to identify any trends in such thermal analysis data.

Johri and Venugopalan [7] have reported a systematic TG investigation of the thermal decomposition behaviour in air of a series of N,N-bis(dithiocarboxy)-o-phenylenediamine metal complexes, including the tin(II) complex. A sketchy thermal decomposition mechanism is given, which indicates thermal stability of the tin(II) complex to 343 K and thereafter, stepwise decomposition to yield SnO_2 as the final residue. Neither the volatile decomposition products nor any stable intermediates are stated.

Kaushik *et al.* [8] have studied the thermal decomposition behaviour of bis(N-X-dithiocarbamato)tin(II), (X= 2-, 3- or 4-chlorophenyl), in a static air atmosphere, using TG and DTA. A complex decomposition process is evident for each of these complexes, which all appear to be stable to 400 K and subsequently decompose stepwise, via SnS_2 to SnO_2. The corresponding thermal decomposition mechanisms, which are not given in detail, appear to be independent of the position of the chloro substituent on the phenyl group of the dithiocarbamato moiety.

Kaushik *et al.* [9] have studied the thermal decomposition behaviour of bis[N-(4-ethoxyphenyl)dithiocarbamato]tin(II) and bis[N-(4-ethoxyphenyl)-dithiocarbamato]-dichlorotin(IV) complexes, in a static air atmosphere by TG and DTA. The tin(II) complex is stable to 408 K and subsequently decomposes in two major steps to SnS_2 and thence to SnO_2. An initial thiocyanate intermediate is postulated on the basis of the corresponding DTA data. Similarly, the tin(IV) complex is stable to 433 K and subsequently decomposes in three major steps, forming $Sn(CNS)_2Cl_2$ and SnS_2 as intermediates and SnO_2 as the final residue. Activation energies for each of the thermal decomposition steps have been evaluated from the corresponding TG data, but since the relevant decomposition mechanisms have been incompletely defined, the derived kinetic data have little significance.

D'Ascenzo *et al.* [10] have studied the thermal stability of bis(N,N-diethyldithiocarbamato)dichlorotin(IV) in dynamic air and nitrogen atmospheres, using TG, DTA and also HTRS and DRS. All the data fundamentally confirm that this complex is nonvolatile. The TG data indicate a two-step thermal decomposition, involving $Sn(CNS)_2Cl_2$ as a stable intermediate and SnS_2 or SnO_2 as the final residue, depending on the atmosphere employed. The spectroscopic data additionally reveal that the complex is stable to 373 K.

Sen Gupta and Kauschik [11] have studied the thermal decomposition behaviour of a series of (N-alkylcyclohexyldithiocarbamato)tin(IV) complexes: $Sn(R, R'dtc)_nCl_{4-n}$: R = methyl, R' = cyclohexyl, n = 2 or 3: R = ethyl, R' = cycloethyl, n = 1 or 2 and R = *i*-propyl, R' = cyclohexyl, n = 1 or 2 and also $Sn(RR'dtc)_4$: R = ethyl, R' = cyclohexyl, in air and in nitrogen atmospheres, using TG and DTA and simultaneous TG-DTA. All these complexes exhibit thermal stability to 350 K and thereafter decompose sequentially to either SnS_2 or SnO_2, depending on the atmosphere involved. A definite intermediate in the decomposition of the chloro complexes is $Sn(CNS)_2Cl_2$ and in the decomposition of $Sn(RR'dtc)_4$, (R = ethyl, R' = cyclohexyl), the intermediate is $Sn(CNS)_4$. Activation energies for the overall decomposition of these complexes are derived from the corresponding TG data, but since the decomposition processes are not completely defined, such data are of little significance.

The most comprehensive thermal analysis study of tin dithiocarbamate complexes is due to Bratspies *et al.* [12–20]. These classical studies are notable for the novel use of mass spectrometry as a thermal analysis technique. The technique, formally known as programmed probe analysis (PPA) is now more appropriately titled thermal degradation mass spectrometry (TDMS) and has been described in detail in the literature [21]. The test sample is heated at a programmed rate to 700 K maximum in the probe of a mass spectrometer. The total ion current, resulting from the generation of fragment ions via thermal decomposition of the sample, is monitored as a function of probe temperature, thereby generating the TDMS profile and quantifying the volatile thermal decomposition products. Mass spectra are obtained at selected intervals throughout the heating programme to characterise the volatile thermal decomposition products. The technique has had widespread application. Another 'pseudo' thermal analysis technique used in these studies was pyrolysis/gas chromatography-mass spectrometry (P/GC-MS). The test sample is heated at a programmed rate to 500 K maximum in a stainless-steel micro tube, surrounded by a cylindrical micro-furnace and attached to the inlet port of a GC-MS system. Helium gas at a constant flow rate, passes through the sample chamber and sweeps the volatile decomposition products directly into the interfaced GC-MS system for 'on-line' analysis. This P/GC-MS system has been described in detail in the literature [22].

These techniques have been applied to study the thermal decomposition behaviour in an inert atmosphere of bis(N,N-diethyldithiocarbamato)tin(II) [12]. The results obtained by Bratspies *et al.* [12] differ markedly from those of Perry and Geanangel [4] and it is concluded that the latter results refer to a $Sn(Et_2dtc)_2/Sn(Et_2dtc)_4$ mixture. Bratspies *et al.* [12] propose two different thermal decomposition mechanisms for $Sn(Et_2dtc)_2$, depending on the temperature involved. At low temperatures, below 600 K, the major volatile products of decomposition in an inert atmosphere are N, N, N', N'-tetraethylthiourea and carbon disulphide and the final residue is tin(II) sulphide. At higher temperatures, the major volatile decomposition products are S-ethyl-N, N'-diethyldithiocarbamate and ethyl-isothiocyanate and tin(II) sulphide is the final residue. $Sn(Et_{2z}dct)_2$ is stated to be volatile in vacuum, but decomposes in air and nitrogen.

Bratspies *et al.* [13] have applied TDMS to study the oxidation of bis(N, N'-diethyldithiocarbamato)tin(II). A complicated sequence of reactions applies, involving the intermediate formation of di-μ-sulphidobis[bis(N, N-diethyldithio-carbamato)tin(IV)]. Other stable intermediates are tetraethylthiuram disulphide and tetraethylthiuram monosulphide. The purity of the $Sn(Et_2dtc)_2$ sample is critical in such studies and this was assessed by mass spectrometry prior to the TDMS study of the oxidation process.

Bratspies *et al.* [14, 15] have applied TDMS to study the thermal decomposition of tetrakis(N, N'-diethyldithiocarbamato)tin(IV) in vacuum and in an inert atmosphere [16]. The complex decomposes initially to bis(N, N'-diethyldithiocarbamato)tin(II) and tetraethylthiuram disulphide – which subsequently decomposes to tetraethylthiuram monosulphide and elemental sulphur. The elemental sulphur and bis(N, N'-diethyl-dithiocarbamato)tin(II) subsequently interact to form di-μ-sulphidobis[bis(N, N'-diethyl-dithiocarbamato)tin(II)]. A wide variety of minor decomposition products is also noted. Bratspies *et al.* [17] have shown that the thermal decomposition mechanism previously evaluated for $Sn(Et_2dtc)_4$, applies to $Sn(R_2dtc)_4$ complexes generally, from their TDMS study of series of the latter complexes (R = methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, benzyl and $-NR_2$ = pyrolidine or piperidine). The thermal decomposition mechanism of the intermediate $S_2Sn_2(R_2dtc)_4$ is also discussed.

Bratspies *et al.* [18] have applied P/GC-MS to study the thermal decomposition of a series of bis(N, N-diethyl-dithiocarbamato)dihalotin(IV) complexes in an inert atmosphere. The major volatile decomposition products are tetraethylthiourea and carbon disulphide with dihalotin(IV) sulphide as a stable intermediate, which subsequently decomposes to tin(II) sulphide with the liberation of free halogen. It is significant that the nature of the halogen ligand bound to the metal centre has no effect on this thermal decomposition mechanism.

Bratspies *et al.* [19] have applied P/GC-MS to study the thermal decomposition of bis(N,N-diethyldithiocarbamato)diphenyltin(IV) in an inert atmosphere. The major volatile decomposition products are S-phenyl-N, N-diethyldithiocarbamate and C-phenyl-N, N-diethyldithiocarbamate with tin(II) sulphide as the final residue. It appears that the stability of the phenyl radical as a reactive intermediate and the unidentate binding mode of the dithiocarbamato ligands in this complex are the major contributing factors to the observed thermal decomposition mechanism.

Bratspies *et al.* [20] have applied P/GC-MS to study the thermal decomposition of several tin(IV) dithiocarbamate complexes in an air atmosphere. The major thermal decomposition mechanism involves two stages, with the formation of N, N, N', N'-tetraethylthiourea and carbon disulphide as volatile decomposition products and X_2SnS (X = halogen) as a stable intermediate, which subsequently decomposes to tin(II) sulphide and free halogen. It appears that the presence of oxygen does not directly influence this primary decomposition process, but dramatically affects several secondary decomposition processes.

Conclusion

Although extensive thermal analysis data are available, relating to the thermal decomposition of tin dithiocarbamate complexes, it is most apparent that the relevant thermal decomposition mechanisms are most complicated and cannot be determined using conventional thermal analysis techniques alone. The extensive work of Bratspies *et al.* [12–20] has clearly shown that in most cases, primary and secondary decomposition mechanisms apply and that these can only be determined when the major decomposition products are unambiguously identified by 'coupled' evolved gas analysis techniques. Overall, at this stage, it is not possible to identify general well-defined trends in the thermal decomposition behaviour of tin dithiocarbamate complexes. However, the mechanisms of thermal decomposition of three series of these complexes appear to have been confirmed: bis(N, N-diethyldithiocarbamato)tin(II) decomposes to N, N, N', N'-tetraethylthiourea and carbon disulphide with a residue of tin(II) sulphide: bis(N, N-diethyldithiocarbamato)dihalotin(IV) complexes decompose to tetraethylthiourea and carbon disulphide with dihalotin(II) sulphide as a stable intermediate and tin(II) sulphide as the final residue and tetrakis(N, N-dialkyldithiocarbamato)tin(IV) complexes to bis(N, N-diethyl-dithiocarbamato)-tin(II) complexes and tetraalkylthiuram disulphide. The latter subsequently decomposes to tetraalkylthiuram monosulphide and elemental sulphur which, in turn, forms the novel complexes di-μ-sulphidobis[bis(N, N-dialkyl-dithiocarbamato)tin(II) with the intermediate bis(N, N-dialkyldithiocarbamato)tin(II) complexes. It appears that for these groups of complexes, the nature of the terminal alkyl group substituents of the dithiocarbamato moiety and the nature of an attached halogen ligand to the tin metal centre, have little, if any influence on the thermal decomposition mechanisms. Hence such mechanisms appear to be governed by the intrinsic features of the dithiocarbamato ligands and their corresponding binding mode to the tin metal centre. The thermal stability of the corresponding primary decomposition products is an important secondary influencing factor. It is significant that structural features of these complexes appear to exert only a minor influence on the corresponding mechanisms of thermal decomposition.

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Zusammenfassung — Es wird ein kurzer Überblick über die thermoanalytischen Angaben gegeben, die über die Dithiocarbamatkomplexe von Zinn(II) und Zinn(IV) zur Verfügung stehen. Da die relevanten Mechanismen der thermischen Zersetzung kompliziert sind, sind – für die Zersetzungen in inerter Atmosphäre – gerade diejenigen Mechanismen verdächtig, die allein auf der Grundlage von thermoanalytischen Daten postuliert werden. Realistische Mechanismen für die thermische Zersetzung dieser Komplexe können nur dann formuliert werden, wenn die relevanten Zersetzungsprodukte eindeutig identifiziert wurden. In vorliegendem Überblick wird ein Versuch unternommen, in speziellem Bezug auf die Struktureigenschaften der entsprechenden Komplexe Trends bei diesen thermoanalytischen Anlaysendaten zu finden.