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Review

THERMAL BEHAVIOUR OF METAL-DITHIOCARBAMATES

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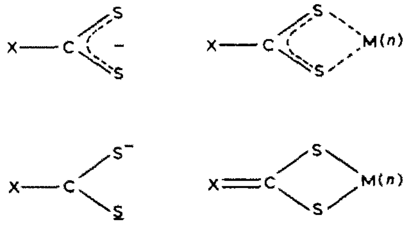
ABSTRACT

Work on the thermal behaviour of metal-dithiocarbamate complexes up to and including 1985 is reviewed.

INTRODUCTION

Carbon disulphide reacts with a variety of nucleophiles such as X^- or X^{2-}, to give rise to compounds known as dithioacids. The deprotonated forms of these compounds interact slowly with metal ions to form complexes, in which with a few exceptions, both the sulphur atoms are bound to a metal atom as shown below



where M is the metal atom and *n* denotes its valency.

There is growing interest in the chemistry of sulphur donor ligands because of their encouraging anticancer, antiviral and antifungal activities as well as their widespread industrial applications. Dithiocarbamates (**I**), xanthates (**II**), dithiolates (**III**), dithiophosphates (**IV**), and dithiocarbamates (**V**) belong to this class of ligand. Of these, dithiocarbamates are the most versatile; much attention has been paid to them by the chemists and a large amount of work has been reported. The present discussion is therefore

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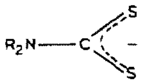
mainly centred on metal-dithiocarbamate complexes.



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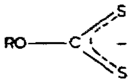

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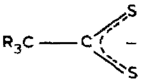

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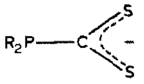

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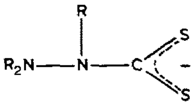
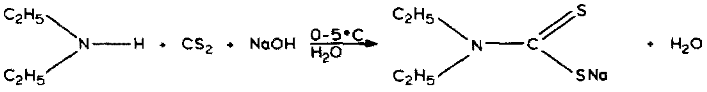


(V)

The dithiocarbamates were discovered as a class of chemical compound during the early study of organosulphur chemistry [1,2]. Carbamates are half-amides of carbonic acid, and their sulphur analogues, the dithiocarbamates are the half-amides of dithiocarbamic acid. The synthesis of the simple diethyldithiocarbamates can be represented as follows



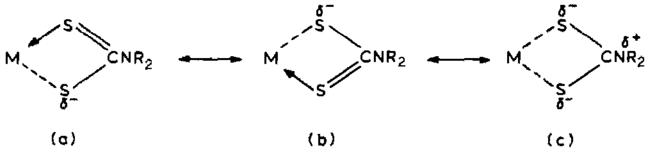
The parent compound dithiocarbamic acid can be obtained as colourless needles from its sodium or ammonium salt by treating with cold water or strong mineral acid. The acids are quite unstable, decomposing to thiocyanic acid and hydrogen sulphide, but can be kept below 5°C for a short time. The synthesis of a number of dialkyl-dithiocarbamates has been described by Klopping and Vander Kerk [3].

Because of the strong metal binding properties of dithiocarbamates much work has been carried out in the past three decades on metal-dithiocarbamate complexes. All this work has been summarised in some excellent reviews and monographs [4–16].

Studies on metal complexes of sulphur donor ligands are interesting because of the peculiarities observed in the donor properties of sulphur compared with its cogener oxygen. In spite of several similarities oxygen and sulphur differ greatly in donor properties, attributed to the lower electronegativity of the sulphur atom compared with oxygen. The comparatively lower electronegativity of sulphur decreases the ionic character and thus alters the relative stabilities of various types of bond and reduces the significance of hydrogen bonding in its compounds.

The spectral features of the metal complexes containing sulphur donor ligands are attributed to the ability of sulphur atom to form multiple (π-bonds) bonds, caused by the presence of vacant $d\pi$ orbitals in sulphur. From a survey of β-(naphelauxetic ratio) values for different sulphur ligands [17] it can be seen that these ligands occupy late positions in the nephelauxetic series of different donor atoms, F < O < N < Cl < Br < S = I < Se suggestive of a strong covalent nature for the metal–sulphur bond. Also sulphur donor ligands have lower positions in the spectrochemical series of ligands [18].

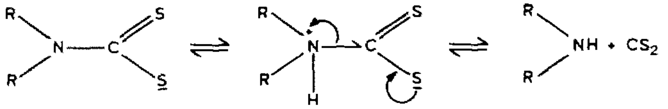
Several canonical forms may be written for the structure of the dithiocarbamate group in $M(R_2NCS_2)_n$, where M is the metal atom and n is its valency.



The canonical form (c) arises from the mesomeric electron-releasing tendency of the R_2N group. This electron drift into the sulphur atoms will increase their electron donor capacity and decrease the electron affinity of the *d*-orbitals. Thus the dithiocarbamate ion permits the formation of strong complexes with the heavy metals with a reduced tendency to *d*-active, π-bond formation from metal to sulphur atom [5].

Among the polyatomic ligands, the dithiocarbamate ligand can stabilize high oxidation states of transition metals in its complexes. As with 1, 1-dithioates, the σ-donation and π-back donation of the sulphur atoms is assumed to be of the same order. The strong metal binding properties of the dithiocarbamates is also seen in the insolubility of metal dithiocarbamate complexes in water (with the exception of those of alkalic and alkaline earth metals) [5].

The stability of metal dithiocarbamate complexes is pH dependent. At low pH, the decomposition proceeds through the dipolar ion according to the following scheme [4].



Even in the solid state slow decomposition takes place, the rate of which increases with temperature [19]. In non-aqueous solutions the dithiocarbamic acids are generally soluble and much more stable [20,21], a property which has led to numerous applications in the extraction of metal chelates from acid solution.

The structure of various metal-dithiocarbamate complexes is well established. The dithiocarbamate group can act as a monodentate or bidentate ligand. IR spectroscopy can distinguish structurally between a monodentate and bidentate dithiocarbamate Whether the dithiocarbamate group is monodentate or bidentate is reflected in their $\nu(C{=}S)$ stretching frequency in the

980–1050 cm^{-1} region [22–27]; the presence of only one strong bend in this region supports the bidentate nature of the dithiocarbamates, whereas the appearance of a doublet in this region indicates one complexed (C–S) group and one uncomplexed (C=S) group, i.e. monodentate bonding. The $\nu(C\overset{\dots}{-}S)$ stretching frequency in the case of $Ru(NO)(S_2CNEt_2)_3$ [28] and $Sn(S_2CNEt_2)_4$ [29] complexes, which possess both monodentate and bidentate $Et_2NCS_2^-$ groups is split into a doublet separated by $\geqslant 20$ cm^{-1}. However, in the case of the eight-coordinated $Ti(S_2CNMe_2)_4$ complex [24] in which all the $Me_2NCS_2^-$ groups are bidentate, a single band appears at ~ 1000 cm^{-1}.

Another important band in dithiocarbamate complexes is the thioureide band ($C\overset{\dots}{-}N$). The frequency for this band lies between those of the C–N bond (1250–1350 cm^{-1}) and the C=N bond (1640–1690 cm^{-1}) stretching vibrations and can be best explained as vibration of a polar $C=N^+$ bond [30,31]. The occurrence of this band at ~ 1500 cm^{-1} implies considerable double bond character in the $S_2C\overset{\dots}{-}NRR$ bond. In general, the $C\overset{\dots}{-}N$ frequency shows a blue shift in these complexes compared with the respective dithiocarbamate ligands. This trend has been reported in complexes where the dithiocarbamate group behaves as a bidentate ligand only [32–36], whereas for a monodentate dithiocarbamate moiety this frequency should either exhibit no change in position or undergo a red shift with respect to the corresponding free ligand frequency [31].

THERMAL STUDIES

The earliest work on the thermoanalytical properties of metaldithiocarbamates was reported in 1908 by Delepine [37,38] who found that nickel(II) and copper(II) di-isopropyldithiocarbamates sublime in vacuum almost without decomposition. The volatility of nickel(II) and cobalt(III) dithiocarbamates in vacuo was later reported by Malatesta [39].

Thermal behaviour of diphenyl- and dibenzyldithiocarbamate complexes of phenyltin, lead, antimony and bismuth was studied by Kupchik et al. [40,41]. Upon thermal degradation in air, diphenyldithiocarbamates gave diphenylamine and the corresponding bis-(organometal) oxide (hydroxide in case of Ph_3Pb) or diphenylmetal oxide. The dibenzyldithiocarbamates upon thermal decomposition yield the corresponding bis-(triphenylmetal) sulphide trimer or diphenylmetal sulphide or phenylmetal sulphide. The conditions and results of thermal decomposition of these complexes are presented in Table 1.

Bernard and Borel [42] studied the thermal behaviour of metaldithiocarbamates of lead(II), zinc(II) and cadmium(II) using TG and DTA and reported that these complexes decomposed with the evolution of hydrogen sulphide or carbon disulphide. The decomposition can be completed either

TABLE 1

Thermal decomposition of some phenyltin, lead, antimony and bismuth dithiocarbamates

Sl. No.	Dithiocarbamate	Condition	Sulphide/oxide	Yield %
1	$Ph_2SnSCSNPh_2$	Neat, 523K, 3 h	$Ph_3SnOSnPh_3$	84
2	$ClPh_2SnSCSPh_2$	Neat, 523K, 3 h	$ClPh_2SnOSnPh_2Cl$	63
3	$Ph_3PbSCSNPh_2$	Neat, 473K, 3 h	Ph_3PbOH	82
4	$Ph_2SbSCSNPh_2$	Neat, 523K, 3 h	$Ph_2SbOSbPh_2$	72
5	$Ph_2Sn(SCSNPh_2)_2$	Neat, 523K, 3 h	Ph_2SnO	96
6	$Ph_2Pb(SCSNPh_2)_2$	Neat, 473K, 3 h	Ph_2PbO	70
7	$ClPh_2SnSCSNHbz$	C_6H_6, Reflux 1 h	$(Ph_2SnS)_3$	93
8	$Ph_3PbSCSNHbz$	C_6H_6, Reflux 1 h	$(Ph_3Pb)_2S$	64
9	$Ph_2Sn(SCSNHbz)_2$	C_6H_6, Reflux 1 h	$(Ph_2SnS)_3$	93
10	$Ph_2Pb(SCSNHbz)_2$	Et_2O, Reflux 10.5 h	$(Ph_2PbS)_3$	60
11	$PhSb(SCSNHbz)_2$	CH_3CN, Reflux 4 h	PhSbS	
12	$Ph_3SnSCSNHbz$	Neat, 403, 4 h	$(Ph_3Sn)_2S$	
13	$Ph_2Sn(SCSNHbz)_2$	C_6H_6, Reflux 4 h	$(Ph_2SnS)_3$	99
14	$Ph_2Sn(SCSNHbz)_2$	C_6H_6, Reflux, 4 h	$(Ph_2SnS)_3$	86
15	$PhSb(SCSNHPh)_2$	CH_3CN, reflux 4 h	PhSbS	72

via the formation of metal thiocyanate as an intermediate which further decomposes and gives metal sulphide or the complex can yield the metal sulphide directly in a single step decomposition.

D'Ascenzo and Wendlendt [43] studied the thermal behaviour of metal complexes of diethyldithiocarbamates with the aid of TG, DTA and HTRS (High Temperature Reflectance Spectroscopy). These authors without reference to earlier work, reported that cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) diethyldithiocarbamates were completely volatile and represented a 'new' class of volatile dithiocarbamates. Later the same authors [44] reported the iron(III) diethyldithiocarbamate, $Fe(Et_2NCS_2)_3$, as a new volatile metal chelate. The cobalt(II) complex, $Na[Co(S_2CNEt_2)_3] \cdot H_2O$ was reported to be volatile [42]. Other workers [39,45–47] showed that the reaction in air of the salts with diethyldithiocarbamate ions liberates the cobalt(III) chelate, $Co(S_2CNEt_2)_3$.

During their studies of the thermal behaviour of the diethyldithiocarbamates of cobalt(III), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), chromium(III) and lead(II) by TG and DTA, Larionov [47,48] observed that the thermal stability of chelates increases in the order, $EtOCS_2^- < (EtO)_2PS_2^- < Et_2NCS_2^-$. Further the volatility behaviour of the complexes was quite evident in an inert argon atmosphere. Nickel complexes were found to be partially volatile, whereas cobalt and chromium complexes were completely volatile. Zinc, lead, cadmium and nickel complexes yield the corresponding metal sulphide at about 623 K. The decomposition of $NiL_2 \cdot n\text{py}$ and $ZnL_2 \cdot n\text{py}$ ($L = Et_2NCS_2$, $EtOCS_2$ or $(EtO)_2PS_2$, py = pyridine) occurred at a lower temperature than for corresponding NiL_2 and ZnL_2 complexes. Further, the temperature for the pyridine molecule in these complexes, increased in the series $(Et_2O)_2PCS_2 > EtOCS_2^- > Et_2NCS_2^-$.

D'Ascenzo et al. [49] also investigated the thermal behaviour of dichlorotin(IV)bisdiethyldithiocarbamate, $Sn(Et_2NCS_2)Cl_2$. They observed the non-volatile nature of this complex and proposed a two-step decomposition mechanism. Layalikov and Kitovskaya [50] used TG and DTA to characterize some active dithiocarbamate fungicides, i.e., Ziram(bis(dimethyldithiocarbamato)zinc(II), Terban(tris(dimethyldithiocarbamato)iron(III), and Zineb(ethylenebis(dithiocarbamato)zinc(II)). Flaherty and McCutcheon [51] studied the thermal properties of cobalt(III), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), chromium(III) and lead(II) diethyldithiocarbamate complexes and concluded that all are partially volatile and undergo further decomposition, which makes analysis of these complexes by gas chromatography quite difficult.

Onuska et al. [52–54] analysed a series of *S*-alkyl-*N*,*N*-dialkyldithiocarbamato and *S*-alkyl-*N*-monoalkyldithiocarbamato complexes by GC–MS (gas chromatography–mass spectrometry) methods. Sceney and Magee [55] studied the thermal volatility behaviour of tris(dialkyldithiocarbamato)-iridium(III) and observed that the volatility is maximum for di-isopropyl and di-isobutyl dithiocarbamato complexes. Sufficiently complete volatilization of dialkyldithiocarbamato complexes of copper(II) is also achieved at reduced pressure [56,57].

Venkappaya and Brown [58] reported that the *N*-α-methylbenzyldithiocarbamates of chromium(III), cobalt(III), nickel(II), zinc(II) and cadmium(II) undergo thermal decomposition with the loss of hydrogen sulphide, resulting in the formation of the respective isothiocyanates and metal sulphides. Annuar et al. [59] investigated the thermal decomposition of monoethanol and diethanol dithiocarbamate complexes of nickel(II) and copper(II) by TG, DTA and mass spectrometry and reported the formation of metal oxide as the end product. They also proposed the mechanism for the nickel(II) monoethanoldithiocarbamate complex. Further, the enthalpy change for the reaction

$$FeCl_3 + 3NaS_2CNEt_2 \rightarrow Fe[S_2CNEt_2]_3 + NaCl$$

was also studied by Annuar et al. [60] and was found to be -82.7 ± 2.0 kJ mol^{-1}.

Data on the vapour pressures of dialkyldithiocarbamates are available only for the diethyl derivatives. The vapour pressures of the chelate compounds of iron(III), cobalt(III), nickel(II), copper(II) and zinc(II) were determined [42,43] using an isoteniscope in the pressure range 1–260 torr at temperatures of 298–493 K. The vapour pressures of the diethyldithiocarbamates of nickel(II), copper(II) and zinc(II) were determined at 393–473 K by a flow method in a stream of nitrogen [61]. The calculated heats of

TABLE 2

Heats of sublimation of metal diethyldithiocarbamates

Complex	ΔH(kcal mol^{-1})	Sublimation temperature (K)	Ref.
$Fe(S_2CNEt_2)_3$	15.7 ± 0.4	519	43
Na $Co(S_2CNEt_2)_3$ [a]	9.3 ± 0.2	530	42
$Ni(S_2CNEt_2)_2$	14.6 ± 0.4	559	42
	36.3 ± 0.5		60
$Cu(S_2CNEt_2)_2$	20.8 ± 0.4	502	42
	35.6 ± 0.6		60
$Zn(S_2CNEt_2)_2$	24.2 ± 0.6	490	42
	34.1 ± 0.6		60

[a] Apparently the complex $Co(S_2CNEt_2)_3$.

sublimation (Table 2) show significant differences in the results for given chelate compounds, and also the changes in volatility in the series of metals, found by different authors [43,61]. The volatilization of metal dithiocarbamates may be due to the sublimation of the solid or evaporation of the molten chelate compound, depending on the temperature. For some compounds, for example $Co(S_2CNEt_2)_3$ [47], $Cu(S_2CNMe_2)_2$ and $Cu(S_2CNi\text{-}pr_2)_2$ [57], fusion is not observed.

X-ray diffraction studies of metal dithiocarbamates [7], including most volatile diethyldithiocarbamates, show that the square $Ni(S_2CNEt_2)_2$ [7] and the distorted octahedral chelate compounds of cobalt(III) [7,62], chromium(III) [63], iridium(III) [64] and iron(III) [65] are monomeric in the solid state. These compounds have a molecular crystal structure, in which the molecules are joined by van der Waals forces, acting only between the organic groups. At the same time, the crystals of the zinc(II) and copper(II) chelate compounds, which are the most volatile diethyldithiocarbamates, and also the cadmium(II) chelate compound, consist of dimers [7] and this does not influence their volatility. The compound $Hg(S_2CNEt)_2$ exists in monomeric and dimeric forms [66]; the lead(II) complex has been assigned both a dimeric [67] and a monomeric [68] structure; the silver(I) chelate compound is a cluster compound having the composition $Ag_6(dtc)_6$ [61]. Replacement of the ethyl group by another group does not lead to marked changes in the structure of the chelate sites [7].

The most volatile chelate compounds $Ir(S_2CNR_2)_3$ [67] contain branched groups (isobutyl and isopropyl). Among copper(II) dialkyldithiocarbamates, in addition to the chelate compounds containing groups having the isostructure, the compound $Cu(S_2CNEt_2)_2$ is appreciably volatile [56,57]. The replacement of the alkyl by the benzyl group in copper(II) chelate compounds leads to a sharp decrease in the volatility [55].

A common technique in the search for volatile compounds involves the introduction of fluorine atoms into the molecule. This decreases the energy of intermolecular interaction in the chelate compounds, and often increases the volatility. This effect is not universal, however, and there are examples where the complexes of fluorine-containing compounds are less volatile than the complexes without fluorine atoms [69,70]. Sodium bis(trifluoroethyl)dithiocarbamate, $(CF_3CH_2)_2NCS_2Na$, was synthesised [74], according to the reaction

$$(CF_3CH_2)_2NH + CS_2 + NaNH_2 \rightarrow (CF_3CH_2)_2NCS_2Na + NH_3$$

This ligand forms chelate compounds, which sublime and have been characterised by mass spectroscopy, with zinc(II) (378), antimony(II) (408), nickel(II) (388), copper(II) (403), lead(II) (423), cadmium(II) (453) and bismuth(III) (463) (temperature of sublimation (K) is given in parentheses; the vacuum was established using a water pump). The introduction of fluorine atoms made the new chelate compounds more volatile than the diethyldithiocarbamates.

The volatility of metal dialkyldithiocarbamates has been used to develop gas chromatographic methods for separating metals [55,71–73]. In particular, a mixture of the diethyldithiocarbamate chelate compounds of palladium(II), nickel(II), copper(II), cadmium(II) and zinc(II) has been separated [71]. The bis(trifluoroethyl)dithiocarbamate complexes have also been used for the gas chromatographic determination of groups of cations (Bi, Sb, Pb, Cd, Ni and Zn) [71]. The volatility of the dialkyl-dithiocarbamates of chromium, cobalt, copper, manganese, nickel and zinc has been used to develop a method for the atomic absorption determination of these metals [74]. Daughtrey et al. [75] reported the use of diethyldithiocarbamates for the gas chromatographic determination of arsenic.

Cardwell and Desarro [76] studied the thermal behaviour of diethyldithiocarbamates of nickel(II), copper(II), palladium(II), zinc(II), cadmium(II), mercury(II), lead(II), platinum(II), silver(I), iron(III) and cobalt(III). Thermograms of the complexes showed that the nickel, zinc, iron and cobalt diethyldithiocarbamates are completely volatile while the remainder are less volatile and decompose slightly. In all cases the complexes investigated proved to be highly stable thermally, with the initial inflection on the TG curves appearing in the range 513 K (copper and silver) to about 573 K (nickel, cobalt, palladium and platinum). Gas chromatographic separation of various volatile metal dithiocarbamates was also achieved by these workers.

Sceney et al [77] described the thermal behaviour of copper(II) dialkyldithiocarbamates, $Cu(R_2NCS_2)_2$, where $R = Me$, Et, *n*-Pr, *n*-Bu, EtPh, pyrrole and piperidine, and reported that the copper(II) diethyldithiocarbamate complex is completely volatile in vacuo but in air and nitrogen only partial volatility is observed. Further, in an atmosphere of nitrogen all these complexes are found to decompose with the formation of copper sulphide. In an air atmosphere $Cu(Et_2NCS_2)_2$ is found to yield Cu_2S as the end product of first step decomposition, and is further oxidised to $CuSO_4$ and CuO, before finally decomposing to CuO at 1073 K. Larionov and Kosareva [78] studied the thermal decomposition of some bis(diethyldithiocarbamate) complexes of nickel(II), zinc(II), cadmium(II) and lead(II) and isolated the corresponding metal sulphide residue as the end product of decomposition. The residues were characterized by chemical analysis and X-ray powder diffraction.

Thermal decomposition of some divalent metal complexes with ethylenebisdithiocarbamate ligands has been studied [79] using TG/DTG and DTA methods. The loss of a CS_2 molecule was observed during the first step of decomposition. A two-step thermal decomposition mechanism was proposed for the bis(dialkyldithiocarbamato)tin(II) complex by Perry and Greanangel [80] on the basis of TG and DTA data. The first decomposition was represented by the loss of one dithiocarbamate ligand followed by the other during the second step decomposition, resulting in the formation of tin metal. This was supported by the mass spectral studies.

$$Sn(S_2CNR_2)_2 \rightarrow Sn(S_2CNR_2) \rightarrow Sn$$

The thermal properties of silver(I) and gold(III) complexes were studied by D'Ascenzo and Bica [81] in an atmosphere of air or nitrogen using TG, DTA and DRS (dynamic reflectance spectroscopy). In a nitrogen atmosphere, the silver compound was found to decompose to Ag_2S, whereas in air, it first decomposed to give a mixture of Ag_2S, Ag_2SO_4 and Ag. Ag_2S was further oxidised to Ag_2SO_4 and finally silver metal was obtained at 1198 K. The gold complexes showed similar behaviour in both air and nitrogen atmospheres and resulted in the formation of metal as a residue.

A comparative study of the thermal behaviour of $Cu(S_2CNR_2)_2$ complexes with different R-groups (R = Me, Et, *i*-Pr, *n*-Bu) was reported by Larionov et al. [82]. Reduction of copper(II), during pyrolysis of the chelates, is studied by EPR (electron paramagnetic resonance). The main product obtained by pyrolysis of the chelates in an inert argon atmosphere was $Cu_{1.96}S$.

The mode of thermal decomposition of tin(IV) complexes of the type $X_2Sn(Et_2NCS_2)_2$ where X = Cl, Br or I, $Ph_2Sn(Et_2NCS_2)_2$ and $Sn(Et_2NCS_2)_4$ in both inert nitrogen and active air atmospheres employing TG, DTA, EGA (evolved gas analysis) and P/GC–MS (pyrolysis gas chromatography–mass spectroscopy) has been reported [83,84]. The authors proposed various decomposition mechanisms for these complexes taking into account bidentate or monodentate behaviour of the dithiocarbamate ligands, but the final product obtained in all the cases was SnS.

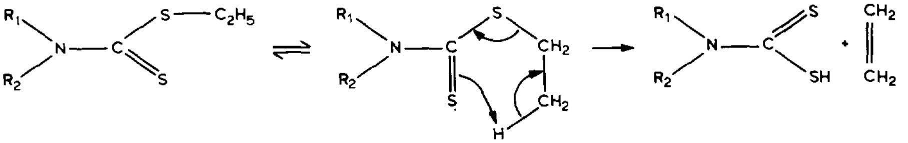
Srivastava et al. [85] carried out thermal investigation on $Ph_2Sn(X)dtc$ where X = Cl, I, N_3, NCS or N_2 and dtc = (Et_2NCS_2) and observed similar results to those reported by Perry and Greanangel [80] for $Sn(S_2CNR_2)_2$ complexes. However, the results of recent investigations by Srivastava and

Bhargava [86] of the thermoanalytical behaviour of tetrakismorpholine-*N*-carbodithioate tin(IV) are slightly different. The complex lost three ligands consecutively and during the fourth step decomposition, gave SnS_2 which after further decomposition finally gave tin metal at 573 K, whereas dichlorotin(IV) bis(morpholine-*N*-carbodithioate) decomposed to tin metal via the formation of $Sn(NCS_2)_2Cl_2$ as the intermediate decomposition product.

Thermal decomposition of chromium(III) dithiocarbamato complexes of the type $Cr(S_2CX)_3$ ($X = Me_2N$, Et_2N, pyrrolidine, hexamethylene, cyclohexyl, morpholine) have been reported by Janicki et al. [87]. A gradual loss of organic fragments followed by the formation of Cr_2S_3 residue has been observed. Neeb and his coworkers [88–90] have reported the thermal stability of a series of metal dithiocarbamate complexes of zinc(II), antimony(III), nickel(II), copper(II), lead(II), cadmium(II) and bismuth(III). The thermal behaviour of uranium(VI) diethyldithiocarbamate complexes of the type $UO_2(Et_2NCS_2)_2 \cdot H_2O$ and $NH_4 \cdot UO_2(Et_2NCS_2)_3$ was described by Dubrovin et al. [91]. The complexes showed a two step decomposition pattern; $UO_2(Et_2NCS_2)_2$ was formed at the end of the first step decomposition and further decomposed to give UO_2 at 773 K as the final decomposition product. Between 1978 and 1979 four papers appeared [92–95] dealing with the DTA and/or DSC of metal-dithiocarbamate complexes. These techniques have been utilised to determine the melting points and/or enthalpies of fusion and sublimation of dithiocarbamate complexes. Kosareva and Larionov [96] investigated the sublimation behaviour of a series of metal dithiocarbamates. It was observed that volatility of the complexes increases as the oxidation state of the metal in the complex decreases and also increases as branching of the alkyl group of the dithiocarbamate ligand increases.

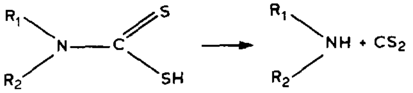
Pyrolytic decomposition of *S*-ethyl *N*-disubstituted dithiocarbamates has been investigated by Chande [97]. The main feature of the pyrolytic derangement was the elimination of ethylene and formation of carbon disulphide, *N*-disubstituted amine and/or trisubstituted thiocarbamide and ethylmercaptan. Ethyl groups on nitrogen and sulphur, were eliminated, depending on the conditions and the nature of substituents. The following mechanisms of pyrolysis were discussed.

(i) Formation of ethylene, in the pyrolysis of the *S*-ethyl *N*-dimethyl-dithiocarbamate (**Ia**) at 533 K, *S*-ethyl *N*-methyl-phenyl-dithiocarbamate (**Ib**) at 588 K and *S*-ethyl *N*-diphenyl dithiocarbamate (**Ic**) at 503–513 K is possible by a cyclic elimination reaction involving the *β*-hydrogen of the ethyl group and the thion sulphur.

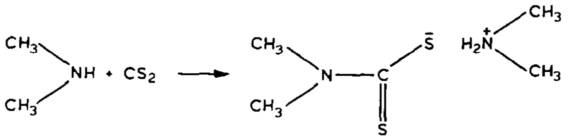


(**Ia**) $R_1 = R_2 = CH_3$; (**Ib**) $R_1 = C_6H_5$, $R_2 = CH_3$; (**Ic**) $R_1 = R_2 = C_2H_5$.

The other products may be formed by further decomposition of the related free dithiocarbamic acid.

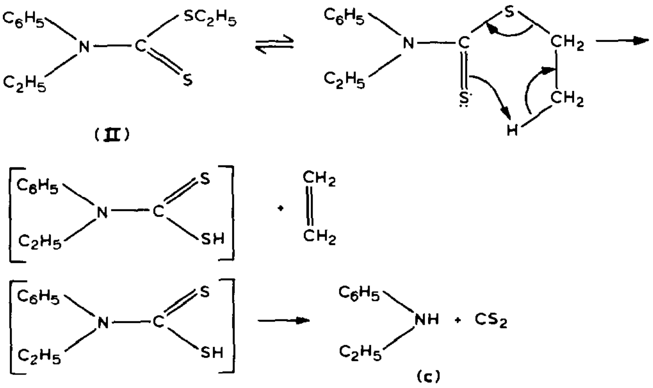


Dimethylammonium dimethyl dithiocarbamate obtained by the pyrolysis of **Ia**, may be formed by the interaction of dimethylamine (**a**) and carbon disulphide.



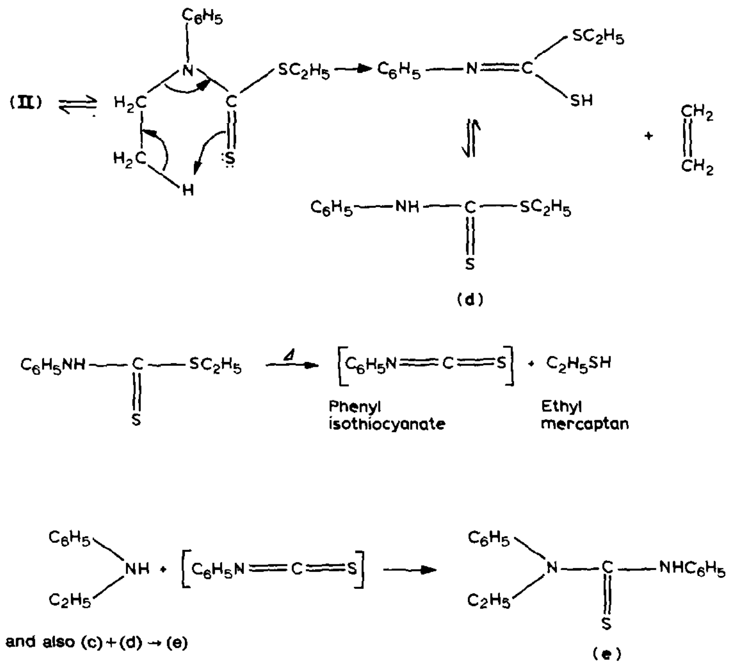
(a) (b) Dimethylammonium dimethyldithiocarbamate

(ii) Pyrolysis of *S*-ethyl *N*-disubstituted dithiocarbamates where at least one of the substituents is an ethyl group appeared to be more complex. For example, on pyrolysis of *S*-ethyl *N*-ethyl phenyldithiocarbamate (**II**) at 558 K, ethylaniline (**c**), 1,3-diphenyl-1-ethylthiocarbamate (**d**) and carbon disulphide are isolated together with unreacted starting materials. The gaseous products are mainly ethylene and smaller quantities of ethyl mercaptan. Formation of (**a**) and (**b**) is suggestive of two independent elimination processes operating simultaneously involving in one case the ethyl group on sulphur and in the other that on the nitrogen.

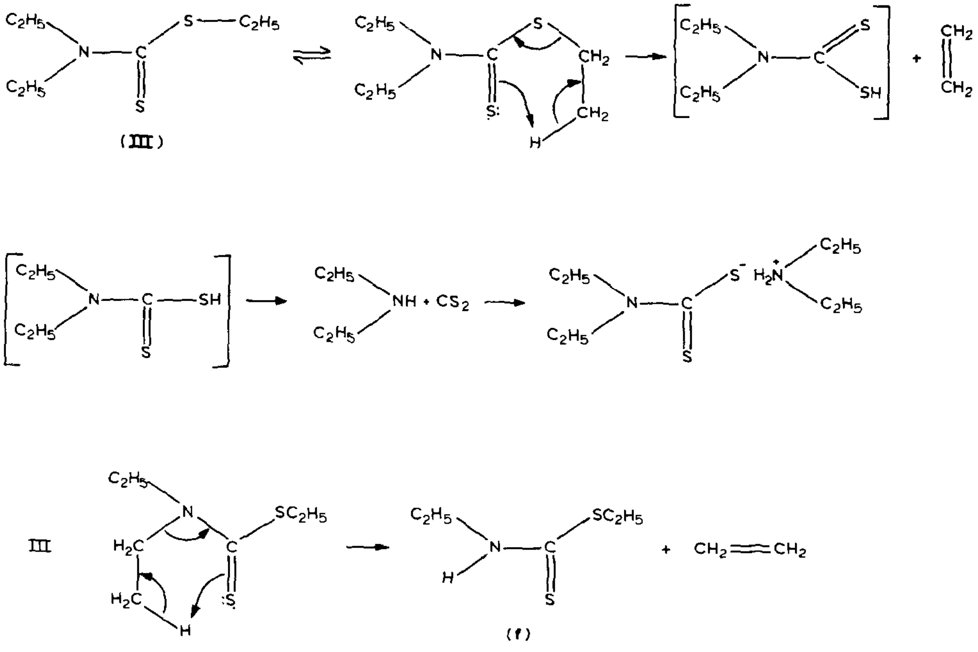


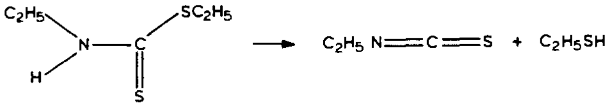
(II)

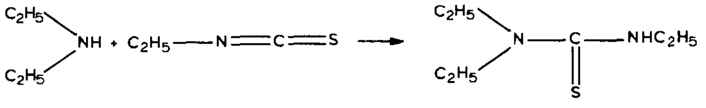
(c)



(iii) Pyrolysis of *S*-ethyl *N*-diethyldithiocarbamate (**III**) at 527 K, gave *S*-ethyl *N*-ethyldithiocarbamate (**f**), carbon disulphide, diethylamine (**g**), triethylthiocarbamide (**h**), ethylene and ethyl mercaptan. The formation of these products can be explained only by invoking a mechanism involving ethyl groups substituted on nitrogen as well as on sulphur.







(g) (h)

or (f) + (g) ——► (h) + C_2H_5SH

From these results it is evident that the ethyl groups substituted on nitrogen as well as those on sulphur, can be eliminated as ethylene. The former elimination is akin to that occurring in tetrasubstituted thiuram disulphides [98]. The latter, i.e. elimination of the S-ethyl group, is perhaps akin to that occurring in the Chugaev reaction [99].

Thermal behaviour of diphenylthallium(III) diethyldithiocarbamate has been studied by Srivastava et al. [100]. The course of the thermogravimetric analysis of this compound can be represented as

$$\begin{tikzcd}
Ph_2Tl(S_2CNEt_2) \arrow[r, "\Delta", "293\text{ K}"'] & CS_2 + (Ph_2Tl)_2S + (Et_2N)_2C{=}S \arrow[d, "\Delta\ 393\text{ K}", "-(Et_2N)_2C{=}S + CS_2"'] \\
Tl_2S_3 & (Ph_2Tl)_2S \arrow[l, "\Delta"', "733\text{ K}"]
\end{tikzcd}$$

This behaviour is similar to that reported by Kupchik et al. [40] for organoantimony compounds.

Bratspies et al. [101,102] have reported thermal investigation of tetrakis-(*N*,*N*-dialkyldithiocarbamate)tin(IV) complexes and have discussed the thermal decomposition mechanism, proposing the formation of tetraalkylthiurem disulphide, tetraalkylthiuram monosulphide, and bis[bis(*N*,*N*-dialkyldithiocarbamato)tin(IV)] complex as decomposition products.

Johri and Venugopalan [103,104] have carried out systematic thermal decomposition studies on copper(II), zinc(II), cadmium(II), cobalt(II), nickel(II), tin(II), oxovanadium(IV) and dioxouranium(VI) complexes with

TABLE 3

Thermal stability data of some bis(dithiocarboxy)-*O*-phenylenediamine metal complexes

Sl. No.	Complex	Decomposition range (K)	Final residue
1.	CuL	333–1073	CuO (black)
2.	ZnL	323–1143	ZnO (white)
3.	CdL	323–1128	CdO (yellowish brown)
4.	CoL	333–1103	Co_3O_4
5.	NiL	323–1033	NiO (black)
6.	SnL	343–1008	SnO_2 (white)
7.	VOL	323–943	V_2O_5
8.	$(UO_2)L$	338–1033	U_3O_8 (olive green)

ammonium N,N-bis(dithiocarboxy)-*O*-phenylenediamine under non-isothermal temperature conditions. The decomposition ranges and residues obtained after decomposition are given in Table 3.

Kaushik and his coworkers [105] have studied the thermal decomposition of N-(ethyl, m-tolyl) dithiocarbamate complexes of Mn(II), Co(III), Ni(II) Cu(II) and Mo(V) with the aid of TG and DTG in a dynamic N_2 atmosphere. All these complexes were thermally stable upto 473 K except that of Ni(II), the thermal stability of which extended to 493 K. Beyond this temperature, the organic portion of the ligand started to decompose resulting in the formation of the metal thiocyanate. However, for this decomposition step two overlapping decomposition reactions have been observed in the Mn(III) and Co(III) complexes. In the first substep one molecule of the ligand is removed from the coordination sphere of the complex reducing the metal from a +3 oxidation state to +2. The second and last decomposition results in the formation of sulphide in the case of cobalt(III) and copper(II) complexes. In nickel and molybdenum(V) complexes the crucible was completely empty at the end of the second step decomposition due to the volatilization of their thiocyanates while in the manganese complex a residue of indefinite composition was obtained as the end product. The various thermal decomposition reactions of these complexes can be represented as follows

1. $Mn(S_2CNRR')_3 \xrightarrow{478-523\ K} Mn(S_2CNRR')_2$

   $Mn(S_2CNRR')_2 \xrightarrow{523-613\ K} Mn(SCN)_2$

   $Mn(SCN)_2 \xrightarrow{733-1083\ K}$ residue of indefinite composition

2. $Co(S_2CNRR')_3 \xrightarrow{453-633\ K} Co(SCN)_3$

   $Co(SCN)_3 \xrightarrow{673-803\ K} Co(SCN)_2$

   $Co(SCN)_2 \xrightarrow{873-1073\ K} CoS$

3. $Ni(S_2CNRR')_2 \xrightarrow{598-633\ K} Ni(SCN)_2$

4. $Cu(S_2CNRR')_2 \xrightarrow{728\ onward}$ volatile product

5. $Cu(S_2CNRR')_2 \xrightarrow{473-563\ K} Cu(SCN)_2$

6 $Cu(SCN)_2 \xrightarrow{573-873\ K} CuS$

5. $Mo_2O_3(S_2CNRR')_4 \xrightarrow{473-643\ K} Mo_2O_3(SCN)_4$

$Mo_2O_3(SCN)_4 \xrightarrow{653-943\ K}$ volatile product

(Where $R = C_2H_5$, $R' = C_6H_4CH_3$)

Kinetic parameters such as apparent activation energy and order of reaction were also calculated by these authors for the first step decomposition reaction of the complexes making use of the graphical method of Coats and Redfern [106]. The plot of $-\log[-\log(1-\alpha)/T^2]$ vs. $1/T \times 10^3$ for $n = 1$ (where α is the fraction decomposed, T is the temperature is K and n is the apparent order of reaction) gives a straight line i.e. the decomposition proceeds through first order kinetics.

Kumar and Kaushik [107,108] have carried out a thermal investigation on $M^{III}(S_2CNRR')_3$ and $M^{II}(S_2CNRR')_2$ complexes (where $M^{III} = As$, Sb, Bi and $M^{II} = Zn$, Cu, Hg; $R = C_2H_5$ and $R' = m\text{-}C_6H_4CH_3$) in N_2 and air/oxygen atmospheres to determine their mode of decomposition. The thermal decomposition ranges and mode of thermal transformations for these complexes are given in Table 4. The intermediates and final residues were identified by chemical analysis and spectral studies. Kinetics for the first step thermal decomposition in a N_2 atmosphere have also been evaluated and it was found that in all cases initial decomposition followed first order kinetics.

Thermogravimetric studies on Ru(III), Rh(III), Pd(II), Os(IV), Ir(III) and Pt(II) complexes of *N*-(ethyl, *m*-tolyl)-dithiocarbamates in a N_2 atmosphere have also been described by the same workers [109]. Ru(III), Rh(III), Os(IV) and Ir(III) complexes yielded the metal sulphides at the end of the first decomposition step at 663, 793, 533 and 593 K respectively. Beyond this temperature, the TG curves showed a little arrest followed by continuous weight loss in each case. Except for Os_2S_3, which is completely volatile in the range 573–873 K, other sulphides lose sulphur, but even at 1273 K, no pure metals were obtained. This is attributed either to incomplete decomposition of the sulphides or to the probable formation of non-stoichiometric sulphides of these metals. Palladium(II) and platinum(II) complexes showed high thermal stabilities (up to 523 and 473 K respectively). After the first step decomposition, metal thiocyanates were obtained at 643 and 613 K for Pd(II) and Pt(II) complexes respectively. These thiocyanates gave metal sulphide in the second step decomposition. The metal sulphides on heating

TABLE 4

Thermal stability data of some $M^{III}(S_2CNRR')_3$ and $M^{II}(S_2CNRR')_2$ complexes ($R = C_2H_5$, $R' = m\text{-}C_6H_4CH_3$)

Complex (atmosphere)	Decomposition range (K)	Decomposition reactions
$As(S_2CNRR')_3$	473–538	$As(S_2CNRR')_3 \rightarrow As_2S_3$
(In N_2)	548–973	Volatilization
$Sb(S_2CNRR')_3$	473–563	$Sb(S_2CNRR')_3 \rightarrow Sb(SCN)_3$
(In N_2)	573–673	$Sb(SCN)_3 \rightarrow Sb_2S_3$
$Bi(S_2CNRR')_3$	433–553	$Bi(S_2CNRR')_3 \rightarrow Bi(SCN)_3$
(In N_2)	573–913	$Bi(SCN)_2 \rightarrow Bi_2S_3$
$As(S_2CNRR')_3$	453–523	$As(S_2CNRR')_3 \rightarrow As_2S_3$
(In air)	553–923	Volatilization
$Sb(S_2CNRR')_3$	493–548	$Sb(S_2CNRR')_3 \rightarrow Sb_2S_3$
(In air)		
$Bi(S_2CNRR')_3$	393–558	$Bi(S_2CNRR')_3 \rightarrow Bi_2(SO_4)_3$
(In air)	673–773	$Bi_2(SO_4)_3 \rightarrow Bi_2O_3$
$Zn(S_2CNRR')_2$	543–643	$Zn(S_2CNRR')_2 \rightarrow Zn(SCN)_2$
(In N_2)	713–943	$Zn(SCN)_2 \rightarrow ZnS$
$Cd(S_2CNRR')_2$	548–613	$Cd(S_2CNRR')_2 \rightarrow Cd(SCN)_2$
(In N_2)	718–943	$Cd(SCN)_2 \rightarrow CdS$
$Hg(S_2CNRR')_2$	453–558	$Hg(S_2CNRR')_2 \rightarrow HgS$
(In N_2)	573–728	Volatilization
$Zn(S_2CNRR')_2$	543–633	$Zn(S_2CNRR')_2 \rightarrow ZnS$
(In O_2)	728–923	$ZnS \rightarrow ZnO$
$Cd(S_2CNRR')_2$	523–628	$Cd(S_2CNRR')_2 \rightarrow CdS$
(In O_2)	728–883	$Cds \rightarrow CdO$
$Hg(S_2CNRR')_2$	443–543	$Hg(S_2CNRR')_2 \rightarrow HgS$
(In O_2)	543–728	Volatilization

at higher temperatures lost sulphur and formed non-stoichiometric metal sulphides.

Kaushik, Chhatwal and Sharma [110] have studied the thermal behaviour of *N*-(*p*-ethoxyphenyl)-dithiocarbamate, (PED) complexes of copper(II), zinc(II), cadmium(II), tin(II), tin(IV), nickel(II), and palladium(II) in a dynamic air atmosphere, using TG, DTA and IR techniques. The following decomposition mechanisms are proposed.

Decomposition of Cu(PED)$_2$

(i) $Cu[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow CuS$
(ii) $2Cu_2S + 5O_2 \rightarrow 2CuO + 2CuSO_4$
(iii) $CuSO_4 \rightarrow CuO + SO_3$

Decomposition of Zn(PED)$_2$

(i) $Zn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow ZnS$
(ii) $ZnS + O_2 \rightarrow ZnO$

Decomposition of Cd(PED)$_2$

The complex is stable upto 398 K. Beyond this it decomposes rapidly. This rapid mass loss may be due to the simultaneous destruction of the organic matter forming the sulphide and metal which are then oxidised to the sulphate and oxide respectively. A mixture of cadmium sulphide and oxide is obtained at 1273 K.

$Cd[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow CdS + CdO$

Decomposition of Sn(PED)$_2$

(i) $Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2Cl_2 \rightarrow SnS_2$
(ii) $SnS_2 + O_2 \rightarrow SnO_2$

Decomposition of Sn(PED)$_2$Cl$_2$

(i) $Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow Sn(CNS)_2Cl_2$
(ii) $Sn(CNS)_2Cl_2 \rightarrow SnS_2$
(iii) $SnS_2 + O_2 \rightarrow SnO_2$

Decomposition of Ni(PED)$_2$

(i) $Ni[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow Ni(CNS)_2$
(ii) $Ni(CNS)_2 \rightarrow NiS$
(iii) $NiS + O_2 \rightarrow NiSO_4$
(iv) $NiSO_4 \rightarrow NiO$

Decomposition of Pd(PED)$_2$

(i) $Pd[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \rightarrow PdS$
(ii) $PdS \rightarrow Pd$
(iii) $Pd + 1/2O_2 \rightarrow PdO$
(iv) $PdO \rightarrow Pd$

Kinetic parameters for the first step decomposition reaction of Cu(II), Zn(II), Sn(II) and Sn(IV) complexes have been calculated using the graphical method of Coats and Redfern. Calculation of heats of reaction from DTA curves for the different decomposition steps of all these complexes has been carried out using the simple expression $\Delta H = KA/N_0$ where ΔH is the heat of reaction, K is the calibration constant, A is the area under the peak and N_0 is the initial number of the specimen.

Thermal behaviour of ammonium-N-(p-ethoxyphenyl)-dithiocarbamate, NH_4(PED) and its gold(III), arsenic(III), iron(III), cobalt(III) and molybdenum(V) complexes have also been reported by the same group [111]. NH_4(PED) is thermally stable to 368 K. Beyond this temperature decomposition began and the crucible was completely empty at 823 K. The DTA profile of the ligand showed one endotherm and one exotherm, corresponding to the melting and burning of the ligand respectively.

The gold(III), arsenic(III) and molybdenum(V) complexes showed two-step decomposition. The first stage in the decomposition, common to all

TABLE 5

Thermal stability data of *N*-(*p*-ethoxyphenyl)-dithiocarbamate (PED) complexes

Sl. No.	Compound	TG decomposition range (K)	DTA	
			Peak temp. (K)	ΔH (kJ mol^{-1})
1.	$Cu(PED)_2$	463–623	468	4.33
			563	13.80
		623–958	710	12.42
			738	12.55
			848	67.80
		958–1173	1008	12.40
2.	$Zn(PED)_2$	423–558	423	2.97
			518	34.07
		653–1073	b	
3.	$Cd(PED)_2$	398–1273	419	3.38
			498	9.69
			565	16.18
			b	
			b	
4.	$Sn(PED)_2$	408–673	410	2.52
			463	5.38
			613	33.24
		723–883	788	12.79
5.	$Sn(PED)_2Cl_2$	433–503	433	6.26
			515	31.22
		523–678	648	6.70
		718–893	778	6.71
6.	$Ni(PED)_2$	508–638	508	2.82
			623	
		638–823	673	17.84
		823–1023	b	
		1023–1173	b	
7.	$Pd(PED)_2$	448–598	498	2.80
			515	10.18
		648–703	693	17.50
		823–1073	b	
		1073–1273	1128	47.35
8.	$Au(PED)_3$	393–553	400	15.7
			478	28.3
		588–723	578	251.3
			678	131.3
9.	$As(PED)_3$	443–588	460	34.1
			573	128.4
		598–873	643	247.2
			b	
10.	$Fe(PED)_3$	473–623	b	
			558	244.9
		623–773	b	
		873–1093	b	

TABLE 5 (continued)

Sl. No.	Compound	TG decomposition range (K)	DTA	
			Peak temp. (K)	ΔH (kJ mol^{-1})
11.	$Co(PED)_3$	413– 573	460	14.6
			528	179.1
		573– 748	600	65.2
		748–1048	b	
		1048–1148	b	
12.	$Mo_2O_3(PED)_4$	398– 583	405	14.9
			423	229.1
			555	77.7
		588– 918	b	

b = Broad.

three complexes, was the formation of sulphide. The second step in the weight loss corresponded to the formation of metal, volatilization of sulphide and oxidation of sulphide to oxide for gold(III), arsenic(III) and molybdenum(V) complexes, respectively. The first endothermic peak in the DTA curves of these three complexes corresponded to the melting of the complexes, while the first stage decomposition of sulphide was represented by the last two exotherms in the case of gold(III) complexes while only one exotherm was obtained for this step in the molybdenum(V) complex. The DTA curve showed one exotherm and one endotherm for the second step in the decomposition of the arsenic(III) complex. The exotherm corresponded to the conversion of sulphide to oxide, while the endotherm was due to the volatilization of the oxide.

The iron(III) complex showed three major thermal changes, corresponding to the formation of sulphide, oxidation of sulphide to sulphate and the decomposition of sulphate to oxide. The DTA profile of the complex showed two endotherms and two exotherms. The first endotherm corresponded to the melting of the compound while the second endotherm was due to the decomposition of iron sulphate to iron oxide. The first broad exotherm corresponded to the decomposition of dithiocarbamate to sulphide, while the next sharp exotherm could have been caused by the oxidation of iron sulphide to iron sulphate. The thermal behaviour of the cobalt(III) complex is almost identical to that of the iron(III) complex, except that the decomposition of sulphide proceeded through the intermediate thiocyanate, as shown by an additional exothermic band in the DTA.

Table 5 shows the TG and DTA analysis of *N*-(*p*-ethoxyphenyl)-dithiocarbamate complexes.

Thermal studies on palladium(II) and platinum(II) complexes of *N*-(methyl, cyclohexyl)-dithiocarbamates have been reported by Sangari et al. [112]. The thermal behaviour of these complexes is similar. Both palladium(II) and platinum(II) complexes undergo a solid-liquid phase transition at 463 K indicated by a sharp endothermic peak in the DTA followed by a three-stage decomposition. The first stage endothermic decomposition between 563 and 618 K in the palladium(II) complex and 593 and 663 K in the platinum(II) complex resulted in the formation of thiocyanate. The second step decomposition observed between 673 and 748 K in the palladium(II) complex and 673 and 728 K in the platinum(II) complex, resulted in the formation of metal sulphide. The curves are not perfectly horizontal beyond these temperatures. A slow continuous loss of sulphur is observed upto 1073 K in the platinum(II) complex, but no pure metal could be isolated. Kinetic parameters for the first stage decomposition of these complexes have been evaluated and first order kinetics are found in both cases.

Jain and Kaushik [113] have reported thermogravimetric studies on some *N*-aryl substituted dithiocarbamato complexes of thallium(I), $Tl(S_2CNRR')$ ($R = H$, $R' =$ *o*-, *m*-, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4; $R = CH_3$, C_2H_5, $R' = C_6H_5$, $CH_2C_6H_5$, *m*-$CH_3C_6H_4$, C_5H_9 and $RR' = C_6H_{12}$). All the complexes showed a two-stage weight loss in an N_2 atmosphere. The first stage decomposition resulted in the formation of thallous sulphide. The horizontal trace on the TG curves after the first stage decomposition in each case indicated the stability of thallous sulphide in an N_2 atmosphere. The second stage weight loss is due to volatilization of thallous sulphide which continued up to 1275 K. Thermogravimetric data for these complexes indicate that thallium(I) complexes with secondary amine dithiocarbamates are thermally more stable than those with primary amine dithiocarbamates. Kinetics for the first stage decomposition of these complexes were also studied and first order kinetics were observed in each case.

Bhushan et al. [114–117] have investigated the thermal decomposition of *N*-(*o*-, *m*-, *p*-chlorophenyl)-dithiocarbamato complexes of Cu(II), Zn(II), Cd(II), Sn(II), Co(II), Ni(II), Pd(II), Pt(II), Au(III), As(III) and Mo(V). The Cu(II) and Co(II) complexes showed a three step decomposition pattern. The first weight loss corresponded to the formation of sulphide. A slight increase in weight was then observed which was followed by a decrease in weight. This increase was due to the oxidation of sulphide to sulphate/oxide while the decrease was caused by decomposition of sulphate to oxide.

Both Zn(II) and Sn(II) dithiocarbamates showed similar two-step thermal decomposition behaviour. In the first step, rapid mass loss corresponded to the formation of sulphide which in the second step decomposition converted slowly to the corresponding oxide.

Thermal decomposition of Cd(II) complexes followed a rapid initial weight loss due to the simultaneous destruction of organic matter and oxidation of sulphide and metal, to sulphate and oxide respectively. A mixture of $CdSO_4$, CdS and CdO was observed at 1273 K.

The Ni(II) complexes showed two-step thermal decomposition. The first step decomposition resulted in the formation of thiocyanate. Afterwards the TG curve showed some abrupt changes which could have arisen from the oxidation of sulphide formed during the decomposition; finally the decomposition gave black NiO as the end product.

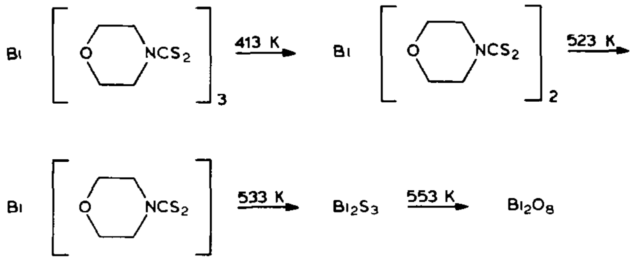
Thermal behaviour of Pd(II) complexes showed four major changes. The first step resulted in the formation of sulphide. In the next step the sulphide oxidised to metallic palladium, which further oxidised to palladium oxide. In the final decomposition this converted to metallic palladium as the end product.

Thermal decomposition of Pt(II)dithiocarbamates is shown by TG to occur in a single step giving metallic platinum. Thermal decomposition of Au(III) and As(III) complexes was completed in two stages. The first stage was common to both types of complexes and resulted in the formation of metal sulphide. In the next step formation of metallic gold was observed from Au(III) complexes while in this step volatilisation of sulphide occurred in As(III) complexes. These results are similar to those reported for *N*-(*p*-ethoxyphenyl)-dithiocarbamate complexes of Au(III) and As(III) by Kaushik et al. [111].

Thermal decomposition of μ-oxo-dioxotetrakis-*N*-[*o*-, *m*-, *p*-chlorophenyl-dithiocarbamato]molybdenum(V), $[(ClC_6H_4NCS_2)_2MoO]_2O$ showed three major changes. The initial decomposition resulted in the formation of sulphide which in the next step oxidised to the oxide. In the final phase of decomposition this oxide sublimed.

Details of the thermal stability data of all these complexes are presented in Table 6.

Srivastava et al. [118] have investigated the thermogravimetric behaviour of $BiX_n(S_2CR)_{3-n}$ X = Cl, NBr or I ($n = 0$, R = morpholino, *N*-phenylpiperazino, Bu_2N, *N*-methylanilino, *N*-ethylanilino; $n = 1$, R = morpholino, *N*-methylanilino, *N*-methylanilino, *N*-ethylanilino, Bu_2N) complexes. The TG curves indicated successive loss of two dithiocarbamate groups at 413 K and 523 K respectively. At 533 K the weight corresponded to Bi_2S_3 which at 553 K changed to bismuth(III) oxide.



The mass spectra of several metal–dialkyl-dithiocarbamate chelates have been determined [119–134]. Mass spectrometric studies of dialkyl-dithiocarbamates of chromium(III), iridium(III), cobalt(III), ruthenium(III) and rhodium(III) [120] and nickel(II) [121], which are monomeric in the solid phase and also the dimeric $Cu(S_2CNEt_2)_2$ [122] showed monomolecular

TABLE 6

Thermal stability data and heats of reaction of some *N*-chlorophenyl-dithiocarbamate complexes

Compound	TG decomposition range (K)	DTA (initial wt. = 500 mg)	
		Peak temp. (K)	ΔH (Kcal mol^{-1})
$NH_4(OCD)$	338– 813	b	
$NH_4(MCD)$	343– 793	b	
$NH_4(PCD)$	368– 803	b	
$Cu(OCD)_2$	373– 1168	398	2.61
		498	14.94
		653	54.32
		808	43.54
		873	91.07
		b	
$Cu(MCD)_2$	423– 1133	448	5.18
		543	37.13
		618	17.11
		b	
		1103	30.73
$Cu(PCD)_2$	393– 1183	408	2.75
		513	14.26
		643	22.87
		678	58.46
		833	88.88
		1103	21.51
$Zn(OCD)_2$	453– 1223	b	
		548	
		788	
		878	
$Zn(MCD)_2$	468– 1123	b	
		573	
		803	
		918	
$Zn(PCD)_2$	413– 1073	448	
		528	
		798	
		923	
$Cd(OCD)_2$	373– 1273	b	
		493	
		573	
		758	
		b	
$Cd(MCD)_2$	453– 1223	b	
		b	
		753	
		858	
		b	
$Cd(PCD)_2$	403– 1273	b	
		698	
		763	
		b	

TABLE 6 (continued)

Compound	TG decomposition range (K)	DTA (initial wt. = 500 mg)	
		Peak temp. (K)	ΔH (Kcal mol^{-1})
$Sn(OCD)_2$	368– 873	398	
		463	
		623	
		783	
$Sn(MCD)_2$	398– 873	423	
		473	
		578	
		808	
$Sn(PCD)_2$	403– 1273	408	
		438	
		613	
		748	
$Co(OCD)_2$	388– 1138	403	7.3
		509	84.6
		603	251
		773	471
		b	
		b	
$Co(MCD)_2$	413– 1148	423	15.8
		518	145
		708	161
		758	209
		933	511
		b	
$Co(PCD)_2$	373– 1198	413	14.1
		573	85.3
		683	388
		803	336
		958	313
		1098	127
$Ni(OCD)_2$	413– 878	423	10.9
		453	22.8
		523	144
		773	477
$Ni(MCD)_2$	453– 873	b	
		528	104
		713	227
		783	457
$Ni(PCD)_2$	438– 923	418	11.5
		458	30.5
		523	114
		778	423
$Pd(OCD)_2$	423– 1223	b	
		578	
		678	
		b	
		1158	

TABLE 6 (continued)

Compound	TG decomposition range (K)	DTA (initial wt. = 500 mg)	
		Peak temp. (K)	ΔH (Kcal mol^{-1})
Pd(MCD)$_2$	473– 1203	498	
		593	
		683	
		b	
Pd(PCD)$_2$	438– 1213	453	
		593	
		658	
		973	
		1163	
Pt(OCD)$_2$	368– 763	388	15.5
		503	99
		743	782
Pt(MCD)$_2$	413– 788	423	18.5
		538	102
		708	329
Pt(PCD)$_2$	383– 773	458	25.6
		543	88.7
		728	438
Au(OCD)$_3$	383– 733	388	
		448	
		608	
Au(MCD)$_3$	418– 728	433	
		528	
		b	
Au(PCD)$_3$	393– 768	423	
		553	
		648	
As(OCD)$_3$	463– 863	503	
		573	
		668	
		823	
As(MCD)$_3$	488– 883	498	
		593	
		648	
		818	
As(PCD)$_3$	378– 873	438	
		558	
		628	
		828	
$Mo_2O_3(OCD)_4$	333– >1073	b	32.65
		478	32.65
		618	230.73
$Mo_2O_3(MCD)_4$	393– >1073	b	
		573	48.15
		778	230.63
$Mo_2O_3(PCD)_4$	343– >1073	b	
		b	
		778	303.55

OCD, MCD, PCD = *o*-, *m*- and *p*-chlorophenyl-dithiocarbamate respectively.

ions, thus indicating the dimer decomposed on volatilization. The mass spectra of $Zn(S_2CNEt_2)_2$ [122], in addition to the peak due to the decomposition products of the dimeric molecule, contain two zinc atoms.

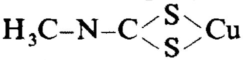
Riekkola [132] has studied the mass spectra of several metal–dialkyldithiocarbamates and has suggested some general fragmentation pathways. The gas phase stability is found to decrease in the order Ni > Pd > Cu > Zn > Cd > Pb > Hg ≫ Se for bis(dithiocarbamates) and Rh > Cr > Co > Fe ≫ In > As for tris(dithiocarbamates). The effect of length and shape of the non-fluorinised alkyl group on the gas phase stability is apparent in the ligand order diethyldithiocarbamate > diphenyldithiocarbamate > diisobutyldithiocarbamate > dibutyldithiocarbamate. Fluorination of dialkyldithiocarbamates decreases the gas phase stability. Gas chromatography –mass spectrometry (GC–MS) thus provides an excellent means of verifying the metal chelates which elute without decomposition under specified conditions.

The mass spectral and thermal decomposition behaviour of the diethyldithiocarbamate of dinitrosylmolybdenum, $[Mo(NO)_2(Et_2NCS_2)]$, (II), and the dimeric disulphidomolybdenum, $[MoS_2(Et_2NCS_2)_2]$ (III) have been reported by Udupa and Nagaraja [133]. The fragmentation of (I) takes place by the stepwise removal of NO followed by the successive loss of CH_2 groups and S, to give the final molybdenum fragmentation MoS_2. Mass spectrum fragments of (II) showed the formation of the dinuclear species $Mo_2O(Et_2NCS_2)_2S_2$, which lost MoS_2 and finally became Mo(MeNHCS). Complex III did not exhibit fragmentation at mass numbers higher than 576–592 for which the parent molecular ion would cover the mass numbers 608–624; this was probably due to non-volatility of the parent complex. Similar observations were made [134] on the spectrum of $Mo_2O_3(Et_2NCS_2)_2$. The other fragments of molybdenum were very weak and could not be detected under the experimental conditions. The fragmentation of the dithiocarbamate moiety was similar in all the complexes; thus in the thermal decomposition in air the ligand Et_2NCS_2 lost an S-atom followed by the stepwise dissociation of CH_2 groups to give NCS. S-containing molybdenum compounds gave rise to MoO_3 through the intermediate molybdenum sulphide [135–137]. The weight loss curve indicated that the nitrosyl complex lost 2 mol of NO in the temperature range 373–423 K and MoO_3 was formed at 753K through the intermediate MoS_3. The oxoisothiocyanate complex on the other hand lost NCS over the temperature range 373–423 K. At higher temperature MoS_3 was formed which was oxidised to MoO_3 at about 773 K. Complex III was stable up to 573 K and decomposed to give a polysulphide of composition Mo_2S_8 between 473 and 573 K. The sulphide was oxidised to MoO_3 at about 753 K.

Thermogravimetric behaviour of some diethyldithiocarbamato complexes of the type ML_2 and ML_3 at reduced pressure has been studied by Leong [138]. Thermogravimetric measurements for ML_2 (HL = diethyldithiocarbamic acid, M = copper, nickel, zinc, lead and cadmium) and ML_3 (M = chromium, iron and cobalt) at reduced pressure indicate complete volatilization for all the chelates below 250 K. ML_2 complexes are more volatile than ML_3 complexes. The order of decreasing volatility is Zn > Cu > Pb > Cd > Ni > Co > Fe,Cr.

The thermal properties of ML_n (HL = $(iso\text{-}Bu)_2NCS_2H$; $n = 2$, M = Ni, Cu, Zn, Cd, Hg, Pb; $n = 3$, M = Cr, Fe, Co, In, As) complexes in an inert atmosphere have been investigated [139]. In spite of slight decomposition (M = As, Fe) which occurred during volatilisation, most of the metal chelates could be successfully separated by gas chromatography on short gas capillary or fused SiO_2 columns. There was no clear correlation between the gas chromatographic behaviour and the thermal stability of these metal chelates.

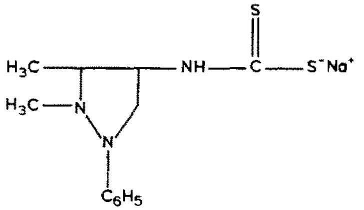
Structure, thermal stability and gas chromatographic behaviour of some dialkyldithiocarbamate chelates of palladium(II) have been studied by Riekkola et al. [140]. The volatility trends observed in TG and DSC are compared with observations made using capillary columns in gas chromatography. Fluorination markedly increased the volatility and thermal stability. For chelates other than $Pd(S_2CNEt_2)_2$, no clear trends were observed in TG and/or DSC data. The chromatographic elution order Et > *n*-Pr ~ *i*-Bu < *n*-Bu, indicated the effects of the molecular weight and the shape of the molecule.

Thermogravimetric studies on piperazine-bis(dithiocarbamate), Pz(bis)dtc $Na_2 \cdot 4.5H_2O$ and its metal complexes with cobalt(II), together with nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) compounds of the type $ML \cdot nH_2O$, have been described [141]. The ligand sodium salt, after losing its water of crystallization between 298 and 423 K, produced a polysulphide of type $Na_2S_{3.5}$ in the range 423–648 K, which then underwent oxidation to Na_2SO_4 and Na_2O. For the complexes, the data up to 1173 K suggested a multistep decomposition. All the complexes except the copper and mercury derivatives, after the loss of the water of crystallization in the range 298–448 K, showed a second step decomposition, leading to the formation of polysulphide ($NiS_{2.5}$, $CoS_{2.5}$, $ZnS_{1.5}$, $CdS_{1.5}$) up to 773 K. The second step (373–623 K) for the copper complex left as residue  $H_3C{-}N{-}C{<}^{S}_{S}{>}Cu$ while for the mercury compound the "intact" ligand moiety was lost between 443 and 569 K. The third step left a MO residue for all the complexes with the exception of mercury and copper derivatives. In the former case complete evaporation of the metal was observed, while in the latter case CuS_2 was formed which then underwent conversion to CuO.

TG and DTA behaviour of molybdenum(V)-μ-dioxo complexes with dithiocarbamates of the type $Mo_2O_4L_2$ (HL = R_2NCS_2H; R = Et; *i*-Pr; *n*-Bu; cyclohexyl, (cy); $Cy(Me)NCS_2H$; $Ph(Et)NCS_2N$; $R'CS_2H$ (R'H = morpholino, piperidino, pyrrolidino) have been discussed recently by Doadrio Villarejo et al. [142]. Study of the thermal transformation routes of $Mo_2S_2(\mu\text{-}S)_2L_2$ (I, HL = bis(2-ethylhexyl)dithiocarbamic acid) complex by

HPLC [143] indicated that on heating in air I was converted to $Mo_2OS(\mu\text{-}S)_2L_2$ (II), and $MoO(S_2)\ L_2$ (III). Compound III further decomposed to a substance which could not be detected by HPLC via MoO_2L_2. Compound II was converted simultaneously to $Mo_2O_2(\mu\text{-}S)_2L_2$ (IV), $Mo_2O_2(\mu\text{-}O,S)L_2$ (V) and an unidentified compound. Compound IV was formed via this unidentified compound as well as directly from II. Compounds IV and V were stable compared with I and II. Compound V was not formed from IV. In oxidation the terminal S in I was more easily replaced by O than a bridging S.

Thermal decomposition of 4-aminophenazone dithiocarbamato complexes of antimony(III) silver(I), lead(II) cadmium(II), platinum(II), uranium(V) and molybdenum(V) have been studied by Singh et al. [144] in an oxygen atmosphere using TG and DTA.



Sodium 4-aminophenazone dithiocarbamate, (4-Apdtc) Na

The apparent activation energies (E^*) values have been calculated by the graphical method of Coats and Redfern for the first step thermal decomposition. The following decomposition reactions apply

(i) $Sb(4\text{-}Apdtc)_3 \xrightarrow{493-653\ K} Sb_2(SO_4)_3 \xrightarrow{673-823\ K} Sb_2O_3$

(ii) $Ag(4\text{-}Apdtc) \xrightarrow{433-703\ K} Ag_2O$

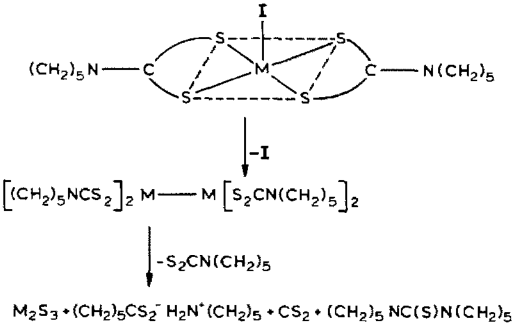
(iii) $M(4\text{-}Apdtc)_2 \xrightarrow{x} MSO_4 \xrightarrow{y} MO$

($M = Pb$, $x = 493\text{–}513$ K, $y = 623\text{–}993$ K; $M = Cd$, $x = 498\text{–}503$ K, $y = 693\text{–}703$ K; $M = Pt$, $x = 493\text{–}673$ K, $y = 703\text{–}963$ K; $M = UO_2$, $x = 493\text{–}693$ K, $y = 693\text{–}873$ K)

(iv) $Mo_2O_3(4\text{-}Apdtc)_4 \xrightarrow{463-693\ K} Mo_2O_3(SO_4)_2 \xrightarrow{693-833\ K} MoO_3$

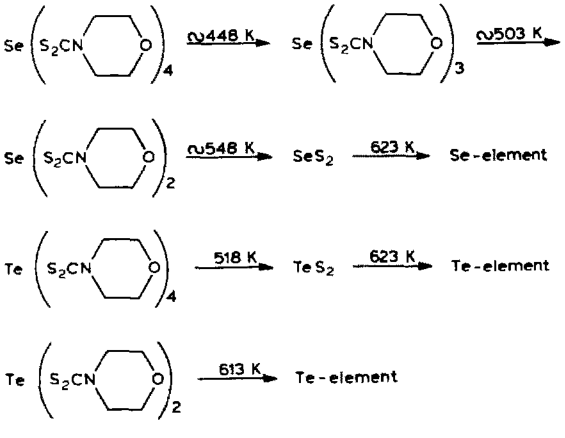
The thermal stability in air of the dithiocarbamato complexes of antimony and bismuth(III), $Sb[S(S)CNR_2]_3$ and $Bi[S(S)CNR_2]_3$ (R = ethyl, *n*-butyl, *n*-isopropyl, *n*-amyl, *n*-isoamyl and *n*-octyl groups) has been investigated using TG, DTG and DTA results by Afanasova et al. [145]. The E^* values have been calculated by Piloyan's methods [146,147] and presumed decomposition reactions, involving release of CS_2, alkene ($RCH{=}CH_2$), amine and isothiocyanate (RNCS) as volatile products of decomposition, were given.

Recently simultaneous TG, DTG and DTA studies under non-isothermal conditions have been carried out in air and in nitrogen atmospheres on tris(piperidyldithiocarbamato), tris(*N*,*N*-disubstitutedithiocarbamato) and halo-bis(piperidyldithiocarbamato) complexes of arsenic(III), antimony(III) and bismuth(III) [148–150]. The apparent activation energies have been calculated using the graphical method of Freeman and Carrol [151] modified by $n = 1$ and 2 methods of Piloyan et al. [146,147]. The intermediates obtained at the end of the decomposition steps have been identified via their elemental analysis, infrared spectral data and x-ray diffraction studies. A possible mechanism of decomposition reactions was suggested. Thermal decomposition mechanism of iodo(piperidyldithiocarbamato) complexes of antimony(III) and bismuth(III)



It is interesting to note that these workers have isolated CS_2 only as the volatile product of the decomposition unlike the mixture of CS_2, alkene, amine and isothiocyanate compounds proposed by Afanasova et al. [145].

The results of thermogravimetric analysis of the morpholine-4-dithiocarbamates of selenium(IV), tellurium(IV) and tellurium(II) showed that these compounds start to decompose at 423, 433 and 428 K respectively [152]. The selenium dithiocarbamate decomposed to selenium disulphide in three steps over the range 423–548 K, while tellurium dithiocarbamate decomposed in a single step. Both disulphides are finally reduced to the elementary state at 623 K. Tellurium(II) dithiocarbamate decomposed to elementary tellurium at 613 K in a single step. Further extension of the curves showed the volatility of the elements.



CONCLUSION

Studies of the thermal behaviour of the majority of metal dithiocarbamate complexes have been discussed in this review. However, incomplete identification of the intermediates and end products obtained during the thermal decomposition of these complexes by earlier workers, due to lack of advanced techniques and paucity of literature in the field, led to confusion regarding the mode of thermal decomposition of these complexes. To overcome this, during the past five years thermal properties of a number of metal-dithiocarbamate complexes have been extensively investigated.

Recent thermal studies on metal-dithiocarbamates indicates that the formation of the metal-thiocyanate intermediate is the essential step in the decomposition of the majority of dithiocarbamate complexes. The decomposition of metal-dithiocarbamates generally proceeds through the following steps.

1. Decomposition of dithiocarbamate to thiocyanate

$$M(R_2NCS_2)_n \rightarrow M(NCS)_n$$

2. Decomposition of thiocyanate to sulphide

$$M(NCS)_n \rightarrow MS_{n/2}$$

3. Oxidation of sulphide to metal or metal oxide

$$MS_{n/2} \rightarrow M \text{ or } MO_{n/2}$$

or volatiliszation of metal sulphide (where n is the valency of metal atom)

The third step is not essential for all metal dithiocarbamate complexes and therefore the end product of decomposition may be the metal sulphide, metal oxide, metal or volatile metal sulphide depending on the nature of the metal and the furnace atmosphere. It should also be pointed out that in some cases (in the majority of platinum metal dithiocarbamates for example) the composition of the end product does not correspond to either pure metal or sulphide; this may be attributed to the formation of non-stoichiometric metal sulphides at that temperature. Mercury(II), arsenic(III) and molybdenum(VI) sulphides and oxides are volatile, although molybdenum(VI) oxide showed volatility at higher temperatures than the others. In gold(II) and platinum group metal dithiocarbamates impure metal was obtained as the end product of decomposition and its composition was highly dependent on the furnace atmosphere. Formation of metal sulphate as the intermediate product and metal oxide as the final product was only observed when decomposition was carried out in an oxidizing atmosphere.

In some comparative studies of metal complexes with different dithioligands it was observed that the thermal stability of chelates increases in the order $EtOCS_s^- < (EtO)_2PS_2^- < Et_2NCS_2^-$. Furthermore in their adducts with pyridine the temperature at which loss of a pyridine molecule occurs increased in the order $(EtO)_2PCS_2^- > EtOCS_2^- > Et_2NCS_2^-$.

Although only a few metal dithiocarbamates and their intermediate and/or end products have been reported to be volatile, these have allowed the use of pyrolysis/gas chromatography for the separation of metal ions as their corresponding metal-dithio complexes. Thus information on the volatility of metal-dithiocarbamate complexes with different R-substituent groups and different metals, and their intermediate and/or final decomposition products has become an important consideration in an attempt to extract some general trends. It is observed that volatility increases as the oxidation state of the metal decreases and further, volatility increases as branching of the alkyl group of the dithiocarbamate ligand increases. However, due to the availability of insufficient data, it is premature at this stage to establish any general correlation between the volatility of the metal-dithiocarbamate complexes with their structure. There is much scope for research in this particular field.

Only a little work has been done in the area of thermal decomposition mechanisms and kinetics in the reactions of metal-dithiocarbamate complexes. In all cases the first step decomposition occurs by first order kinetics. A DTA study of metal-dithiocarbamate chelates has been made to obtain data on melting points and phase changes, but the results obtained for the melting points are often different from those obtained by other methods. Enthalpies of reaction are known for only a few complexes and only a little work has been reported using DSC.

These remarks indicate that confusion still prevails regarding thermal decomposition mechanisms, kinetics and identification of intermediate and end products of the thermal decomposition of metal-dithiocarbamate compounds. Further research in the field using complexes with different dithiocarbamate ligands and different metals is necessary to elucidate the decomposition mechanism of these complexes.

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