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Thermal stability of dithiocarbamates derived from α-amino acids with different metal ions

B. Macías *, J.J. Criado, M.V. Vaquero and M.V. Villa

Departamento de Química Inorgánica, Facultad de Farmacia, Avda. del Campo Charro s.n., 37007-Salamanca (Spain)

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Abstract

The thermal stability of compounds formed by dithiocarbamates prepared from several amino acids (glycine, alanine, α-aminobutyric acid, norvaline, valine, norleucine, isoleucine) with Ba^{2+}, Pb^{2+}, Cd^{2+}, Mo^{4+} and Mo^{5+} has been studied. Owing to its larger ionic character, the barium derivatives decompose at higher temperatures than the other compounds. In general terms, the stability decreases as the molecular weight increases. In all cases, the first step corresponds to dehydration, followed by decarboxylation and pyrolysis of the organic chain. The final residues have been identified by X-ray powder diffraction as oxides, sulphates and oxosulphates.

INTRODUCTION

Dithiocarbamates have attracted considerable attention in the last two decades, not only because of their academic interest, but also because of their industrial applications [1, 2]. Their thermal stability has been reviewed twice in the last decade [3, 4]. The general conclusion emerges that the thermal decomposition follows complex patterns, with regards to both the mechanisms governing this reaction, and the nature of the intermediate and final products formed; the formation of volatile intermediates represents an additional complication in the elucidation of these processes [5]. In general terms, volatility increases with the oxidation state of the metal (due to the increasing covalent character) and in the presence of branched organic chains in the starting material.

Although no general reaction pattern has been proposed, the formation of thiocyanate is indicated in the early stages of decomposition, and this is then transformed into a sulphide and finally into an oxide, although in some cases (depending on the particular nature of the metal and on the reaction temperature) the zero-valent metal is also formed. The formation of mixed

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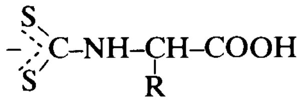
* Corresponding author.



Formula 1. Dithiocarbamate derivatives of α-amino acids.

phases and non-stoichiometric compounds (mainly sulphides) seems to be the general rule. If the decomposition is carried out in air, oxides, sulphides and sulphates predominate as the intermediate and final products.

It is evident that the nature and oxidation state of the metal, the type of dithiocarbamate, the use of an inert or oxidizing atmosphere, the temperature, etc., all influence the particular decomposition paths in every case, and that no general conclusions have been reached. In order to provide more information about this subject, we have studied the thermal stability of dithiocarbamate derivatives of α-amino acids with the general formula given in Formula 1 where R is H, glycine (gly); $-CH_3$, alanine (ala); $-CH_2-CH_3$, α-aminobutyric acid (α-ambut); $-CH_2-CH_2-CH_3$, norvaline (norval); $-CH-(CH_3)_2$, valine (val); $-CH_2-CH_2-CH_2-CH_3$, norleucine (norleu); $-CH_2-CH-(CH_3)_2$, leucine (leu); $-CH-(CH_2-CH_3)(CH_3)$, isoleucine (isoleu). In this way, the effect of the nature of the side chain on the thermal stability has been studied. In order to analyse the effect of the nature of the metal cation, several cations have been used to prepare salts or coordination complexes with these dithiocarbamates: mostly ionic compounds with Ba^{2+}, and covalent compounds with Pb^{2+}, Cd^{2+}, and with molybdenum in two different oxidation states, Mo^{5+} and Mo^{4+}.

EXPERIMENTAL

Thermogravimetric (TG) curves were recorded on a Perkin-Elmer model TGS-2, and differential thermal analysis (DTA) was performed on a Perkin-Elmer 1700, using alumina to dilute the samples. The curves were recorded in a dynamic atmosphere of pure air (20 ml min^{-1}) at a heating rate of 10°C min^{-1}. X-ray powder diffraction (XRD) analysis of the residues was performed in a Siemens D-500, model Kristalloflex 810 diffractometer.

Preparation of the compounds

Barium salts of the dithiocarbamates are easily prepared by reaction of the corresponding amino acid with carbon disulphide in the presence of barium hydroxide. The characterization of these compounds has been published elsewhere [6, 7]. Their general formula is Ba(dtc a.a.) · $3H_2O$, where a.a. is the particular amino acid. Reaction of aqueous solutions of these compounds with soluble salts of Pb^{2+} and Cd^{2+} leads to formation of Pb(dtc a.a.) and Cd(dtc a.a.) · H_2O compounds, respectively [8]. The reactivity of molybdenum with these compounds depends on the reaction conditions. The reaction of sodium molybdate with sodium salts of the dithiocarbamates in 6 M HCl leads to the formation of [Mo_2O_3(dtc a.a.)$_4$] · $2H_2O$. In a weaker acid medium (0.1 M HCl) and extracting the compound in an organic solvent, e.g. diethyl ether, as it is formed, leads to the formation of [MoO(dtc a.a.)$_2$] compounds. Finally, the reaction of the dithiocarbamates with molybdenum pentachloride under a non-oxidizing atmosphere leads to [Mo_2O_4(dtc a.a.)$_2$] · $2H_2O$ compounds [9].

RESULTS

Barium derivatives

All the DTA and TG profiles for the barium compounds were very similar. Those for the valine derivative are shown in Fig. 1. The first weight loss at around 100°C coincides with the endothermic DTA peak and represents approx. 3 water molecules per molecule of compound. A second weight loss is recorded between 200 and 400°C, where a change in the slope of the curve is observed in some cases: this can be related to the evolution

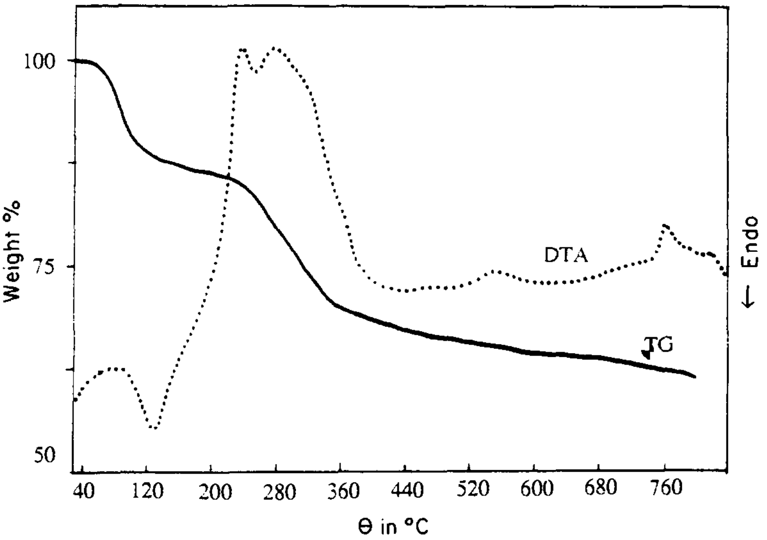


Fig. 1. TG and DTA profiles for Ba(dtc val) · $3H_2O$.

of the hydrocarbon chain. In some cases, especially with the short-chain derivatives, the first weight loss corresponds to CO_2 evolution, thus suggesting that the first step during decomposition corresponds to decarboxylation. Exothermic peaks are recorded in the DTA profiles of the long-chain derivatives, indicating a pyrolisis process. XRD analysis of the residues indicates barium sulphate as the major decomposition product, with small amounts of barium sulphide. The total weight losses in all cases coincide with those expected for total conversion to barium sulphate.

Lead derivatives

As with the barium compounds, all the DTA and TG curves were very similar; as an example, those for the valine derivative are shown in Fig. 2. According to elemental analysis results [8], these compounds do not contain crystallization water molecules, and the first weight loss is recorded between 125 and 155°C as two unresolved steps that, according to the weight losses recorded, should correspond to the loss of CO_2 and H_2S. The evolution of H_2S during the thermal decomposition of lead dialkyldithiocarbamates has been previously reported [10], with formation of lead thiocyanate. Exothermic peaks are recorded in this temperature range in the DTA profile. XRD analysis of the residues indicates formation of $Pb_2O(SO_4)$ as the major component (JCPDS file 18-702), although $PbSO_4$ is also present. The oxosulphate has also been identified after decomposition of lead alkyldithiocarbamates, through oxidation of intermediates (mainly sulphides and thiocyanates) [10]. As above, total weight losses up to 800°C

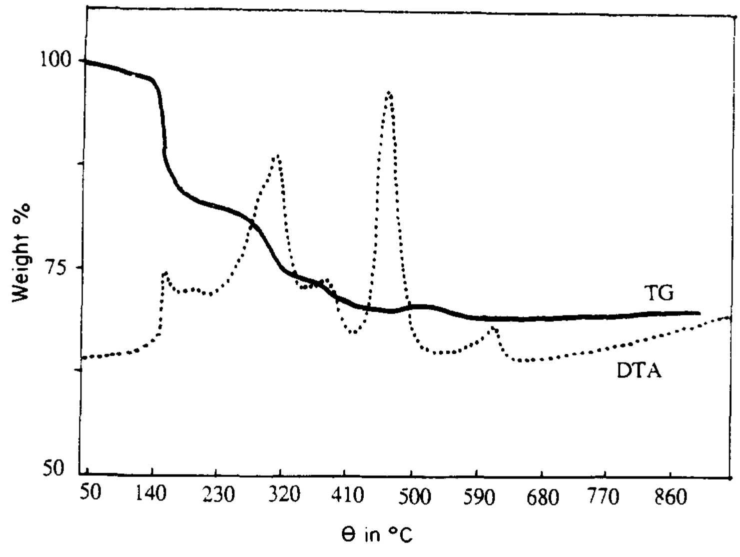


Fig. 2. TG and DTA profiles for Pb(dtc val).

in all cases coincide with those expected if formation of $Pb_2O(SO_4)$ is assumed.

Cadmium derivatives

The behaviour shown by these complexes during their thermal decomposition is not as uniform as was observed for the barium and lead derivatives. The curves recorded for the valine derivative are shown in Fig. 3. The removal of a water molecule corresponds with the weight loss measured between 60 and 120°C. Two differentiated steps are then apparent, the first one ending at 330°C and the second at 440°C, but the weight losses corresponding to these two steps are not constant, nor do they change steadily as the molecular weight of the compound increases. XRD analysis of the residues indicates the presence of a complex mixture: CdO, $Cd_3O_2SO_4$ (JCPDS file 26-382) and even metallic Cd have been identified, despite the oxidizing atmosphere during decomposition. However, it should be noted that these same compounds have also been identified upon decomposition of other cadmium dithiocarbamates [4].

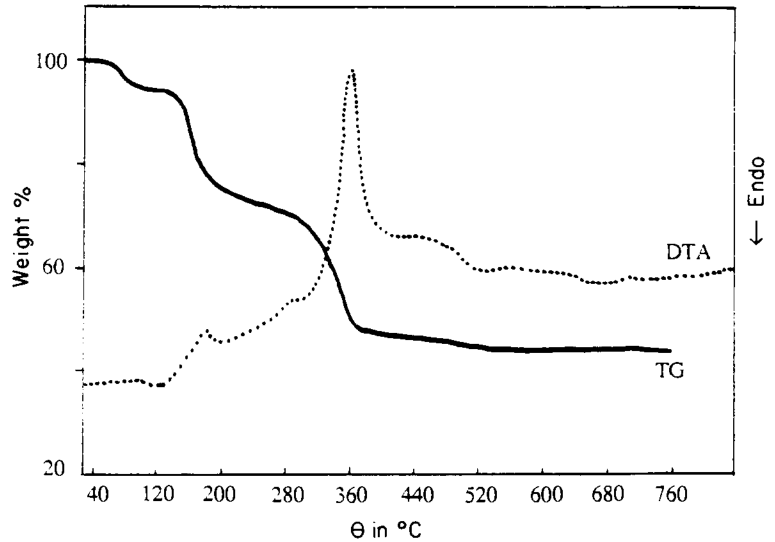


Fig. 3. TG and DTA profiles for Cd(dtc val) · H_2O.

Molybdenum derivatives

As expected, the thermal behaviour of the molybdenum derivatives depends on the stoichiometry of the compound, $[Mo_2O_3(\text{dtc a.a.})_4] \cdot 2H_2O$,

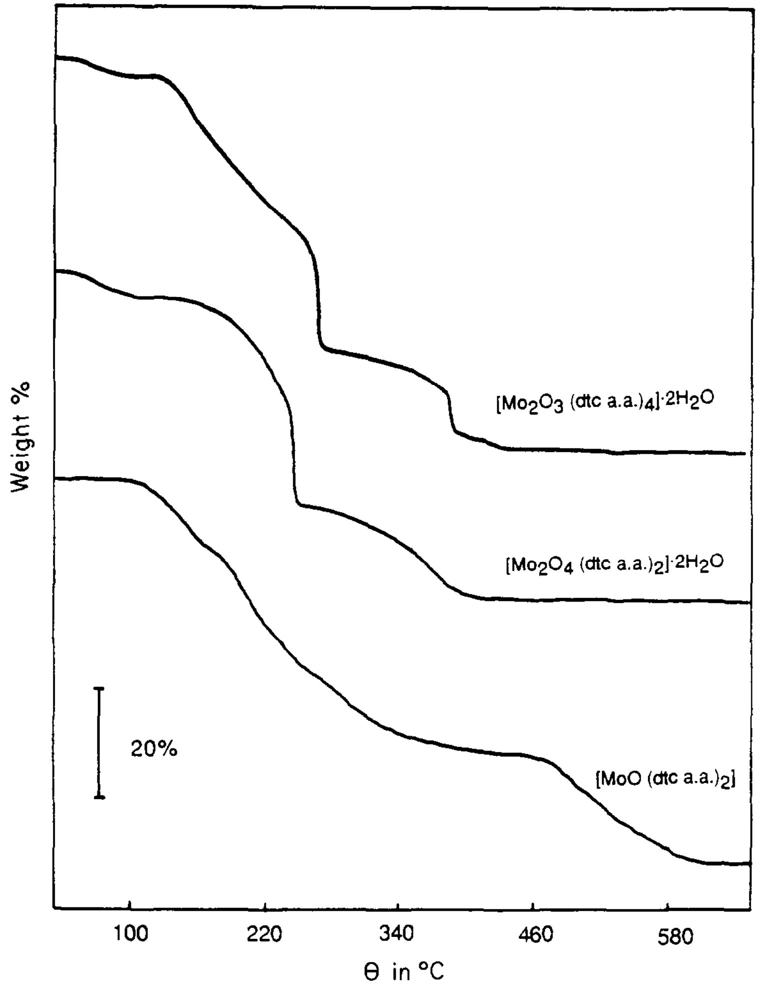


Fig. 4. TG curves for different molybdenum complexes.

$[Mo_2O_4(dtc\ a.a.)_2]\cdot 2H_2O$ or $[MoO(dtc\ a.a.)_2]$. Representative curves for complexes of each of these three types are shown in Fig. 4.

For the Mo(V) derivatives with the general formula $[Mo_2O_3(dtc\ a.a.)_4]\cdot 2H_2O$, the first weight loss (3.5–4%) corresponds to the removal of crystallization water molecules. The second weight loss, between 135 and 270°C, coincides with that calculated for removal of two ligands. This behaviour has been already reported [3, 4, 11], although the evolved species simultaneously decomposes. Singh et al. have reported [12] that dialkyldithiocarbamates with the general formula $Mo_2O_3(dtc\ a.a.)_4$, i.e. corresponding to our compounds, once the water molecules have been removed, undergo oxidation to $Mo_2O_3(SO_4)_2$ when heated at 420°C in air. The weight losses recorded up to this temperature for our complexes coincide fairly well with those expected for this transformation. Finally, a new weight loss leads to formation of the final products, where MoO_3 has been characterized by XRD as the major component, as reported by other authors for decomposition of molybdenum complexes under oxidizing conditions [3, 4, 13], although in our case the diffraction peaks of MoO_2 were also detected, probably due to the reducing ability of dithiocarbamates.

The weight loss corresponding to removal of crystallization water molecules is recorded in the same temperature range for complexes with the general formula $[Mo_2O_4(\text{dtc a.a.})_2] \cdot 2H_2O$, decomposition starting at 160°C. The weight loss up to the plateau starting at 270°C coincides with that calculated for $Mo_2O_3(SO_4)_2$ formation. A weaker weight loss is recorded above this temperature, corresponding to the formation of MoO_3, with appreciable amounts of MoO_2, according to the XRD analysis. It should be noted that the amount of MoO_2 seems to be larger than for the previous complexes, thus giving rise to darker residues.

Finally, complexes with the general formula $[MoO(\text{dtc a.a.})_2]$ show similar thermogravimetric curves. As expected from their stoichiometry, no weight loss is observed at low temperatures, due to the lack of crystallization water molecules, because these complexes were extracted in an organic solvent [9]. The most important weight loss extends from 105 to 430–460°C, although no flat line is attained, even at 600°C in some cases; therefore, sublimation of MoO_3 cannot be ruled out. In agreement, the total weight losses are larger than those expected for formation of MoO_3 as the final product, although this is the major component of the residue.

DISCUSSION

It is not easy to draw a general conclusion about the thermal behaviour of these compounds. Nevertheless, some general trends can be observed, not only from the curves shown in Figs. 1–4, but more clearly from the data given in Table 1. This table includes temperatures for the start of the decompositions; the loss of molecular water was not taken into account because it does not seem to affect the general stability patterns.

The highest decomposition temperatures are observed for the Ba derivatives, probably due to their ionic character. For the Ba, Pb and Cd derivatives, the thermal stability decreases, i.e. the onset temperature for decomposition is lower, as the molecular weight of the compound increases; in other words, as the relative amount of organic component increases. In some cases, the differences are not as large as those previously reported for dialkyl-dithiocarbamates, probably because the presence of the carboxylate moiety makes the differences in the molecular weights less important. Similar conclusions can be drawn for $[Mo_2O_4(\text{dtc a.a.})_2] \cdot 2H_2O$, but not for $[Mo_2O_3(\text{dtc a.a.})_4] \cdot 2H_2O$ and $[MoO(\text{dtc a.a.})_2]$. The greatest thermal stability is observed for compounds with the formula [Mo_2O_4(dtc

TABLE 1

Onset temperatures (°C) for thermal decomposition of dithiocarbamate derivatives[a]

	gly	ala	α-ambut	norval	val	norleu	leu	isoleu	Residue[b]
Ba(dtc a.a.) · $3H_2O$	275	250	220	190	200	200	210	200	$BaSO_4$, (BaS)
Pb(dtc a.a.)	150	155	140	135	130	127	125	130	$Pb_2(SO_4)O$, ($PbSO_4$)
Cd(dtc a.a.) · H_2O	165	135	140	143	145	137	135	140	CdO, $Cd_3O_2SO_4$, (Cd)
[Mo_2O_3(dtc a.a.)$_4$] · $2H_2O$	127	130	135	130	130	130	135	132	MoO_3, (MoO_2)
[Mo_2O_4(dtc a.a.)$_2$] · $2H_2O$	172	169	164	163	160	150	140	145	MoO_3, (MoO_2)
[MoO(dtc a.a.)$_2$]	101	102	105	102	103	105	105	100	MoO_3, MoO_2

[a] Water evolution has been ignored. [b] From XRD, minor components in parentheses.

a.a.)$_2$] · $2H_2O$, which is probably related to the presence of the double-oxygen bridge structure, Mo–O_2–Mo. In any case, the presence of the $Mo_2O_3^{4+}$, $Mo_2O_4^{2+}$ and MoO_2^{2+} moieties in the molybdenum derivatives seems to increase their thermal stabilities. Whether this behaviour is related to their larger covalent character and/or to the Mo–O bonds remains unclear.

As stated above, water release seems to affect only very slightly (if at all) the stability of the compounds. This process is followed by the main weight losses, consisting of decarboxylation and pyrolysis of the organic chain, as shown by the intense exothermic DTA peaks. The behaviour found here is similar to that previously reported for dithiocarbamate derivatives of α-amino acids with other metal cations [14–16]. The residues are mainly oxides, sulphates and oxosulphates, as expected when decomposition is carried out in air.

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