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Thermal and spectroscopic study of several dithiocarbamates

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Abstract

The thermal decomposition of several dithiocarbamates has been studied by TG and DTG techniques in a dynamic atmosphere of air. Various structures are proposed for the solid compounds, and the decomposition processes have been followed by IR spectroscopy as an approach to the establishment of possible thermal breakdown pathways.

INTRODUCTION

Dithiocarbamates (N–C(=S)–SX) and their derivatives make up one of the most important groups among organic fungicides used for disease control of plants. Thiram was suggested in 1934 for this purpose, and since then a series of salts of *N*-methyl- and *N,N*-dimethyldithiocarbamic acid have been proposed, as well as a group of ethylenebisdithiocarbamates (nabam, zineb, maneb, etc.). A remarkable characteristic of these compounds is their thermal instability, knowledge of which becomes especially necessary for their storage and agricultural applications, particularly in greenhouses. In the same way, this thermal instability makes impossible their direct analysis by gas–liquid chromatography (GLC).

Little work has been published concerning the thermal properties of dithiocarbamates, but some about their metal complexes, such as those of Cu^{2+} [1], Sn^{4+} [2] and other metal cations [3]. The purpose of this paper is the study of various dithiocarbamates using TG and DTG techniques and monitoring of the thermal decomposition processes by IR spectroscopy.

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EXPERIMENTAL

Materials

All the dithio- and ethylenebisdithiocarbamates used in this work were supplied by Riedel-de Haën as Pestanal Standard Quality.

Apparatus and procedures

The TG studies were carried out in air on a Mettler TA-3000 thermobalance using samples weighing between 5 and 15 mg, at a heating rate of 10°C min^{-1}. The DSC curves were recorded in a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5°C min^{-1} using sample weights from 3 to 6 mg. The range of temperatures was between 40 and 700°C. The infrared spectra of the compounds were recorded on KBr pellets made with the different dried compounds at room temperature, and with the same compounds after one hour of heating at 175, 225 and 420°C, in the range 4000–300 cm^{-1}, using a Perkin-Elmer 983 spectrophotometer.

RESULTS AND DISCUSSION

The TGA curves obtained are shown in Fig. 1. In Table 1 are listed the temperatures at which steps appear in the TGA, as well as the mass losses in percentages.

The decomposition processes start at ≈100°C for metham, (NH_4)APD, NaDDC and nabam and at higher temperatures (≈200°C) in the cases of ferbam, zineb, maneb and thiram. The processes leading to pyrolysis take place in three or four steps in all cases except for thiram, ferbam and zineb, which experience the pyrolysis process in only one well characterized step. Ferbam decomposes at 217°C, thiram at 215°C and zineb at 183°C. The lower temperature in the last case may be a consequence of its polymeric character; on the other hand, a greater thermal stability is observed for the compounds which are metal complexes than for those which are not. The decomposition products cannot be established for zineb because of its aforementioned polymeric character. (NH_4)APD and thiram are totally volatilized during the process and they leave no residue. Ferbam, zineb, NaDDC and nabam experience pyrolytic processes that lead to the metallic sulphides (ferbam: residue FeS_2 24.95%, found 25.65%; zineb: residue ZnS 35.34%, found 42.97%; nabam: residue Na_2S 40.65%, found 39.63%, NaDDC: residue Na_2S 22.78%, found 24.69%). Metham yields a sulphate (metham: residue Na_2SO_4 54.98%, found 52.76%); it is not possible to identify the decomposition product for maneb as the oxide or sulphide from TGA data (maneb: residue MnO_2 32.77%, MnS 32.79%, found 32.45%).

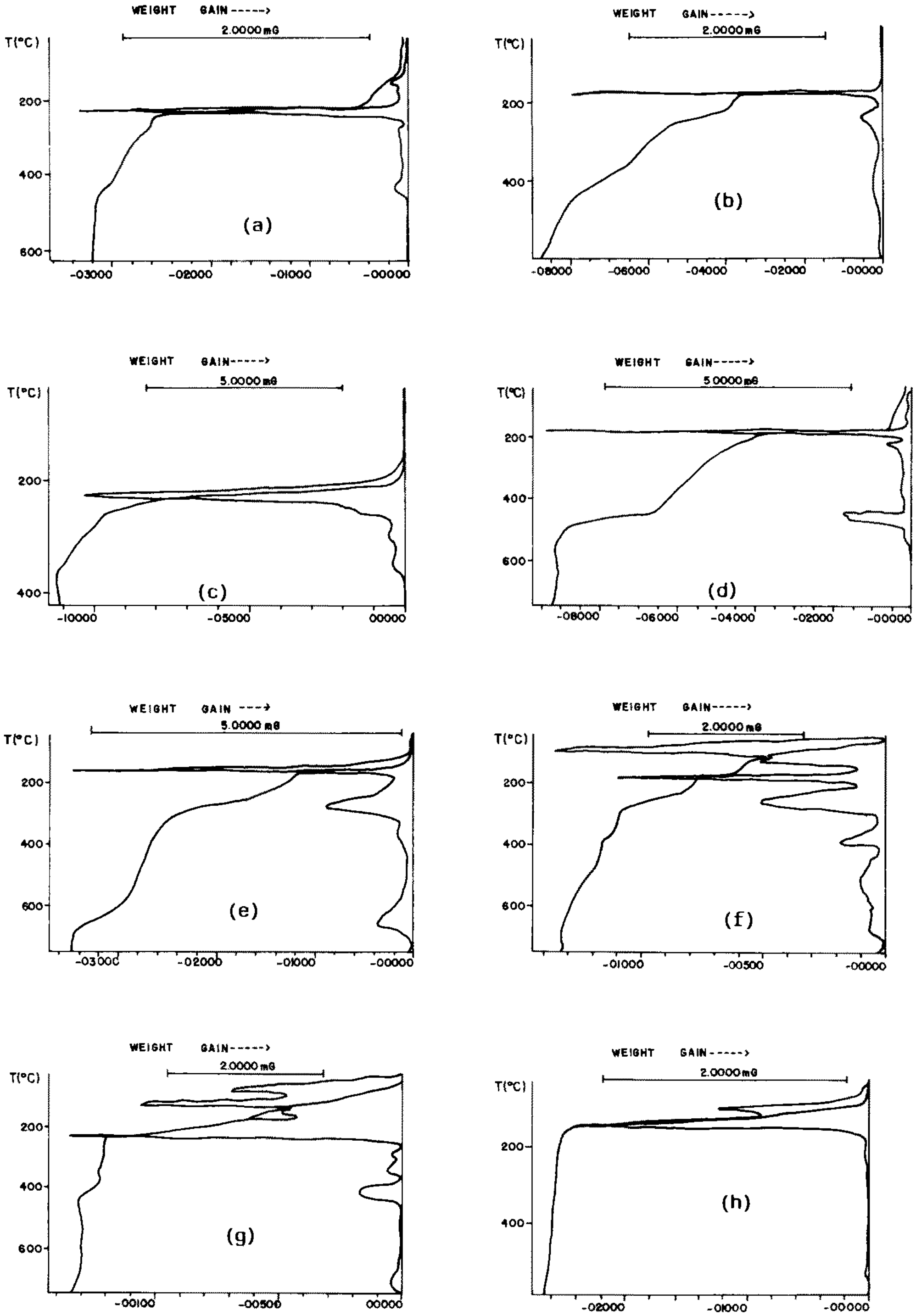

Fig. 1. Thermogravimetric curves: (a) ferbam; (b) zineb; (c) thiram; (d) maneb; (e) NaDDC; (f) nabam; (g) metham; (h) (NH_4)APD.

TABLE 1

Mass losses in TGA processes

Compound	Formula	T_1 (°C)	Loss (%)	T_2 (°C)	Loss (%)	T_3 (°C)	Loss (%)
Ferbam	$[(CH_3)_2NC(=S)S]_3Fe$	217	74.35				
Zineb	$[(CH_2NHC(=S)S)_2Zn]_x$	183	28.92	<600	28.11		
Thiram	$[(CH_3)_2NC(=S)S]_2$	215	100.00				
Maneb	$[\{CH_2NHC(=S)\}_2]_2Mn$	189	37.62	<550	24.01		
NaDDC	$[(C_2H_5)_2NC(=S)S]Na$	99	19.51	167	12.75	255	42.91
Nabam	$[(CH_2NHC(=S)S)_2]Na$	97	27.61	178	8.46	383	11.03
Metham	$[CH_3NHC(=S)SH]Na$	97	?	183	51.76	400	3.41
(NH_4)APD	$[(CH_2)_4NC(=S)S](NH_4)$	103	?	144	103.94		

Infrared study

Structure of dithiocarbamates

Figure 2 is a proposed representation of the studied compounds, classified as Type A (methyl- and dimethyldithiocarbamates) and Type B (ethylenebisdithiocarbamates). The structure of the compounds can be studied by IR spectroscopy according to the frequency of the absorption bands (see Table 2) assigned [4, 5] to C–N (1390–1325 cm^{-1}, band 1), C=S (1160–1130 cm^{-1}, band 2), S–CS–N (1060–1040 cm^{-1}, band 3) and C–N (1000–970 cm^{-1}, band 4). Depending on the studied band, an increase in electronegativity of the metal increases the shifts of the absorptions toward higher (band 3) or lower frequencies (bands 1, 2 and 4), keeping in all the cases the same order of displacement Fe > Zn > Mn > Na. The corresponding absorptions for the ammonium compound appear at each side of this scale, depending on the band studied.

The ligand–metal association has a higher ionic character for Na^+ compounds, which explains its higher batho- or hypsochromic shift. This greater ionic character also produces a higher lability of sodium compounds in comparison with the less ionic ones. The localisation of charges in the anion makes its breakdown easier; thus, NaDDC, metham and nabam decompose at ≈100°C, implying a lower thermal stability than that of the Zn^{2+} derivatives. The behaviour of the ammonium derivative is attributable to its possibilities of hydrogen bond formation.

A structural difference can be noted between the compounds having an amidic hydrogen atom and the *N*,*N*-dialkyl derivatives: in the latter, a specially favourable structure is obtained when the non-bonding electrons of nitrogen partially overlap with the C=S system; in the former, a greater stability is reached instead by hydrogen bonding, although a part of the delocalised system is then broken. These hydrogen bonds appear in

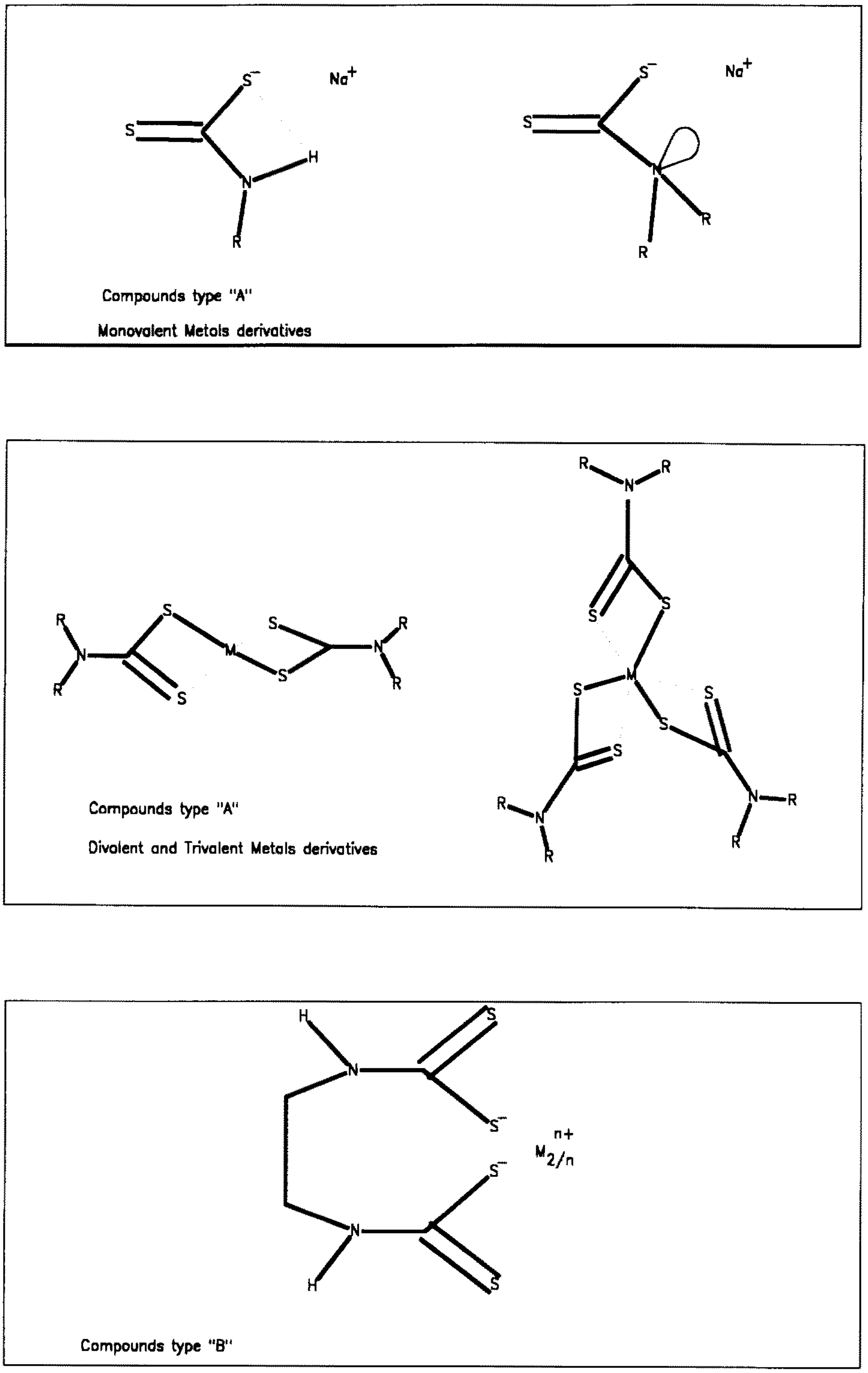

Fig. 2. Proposed structures for the two types of dithiocarbamates with various cations.

TABLE 2

Absorption bands in the IR spectra

Compound	Assignment			
	C–N	C=S	S–CS–N	C–N
Ferbam	1390	1147	1048	978
Zineb	1380	1105	1040	975
Thiram	1373	1148	1038	970
Maneb	1360	1140	1055	966
NaDDC	1354	1136	1040	965
Nabam	1348	1132	1046	959
Metham	1336	1128	1055	966
$(NH_4)_APD$	1325	1159	1037	998

the IR spectra as broad bands (around 3300 cm^{-1}) for the compounds of Type B as well as for metham.

Finally, the derivatives of Type A with di- or trivalent metal cations could show a certain delocalisation of the anionic charge between the two sulphur atoms in the dithiocarbamate group, but we have found in the IR spectra the characteristic band of C=S at ≈1050–1040 cm^{-1}, as expected [4]. This fact allows us to propose a structure for these compounds in which the dithiocarbamic nitrogen (with its lone pair) is bonded to the metal cation along with a formally charged sulphur atom, as is depicted in Fig. 2.

Decomposition processes

Thiram remains without change in its spectrum (and presumably in its structure) up to 225°C, but two new bands appear (at 630 and 480 cm^{-1}), probably indicating a partial decomposition with possible formation of an N≡C–S$^-$ species. The same behaviour is exhibited by NaDDC and

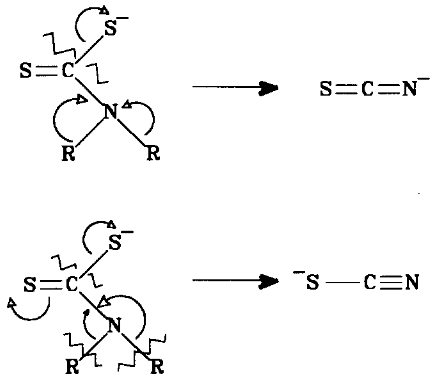

Fig. 3. Alternative routes of thermal breakdown.

ferbam (Type A compounds in Fig. 2). Other compounds (those of Type B) exhibit three bands during their decomposition, at 2075, ≈675 and 470 cm^{-1}. These absorptions correspond to an S=C=N$^-$ association which absorbs at 2050 cm^{-1} and gives two peaks between 700 and 500 cm^{-1} [5]. In despite of the structural similarity observed for both types of compounds from the IR studies at room temperature, there is not a unique route for their thermal breakdown (see Fig. 3).

Thus, although the decomposition residue is in most cases the corresponding metal sulphide with a good agreement between the measured values and the calculated ones, there are some cases in which the metallic oxide (or indeed the sulphate) seem to be formed preferably. The differences in composition of the residues are a consequence of the fragmentation pathways followed in each case, and also of the relative stability of the various metal oxides and salts.

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