Thermal Analysis of Some Metal Diethyldithiocarbamates

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Abstract

Thermal decomposition studies of diethyldithiocarbamates of Ca(II), Mn(II), Fe(III), and Ni(II), were carried out in two distinct atmospheres, viz., dynamic air and dynamic nitrogen using simultaneous TG-DTA techniques with a view to compare their thermal behaviour. Thermal stabilities in the two atmospheres have been compared, and the thermal stabilities among the four metal derivatives of diethyldithiocarbamate have also been compared. Thermal decomposition reactions of these compounds have been suggested in both the atmospheres.

1. Introduction

Sodium diethyldithiocarbamate is used as a chelating agent with strong affinity for mercury, copper, nickel and zinc. Diethyldithiocarbamic acid derivatives have been reported for a great number of metals. They have been used extensively in analytical chemistry (Duval, 1963). Moreover, diethyldithiocarbamate and its metal derivatives have been used with success as fungicides, pesticides, vulcanization accelerators, floatation agents, and high pressure lubricants(Thorn&Ludwig,1962). In recent years a great deal of interest has been shown in metal dithiocarbamates due to their diverse applications. As a part of the programme for the thermal analysis of solids of versatile applications, presently thermal decomposition studies of some metal derivatives of diethyldithiocarbamate have been carried out with a view to compare their thermal behaviour. Thus, diethyldithiocarbamates of Ca(II), Mn(II), Fe(III),, Ni(II) have been studied using simultaneous TG-DTA techniques in two distinct atmospheres, viz., in air (an oxidizing atmosphere) and in nitrogen (an inert atmosphere). The TG data of these compounds have been studied further with a view to evaluate the kinetics and mechanism of the thermal decomposition of these compounds.

2. Experimental

The metal derivatives of diethyldithiocarbamate were prepared with Ca(II), Mn(II), Fe(III), and Ni(II). All these compounds were prepared by a common procedure(Thorn&Ludwig,1962., Coucouvanis &Lippard, 1970) Each of the metal salts and sodium diethyldithiocarbamate were dissolved separately in water, and these solutions were mixed together in 1:2 mole ratio (for Fe derivative 1:3 ratio) with stirring. The metal derivative precipitated in each case was filtered and dried *in vacuo* over phosphorous(V) oxide.. The TG, DTG and DTA curves of all the compounds were recorded on a Mettler Toledo STARe thermal analysis system consisting of the STARe software and the TGS/SDTA 851e module. The instrumental curves obtained were exactly traced on tracing sheets for presentatiom. The plateaus in the TG curves, and the peak temperatures and the peak width in the DTG and DTA curves were tabulated. The final residue in each case was identified by performing the pyrolysis experiment in air or in nitrogen, as the case may be, and the residue was identified by chemical analysis. The mass losses obtained from the TG and pyrolysis experiments were compared with the theoretical values.

3. Results

The TG, DTG and DTA curves of the complexes in air and in nitrogen are traced. Two sample figures are given in Figures1 & 2. The thermal decomposition data of the complexes are presented in Tables 1 and 2 . These figures and tables are given at the end . The salient features of the thermal decomposition of the compounds studied are discussed below.

3.1 Calcium(II) Diethyldithiocarbamate

The compound, $Ca[(C_2H_5)_2NCS_2]_2.H_2O$ is stable up to ~180^0C in air, and then it undergoes decomposition in two stages as indicated by the DTG peaks at 198 and 701^0C, and the corresponding endothermic DTA peaks at 198 and 700^0C . The first decomposition stage is the dehydration stage, during which the lone water molecule present in the compound is removed in the temperature regime 180 - 230^0C. The mass loss obtained from the TG curve for the first decomposition stage (4.8%) agrees with the theoretical value calculated for the removal of one water molecule (5.1%). The anhydrous compound is stable in the temperature region 230 - 620^0C, and then it undergoes further decomposition in the temperature region 620 - 730^0C to give $Ca[(SCN)_2]$ as the final product in conformity with the mass loss data obtained from the TG curve (44.8%), pyrolysis experiment (44.7%) and the theoretical value (44.9%). The $Ca[(SCN)_2]$ formed is stable up to ~800^0C, the temperature limit used for the TG studies. The decomposition reaction of the compound in air is represented by the following equation.

$$Ca[(C_2H_5)_2NCS_2]_2.H_2O \rightarrow Ca[(C_2H_5)_2NCS_2]_2 \rightarrow Ca[(SCN)_2$$

The compound is stable up to ~170^0C in nitrogen atmosphere, and it decomposes in two stages almost similar to that in air. These two decomposition stages are denoted by the DTG peaks at 218 and 701^0C, and the corresponding endothermic DTA peaks at 221 and 707^0C . The first decomposition stage is the dehydration step, which is in conformity with the mass loss obtained from the TG curve (5.2%) and the theoretical value (5.1%). The anhydrous calcium diethyldithiocarbamate is stable in the temperature region 230 - 610^0C, after which it decomposes to give $Ca(SCN)_2$ as the final product. The mass loss data obtained from the TG curve (44.1%), pyrolysis experiment (44.2%) and the theoretical value (44.9%) support the above suggested decomposition reaction. The decomposition reaction of the compound in nitrogen is the same as that in air, which is illustrated by the equation given above.

3.2 Manganese(II) Diethyldithiocarbamate

The compound, $Mn[(C_2H_5)_2NCS_2]_2$ is stable up to ~170^0C in air, and then it undergoes decomposition in a single stage as shown by the DTG peak at 221^0C and the exothermic DTA peak at 230^0C . The peak width in the DTG curve shows that the decomposition starts at ~ 170^0C and ends at ~ 260^0C with a minor and gradual mass loss up to ~470^0C. The product obtained after this temperature is found to be MnO_2, which is supported by the mass loss data obtained from the TG curve (75.6%), pyrolysis experiment (75.4%) and the theoretical value (75.2%). The exothermic DTA peak obtained indicates that the decomposition is oxidative decomposition. The decomposition reaction of the compound in air is represented by the following equation.

$$Mn[(C_2H_5)_2NCS_2]_2 \rightarrow MnO_2$$

The compound shows a stability up to ~180^0C in nitrogen atmosphere, and it decomposes in a single stage as indicated by the DTG peak at 206^0C and the corresponding endothermic DTA curve at 214^0C (*vide* Fig 3.8 and Table 3.2). The decomposition starts at ~180^0C and ends at ~250^0C with a gradual but minor mass loss up to ~470^0C. The final residue obtained after ~470^0C is found to be MnS, which is in conformity with the mass loss data obtained from the TG curve (75.1%), pyrolysis experiment (75.2%) and the theoretical value (75.2%). The decomposition reaction of the compound in nitrogen is represented by the following equation.

$$Mn[(C_2H_5)_2NCS_2]_2 \rightarrow MnS$$

3.3 Iron (III) Diethyldithiocarbamate

Iron(III) diethyldithiocarbamate is stable up to ~200°C in air, and thereafter, it decomposes in a single stage as indicated by the DTG peak at 239^0C and the exothermic DTA peak at 247^0C . The peak width in the DTG curve shows that the compound starts decomposition at ~200^0C and ends at ~280^0C with a gradual but minor mass loss up to ~600°C.

The final decomposition residue obtained after ~600°C is found to be Fe_2O_3, which is in conformity with the mass loss data obtained from the TG curve (68.4%), pyrolysis experiment (68.3%) and the theoretical value (68.1%). The decomposition reaction of the compound in air is illustrated by the equation given below.

$$Fe[(C_2H_5)_2NCS_2]_3 \rightarrow Fe_2O_3$$

The compound is stable up to ~220^{0}C in nitrogen atmosphere and then it decomposes in a single stage as denoted by the DTG peak at 274^{0}C and the endothermic DTA peak at 260^{0}C. The final decomposition product is found to be FeS, which is confirmed by the mass loss data obtained from the TG experiment (82.2%), pyrolysis experiment (82.2%) and the theoretical value (82.4%). The thermal decomposition reaction of iron (III) diethyldithiocarbamate in nitrogen is represented by the equation given below.

$$Fe[(C_2H_5)_2NCS_2]_3 \rightarrow FeS$$

3.4 Nickel (II) Diethyldithiocarbamate

The TG curve of $Ni[(C_2H_5)_2NCS_2]_2$ exhibits a plateau up to ~260^{0}C in air. Thereafter, the compound stable up to ~260^{0}C, and thereafter, it undergoes decomposition in a single stage as denoted by the DTG peak at 335^{0}C and the corresponding exothermic DTA peak at 341^0. The peak width in the DTG curve shows that decomposition starts at ~260^{0}C and ends at ~360^{0}C resulting in the formation of NiO as the decomposition product. The mass loss data obtained from the TG curve (78.7%), pyrolysis experiment (78.8%) and the calculated value (78.9%) support the above suggested decomposition, which is represented by the following equation.

$$Ni\ [(C_2H_5)_2NCS_2]_2 \rightarrow NiO$$

The compound, $Ni\ [(C_2H_5)_2NCS_2]_2$ shows a stability up to ~280^{0}C in nitrogen atmosphere, and then it decomposes in a single stage. The decomposition is indicated by the DTG peak at 357^{0}C and the corresponding endothermic DTA peak at 367^{0}C. The decomposition starts at ~280^{0}C and ends at ~380^{0}C as indicated by the DTG peak width, and the residue obtained is found to be NiS. The mass loss data obtained from the TG curve (74.2%), pyrolysis experiment (74.3%) and the calculated value (74.4%) support the above suggested reaction. The TG plateau obtained above ~380^{0}C continues up to ~800^{0}C indicating that NiS is stable up to that temperature. The decomposition reaction of the compound is represented by the following equation.

$$Ni\ [(C_2H_5)_2NCS_2]_2 \rightarrow NiS$$

4. Discussions

Among the four metal diethylditiocarbamates studied in air only calcium(II) diethyldithiocarbamate contain water of hydration, while the remaining three do not contain any water of hydration. Out of the four metal diethyldithiocarbamates studied, three of them, *viz*., diethyldithiocarbamates of Mn(II), Fe(III), Ni(II), decompose in single step, and one decompose in two stages in air. In all the cases of four compounds, the final decomposition residues are the respective metal oxides. Among the four metal diethyldithiocarbamates studies, the anhydrous calcium salt is remarkably stable showing the highest thermal stability in air (up to ~620°C). while the Manganese salt shows the least thermal stability (up to ~170°C). The stability order of the anhydrous metal diethyldithiocarbamates in dynamic air is as follows (the temperatures of stability are given in parentheses).

Ca	>	Ni	>	Fe	>	Mn
(620°C)		(260°C)		(200°C)		(170°C)

The exothermic peak in DTA shows that oxidation has taken place in most of the decomposition reactions. The ligand and their probable decomposition products are easily combustible in the oxidizing atmosphere used. The DTG peak width of the compounds is more or less the same which shows the decomposition to be the same.

Among the four compounds studied in nitrogen atmosphere, three compounds, *viz*., the dietheyldithiocarbamates of Mn(II), Fe(III), Ni(II), decompose in single stage, while the other decompose in two stages. In nitrogen atmosphere also the Ca(II) salt in the anhydrous form shows the highest stability (up to ~610°C), and the Mn(II) salt shows the least stability (up to ~180°C). In nitrogen atmosphere the final decomposition residues for all the four compounds except the calcium salt are the respective metal sulphides, and in the case the calcium salt the final decomposition residue is calcium(II) thiocyanate. The stability order among the four metal diethyldithiocarbamates in nitrogen atmosphere is as given below (the temperatures of stability are given in parentheses).

Ca	>	Ni	>	Fe	>	Mn
(610°C)		(280°C)		(220°C)		(180°C)

The endothermic peak in DTA shows that oxidation is not taking place in most of the decomposition reactions. The DTG peak width of the samples is more or less the same which shows the decomposition to be the same in all the samples.

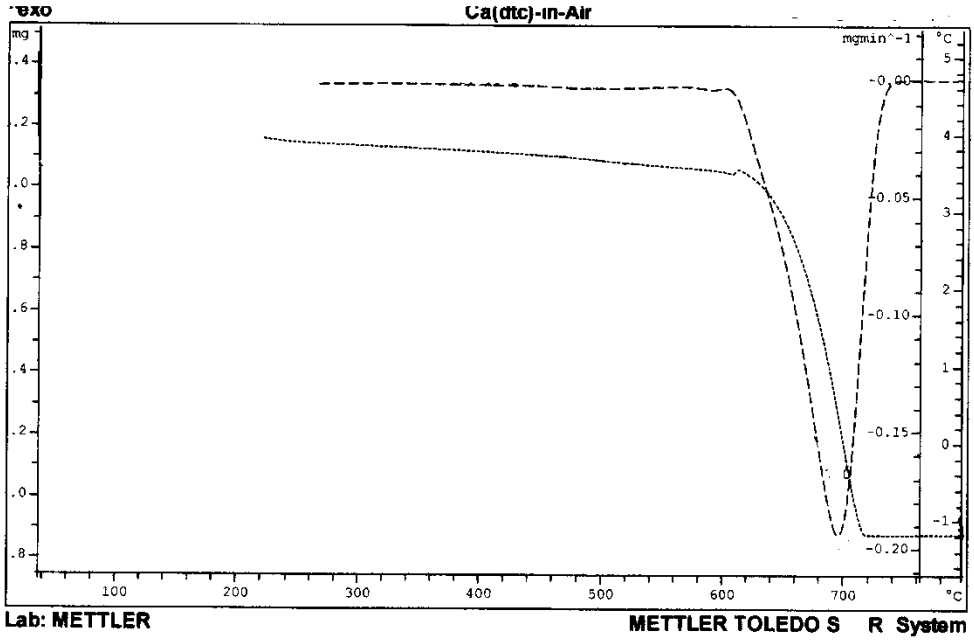

Figure 1

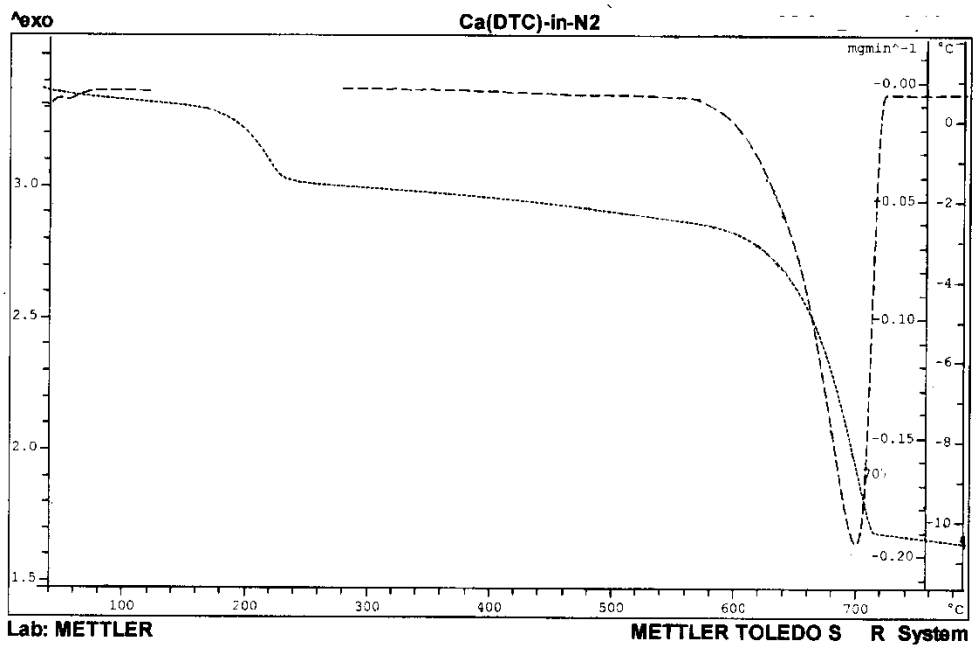

Figure. 2

Table 1: Thermal Analysis Data of Metal Diethyldithiocarbamates in Air

Compound	Plateau in TG (^{0}C)	Peak in DTG (^{0}C)	Peak width in DTG (^{0}C)	Peak in DTA (^{0}C)	Peak width in DTA (^{0}C)	Mass loss (%)			Residue
						TG	Pyrolysis	Calculated	
$Ca[Et_2NCS_2]_2 .H_2O$	Upto 180 230-620 After 730	198 701	180-230 620-730	198 700	190-230 640-730	4.8 44.8	… 44.7	5.1 44.9	$Ca[Et_2NCS_2]_2$ $Ca(SCN)_2$
$Mn[Et_2NCS_2]_2$	Upto 170 After 250	221	170-260	230	210-250	75.6	75.4	75.2	MnO_2
$Fe[Et_2NCS_2]_3$	Upto 200 After 280	239	200-280	247	220-260	68.4	68.3	68.1	Fe_2O_3
$Ni[(Et)_2NCS_2]_2$	Up to 260 Above 360	335	260-360	341	320-360	78.7	78.8	78.9	NiO

Table 2: Thermal Analysis data of Metal Diethyldithiocarbamates in Nitrogen

Compound	Plateau in TG (^{0}C)	Peak in DTG (^{0}C)	Peak width in DTG (^{0}C)	Peak in DTA (^{0}C)	Peak width in DTA (^{0}C)	Mass loss (%)			Residue
						TG	Pyrolysis	Calculated	
$Ca[Et_2NCS_2]_2 .H_2O$	Up to 170 230-610 Above 710	218 701	170-230 610-710	221 707	210-230 700-720	5.2 44.1	… 44.2	5.1 44.9	$Ca[Et_2NCS_2]_2$ $Ca(SCN)_2$
$Mn[Et_2NCS_2]_2$	Up to 180 Above 250	206	180-250	214	210-230	75.1	75.2	75.2	MnS
$Fe[Et_2NCS_2]_3$	Up to 220 Above 320	274	220-320	260	250-290	82.2	82.2	82.4	FeS
$Ni[(Et)_2NCS_2]_2$	Up to 280 Above 380	357	280-380	367	340-380	74.2	74.3	74.4	NiS

5. Conclusion

Metal diethyldithiocarbamates behave differently in air and in nitrogen atmospheres. The following differences have been noted from the thermal analysis using simultaneous TG/DTA techniques.

1. Out of the four metal diethyldithiocabamate studies, those of Mn(II), Fe(III), Ni(II), decompose single stage in air,and in nitrogen atmospheres.
2. Generally, the metal diethyldithiocarbamates exhibit enhanced stability in nitrogen atmosphere than in air
3. The decomposition residues obtained in air are the respective metal oxides, while the final residues obtained in nitrogen are the respective metal sulphides, in all the salts except that of Ca(II), for which the final residue is $Ca(SCN_2)$.

References

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