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The thermal behaviour of the ethylenebis-dithiocarbamates Maneb, Zineb and Mancozeb. Part 1. The mechanism of the thermal decomposition

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Abstract

The thermal decomposition of Maneb, Zineb and Mancozeb has been investigated by means of thermal analysis techniques. IR, X-ray diffraction, gas chromatography, high pressure liquid chromatography, etc. were carried out on the samples, which were withdrawn at various stages during thermogravimetric testing or during thermal decomposition in vacuum at constant temperature. The mechanisms of the thermal decomposition and the molecular structures of Maneb, Zineb and Mancozeb are proposed.

INTRODUCTION

The ethylenebisdithiocarbamates Maneb, Zineb and Mancozeb are important fungicides. In recent years a great deal of interest has been shown in the field of metal dithiocarbamates, due to their diverse applications. Although there is extensive literature on the metal dithiocarbamates, little of it is concerned with the investigation of the thermal behaviour of these complexes. In order to put these fungicides to correct use, it is important to study their thermal behaviour.

The mechanisms of the thermal decomposition of $Cu(R_2Dtc)_2$, AgR_2Dtc (where R is Me or Et, and Dtc is dithiocarbamate) and $M(S_2CN(CH_2)_5)_3$ (where M is As, Sb or Bi) have been extensively studied [1–3]. The first step in the thermal decomposition of these compounds is the splitting off of a carbon disulphide molecule. Another main intermediate product in the decomposition processes is ethylene thiourea. The final products of the decomposition in nitrogen and air atmospheres are the sulphide and the

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oxide, respectively. The thermal decomposition of sodium ethylenebisdithiocarbamate (Nabam), which is an intermediate in the synthesis of Maneb, Zineb and Mancozeb, has also been widely studied. Hylin [4] analysed the thermal decomposition products by gas chromatography (GC), high pressure liquid chromatography (HPLC) and thin layer chromatography (TLC), and proposed a decomposition mechanism for Nabam in aqueous conditions.

The available information on the thermal decomposition of Maneb, Zineb and Mancozeb is very poor, due partly to their molecule structures not being completely identified. Using TG and DTA, Lyalikov and Kitovskaya [5, 6] have suggested that the first step in the thermal decomposition of Maneb, Zineb and some metal dithiocarbamates is the splitting off of the carbon disulphide group. Day and Hamilton [7] have also studied the decomposition of Maneb, Zineb and Mancozed, using DTA in a nitrogen atmosphere and found that the endothermic peaks corresponded to the evolution of carbon disulphide and hydrogen sulphide respectively. However, they have not proposed a mechanism for the thermal decomposition. These fungicides can decompose to produce toxic products H_2S and ethylene thiourea (ETU) so it is important to study their thermal decomposition.

EXPERIMENTAL

Apparatus

Thermal analyses were carried out using a Perkin-Elmer thermogravimetric analyser model TGS-2, and a differential scanning calorimeter, model DSC-2C, and by the combined technique of TG–DTG. IR spectra were measured on a Nicolet Model 60SXR FT-IR spectrometer. Analysis was carried out as follows. Once a weight-loss peak during decomposition appeared in the thermogram or at any stage of the decomposition, the reaction was quenched and the residue was removed from the TG cell, ground in KBr, and a KBr plate made. This was used for IR analysis of the product.

The thermal analysis was conducted using an Al cell at lower temperatures and a Pt cell at higher temperatures, with a nitrogen flow rate of about $40.0\,\mathrm{cm^3\,min^{-1}}$, and a sample size of about 2.0 mg.

In addition, intermediate products (solids and gases) were analysed using high pressure liquid chromatograph Model SP8100 and a gas chromatograph Model 103 type. Both instruments were made in China.

Samples

Maneb is a yellow powder, Zineb a greyish powder and Mancozeb a yellow powder.

TABLE 1

Zinc content (wt.%) of Mancozeb samples

Sample No.				
D-1	D-2	D-3	D-4	D-5
1.66	2.96	4.29	7.80	9.0

The Mancozeb samples contained various quantities of zinc ion, as shown in Table 1.

RESULTS AND DISCUSSION

The structures of Maneb, Zineb and Mancozeb

Purification and recrystallization of Maneb, Zineb and Mancozeb cannot be readily carried out, so it is difficult to establish their structures. There is some disagreement about whether Mancozeb is a chemical compound or a mixture. It has generally been believed that the structures of Maneb and Zineb are either those of cyclic coordinated or dimeric compounds [7]. In order to establish the decomposition mechanisms, possible structures were proposed on the basis of their IR and thermal decomposition products.

The FT-IR spectra of Maneb, Zineb and Mancozeb (7.80 wt.% Zn) are shown in Fig. 1. The medium doublet absorption bands at 3297 and 3154 cm^{-1} are attributable to the N–H stretching frequency and the strong

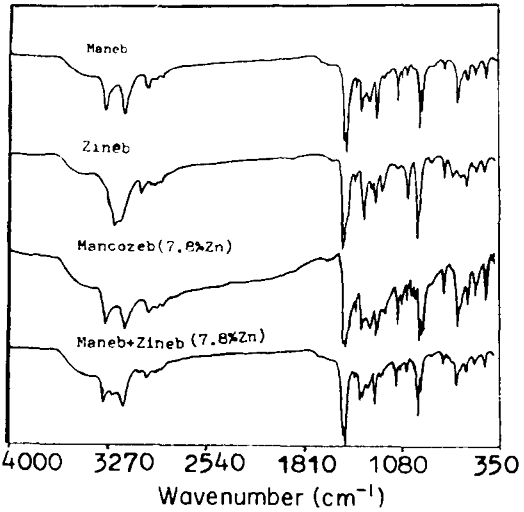
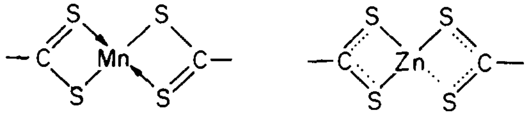


Fig. 1. IR spectra of Maneb, Zineb, Mancozeb (7.80 wt.% Zn) and the mechanically mixed sample of Maneb with Zineb (7.80 wt.% Zn).

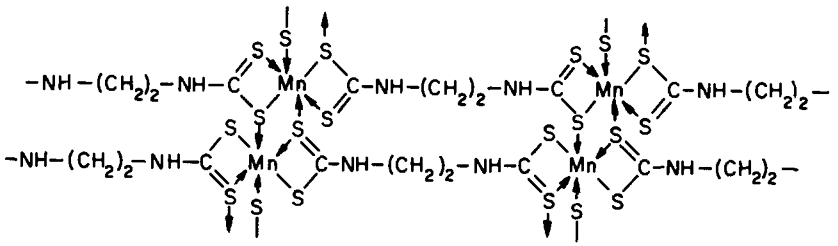


Formula 1.

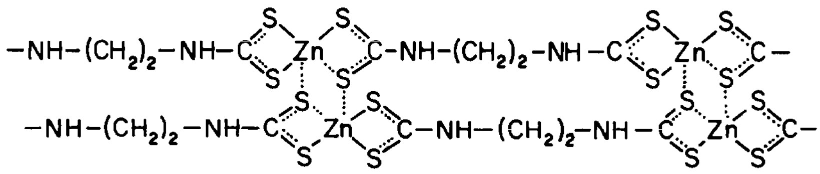
absorption bands at 965 and 945 cm^{-1} are attributable to the C–S bond in the spectrum of Maneb; in the spectrum of Zineb the single medium absorption at 3230 cm^{-1} is due to N–H and the medium and strong absorptions at 1048 and 977 cm^{-1}, respectively, are attributable to C–S. The doublet attributable to the N–H bond in the IR spectrum was probably due to the existence of cis and trans isomers in the Maneb molecule; in the Zineb molecule, the single absorption band at 3230 cm^{-1} was considered to be caused by the absence of cis and trans isomers in Zineb. On the basis of the viewpoint of Bonati and Ugo [8], if a single absorption band due to the C–S group appears at about 1000 cm^{-1}, bidentate coordination exists in the molecule; if two absorption bands appear, no bidentate coordination exists (see Formula 1).

Nabam, which is an intermediate in the synthesis of Maneb, has a linear dimeric structure with close proximity of the Na atoms (i.e. Na–Na). Thus, it is very possible in the synthesis that Mn^{2+} is substituted for two adjacent Na^+ atoms. Maneb is a linear polymer. In addition, it will be shown that the first stage of the thermal decomposition of Maneb and Zineb involves the splitting off of one carbon disulphide group only, with the formation of an intermediate product with the –N=C=S group. This is similar to the thermal decomposition of copper diethyldithiocarbamate, which also has a polymeric structure [1]. On the basis of these results, Maneb and Zineb are postulated to have the structures shown in Formulae 2 and 3.

Figure 1 also shows that the IR spectrum of Mancozeb is different from that of Maneb, Zineb or the mechanically mixed sample of Maneb plus Zineb. Subtraction of the FT-IR spectra of the mechanically mixed sample from that of Maneb gave the spectrum of Zineb; a similar process for Mancozeb and Maneb produced more new absorption bands, particularly as the zinc ion content increased (see Fig. 2). The thermal decomposition



Formula 2.



Formula 3.

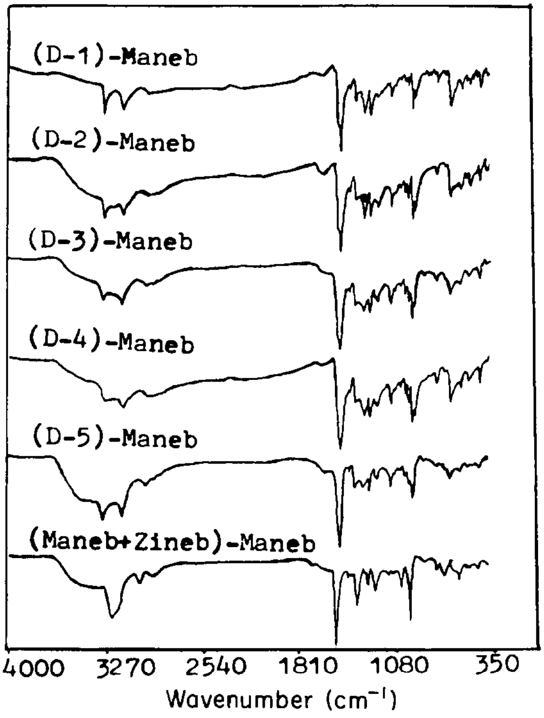
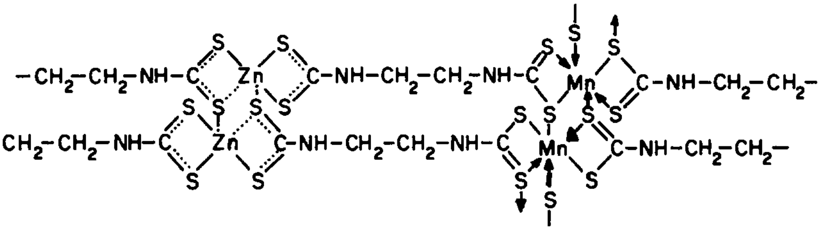


Fig. 2. Difference spectra of Maneb from D-1–D-5 and mixtures of Maneb and Zineb.



Formula 4.

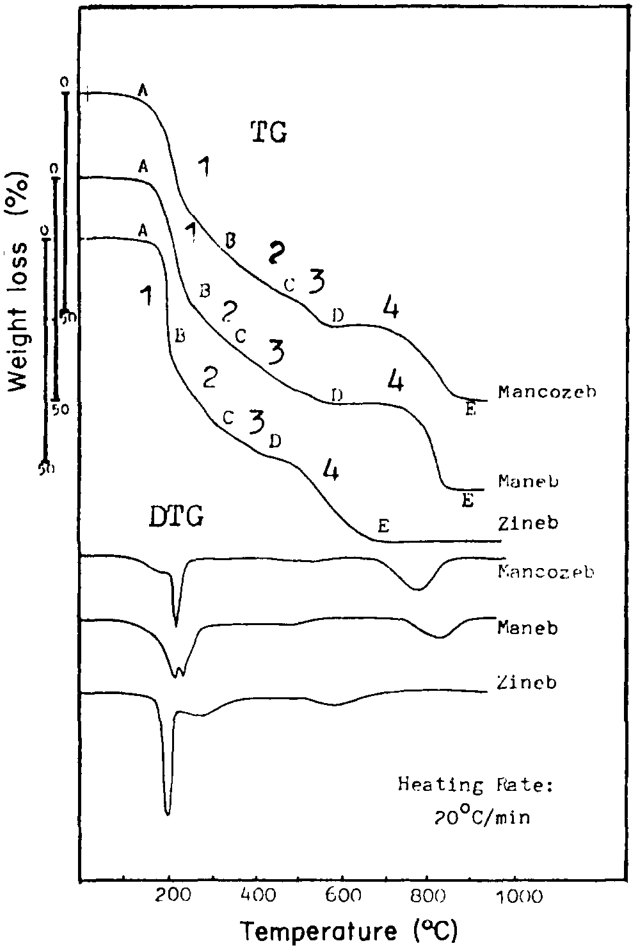


Fig. 3. The TG–DTG of Maneb, Zineb and Mancozeb.

process of Mancozeb contained similarities to those of Maneb and Zineb, as will be shown below. It was postulated that Mancozeb was a compound distinct from both Maneb and Zineb (see Formula 4).

The mechanism of the thermal decomposition of Zineb

As shown in Fig. 3, the TG curve of Zineb consists of a four stage weight loss designated A → B → C → D → E. The weight losses corresponding to each stage measured by the TG curve and calculated according to possible intermediates, are listed in Table 2.

The weight loss of 28.0% for the first stage (A → B) of Zineb

TABLE 2

Weight loss (%) obtained from TG–DTG of Zineb

	Stage 1	Stage 2	Stage 3	Stage 4
Found	28.0	44.5	52.0	71.0
Calc.	27.6	44.0	52.5	72.2

decomposition is in good agreement with the calculated value of 27.6% for one mole of Zineb losing one mole of carbon disulphide. In order to examine this result, the gas phase products of thermal decomposition at this stage were analysed by GC.

Zineb samples were heated at 220°C. After 15 min, the sample was cooled to room temperature under nitrogen. The gaseous products released from the sample were analysed by GC, as shown in Fig. 4; the results are shown in Table 3.

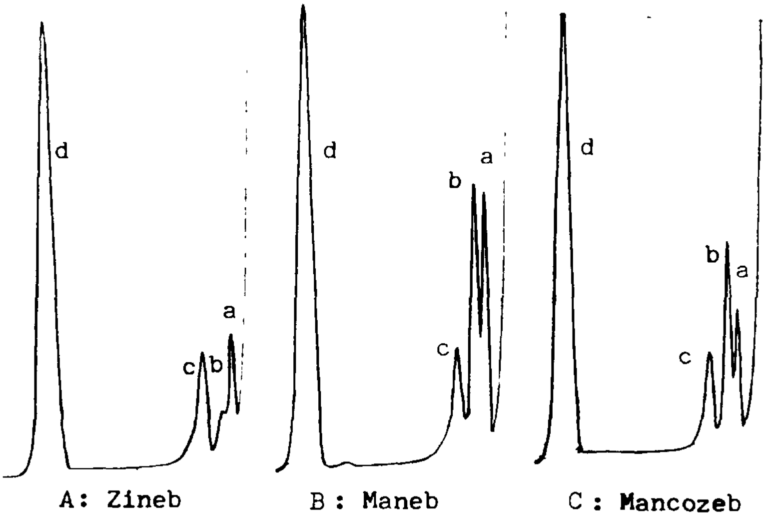


Fig. 4. Chromatograms of the gaseous products of decomposition from Zineb, Maneb and Mancozeb: a, COS; b, H_2S; c, H_2O; d, CS_2.

In Fig. 4A, there are four peaks, which were identified as (d) CS_2, (b)

TABLE 3

The products of Zineb decomposition for 15 min at 220°C

Sample size (mmol)	Weight loss (%)	Found (mmol)	Calc. (mmol)
0.100	29.1	0.098	0.100
0.106	28.3	0.106	0.106

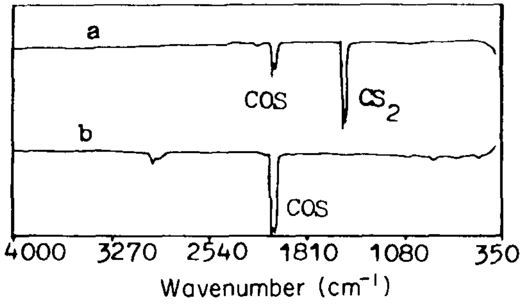


Fig. 5. Comparison of IR spectra: a, the gaseous products of decomposition of Zineb; b, COS standard.

H_2S, (c) H_2O and (a) COS, respectively. The amount of CS_2 evolved as measured by GC was in agreement with that calculated for elimination of one mole of carbon disulphide from Zineb, and with the weight loss at the first stage in the TG test. The product (COS) was identified by comparison with a standard sample and also by the IR spectrum (see Fig. 5).

The weight loss (16.5%) of the second stage of the TG curve was in agreement with that (18.5%) calculated for the loss of one mole of ETU from two moles of Zineb. The residues from Zineb decomposition up to positions B and C on the TG curve (Fig. 3), were identified by HPLC (Fig. 6).

The contents of ETU in the residues at positions B and C were 16.4% and zero respectively, which is consistent with two moles of Zineb decomposing to form one mole of ETU at the first stage, and the sublimation of ETU at the second stage. The product ETU was also

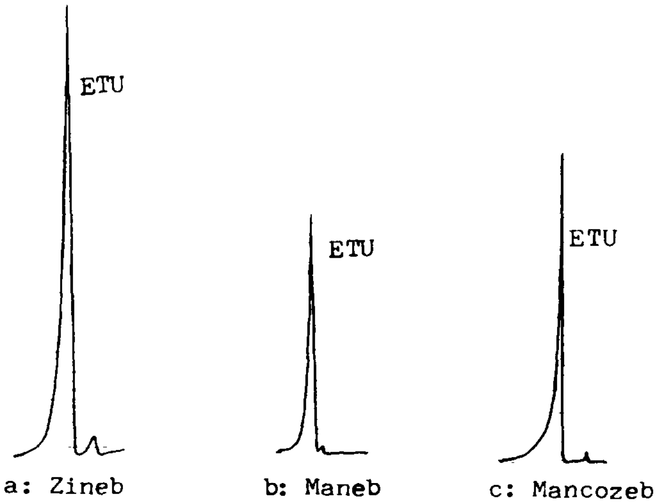


Fig. 6. HPLC spectra of ETU evolved from Zineb, Maneb and Mancozeb.

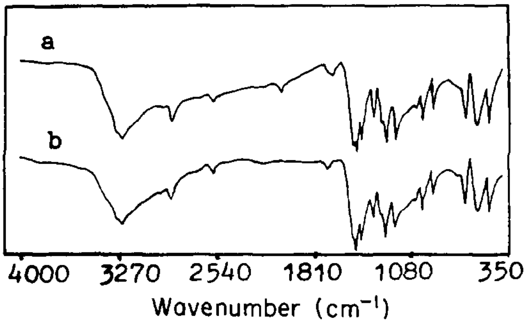


Fig. 7. Comparison of IR spectra: a, ETU separated from residue; b, ETU standard.

identified by preparing a sample and comparing the IR spectra (see Fig. 7). In addition, the relatively strong band at about 2080 cm^{-1} in the IR spectrum of the residue at position B on the TG curve indicated that another product is formed at the first stage (see Fig. 8). Although this product could not be separated by TLC, it could be a coordinate compound of zinc with the isothiocyanic group –N=C=S, because the band at 2080 cm^{-1} is attributable to conjugated double bonds and appears in the IR spectra of some analogous compounds [9]. The formation of gaseous product COS was also considered to be the result of the reaction of the –N=C=S group with H_2O.

The residues obtained at positions D and E on the TG curves were identified by IR as $ZnSO_4$ and ZnO, respectively. Their IR spectra are shown in Fig. 9. The percentage weight losses found for the third and fourth stages on the TG curve were consistent with those calculated for Zineb decomposing and forming these two products, respectively. In addition, X-ray diffraction analysis showed that ZnS was also formed in the third stage of Zineb decomposition (see Fig. 10).

On the basis of these results, a mechanism of the thermal decomposition of Zineb is postulated in Fig. 11.

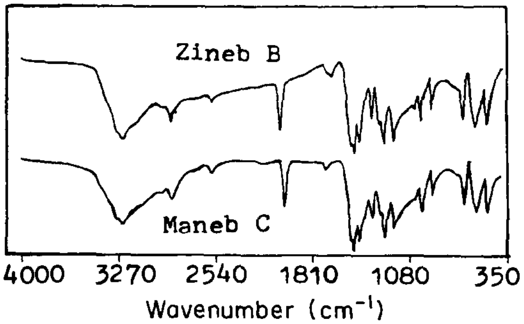


Fig. 8. IR spectra of the residues at positions B and C on the TG curves of Zineb and Maneb.

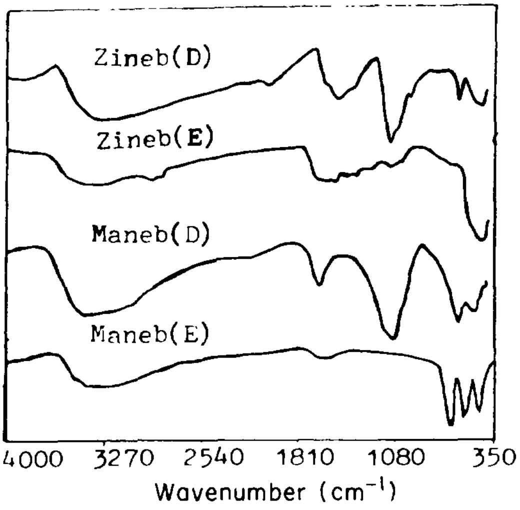


Fig. 9. IR spectra of the decomposition products obtained for both Zineb and Maneb at positions D and E on the TG curves.

The thermal decomposition of Maneb

The TG curves of Maneb are shown in Fig. 3. They consisted of four stages, similar to those obtained for Zineb decomposition, but the first stage involes two consecutive steps. The percentage weight losses for each stage are listed in Table 4. The weight losses in Table 4 are in agreement with those calculated for each stage.

The weight loss (14.0%) found by TG for the first stage was consistent

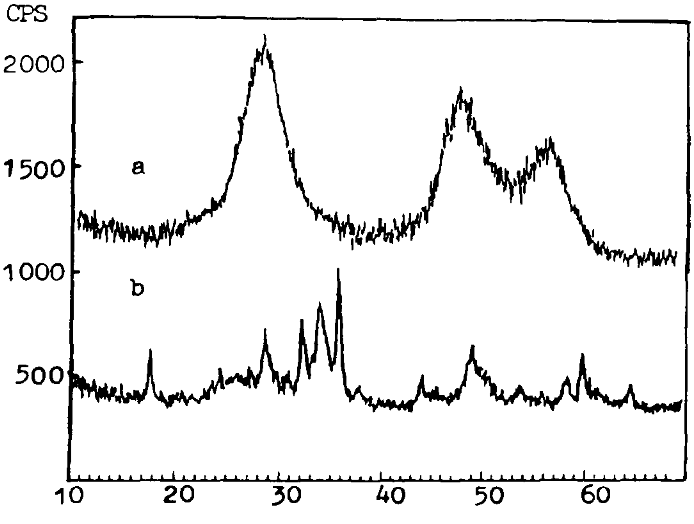


Fig. 10. X-Ray diffraction spectra of the products of decomposition: a, Zineb; b, Maneb.

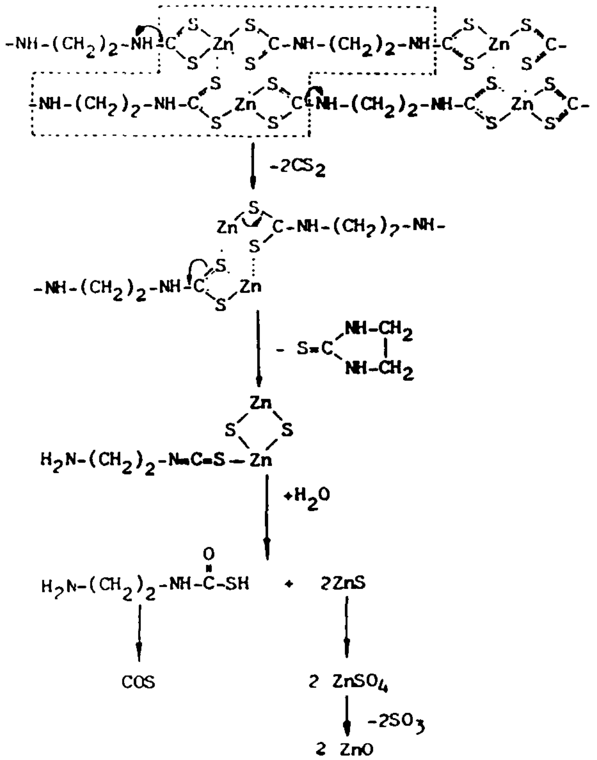


Fig. 11. A mechanism for the thermal decomposition of Zineb.

with the loss of one mole of CS_2 from two moles of Maneb (14.3%). Moreover, it was considered that both steps of the first stage were similar and Maneb continuously decomposed to split off one mole of CS_2 for every two moles of Maneb. This was supported by GC analysis, as shown in Table 5.

The products of the decomposition were identified and measured by GC, HPLC, IR and X-ray diffraction in a similar way to that for Zineb. In the first stage, HPLC (Fig. 6) showed that the 6.2% weight loss due to ETU was lower than that calculated (19.2%) for two molecules of Maneb splitting off

TABLE 4

Weight loss (%) obtained from TG-DTG of Maneb

	Stage 1		Stage 2	Stage 3	Stage 4
	Step 1	Step 2			
Found	14.0	30.0	44.0	53.7	72.5
Calc.	14.3	28.7	44.7	54.0	73.3

TABLE 5

The products of Maneb decomposition (15 min at 220°C)

Sample size (mmol)	Weight loss (%)	CS_2 (mmol)		H_2S (mmol) Found
		Found	Calc.	
0.097	32.1	0.110	0.097	0.041
0.101	32.0	0.108	0.101	0.036

one molecule of ETU. Figure 4B shows that considerable quantities of H_2S are present in the gaseous products from Maneb decomposition. This indicates that two decomposition routes are followed after the loss of CS_2. Like CS_2, ETU was formed in a similar fashion to its formation in Zineb, but H_2S was formed by a different mechanism. It was also found from the analyses that the second stage involved sublimation of ETU and the splitting off of H_2S; the third stage involved the formation of $MnSO_4$; and the fourth stage involved the decomposition of $MnSO_4$ to Mn_3O_4 (Fig. 9). X-ray diffraction studies showed that the third stage was the oxidation of MnS to $MnSO_4$ (Fig. 10). In addition, a coordination compound with the -N=C=S group was also present in the residue of the partial decomposition of Maneb (Fig. 8).

Therefore, on the basis of the above results, a mechanism for the thermal decomposition of Maneb is postulated in Fig. 12.

Thermal decomposition of Mancozeb

The TG curve obtained from Mancozeb is shown in Fig. 3. It also consisted of four stages, similar to those of Zineb and Maneb. The first stage was complicated and consisted of three steps of weight loss as denoted by the DTG curve — the second peak of the DTG curve overlapped the first. The weight loss corresponding to the first peak of the DTG curve increased in line with the zinc ion content of the Mancozeb. Moreover, the percentage weight loss corresponding to several stages of the Mancozeb decomposition is dependent on the zinc ion content. For example, the percentage weight losses corresponding to several stages of sample D-2 (containing 2.96% Zn) decomposition in the TG are shown in Table 6.

It can be seen from Table 6 that the percentage weight loss for the first peak of the DTG curve is in approximate agreement with that calculated according to the zinc ion content in Mancozeb. In addition, analysis with IR spectroscopy showed that the residue of Mancozeb decomposition at the end of the first peak of the DTG curve was mainly Maneb (see Fig. 13). These results showed that the first step in Mancozeb decomposition was elimination of one mole of CS_2 from the ethylenebisdithiocarbamic group

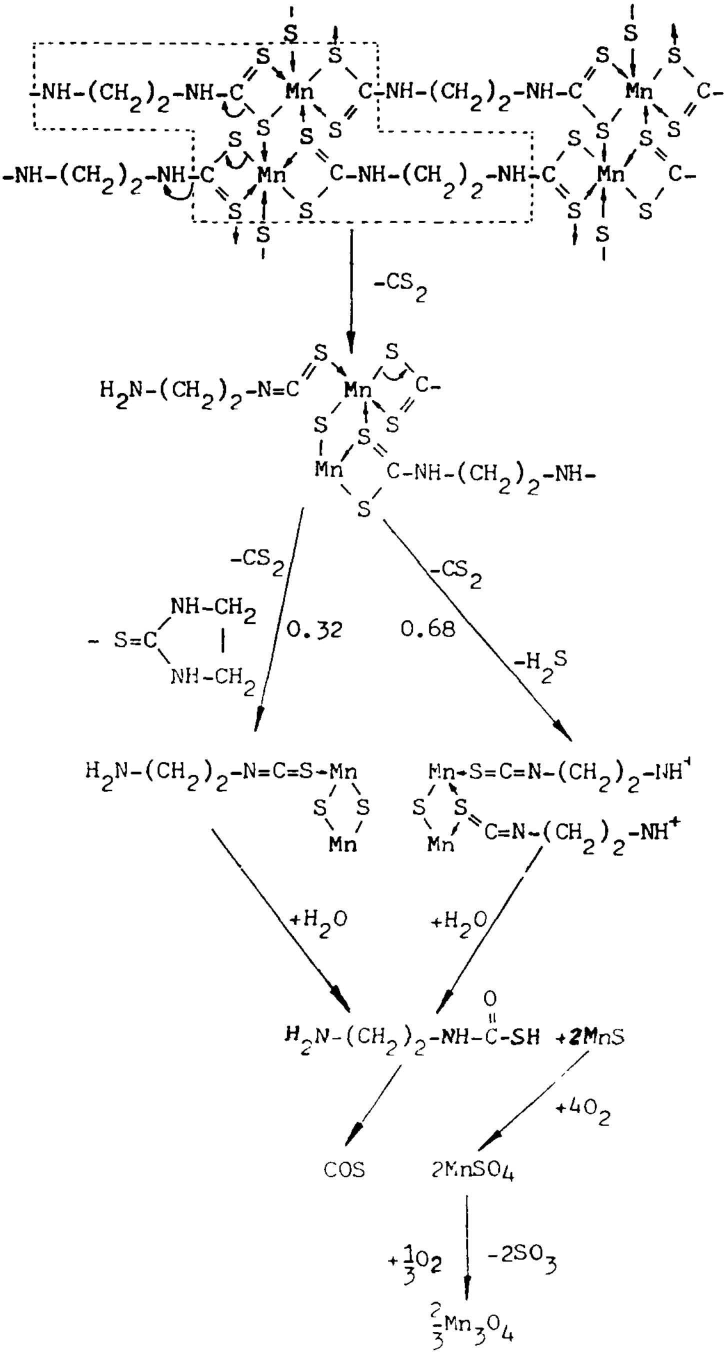


Fig. 12. A mechanism for the thermal decomposition of Maneb.

TABLE 6

Weight loss (%) obtained from TG–DTG of Mancozeb (sample D-2)

	Stage 1			Stage 2	Stage 3	Stage 4
	Step 1	Step 2	Step 3			
Found	3.5	13.0	29.0	43.2	55.0	71.8
Calc. [a]	3.8	14.2	28.7	44.6	53.9	73.2

[a] These values are the sums of calculated weight losses of every decomposition stage (steps) of Maneb with Zineb according to zinc ion content (2.96% Zn) in Mancozeb (sample D-2).

attached to the zinc ion in Mancozeb. The percentage weight loss measured after the first stage involves three steps in the TG test and corresponds to elimination of one mole of CS_2 from one mole of Mancozeb. This is supported by the GC data in Table 7. The quantities of ETU and H_2S formed from Mancozeb were intermediate between those of Zineb and Maneb. The formation of $MnSO_4$ and a small quantity of $ZnSO_4$ in the third stage, and of Mn_3O_4 with a small quantity of ZnO in the fourth stage were identified by IR analysis. A compound with the $-N{=}C{=}S$ group was also found in the solid residue of the partial decomposition of Mancozeb. Moreover, the percentage weight losses measured from several stages in the

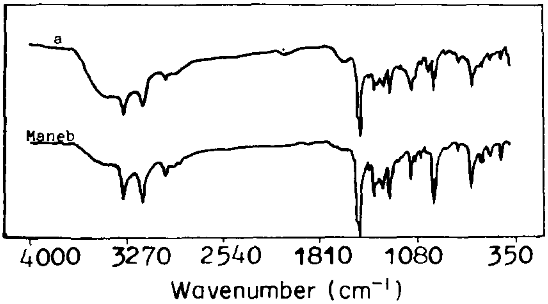


Fig. 13. Comparison of IR spectra: the residue of Mancozeb decomposition after the first DTG peak; and Maneb.

TABLE 7

The products of Mancozeb decomposition for 15 min at 220°C

Sample size (mmol)	Weight loss (%)	CS_2 (mmol)		H_2S (mmol) Found
		Found	Calc.[a]	
0.115	31.2	0.100	0.115	0.034
0.104	31.5	0.095	0.104	0.029

[a] See footnote a of Table 6.

TG test were consistent with those calculated according to the formation of above mentioned products in the respective stages.

The thermal decomposition of Mancozeb can be considered to be a combination of the decomposition of both Maneb and Zineb.

REFERENCES

1 C.G. Sceney, J.F. Smith, J.O. Hill and R.J. Magee, J. Therm. Anal., 9 (1976) 415.
2 G. D'Ascenzo and T. Bica, Thermochim. Acta, 18 (1977) 301.
3 M. Lalia-Kantouri, A.G. Christofides and G.E. Manoussakis, J. Therm. Anal., 29 (1984) 279.
4 J.W. Hylin, Bull. Environ. Contam. Toxicol., 10(4) (1973) 227.
5 Yu.S. Lyalikov and M.I. Kitovskaya, J. Therm. Anal., 4 (1972) 271.
6 Yu.S. Lyalikov and M.I. Kitovskaya, J. Therm. Anal., 7 (1975) 301.
7 F.R. Day and D.J. Hamilton, J. Therm. Anal., 29 (1984) 317.
8 F. Bonati and R. Ugo, J. Organomet. Chem., 10 (1967) 257.
9 Q.T. Liu, Coordination Chemistry, University of Liao-Ning, 1988, p. 14.