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The thermal behaviour of the ethylenebis-dithiocarbamates Maneb, Zineb and Mancozeb. Part 3. Thermal stability of Maneb, Zineb and Mancozeb

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Abstract

In this paper, the thermal stability and decomposition characteristics of Mancozeb containing different zinc ion contents have been investigated by means of thermal analysis, ESCA and FT-IR spectroscopy incorporating a photoacoustic cell. It was found that the thermal stability of Mancozeb was improved by having the zinc ion content within certain limits.

INTRODUCTION

The thermal stability of metal dithiocarbamates is influenced by temperature, humidity, available oxygen and the pH of the system. Hylin [1] analysed the gases CS_2 and H_2S produced on decomposition and found that these were evolved considerably more rapidly from solutions and suspensions than from moist soil. He passed a stream of moist air through the sample tubes and trapped the volatile decomposition products. If nitrogen was substituted for air as the carrier gas, virtually no CS_2 was evolved. A similar result was obtained by Marshall [2] in studying the kinetics of thermal decomposition of Nabam in aqueous media. He found a change in the mechanism of the decomposition of Nabam in solution of pH about 6, and that the rate was accelerated by the presence of oxygen in the air. Marshall also found that the rates of decomposition of metal dithiocarbamates to CS_2 and H_2S were affected by temperature and the nature of the atmospheric gas. At low temperatures, the rate constant of

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decomposition in air was higher than that found in nitrogen, but the effect of the atmospheric gas gradually decreased as the temperature increased.

The influence of metal ions on the thermal stability of Maneb has been reported extensively in the literatures [3–9]. Maneb is more stable to heat and moisture and causes less damage to plants when it contains 0.5–5.0% of Zn^{2+}, Fe^{2+}, Cu^{2+} or another heavy metal ion. By investigating three types of metal dithiocarbamate at elevated temperature and humidity, Bontoyan and Looker [10] found that the rate and amount of ethylene thiourea (ETU) formed from the decomposition of the Maneb was greatest in the absence of zinc, that Zineb degraded less rapidly and at a steadier rate than Maneb containing little or no zinc, and that Mancozeb degraded very slowly with the formation of a very small amount of ETU. The results showed that the thermal stability of Mancozeb was improved by containing zinc ion. However, they only studied Mancozeb containing 1.0% zinc ion and did not investigate the influence of greater amounts.

In this paper, as an extension of the investigation of the mechanism of the thermal decomposition of Maneb, Zineb and Mancozeb [11, 12], the influence of zinc ion content in the range 1.66–9.0% on the thermal stability of solid Mancozeb and its decomposition characteristics have been investigated in more detail.

EXPERIMENTAL

Apparatus

The thermal analyses were carried out on a Perkin-Elmer differential scanning calorimeter, model DSC-2C, and a thermogravimetric analyser, model TGS-2, with sample mass of about 2 mg and Al pans. The measurements were performed in a dynamic atmosphere of nitrogen with a flow rate of 40.0 cm^3 min^{-1}.

In addition, a Nicolet FT-IR spectrometer, model 60 SXR, with a photoacoustic cell and an electronic spectroscopy for chemical analysis (ESCA) apparatus, model PHI-5400, were used to study the structure and characterize the surface of Mancozeb.

Samples

The Mancozeb samples used, containing various quantities of zinc ion, are listed in Table 1.

RESULTS AND DISCUSSION

Thermal stability of Mancozeb

DSC and TG–DTG analyses of Maneb, Zineb and the five Mancozeb samples containing various amounts of zinc ion are shown in Figs. 1 and 2

TABLE 1

The zinc ion content (wt.% Zn) of Mancozeb samples

Sample No.				
D-1	D-2	D-3	D-4	D-5
1.66	2.96	4.29	7.80	9.00

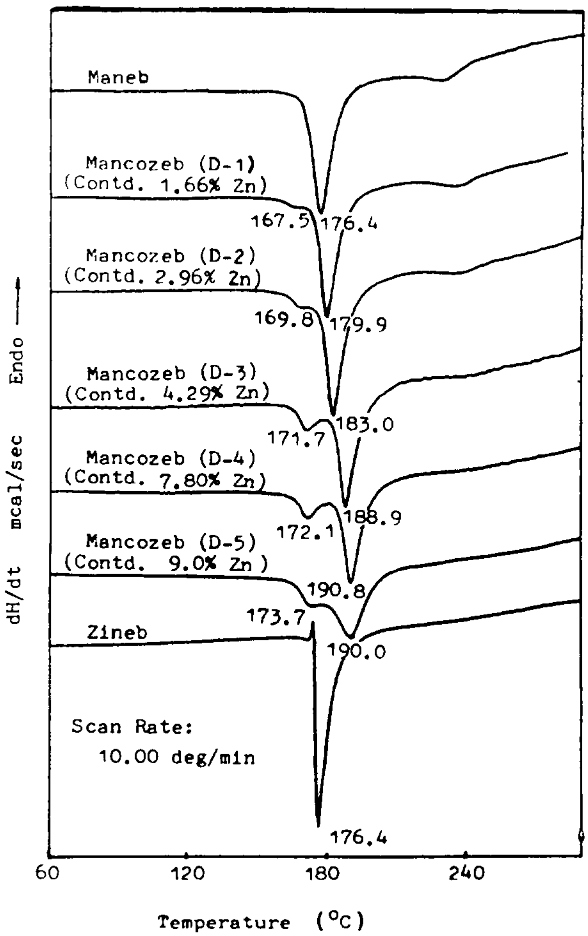

Fig. 1. The DSC analysis of Maneb, Zineb and the five samples of Mancozeb.

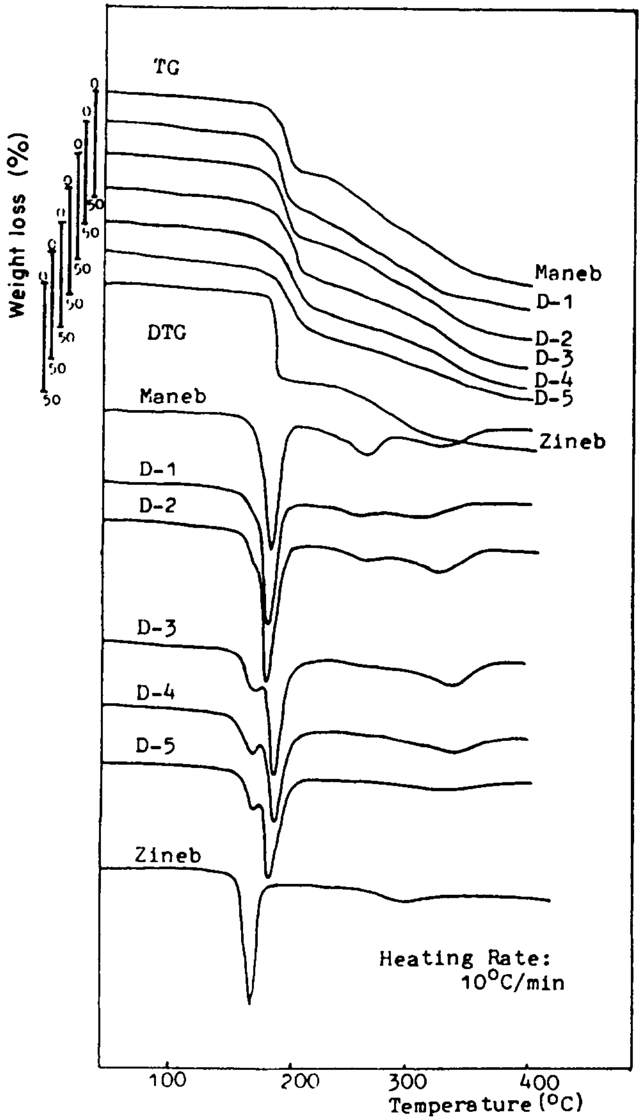

Fig. 2. The TG–DTG analysis of Maneb, Zineb and the five samples of Mancozeb.

and Table 2. From previous studies on the mechanism of the thermal decomposition of Mancozeb, the first and second decomposition peaks correspond to the decomposition of the ethylenebisdithiocarbamic group linked with Zn^{2+} and Mn^{2+}, respectively [11].

From Fig. 1 and Table 2 it can be seen that the peak temperatures T_{m_2} corresponding to Maneb in the DSC and DTG analyses of Mancozeb were increased with increasing zinc content, starting from 176.4°C in DSC and 178.0°C in DTG of Maneb, to 190.8°C in DSC and 193.0°C in DTG for D-4; however, there is a limit to the increase. For a given grain size of solid

TABLE 2

Peak temperatures T_{m_1} and T_{m_2} in °C from TG–DTG

	Sample						
	Zineb	Maneb	D-1	D-2	D-3	D-4	D-5
T_{m_1}	178.0	178.0	170.0	173.0	174.0	174.5	175.5
T_{m_2}	–	–	182.0	185.0	190.0	193.0	192.0

TABLE 3

The peak temperatures T_{m_1} and T_{m_2} in °C of Mancozeb and the mechanically mixed sample of Maneb and Zineb in DSC and TG–DTG

Wt.% Zn		DSC		TG–DTG	
		Mixed sample	Mancozeb	Mixed sample	Mancozeb
2.96	T_{m_1}	160.9	169.8	162.0	173.0
	T_{m_2}	170.0	183.0	178.5	185.0
7.80	T_{m_1}	161.6	172.1	163.0	174.5
	T_{m_2}	168.7	190.8	180.0	193.0

Mancozeb, as the zinc ion content increased so the peak temperatures T_{m_2} reached a limit (e.g. D-5). Therefore, the thermal stability of Mancozeb could only be improved within certain limits.

It can also be seen from the data shown in Table 3 that all the peak temperatures of the mixtures of Maneb and Zineb are lower than those of Mancozeb containing the same zinc ion content. Therefore, the thermal stability of Mancozeb was better than that of the mechanically mixed sample. The peak temperatures from DSC and DTG measurements of the mechanically mixed samples did not increase with zinc ion content, and the DSC and TG–DTG analyses were a combination of Zineb with Maneb only. IR spectra of the mechanically mixed samples of Maneb and Zineb indicate that they are mixtures and not compounds [11].

The kinetic parameters of thermal decomposition

The decomposition peak temperatures obtained at various heating rates ϕ (2.5–40 K min^{-1}) were used. In the DSC analysis, the activation energy was determined from plots of $\ln(\phi/T_m^2)$ vs. $1/T_m$, using Kissinger's equation [13]

$$\ln(\phi/T_m^2) = \ln(AR/\Delta E_a) - \Delta E_a/RT_m$$

TABLE 4

The kinetic parameters of the thermal decomposition

Sample	ΔE_a (kJ mol^{-1})	lg A (s^{-1})	r	K(s^{-1})		
				20°C	100°C	150°C
Maneb	116.4	13.3	0.9948	35.2×10^{-9}	10.0×10^{-4}	8.4×10^{-2}
Zineb	127.0	14.6	0.9966	9.1×10^{-9}	6.5×10^{-4}	8.2×10^{-2}
D-1	126.1	14.4	0.9986	8.3×10^{-9}	5.5×10^{-4}	6.2×10^{-2}
D-2	126.6	14.3	0.9963	5.2×10^{-9}	3.7×10^{-4}	4.6×10^{-2}
D-3	130.5	14.6	0.9959	2.2×10^{-9}	2.1×10^{-4}	3.1×10^{-2}
D-4	135.8	15.1	0.9964	0.8×10^{-9}	1.2×10^{-4}	2.1×10^{-2}
D-5	130.8	14.6	0.9975	1.9×10^{-9}	1.9×10^{-4}	2.8×10^{-2}

where ΔE_a is the activation energy and A is the pre-exponential factor. These parameters and the correlation coefficients r obtained by regression analysis are listed in Table 4.

According to the Arrhenius equation, the rate constant K is calculated from ΔE_a and A. It can be seen from Table 4 that the K values for the samples D-1–D-5 are lower than those of Maneb at each temperature, indicating that the thermal stability of Maneb is less than that of Mancozeb. Similarly, the thermal stability of Zineb is better than that of Maneb, so Zineb should stabilize Maneb, and has been considered as a protecting agent.

The characteristics of the thermal decomposition of Mancozeb

The structure at the surface and at various depths into the solid sample was identified using FT-IR spectroscopy with a photoacoustic cell. The photoacoustic spectra of D-2 and D-4 are shown in Fig. 3 as a function of depth into the solid Mancozeb. Relatively shallow absorption bands at 1022 and 955 cm^{-1} characteristic of Mancozeb appear in the spectra of the surface layer, but as the depth increases the spectra change on the whole to that of Maneb. The interior of the Mancozeb grains is essentially Maneb. In addition, ESCA shows that the ratio Zn/Mn on the surface of Mancozeb grains (1.81) was higher than that in ground Mancozeb (0.97), and higher than that determined by atomic absorption spectroscopy (0.51). The grain breaks up on grinding, so the ratio Zn/Mn for the sample of Mancozeb is lower in ESCA. This was interpreted as indicating that the zinc ions in Mancozeb appear on the surface of the grain, and that substitution of manganese ions occurs only on the surface layer. From thermal stability studies and the decomposition mechanism suggested in a previous work [11], we consider that the ethylenebisdithiocarbamic group attached to zinc

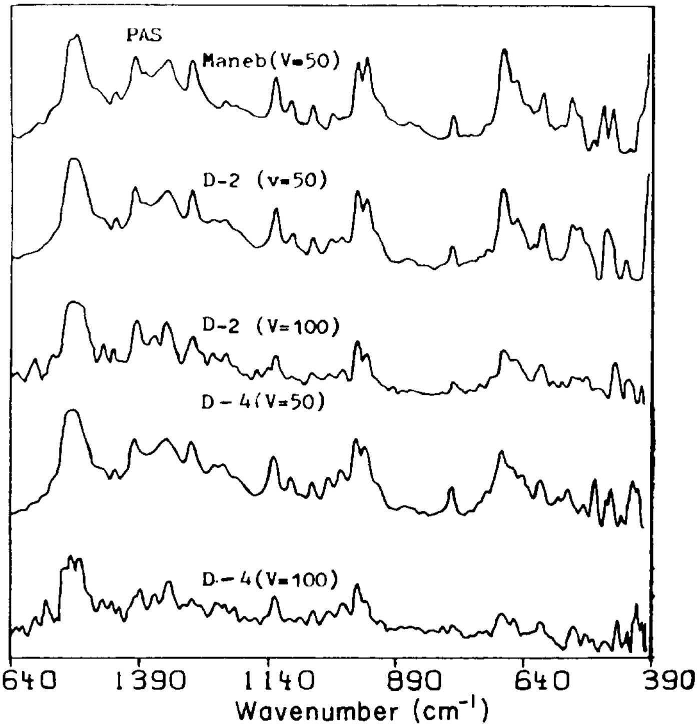

Fig. 3. The photoacoustic spectra of D-2 and D-4; V is the velocity of the moving mirror in cm s^{-1}.

ions in Mancozeb decomposed first and therefore it seems that the zinc ion or Zineb acts as a protective agent during the thermal decomposition of Maneb. Thus, it was considered that the thermal stability of Mancozeb was improved by zinc ions, and that it was more effective in a certain concentration range. However, once the surface layer was completely covered by Zineb or zinc ions, the peak temperature T_{m_2} of Mancozeb could not be further increased by more zinc ions, and the stability could not be further improved.

This behaviour was explained by the characteristics of the solid state thermal decomposition. On the surface of the crystal or grain there are some defects or small cracks, which might form many potential reaction centres (nuclei). Decomposition begins at these centres and consequently more reaction centres are formed on the surface. Similarly, the decomposition begins on the surface of Mancozeb (which is Zineb). The condensed phase products, which have higher thermal stability, form at the surface of the grain and act as a deactivator so Mancozeb or Maneb thereby lose activity and are prevented from decomposing. As the temperature is increased, the deactivation is lost, and decomposition occurs from the inside of the grains (which is Maneb). Therefore, Mancozeb containing zinc ions or Zineb has a higher thermal stability than Maneb which has no zinc ions.

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