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The thermal behaviour of the ethylenebis-dithiocarbamates Maneb, Zineb and Mancozeb. Part 2. Heat changes associated with the thermal decomposition of Maneb and Zineb

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Abstract

An investigation of the heat changes on thermal decomposition of Maneb and Zineb has been carried out using DSC. It has been shown that both endothermic and exothermic processes are present in their initial decomposition. Significant differences occur between the heat changes observed which are atmosphere dependent (nitrogen and air) and gas flow rate dependent.

INTRODUCTION

In a previous paper [1] we proposed a mechanism for the thermal decomposition of Maneb and Zineb. It was shown that the decomposition processes consisted of four stages. In the first stage, carbon disulphide was lost. However, there is some disagreement in the literature of the heat changes associated with the first stage of the dithiocarbamate decomposition process. Sceney et al. [2] studied the thermal decomposition of $Cu(Et_2Dtc)_2$ and $Cu(Me_2Dtc)_2$ (where Dtc is dithiocarbamate) in nitrogen and air atmospheres using DTA and TG, and found an endothermic peak. However, D'Ascenzo and Bica [3] found that the thermal decomposition of $AgEt_2Dtc$ and $Au(Et_2Dtc)_3$ in nitrogen atmosphere were endothermic reactions, but exothermic in air. Using DTA, Lalia-Kantouri et al. [4] also studied the decomposition of dithiocarbamates such as $M(S_2CN(CH_2)_5)_3$ (where M is As, Sb and Bi), but the results obtained were similar to those obtained by D'Ascenzo and Bica [3]. It was considered that the thermal

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decomposition of the dithiocarbamate complexes follows the general rule that decomposition in nitrogen is endothermic but decomposition in air is exothermic. It was considered that the thermal decomposition reactions of both Maneb and Zineb (which are also dithiocarbamates) behaved in the same way as the above complexes [5–8].

EXPERIMENTAL

This work was performed with a Perkin-Elmer differential scanning calorimeter, model DSC-2C, using an Al cell. Sample size was about 2 mg.

RESULTS AND DISCUSSION

The DSC analysis of the first stage of the decomposition of Maneb and Zineb in nitrogen and air atmospheres at various flow rates are shown in Figs. 1–4 and Table 1. It can be seen from the DSC thermograms that endothermic and exothermic processes appear almost simultaneously in the first decomposition stage of Maneb and Zineb, and that the exotherms are far larger than the endotherms. As can be seen, both the atmosphere and the gas flow rate influence the heat changes observed. Under high flow rates of nitrogen, the endotherm dominates, and no exothermic process was observed for Maneb with nitrogen flow rates higher than 40.0 $cm^3 min^{-1}$. On decreasing the flow rate, the endotherm gradually decreases and the

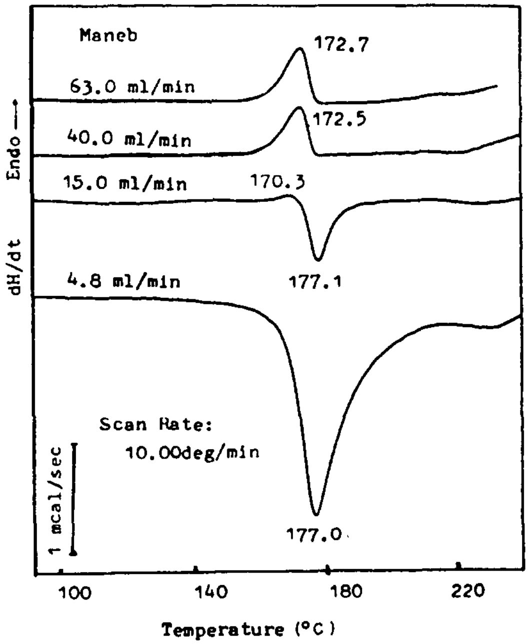

Fig. 1. DSC analysis of Maneb in a nitrogen atmosphere at various gas flow rates.

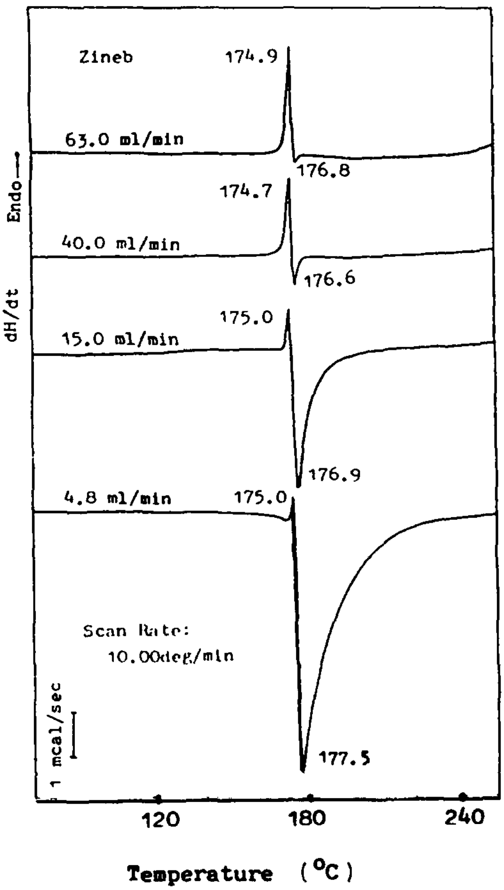

Fig. 2. DSC analysis of Zineb in a nitrogen atmosphere at various gas flow rates.

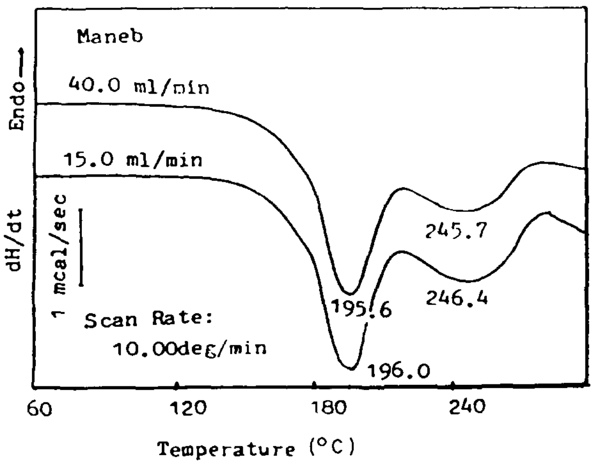

Fig. 3. DSC analysis of Maneb in air at gas flow rates of 40.0 and 15.0 cm^3 min^{-1}.

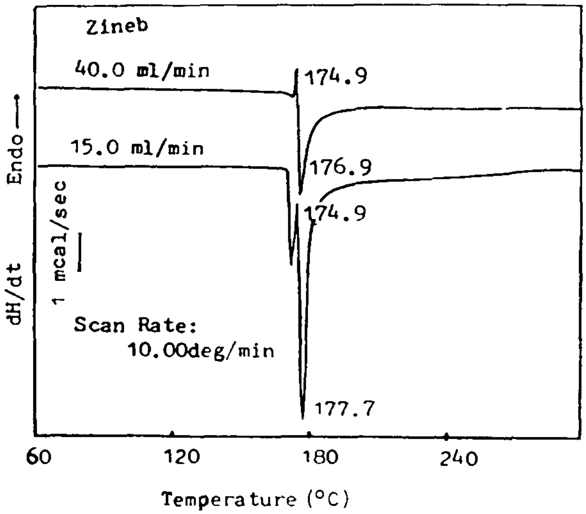

Fig. 4. DSC analysis of Zineb in air at gas flow rates of 40.0 and 15.0 $cm^3 min^{-1}$.

TABLE 1

DSC peak temperatures and apparent enthalpy changes on the decomposition of Maneb and Zineb at various flow rates of nitrogen and air

Flow rate ($cm^3 min^{-1}$)	Atmosphere							
	Nitrogen				Air			
	Maneb		Zineb		Maneb		Zineb	
	Peak temp. (°C)	Heat change ($J g^{-1}$)	Peak temp. (°C)	Heat change ($J g^{-1}$)	Peak temp. (°C)	Heat change ($J g^{-1}$)	Peak temp. (°C)	Heat change ($J g^{-1}$)
Endothermic								
4.8	–	–	175.0	14.5	–	–	–	–
15.0	170.3	6.9	175.0	18.5	–	–	174.9	–
40.0	172.5	96.0	174.7	59.3	–	–	174.9	10.4
63.0	172.7	113.1	174.9	78.4	–	–	–	–
Exothermic								
4.8	177.0	477.9	177.5	1252.4	–	–	–	–
15.0	177.1	100.8	176.9	237.6	196.0	1770.0	177.7	966.3
40.0	–	–	176.6	15.4	195.6	1599.9	176.9	310.9
63.0	–	–	176.8	4.1	–	–	–	–

exotherm increases rapidly, while the endotherm of Maneb completely disappears.

It is known from the literature [5, 7, 8] that the process of splitting off carbon disulphide in the first stage of the decomposition is endothermic, whereas further decomposition or molecular rearrangement can be exothermic.

If Q_1 is the heat of the endothermic reaction, Q_2 is the heat of exothermic reaction, Q_3 is the enthalpy of sublimation of the products and Q_4 is the difference in the heats taken away by gas flow from the two cells of the DSC apparatus. Then at high flow rates, Q_4 increased, and $Q_1 + Q_3 + Q_4 > Q_2$. An apparent endothermic process occurs in the DSC analysis. When Q_4 decreases with decreasing flow rates, $Q_1 + Q_3 + Q_4 < Q_2$, and an exothermic process is apparent in the DSC analysis.

Therefore, the overall process, in which endothermic and exothermic effects are almost simultaneous or occurs in succession, significant differences in apparent heat changes occur with different gas flow rates.

However, the influence of the gas flow rates on the observed heat changes are related to the atmosphere and the sample.

At the same flow rate (40.0 $cm^3\ min^{-1}$) (see Fig. 5) in nitrogen the overall change is endothermic for Zineb. However, the heat change is reversed in air. The exothermic change in air is greater than in nitrogen. The apparent endothermic effect in air at a flow rate of 40.0 $cm^3\ min^{-1}$ is approximately equal to that in nitrogen at 15.0 $cm^3\ min^{-1}$. In addition, the larger exothermic effect occurs at the initial decomposition stage of Zineb in air and the endothermic effect is only superimposed on the exothermic.

Unlike Zineb, the exothermic and endothermic processes in Maneb in nitrogen simultaneously appeared in the DSC analysis only at a suitable flow rate (e.g. 15.0 $cm^3\ min^{-1}$). At lower flow rates of nitrogen, the

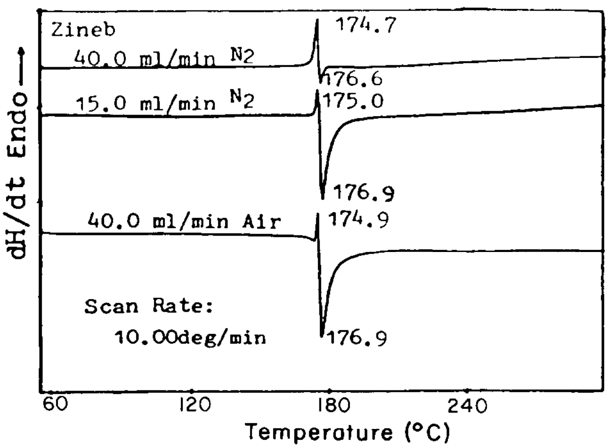

Fig. 5. DSC analysis of Zineb in air and nitrogen at various flow rates.

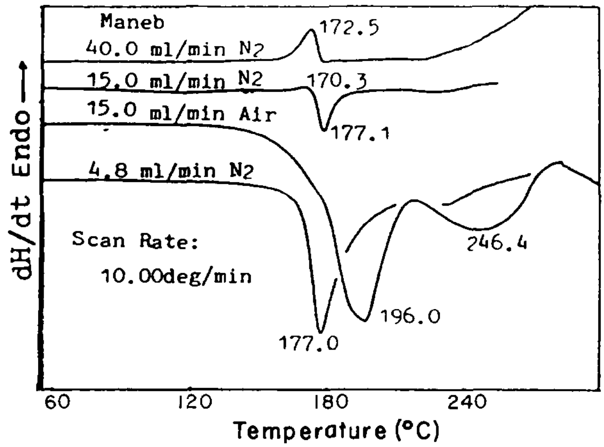

Fig. 6. DSC analysis of Maneb in air and nitrogen at various flow rates.

exothermic process is rapidly increased. When the flow rate is low enough (e.g. 4.8 $cm^3 min^{-1}$) the endothermic effect is removed (see Fig. 6). It can be seen from the DSC analysis that the endothermic process at the first stage of decomposition of Maneb is slower than that ot Zineb and is initially hidden by the exothermic decomposition. The process of losing carbon disulphide corresponds to the endothermic reaction and is conducted stepwise, whereas in Zineb it occurs in one step.

It can also be seen from Figs. 1–6 and Table 1 that both endothermic and exothermic peak temperatures of these two complexes are independent of the gas flow rates and essentially constant, those of Zineb also being independent of the atmosphere. The initial decomposition temperature of Maneb in air are greatly decreased compared with that in nitrogen, whereas those of Zineb do not significantly change. This fact indicates that the thermal decomposition of Maneb is accelerated and is exothermic process accelerated in air or oxygen gas (see Table 2).

TABLE 2

Initial decomposition temperatures (°C) obtained by DSC for Maneb and Zineb

Flow rate ($cm^3 min^{-1}$)	Atmosphere			
	Nitrogen		Air	
	Maneb	Zineb	Maneb	Zineb
4.8	–	169.2	–	–
15.0	159.2	170.1	116.0	168.3
40.0	155.1	169.0	118.0	169.3
63.0	153.5	168.0	–	–

Therefore, Maneb and Zineb must be packed in sealed containers, preferably under nitrogen gas, to prevent loss of fungicide activity and to prevent self-ignition due to partial decomposition during storage and transport.

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