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ETHYLENEBISDITHIOCARBAMATE FUNGICIDES

Differential thermal analysis

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DTA curves were run for the ethylenebisdithiocarbamate fungicides maneb, mancozeb and zineb in a nitrogen atmosphere. Zineb produces a curve quite different from the others, with weak endothermic peaks at 166°C, 252°C and 293°C. Maneb and mancozeb have a relatively strong endothermic peak at 185–190°C corresponding to carbon disulphide evolution and a weaker endothermic peak at 290°C corresponding to hydrogen sulphide evolution.

Maneb samples and some mancozeb samples also had a minor endothermic peak at 235°C, but this peak was lost after solvent extraction, which proved that it was due to an impurity or impurities. Elemental sulphur was found in the extract and on mixing sulphur with mancozeb, the peak at 235°C made its appearance.

There is no distinguishing feature between the DTA curves for maneb and mancozeb. The shapes of the curves are, within experimental limits, indistinguishable, which means that the temperatures and energies of decomposition are the same.

The chemist is left with the question whether differences in structure between maneb and mancozeb should lead to different DTA curves.

The characterization and identification of the ethylenebisdithiocarbamate fungicides has been a long-standing problem. The Pesticides Analysis Advisory Committee Dithiocarbamates Panel has conducted a number of collaborative tests and has produced MT-130 [2] involving colour reactions. Riassetto [8] has also proposed some colour reactions to solve the problem. The main difficulty is to distinguish mancozeb from maneb or, in reality, from maneb containing a quantity of zinc compounds.

We have examined the problem a number of times and have tried infra-red spectrophotometry and X-ray powder patterns without finding substantial differences which could distinguish maneb from mancozeb.

Lyalikov and Kitovskaya [6] have reported thermogravimetric and differential thermal analysis (DTA) studies on some dithiocarbamates, but did not include maneb or mancozeb. These studies were conducted in an atmosphere of air where the predominant reaction at higher temperatures is combustion.

Kennedy, Stojanovic and Shuman [5] used DTA of a number of pesticides to establish temperatures for complete combustion. Zineb was included in the study.

This paper reports the DTA curves for maneb, mancozeb and zineb in a nitrogen atmosphere.

Principles involved in identification

When a chemist tries to establish whether two samples consist of the same compound or are different, he sets up the hypothesis that the two are identical, and then goes through a series of tests to disprove the hypothesis. When he has done a sufficient number of sufficiently stringent tests which give the same results for the two samples the chemist accepts the hypothesis.

If the two samples are both perfectly pure, then the slightest experimentally detectable difference would be enough to disprove the hypothesis. In the practical situation, samples are never perfectly pure, and in some cases are quite impure and very difficult to purify. Then if two samples give differences in the tests, the chemist has to judge whether the differences are attributable to impurities or whether they prove that the samples consist of different substances.

Entering into the chemist's judgement will also be the nature of the test. For example, a minor impurity would not be expected to have much influence on a boiling point or a chromatographic property such as an R_F value, but it could very well be the major or even sole contributor to a colour reaction.

A reaction which gives a colour with an impurity being taken as a test for the main component is well illustrated by the test for benzene prepared from coal tar [9].

In 1882, Victor Meyer was lecturing on benzene derivatives, and during the course of a lecture demonstrated the indophenin reaction (isatin, sulphuric acid) which was at that time held to be characteristic of benzene. To his surprise, not a trace of the characteristic blue colour made its appearance, although he had rehearsed the experiment just prior to the lecture. It happened that his assistant had handed him a sample of benzene which had been made in the lecture course by heating benzoic acid with lime while the rehearsal had been made with the ordinary laboratory supply which was derived from coal tar. Meyer's first thought was that the reaction was caused by an isomeric form of benzene, but he went on to discover thiophene.

This shows the danger of using a colour reaction (or other reaction) in an empirical way for identifications. The reaction should be characterized and it should be clear that it is a reaction of the main component.

Perhaps some of the tests for distinguishing the dithiocarbamates depend on residual amounts of manganese and zinc compounds in the technical material. If different manufacturing processes are followed, it is quite likely that different sets of by-products, impurities or starting materials are present in products from different sources, even if the major component is the same. The chemist must be careful that identification tests do not depend on these different sets of impurities.

Properties of dithiocarbamates

The properties of the dithiocarbamates maneb, mancozeb and zineb present difficulties for chemists attempting their identification. Their insolubility and nonvolatility rule out chromatographic identification. For the same reasons, purification is difficult.

These three dithiocarbamates are usually represented as polymers of unknown chain lengths. The distribution of chain lengths may vary from batch to batch and from factory to factory, which would also be expected to influence some properties.

The Chemical Abstracts [3] names for these dithiocarbamates are:

Maneb:
[[1,2-ethanediylbis[carbamodithioato]](2−)]-manganese

Zineb:
[[1,2-ethanediylbis[carbamodithioato]](2−)]-zinc

Mancozeb:
[[1,2-ethanediylbis[carbamodithioato]](2−)]-manganese
mixt with
[[1,2-ethanediylbis[carbamodithioato]](2−)]-zinc

The Chemical Abstracts classification treats mancozeb as a mixture and, incidentally, treats Vondozeb as mancozeb.

Experimental

Instrument: Bureau de Liaison Modele M4 Micro Analyser. Thermique Differential.

Sample cup: Volume, 25 μL. Materials, platinum. Shape, truncated cone.

The sample cups are placed in platinum alloy receptacles forming the thermocouple junctions onto which (+) and (−) wires are directly soldered. The whole system is enclosed in a small chamber to ensure uniform heat distribution.

Sample atmosphere: Nitrogen gas at 2–3 cm^3/min. Sample weight: 0.02 g. Rate of temperature increase: 5–10 deg/min. Materials: Samples of maneb, mancozeb and zineb were obtained from the Dithiocarbamates PAAC panel and from pesticide companies. Formulation samples were received from the marketplace.

Results and discussion

DTA was considered a possibility for dithiocarbamate identification for the experimentally convenient reasons that it does not require test substances to be volatile or to be dissolved in a solvent.

The merit of the DTA curve is that all energy changes occurring in the sample during heating are clearly observable (provided sensitivity is adequate) and that the peak area reflects the energy involved (Mackenzie [7]). Slight differences in chemical composition or crystal structure are reflected in differences in either the temperature at which a reaction occurs or the heat of reaction, or usually both. Because of this, each substance gives a characteristic DTA curve which is peculiar to that substance

The effect of heating rate on the measured peak temperature is shown in Table 1. The temperature for phase transition in potassium nitrate is 127.7°, so it can be seen that fast heating rates produce an error in the measured peak temperature. Fast heating rates also have quite an effect on the measured peak temperature in a maneb decomposition (Table 1). Under the chosen operating conditions, the rate of temperature increase was close to 10 deg/min at 200°. Variations in this rate from run to run contribute to variations in measured peak temperature.

Table 1 Effect of heating rate on peak temperature

Potassium nitrate		Maneb	
Heating rate, deg min^{-1}	Peak temp., °C	Heating rate, deg min^{-1}	Peak temp., °C
4.6	127	4.3	181
11.0	130	9.9	192
17.6	133	17.2	198
25.8	136	28.7	206

Typical curves for maneb, mancozeb and zineb are shown in Fig. 1. (Table 2 – D, A, G). Zineb produces a curve quite different from the other two, the peaks being of a smaller area and the first peak at a lower temperature. DTA curves for commercial formulations of maneb and mancozeb are shown in Figs 2 and 3. All maneb samples examined, both technical and formulated, have given the typical 3-peak curve (Figs 1,

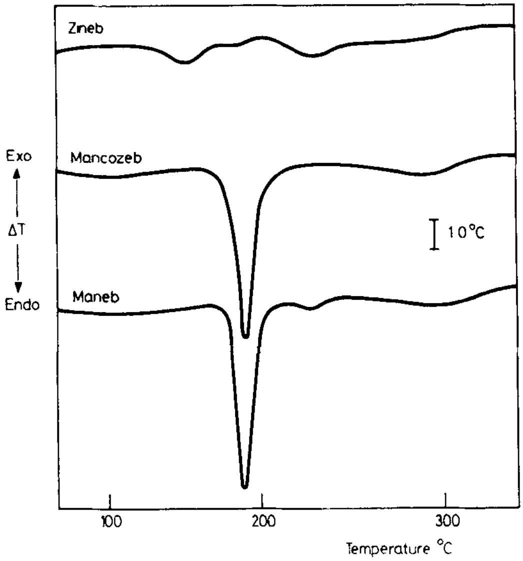

Fig. 1 DTA curves for zineb, mancozeb and maneb (PAAC technical sample)

2, 4). Mancozeb supplied by the Dithiocarbamate PAAC panel has given a 2-peak curve (Fig. 1). However, some formulations claiming to be mancozeb have produced curves very similar to that of maneb.

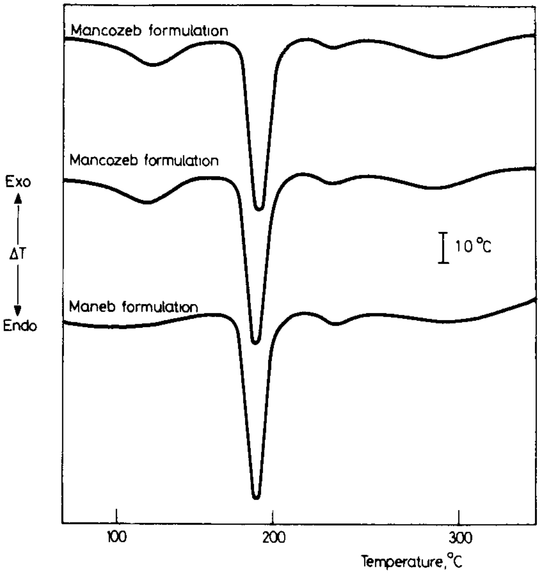

Fig. 2 DTA curves for commercial formulations of mancozeb and maneb

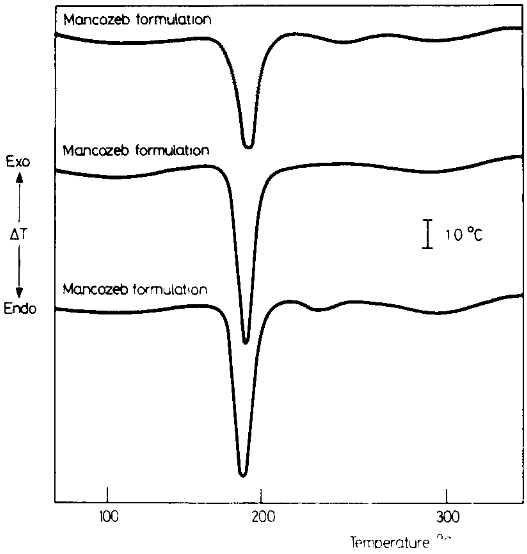

Fig. 3 DTA curves for commercial formulations of mancozeb

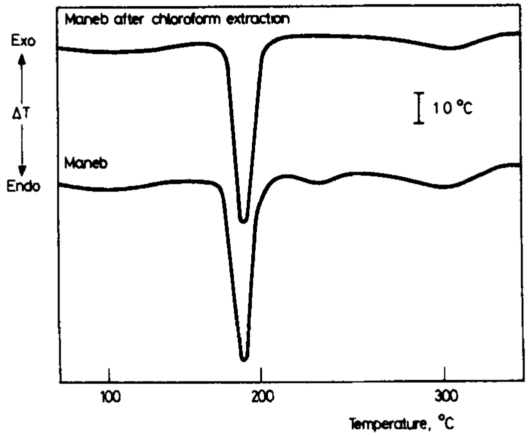

Fig. 4 DTA curves for a commercial maneb formulation before and after chloroform extraction

The temperature and relative areas of the peaks for some of the samples examined are shown in Table 2. These were obtained under the experimental conditions listed. It will be seen that the peak at approx. 235° is the critical one, appearing in all maneb samples, but not in all mancozeb samples. It amounts to only about 5% of the total area of a maneb DTA curve, so its presence as the result of an impurity could not be excluded.

With this thought, samples of maneb and mancozeb were exhaustively extracted (6 hours, Soxhlet) with acetone and chloroform to see if any changes were produced. If impurities present had slight solubility in those solvents, then any peaks due to the impurities should be reduced.

Two mancozeb samples after extraction with choloform or acetone had no changes in their DTA curves (Table 2 – A, B). On the other hand, the extraction of two maneb

Table 2 Dithiocarbamates – DTA peaks, temperatures and relative areas

		Peak 1		Peak 2		Peak 3	
		Temp., °C	Rel. area	Temp., °C	Rel. area	Temp., °C	Rel. area
Mancozeb tech (PAAC)	(A)	194	211	–	–	293	55
Mancozeb formulation	(B)	189	205	–	–	290	41
Mancozeb formulation	(C)	187	212	238	14	297	62
Maneb tech (PAAC)	(D)	186	199	233	14	293	55
Maneb formulation	(E)	189	230	238	24	295	70
Maneb formulation	(F)	184	207	233	11	290	58
Zineb tech (PAAC)	(G)	166	28	252	49	293	55

Note: Relative peak areas were determined by cutting from the chart, the area bounded by the peak and baseline and weighing.

samples (Table 2 – D, E) with either chloroform or acetone removed the peak at 235–240° and produced curves indistinguishable from mancozeb curves (Fig. 4). This was convincing evidence that an impurity or impurities were making a contribution. The extracts appeared to contain elemental sulphur, with extracts from the maneb samples containing the larger quantities. Elemental sulphur was identified in the extracts by thin-layer chromatography [4].

Precipitated sulphur was run on the DTA apparatus and endothermic peaks at 100°, 119°, 166° were the only responses in the temperature range of interest. However, when sulphur was mixed with mancozeb (PAAC technical) at the 5% and 10% levels, the peak at 235–240° made its appearance (Fig. 5). This suggested that elemental sulphur in the presence of the dithiocarbamate or the decomposed dithiocarbamate was the agent responsible for this peak. This is not the complete story, because in these synthetic mixtures, peaks in the region of the sulphur melting point were observed (110–120°) but these were not observed on the original maneb DTA curves.

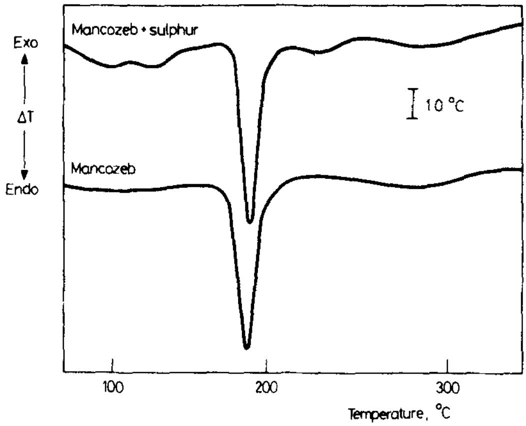

Fig. 5 DTA curve for mancozeb (PAAC technical) with added elemental sulphur (5%)

The question also arose – would storage of samples produce impurities which would make a significant contribution to the peaks? Samples of mancozeb and maneb were stored at 54° for 14 days according to CIPAC MT-46 [1]. The DTA curves after storage showed no observable changes.

The gases evolved during the decompositions were examined. During the peak at 190° carbon disulphide is evolved and during the peak at 290° hydrogen sulphide is produced. This is the case for both maneb and mancozeb.

A DTA curve for a maneb/zineb mixture in the ratio 8.6/1 was run. The Mn/Zn ratio of this mixture is the same as that for mancozeb. It was not experimentally distinguishable from a maneb curve allowing for the reproducibility of the method and equipment.

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Zusammenfassung – DTA-Kurven der Äthylen-bis(dithiocarbamat)-Fungicide Maneb, Mancozeb und Zineb wurden in Stickstoffatmosphäre aufgenommen. Die Kurve für Zineb unterscheidet sich mit schwach endothermen Peaks bei 166, 252 und 293°C deutlich von denen der anderen Substanzen. Maneb und Mancozeb zeigen einen verhältnismaßig stark endothermen, der Abspaltung von Schwefelkohlenstoff zuzuschreibenden Peak bei 185–190°C und einen schwächeren endothermen Peak bei 290°C, der durch die Freisetzung von Schwefelwasserstoff bedingt ist. Maneb-Proben und einige der Mancozeb-Proben zeigten einen geringen endothermen Effekt auch bei 235°C, der jedoch nach Lösungsmittelextraktion nicht mehr auftrat, was beweist, daß dieser Peak einer oder mehreren Verunreinigungen zuzuschreiben ist. Im Extrakt wurde elementarer Schwefel nachgewiesen, und Vermischung von Mancozeb mit Schwefel hat das Wiederauftreten des Peaks bei 235°C zur Folge. Maneb und Mancozeb unterscheiden sich nicht im Verlauf der DTA-Kurven, woraus folgt, daß die Zersetungstemperaturen und -energien gleich sind. Die Frage bleibt offen, ob Unterschiede in der Struktur von Maneb und Mancozeb zu unterschiedlichen DTA-Kurven führen sollten.

Резюме – В атмосфере азота были сняты кривые ДТА для этиленбисдитиокарбаматных фунгицидов манеб, манкозеб и цинеб. Последнее соединение дает кривую, полностью отличающуюся от других соединений, со слабыми эндотермическими пиками при 166°, 252° и 293°. Манеб и манкозеб дают относительно сильный эндотермический пик при 185–190°, соответствующий выделению сероуглерода, и ьолее слабый эндотермический пик при 290°, соответствующий выделению сероводорода. Образцы манеба и некоторые из образцов манкозеба показали главный эндотермический пик при 235°, который, однако, не проявлялся после экстракционной очистки этих веществ. Это свидельствовало, что появление этого пика обусловлено наличием примеси или же примесей. В экстракте была найдена элементарная сера. Смешивание ее с манкозебом приводило к появлению пика при 235°. Не наблюдалось каких-либо различий между кривыми ДТА манеба и манкозеба. В пределах экспериментальных ограничений, форма кривых для овоих соединений была неразличима, что означает близость температур и энергий разложения для обоих веществ.