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A THERMOGRAVIMETRIC STUDY OF SOME DITHIOCARBAMATE FUNGICIDES

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A series of dithiocarbamate-based fungicides was investigated by thermogravimetry and differential thermal analysis. The differences in the thermal decompositions of various dithiocarbamate derivatives were traced to differences in their structures. The characteristic sections of the thermogravimetric curves of the group of fungicides based on ethylene-bis-dithiocarbamates of bivalent metal ions were established. On the basis of the differences in the shapes of the T and TG curves some fungicides can be identified. A group-method was developed for the quantitative determination of the active ingredient in fungicides based on the ethylene-bis-dithiocarbamates of bivalent metals, the characteristic shape of the TG curve being utilized for analytical purposes.

Many biologically active dithiocarbamates are extensively used as fungicides and insecticides. However, analytical procedures described in the literature [1–4] for pesticides based on dithiocarbamates are unsatisfactory. They have the common deficiency that the effect of additives is not eliminated in the analytical procedure. The results are therefore inaccurate and usually substantially higher than the true values. The further study of dithiocarbamates was thus necessary.

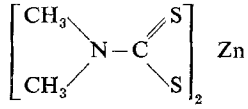
Several literature data can be found on the thermal investigations of pesticides of a dithiocarbamate type [5–7].

We earlier studied a fungicide based on zinc ethylene-bis-dithiocarbamate (Zineb) by means of chemical and thermogravimetric procedures. Based on the results of the chemical investigations, we developed a chemical phase analysis procedure for the determination of the biologically active constituent, zinc ethylene-bis-dithiocarbamate, in Zineb [8]. The thermogravimetric studies revealed that the weight loss of Zineb proceeds in steps, and that the weight loss at 160° is proportional to the content of the biologically active constituent, calculated from the results of the phase analysis of Zineb [9]. This allows the utilization of the TG curve of Zineb for analytical purposes, and the calculation of the active constituent content in the fungicide, which is a mixture of several constituents.

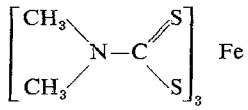
In the present work, we report the results of differential thermal analytical and thermogravimetric investigations of other dithiocarbamate-based fungicides. These are highly complex mixtures of various organic and inorganic compounds. The objective of our research was the development of a quantitative thermogravimetric procedure for the determination of the true content of biologically active

constituents in fungicides. The investigations were performed with a Paulik–Paulik–Erdey system Derivatograph. The investigated fungicides were:

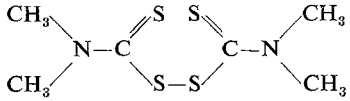
1. Ziram (active constituent: zinc dimethyldithiocarbamate)



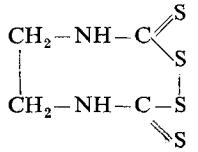
2. Ferbam (active constituent: iron dimethyldithiocarbamate)



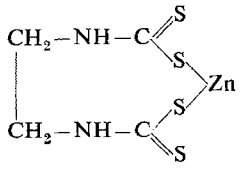
3. Tiram (active constituent: tetramethylthiuramdisulphide)



4. Polycarbazine (active constituent: ethylene-bis-thiuramdisulphide)



and zinc ethylene-bis-dithiocarbamate



in a ratio of 1 : 3.

Industrial products were used as samples.

Measuring conditions were: sample weight 100 mg, TG – 100, DTA – 1 : 5, T – 900°, heating rate 10°/min, reference material – Al_2O_3, platinum crucibles, Pt–Pt/Rh thermocouple, air atmosphere.

It can be seen from Fig. 1 that the TG curves of Ziram, Ferbam and Tiram do not proceed stepwise. The organic part of the main constituent and the organic additives are burnt away completely in the temperature range 270–320°. The great weight loss is accompanied by slight thermal effects – endothermic in the case of Tiram and Ziram and exothermic in the case of Ferbam. The inorganic compounds formed undergo only insignificant weight changes on further heating.

When the metal-containing compounds were heated, the final product contained sulphides, 29 and 26% by weight for Ferbam and Ziram, respectively, compared with the calculated stoichiometric values of 21 and 31%, respectively. The differences are due to the effect of the additives. Tiram, which does not contain any metal, burns away completely.

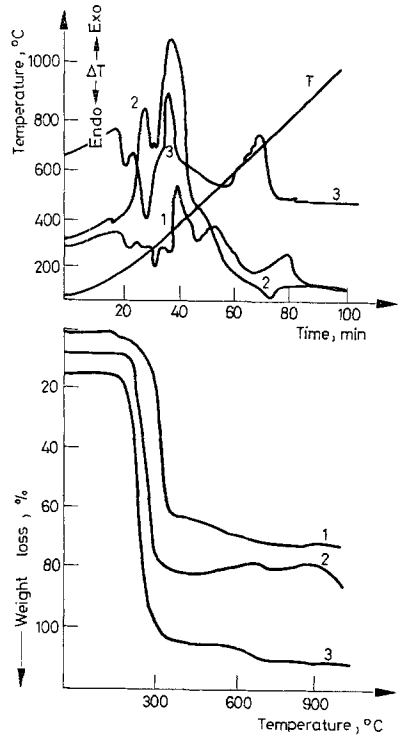


Fig. 1. TG and DTA curves of some fungicides. 1 — Ziram, 2 — Ferbam, 3 — Tiram. The T curve is that of Ziram

In contrast to Ferbam, Ziram and Tiram, the TG curve of Polycarbazine exhibits steps (Fig. 2). This fungicide, like Zineb, contains zinc ethylene-bis-dithiocarbamate. This is apparently the reason why the thermal decomposition of Polycarbazine proceeds similarly to that of Zineb; the first decomposition reaction starts at 150° and is accompanied by an explosion-like exothermic effect (sharp peak on the DTA curve, and change in the course of the T curve).

The weight loss occurs within a narrow temperature interval of 10 to 15°. Consequently, the corresponding section of the TG curve is almost vertical. The solid decomposition product is stable from the final temperature of the reaction up to 220° (horizontal section in the TG curve). The further course of the TG curve for Polycarbazine is also very similar to the TG curve of Zineb.

It seemed probable that the differing mechanisms of thermal decomposition are due to the structural differences of the studied dithiocarbamates. Iron and zinc dimethyldithiocarbamates, and tetramethylthiuramdisulphide are open-chain compounds. In contrast, zinc dithiocarbamate, containing an ethylene group instead of methyl groups, is a bis-dithiocarbamate in which a zinc atom links two

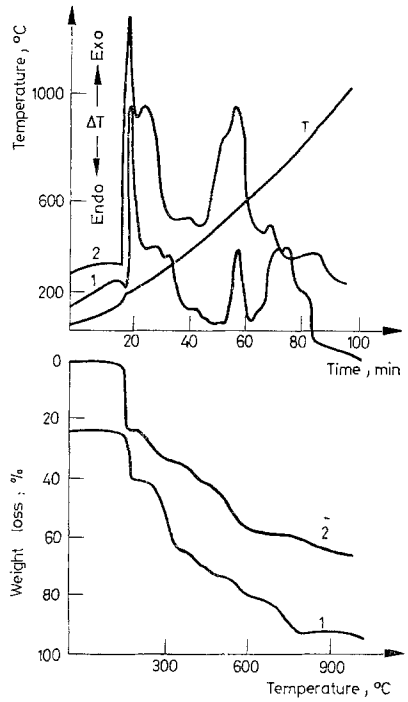
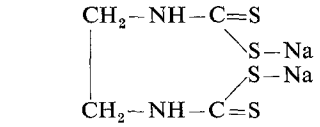


Fig. 2. TG and DTA curves of some fungicides. 1 — Polycarbazine, 2 — Zineb. The T curve is that of Zineb

dithiocarbamate groups of one radical, thereby forming a compound which may be regarded as cyclic. It was assumed that stepwise thermal decomposition is characteristic of dithiocarbamates with cyclic structures. Since ethylene-bis-dithiocarbamates of bivalent metals have this structure, the validity of our assumption was checked by studying their behaviour.

These compounds were prepared in our laboratory without any special purification.

For this purpose, the thermal curves were taken of Cd, Ni, Cu and Mn ethylene-bis-dithiocarbamates, the structures of which are analogous to that of the main constituent of Zineb. The curve was also taken of the fungicide Nabam, whose biologically active constituent is sodium ethylene-bis-dithiocarbamate



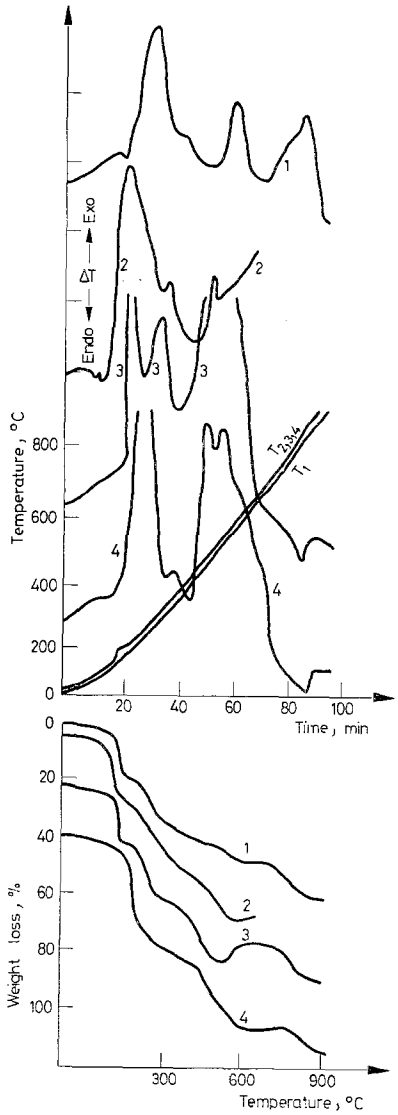


Fig. 3. TG and DTA curves of ethylene-bis-dithiocarbamates of bivalent metals. 1 — Cadmium salt, 2 — manganese salt, 3 — copper salt, 4 — nickel salt. T_1 is the temperature curve of the cadmium salt, $T_{2,3,4}$ temperature curve characteristic of the manganese, copper and nickel salts

This is a salt of the same dithio acid, but is not cyclic in structure, since the hydrogen atoms of the acid are substituted by two atoms of a monovalent metal. All curves were taken under identical conditions, and compared with each other and with the thermal curves of the dimethyldithiocarbamates obtained earlier.

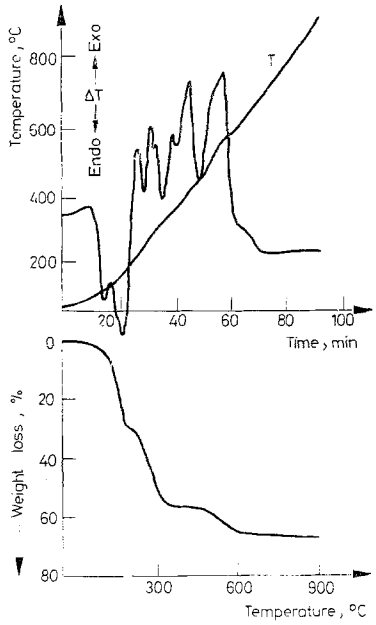


Fig. 4. T, TG and DTA curves of Nabam

Fig. 3 indicates that the curves of the ethylene-bis-dithiocarbamates of bivalent metals are similar in type. The decompositions of these compounds proceed in several steps. Independently of the metal, the first weight loss step occurs in a narrow temperature interval of $10-15°$ and in a short period of time, and therefore the corresponding section of the TG curve is almost vertical. As in the case of Zineb, exothermic peaks on the DTA curve and a change in the course of the T curve correspond to these sections. The course of the T curve remained unchanged only in the case of cadmium ethylene-bis-dithiocarbamate. The solid decomposition products are stable up to temperatures $50-60°$ higher than the final temperature of the first reaction. On further heating, decomposition continues. The characters of the TG and DTA curves up to the end of the heating process are similar to those of Zineb (cf. Figs 3 and 2). The residues found from the thermogravimetric curves are 38, 23 and 32% by weight for the ethylene-bis-dithiocarbamates of Cd, Ni and Cu, respectively, compared with the calculated stoichiometric 44, 34 and 34.8%. From the difference between the calculated and found values of the residues, the degree of contamination of the fungicide by additives can be estimated.

The thermal curves of Nabam (Fig. 4) differ completely from the thermal curves shown in Fig. 3. For Nabam, the TG curve consists of two approximately equal steps. The first decomposition step proceeds in a relatively broad temperature range, from 100 to 160°, and is accompanied by an endothermic effect.

A comparison of all curves obtained in the present work shows that the curves of the ethylene-bis-dithiocarbamates of bivalent metals are similar in type and differ not only from the curves of dimethyldithiocarbamates, but also from the curves of the salt of the same acid with the monovalent metal sodium which is therefore acyclic in structure. These findings confirm our assumption that thermal decomposition of the type found with Zineb occurs only with ethylene-bis-dithiocarbamates of bivalent metals and is connected with their cyclic structure.

The first step of the thermal decomposition of zinc ethylene-bis-dithiocarbamate was discussed in detail in an earlier paper [9], where it was concluded that the weight loss corresponding to the vertical section in the TG curve (at 160°) is due to the splitting-off of one carbon disulphide group from the ethylene-bis-dithiocarbamate molecule, and that there are no other thermogravimetric effects in this section of the TG curve. The similar DTA and TG curves of ethylene-bis-dithiocarbamates of bivalent metals indicate that the thermal decomposition mechanism is identical for this group of dithiocarbamates. It may therefore be concluded that for the ethylene-bis-dithiocarbamates of bivalent metals, the first step of thermal decomposition is the splitting-off of one carbon disulphide group. This mechanism was confirmed by a specific qualitative test for carbon disulphide. The evolved gas was absorbed in a 1% alcoholic solution of diethylamine, and a 0.05% alcoholic solution of a copper salt was added, giving rise to the characteristic intense brown colour of copper diethyldithiocarbamate [10]. On the other hand, no carbon disulphide could be detected in the gaseous decomposition product of Nabam.

The temperature at which the first thermal reaction starts is specific for the salt-forming metal. This temperature was found to be 120, 140, 150 and 200° for Cd, Cu, Mn and Ni ethylene-bis-dithiocarbamates, respectively. The change in the course of the TG curve can therefore be utilized for a qualitative identification of ethylene-bis-dithiocarbamates. Also, since the weight loss is proportional to the amount of the thermoactive substance, the TG curve may serve for the quantitative determination of ethylene-bis-dithiocarbamates in pesticides.

It is frequent in the manufacture of commercial chemicals that the main product is not isolated, either for technological reasons or else because the application of the product does not require its separation from the by-products. Both these conditions apply to fungicides based on dithiocarbamates. In the general case, if the constituent to be analyzed cannot be isolated from the mixture, a quantitative thermogravimetric analysis necessitates the knowledge of the composition of the mixture, and reference TG curves for all constituents must be available. In the case of complex multi-constituent mixtures like the pesticides in question, these requirements are difficult or impossible to satisfy. Our investigations resulted

in a procedure for the thermogravimetric analysis of dithiocarbamate fungicides which eliminates the need to isolate the constituent to be determined, without requiring the knowledge of the product composition and the possession of reference curves for all constituents.

The interpretation of the thermogravimetric curves also served as the basis for the development of a simple analytical procedure not requiring any special equipment. The procedure consists in the collection and quantitative determination of the evolved carbon disulphide. The applied apparatus and procedure were described earlier [9] for Zineb.

0.2000 g of the fungicide is heated in a flask on an oil bath at a heating rate of $5-6°$/min to a bath temperature $20-25°$ higher than the starting temperature of the decomposition. The temperature difference of $20-25°$ ensures that the reaction temperature is reached in all parts of the sample, and also that the experimental results are not distorted, since the TG curves indicate that in this temperature range the solid decomposition product is stable.

The determination is then continued by carrying out the well-known xanthogenate reaction [10]. The evolved carbon disulphide is transferred to an absorber vessel containing an alcoholic solution of caustic soda, by blowing nitrogen or argon, free from oxygen and carbon dioxide impurities, through the reaction mixture. The xanthogenate formed in the absorber is then titrated with standard iodine solution.

Analysis results obtained by this method and by thermogravimetry are listed in Table 1. The satisfactory agreement is understandable in view of one and the same thermal reaction being utilized in both analytical procedures.

Table 1

Content of main constituent in the mixture

Product	Percentage of main constituent	
	by thermogravimetry	by the carbon disulphide method
Copper ethylene-bis-dithiocarbamate	46.7	45.1
Nickel ethylene-bis-dithiocarbamate	60.2	58.0
Zinc ethylene-bis-dithiocarbamate	76.1	75.0

However, the chemical method is more time-consuming, several reagents are required and the operation of freeing nitrogen or argon of interfering gas impurities is rather difficult in practice. In addition, the results depend to a certain extent on the skill of the operator. Direct thermogravimetric determination has undoubtedly important advantages compared with the chemical method. None the less, in laboratories that have no thermogravimetric equipment, the chemical method provides a reliable procedure for analyzing dithiocarbamate fungicides.

The authors hope that the approach used in this investigation may be found useful in the study of mixtures with multi-step thermogravimetric curves, since in such cases it is highly probable that at least one section of the thermogravimetric curve will be specific for an individual constituent of the mixture.

Conclusions

1. It has been demonstrated on the example of dithiocarbamate pesticides that in some cases thermal investigation of mixtures of solid substances yields sections in the thermogravimetric curves of the mixtures, which are characteristic of an individual constituent. By utilizing these sections, thermogravimetric methods can be developed for the quantitative determination of the constituent in question, eliminating the need for its isolation, for reference curves and for the knowledge of the composition of the mixture.
2. The mechanism of thermal decomposition has been elucidated for some groups of dithiocarbamates.
3. A thermogravimetric method for determining ethylene-bis-dithiocarbamates in fungicides has been developed. The method is a group method for all dithiocarbamates having analogous structures.

References

1. D. G. CLARKE, H. BAUM, L. STANLEY and W. F. HESTER, Anal. Chem., 23 (1951) 1842, C. A. 46, 2964e.
2. A. STEVENSON, J. Sci. Food and Agric., 15 (1964) 509.
3. R. BONTOYAN WARREN, J. Assoc. Off. Agric. Chemists, 48 (1965) 562.
4. G. BALIF, Comun. Acad. RPR, 10 (1960) 853.
5. J. PFEIFER and T. FLÓRA, Acta Chim. Acad. Sci. Hung., 51 (1967) 223.
6. T. FLÓRA, Hung. Sci. Instr., No 19 (1970) 3.
7. M. V. KENNEDY, B. J. STOJANOVIC, F. L. SHUMAN, Residue Rev., 29 (1969) 89.
8. YU. S. LYALIKOV and M. I. KITOVSKAYA, Ukr. Khim. Zh., 24 (1968) 964.
9. YU. S. LYALIKOV and M. I. KITOVSKAYA, Ukr. Khim. Zh., 25 (1969) 719.
10. A. N. BLAZHENOVA, A. A. ILINSKAYA and F. M. RAPPOPORT, Analiz gazov v khimicheskoy promyshlennosti, Moscow, 1954, p. 176.

RÉSUMÉ — Etude d'une série de fongicides à base de dithiocarbamate par thermogravimétrie et analyse thermique différentielle. On a trouvé une relation entre la structure de divers dithiocarbamates et leurs différences de comportement thermique. On a établi les parties caractéristiques des courbes thermogravimétriques du groupe des fongicides à base d'éthylène-bis-dithiocarbamates d'ions métalliques bivalents. Plusieurs fongicides peuvent être identifiés d'après la forme différente des courbes T et TG. On a élaboré une méthode de dosage de la partie active des fongicides à base d'éthylène-bis-dithiocarbamate de métaux bivalents où l'on utilise à des fins analitiques la forme caractéristique de la courbe TG.

ZUSAMMENFASSUNG — Fungizide auf Dithiocarbamat-Basis wurden thermogravimetrisch und mit Hilfe der Differentialthermoanalyse untersucht. Unterschiede in der thermischen Zersetzung konnten mit den entsprechenden Strukturen in Zusammenhang gebracht werden. Die charakteristischen Bereiche der TG Kurven von Fungizid-Gruppen, basiert auf Äthylen-bis-dithiocarbamate zweiwertiger Metalle, wurden ermittelt. Aufgrund der Unterschiede in den TG und T Kurven lassen sich verschiedene Fungizide identifizieren. Eine Methode zur Bestimmung der aktiven Gruppen von Äthylen-bis-dithiocarbamate zweiwertiger Metalle enthaltenden Fungiziden wurde unter Berücksichtigung der charakteristischen Form der TG Kurve ausgearbeitet.

Резюме — Выполнены термографические и термогравиметрические исследования ряда фунгицидных препаратов на основе дитиокарбаматов. Различия в механизме термической деструкции дитиокарбаматов различных групп объяснены в связи с их строением. Для группы фунгицидов на основе этиленбисдитиокарбаматов двухвалентных металлов обнаружен характеристический участок термогравиметрической кривой. По температуре изменения хода кривых Т и ТГ проводится идентификация некоторых фунгицидов. Разработан групповой метод количественного определения активного вещества в фунгицидах на основе этиленбисдитиокарбаматов двухвалентных металлов, в котором в аналитических целях используется характеристический участок кривой ТГ.