# Oxidative Decomposition of Ethylene-Bis-Dithiocarbamates

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The most extensively used organic fungicides worldwide are the ethylenebisdithiocarbamates (EBDC). In many instances, these materials are the only successful counteragent for controlling fungal diseases of major food crops. Recently concern over the safety of the EBDC's has been expressed as a result of renewed awareness that commercial formulations contain significant amounts of ethylene thiourea (ETU) (Czezlédi-Jankó 1976, Vonk and Kaars Sijpesteijn 1970, Bontoyan et al. 1972). ETU has been shown to cause thyroid hyperplasia (Graham and Hansen 1972) and at high doses thyroid carcinoma (Graham et al. 1973).

ETU is formed as a byproduct during the manufacture of the EBDC's. It is also formed when solutions of EBDC age (Vonk and Kaars Sijpesteijn 1970) or are aerated (Thorn and Ludwig 1962). However, it is not known whether ETU may also be formed during the process of the application of EBDC's to plants or in the residues remaining on plant and soil surfaces following application. This report describes preliminary results obtained in an effort to answer these questions.

## Experimental Procedures and Results

The original concept for this study was to prepare soil samples containing 100 ppm maneb and to observe its decomposition by passing a stream of moist air through the soil and trapping volatile decomposition products. Additionally, samples were to be taken from the soil and assayed for non-volatile decomposition products. To accomplish this the reaction train shown in Figure 1 was assembled from available glassware. The gas washing bottles

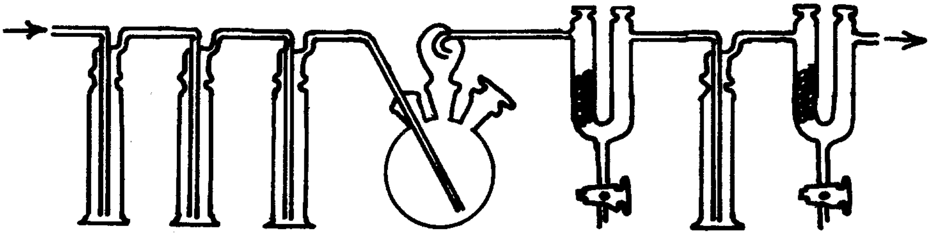

Figure 1. Gas absorption train: 1, 5M NaOH; 2, 1M $H_2SO_4$; 3, $H_2O$; 4, reaction; 5, $H_2S$ trap; 6, 1M NaOH; 7, $CS_2$ trap.

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were to remove $CO_2$ from the entering air, to prevent entrainment of NaOH, and to saturate the air with water. The gas absorbing traps following the reaction flask were to collect $H_2S$ in zinc acetate, other acidic volatiles in NaOH, and $CS_2$ in Viles reagent (Viles 1940). The $H_2S$ and $CS_2$ traps were to be changed at regular intervals (30-60 minutes) so that the kinetics of decomposition could be studied.

Before actual experiments with soil were attempted preliminary studies were made to determine the efficiency of $CS_2$ collection (95-98%) and to optimize air flow. Then a sample of commercial maneb formulation containing 20 mg of maneb was suspended in 100 ml. 0.1 M phosphate buffer pH 7.0 in the reaction flask and air was drawn through the system. After approximately 30 minutes a measurable amount of $CS_2$ had evolved and the rate of evolution continued to increase until approximately 20% of the theoretical $CS_2$ had been released. Evolution then stopped. This unexpected result was confirmed when the experiment was repeated. It was first thought that the commercial formulation was defective, but maneb, synthesized as described by Engst and Schnaak (1967) gave the same results as did pure nabam. EBDC decomposition was affected by pH and available moisture. Neutral and acidic solutions or suspensions evolved $CS_2$ at rapid though comparable rates while reduced evolution was observed at alkaline pH. Gas production was considerably more rapid from solutions and suspensions than from moist soil. (Figure 2). If nitrogen were

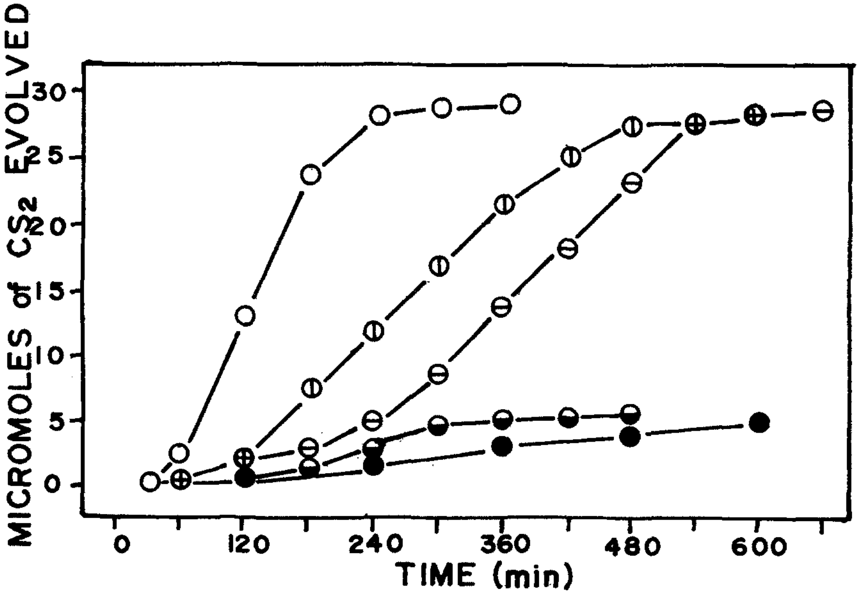

Figure 2. Evolution of $CS_2$ from EBDC solutions and suspensions, all at 20mg. per 100 ml. buffer or 100gm. soil:○maneb pH=6; ⦶ nabam pH=7; ⊖ maneb pH=7; ◒ maneb pH=8; ● maneb+soil pH=7.

substituted for air as the carrier gas, almost no $CS_2$ was evolved. The small amounts that were detected were subsequently shown to be due to the presence of residual air in the reaction train. If the nitrogen were then replaced by air, $CS_2$ evolution began again after a brief induction period the latter probably related to the time required to displace residual nitrogen in the system. (Figure 3).

Examination of the contents remaining in the reaction flask by thin-layer chromatography (Czeztédi-Jankó 1967, Onley and Yip 1971) revealed ETU, ethylene thiuram monosulfide (ETM), elemental sulfur, and a trace of either ethylene diamine (EDA) or unreacted maneb. ETU and ETM were confirmed by co-chromatography with authentic specimens. These results agree with those described by Thorn and Ludwig (1962) with the exception that alkaline conditions were not required to produce ETU. The pH of the reaction mixture remained unchanged throughout the course of the experiment.

To obtain better quantitation of the reaction products and also to follow the course of the decomposition more closely a larger scale experiment was performed using 250 mg of maneb suspended in 250 ml pH 6.0 phosphate buffer. Air was passed through the mixture and the volatile products were collected as before. Aliquots of the reaction mixture was periodically removed and examined by thin-layer chromatography. (Figure 4). When $CS_2$ evolution ceased, the residual reaction mixture was analyzed for ETU by the method of Newsome (1972). EDA was determined by gas

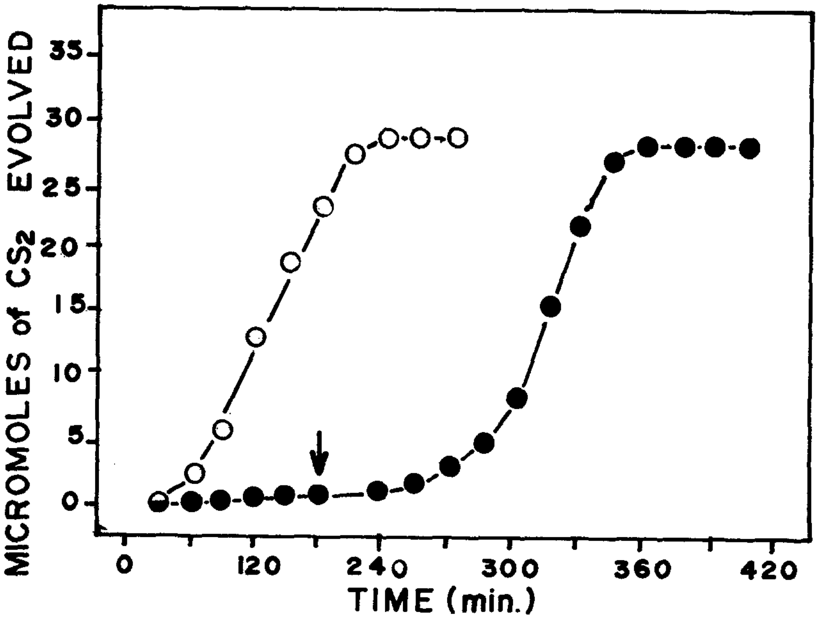

Figure 3. Effect of oxygen on the evolution of $CS_2$ from a suspension of 20 mg. maneb in 100 ml. buffer pH=6. Carrier gases: ○ air; ● nitrogen replaced by air at the arrow.

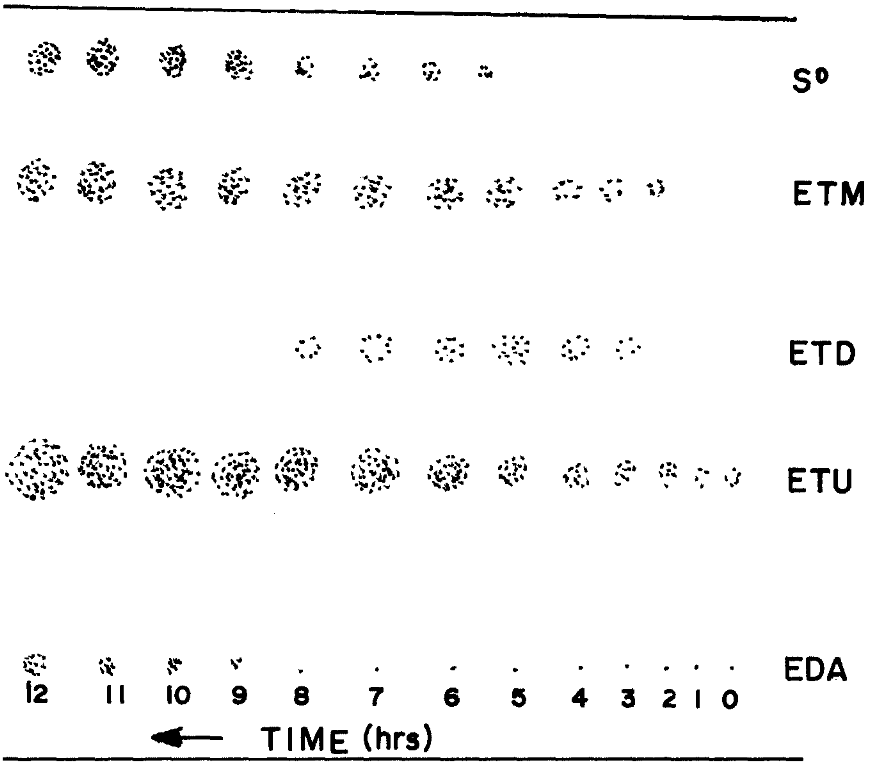

Figure 4. Thin Layer Chromatogram Tracing of Aerated Maneb Suspension.

chromatography of the trifluoroacet-di-amide derivative using a 6-foot column containing 80-100 mesh Chromosorb W coated with 2% DEAS and operated at 190°C with electron capture detection. ETM was estimated gravimetrically following exhaustive extraction of the reaction mixture with chloroform followed by purification as described by Pluigers et al. (1971). Elemental sulfur was estimated on a benzene extract of the reaction mixture by gas chromatography using the column and conditions described above but with a sulfur specific flame photometric detector. The results of these determinations, performed in duplicate on replicate experiments, are presented in the Table.

Recovery of Degradation Products from and Aerated Suspension of 0.97 Millimoles of Maneb in 250 Ml. of Buffer pH = 6.

| | millimoles | |
|---|---|---|
| Substance | Theory | Found |
| ETM | | 0.33 |
| ETU | | 0.54 |
| EDA | | 0.07 |
| total | 0.97 | 0.94 |
| $CS_2$ | 0.68 | 0.60 |
| $S^{o2}$ | 0.87 | 0.72 |

The results observed in the present study are qualitatively similar to those reported by others studying the decomposition of EBDC's. Cox et al. (1951) found EDA and $CS_2$, Barratt and Horsfall (1947) $H_2S$, Clarke et al. (1951) ETU and Klöpping and van der Kerk (1951) ethylene thiuram disulfide (ETD). Thorn and Ludwig (1962) reported that aeration of dilute solutions of nabam resulted in the formation of ETM and ETU. They also mention that ETU can be formed from ETM and that ETD is present, but without experimental evidence and without further comment. In the study most similar to the present one, Engst and Schnaak (1970) observed the formation of ETD, ETM, ETU, and sulfur in aerated solutions and suspensions of EBDC's. They accepted the statement that ETU could be formed from ETM and included such a reaction in their degradation scheme (as have all other previously published schemes) even though their data showed no such transformation. This is not too surprising since all these schemes have included a structure for ETM which has only recently been shown to be incorrect (Pluigers et al. 1971, Benson et al. 1972). The new structure makes it difficult to imagine the formation of ETU from ETM.

Taking into consideration the results reported by others, the quantitative data obtained in the present study, and the presumably correct structure of ETM, a mechanism for the oxidative degradation of EBDC's has been developed. (Figure 5).

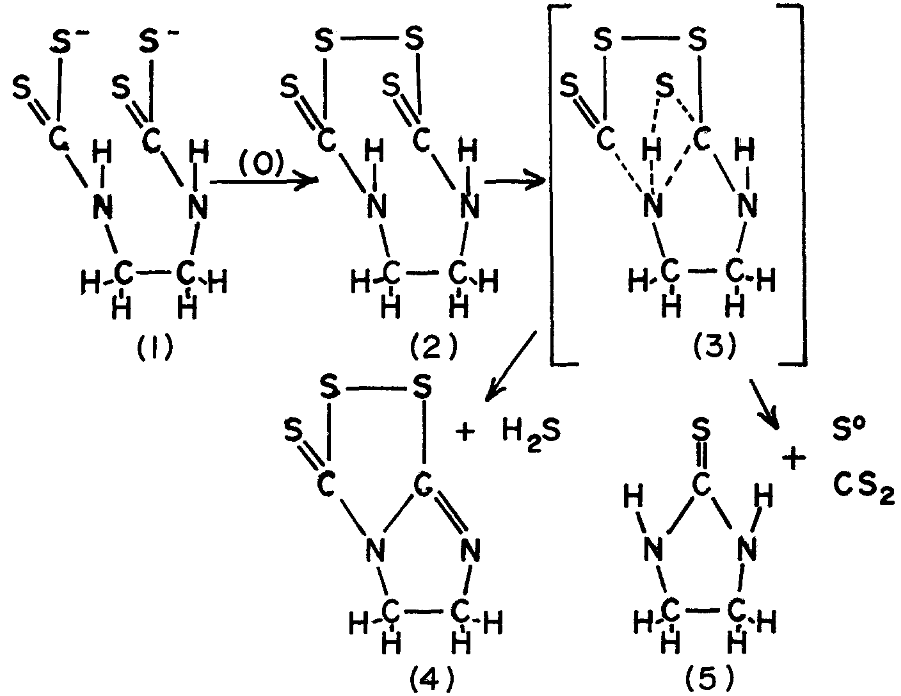

Figure 5. Proposed mechanism for the oxidative decomposition of EBDC's. (1) EBDC; (2) ETD; (3) transient intermediate;(4) ETM;(5) ETU.

It can be seen that ETD, the first product, is the key intermediate. Examination of this structure reveals a strong tendency for hydrogen bonding between one double bonded sulfur and a proton attached to nitrogen on the opposite side of the eight membered ring. This bonding reshapes the ring and brings the carbon to which the sulfur is attached into bonding proximity to the nitrogen containing the proton. Calculations of bond lengths and angles show that such bonding is probable. This can also be demonstrated with accurate molecular models. The transient intermediate formed can decay in several ways. Based on the present work and previous studies the two most probable modes of decay are the formation of ETU with the elimination of $CS_2$ and $S^0$, and rearrangement and transelimination of $H_2S$ to give ETM. In this study, $H_2S$ was rapidly oxidized by air to $S^0$. It is believed that this reaction sequence is valid for dilute solutions and suspensions of EBDC's as would occur in spray tanks and on the surface of leaves and soils. Other degradation products can be formed from ETD and ETM but since these were not observed experimentally they are not included. Additional degradation products of EBDC's have been observed but not identified (Czezledi-Janko 1967, Bontoyan et al. 1973).

From the results presented in this report it appears that ETU is formed as a direct consequence of the more or less spontaneous breakdown of ETD, which is formed by the oxidation of EBDC's. To minimize formation of ETD, oxygen should be excluded during the storage and use of EBDC's. How this can be practically accomplished is not known at present.

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