

Thermal Decomposition of Ethylenebisdithiocarbamate Fungicides to Ethylenethiourea in Aqueous Media

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The kinetics of thermal decomposition of nabam in aqueous media was investigated. The rate of conversion of the dithiocarbamate to ethylenethiourea (ETU) was influenced by temperature, available oxygen, and the pH of the system. Ethylenethiuram monosulfide and β -aminoethylthiocarbamate but not ethylene diisothiocyanate were confirmed as intermediates in the conversion of nabam to ETU at elevated temperature. A degradation scheme consistent with the decomposition kinetics is proposed. Parameters which control the conversion of ethylenebisdithiocarbamate fungicides to ETU are discussed.

The boiling of vegetables containing residues of ethylenebisdithiocarbamate (I) (EBDC) fungicides results in a significant conversion of these residues to ethylenethiourea (II) (ETU) (Newsome and Laver, 1973; Watts et al., 1974). The teratogenic and tumorigenic character of this decomposition product to rats and mice is well documented (Graham et al., 1975; Graham, 1973; Graham and Hansen, 1972; Khara, 1973; Innis et al., 1969). Thus, the preparation of foods containing EBDC residues by heat treatment constitutes a potential hazard to man.

Several workers (Hylin, 1973; Bontoyan and Looker, 1973; Engst and Schnaak, 1967, 1971; Czeglédi-Janko, 1967; Morehart and Crossan, 1965) have studied the chemical decomposition of EBDC fungicides at room temperature under a variety of conditions. Decomposition products which have been identified include carbon disulfide, hydrogen sulfide, ethylenediamine (EDA) (III), ETU, ethylenethiuram disulfide (ETD) (IV), ethylenethiuram monosulfide (ETM) (V), and elemental sulfur. However, to our knowledge no high-temperature kinetic study has been carried out. As a prelude to attempting to control the thermal conversion of EBDC fungicides to ETU, a kinetic study of this conversion was undertaken.

EXPERIMENTAL SECTION

Materials. Nabam (disodium ethylenebisdithiocarbamate) was synthesized according to the method of Engst and Schnaak (1967). The crude product, recrystallized from 80% methanol-water, yielded a pale yellow product (mp 75–77 °C). Anal. Calcd for $C_4H_6N_2S_4 \cdot 2Na \cdot 3H_2O$: C, 15.47; H, 3.90; N, 9.02; S, 41.32. Found: C, 15.18; H, 4.03; N, 9.08; S, 41.22.

β -Aminoethylthiocarbamate (inner salt) (VI) was obtained by reaction of ethylenediamine with 1 equiv of carbon disulfide in the presence of 1.1 equiv of sodium hydroxide (mp 199–201 °C). Anal. Calcd for $C_3H_6N_2S_2$: C, 26.45; H, 5.92; N, 20.56; S, 47.07. Found: C, 26.52; H, 6.09; N, 20.40; S, 47.05.

Ethylene diisothiocyanate (EDI) (VII) was prepared by the thermal decomposition of the corresponding carbethoxydithiocarbamate (Klopping and van der Kerk, 1951). Vacuum distillation of the crude product yielded a spectroscopically and chromatographically (HPLC and TLC) pure fraction. Ethylenethiuram monosulfide (ETM) was obtained by vigorous aeration of a dilute solution of nabam according to the method of Thorn and Ludwig (1962). Final purification was achieved by preparative liquid chromatography on alumina. The yellow crystalline

product melted at 120–121 °C. Ethylenethiuram disulfide monomer (IV), similarly purified, was obtained as a minor product from the same oxidation. Ethylenethiourea (ETU) (2-imidazolidinethione) and ethylenediamine (III) were purchased from Fisher Scientific Co.

Method. Decomposition studies were performed in an apparatus as shown in Figure 1. The reaction flask was charged with a 7.8 mM solution of nabam and maintained at constant temperature by means of an oil bath. Volatile products were entrained into a series of traps with a stream of compressed air or nitrogen at 50 ml/min. The first trap contained 6 N potassium hydroxide to remove hydrogen sulfide while successive traps contained Viles reagent (Keppel, 1969) to remove carbon disulfide. Aliquots of the reaction solution were removed at convenient intervals and immediately assayed for ETU or for EDA (after derivatizing) by liquid chromatography. Aliquots from trap 2 were assayed spectrophotometrically at 298 nm. The amount of carbon disulfide was then determined by comparison of the absorption with those of standards.

Decomposition studies at constant pH were effected using the following buffer systems: pH 8.0–10.0, borate; pH 5.8–8.0, phosphate; pH 4.1–5.9, phthalate; pH 3.6–5.6, acetate; pH 1.0–2.2, potassium chloride/hydrochloric acid; or pH 2.2–8.0, citric acid/phosphate.

Liquid Chromatography. Analyses were performed using a Waters Model 6000A solvent delivery system, a 0.30 $\times$ 25.0 cm column packed using a balanced density slurry technique with 10- μ m silanized LiChrosorb SI60, and an LDC spectromonitor 1 (scanning wavelength) UV detector. A stop flow injection technique using a ball valve (Cassidy and Frei, 1972) was used. ETU was analyzed at 240 nm using 15% methanol-water at 1 ml/min as eluent while EDA in aqueous solution at pH 8 was reacted with excess fluorescamine (4-phenylspiro[furan-2(3H),1'-phthalan]-3,3'-dione; Hoffmann-La Roche, Inc.) in acetone and monitored at 410 nm using 20% methanol-borate buffer (pH 8, 0.05 M) at 1 ml/min as eluent (Samejima, 1974).

Gas-Liquid Chromatography. Analyses for volatile products from the decomposition of EDI were performed on a Microtec 220 gas chromatograph fitted with a Tracor flame photometric detector operated in the sulfur mode and a 3 ft $\times$ 4 mm i.d. glass column packed with Deactigel, 80–100 mesh. Operating parameters were as follows: column flow, nitrogen, 50 ml/min; hydrogen, 35 ml/min; oxygen, 10 ml/min; compressed air, 60 ml/min; and an on-column injection technique was used.

Equipment. IR spectra were determined as films or KBr pellets using a Beckman IR-20A spectrophotometer. Proton NMR spectra were obtained in $CDCl_3$ solution with Me_4Si as an internal standard on a Varian T-60 NMR

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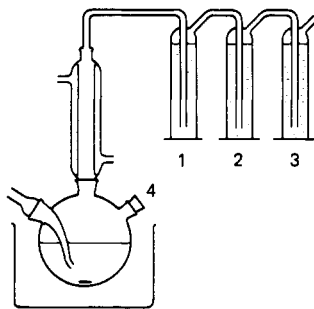


Figure 1. Decomposition apparatus and absorption train.

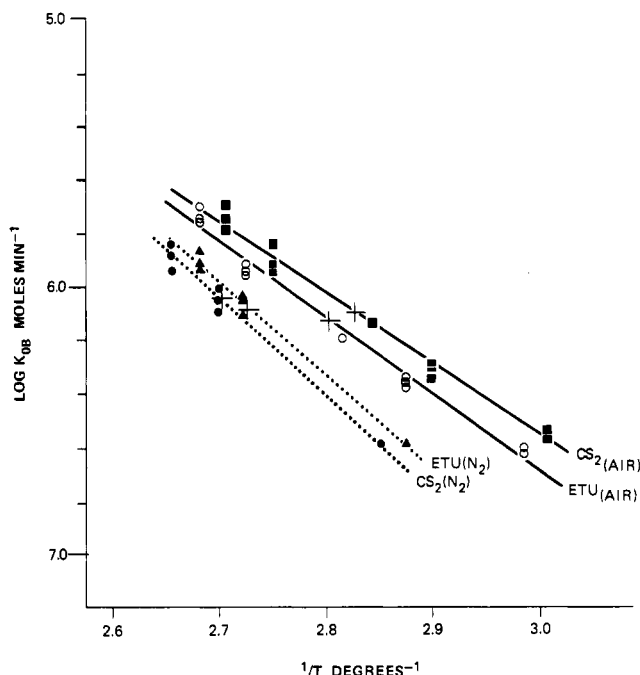


Figure 2. Variation in reaction rate with temperature using compressed air (■, ○) or nitrogen (▲, ●) to entrain volatile products.

spectrometer. The MS were determined on a Finnigan 3100 GC-MS coupled to a D6000 data acquisition system.

RESULTS AND DISCUSSION

Preliminary kinetic runs were carried out in distilled deionized water. Plots of the concentration of ETU and of carbon disulfide vs. time at five temperatures when nabam was dissolved in water were found to be linear over the course of the reaction.

The results of these experiments are conveniently summarized by using the Arrhenius equation which relates the observed rate constant (K_{obsd}) to the temperature according to the expression:

$$\log K_{\text{obsd}} = \log A_{\text{obsd}} - E_{\text{obsd}}/2.303RT$$

where A is a constant known as the frequency or collision factor and R is the gas constant having the value $1.986 \text{ deg}^{-1} \text{ mol}^{-1}$. In Figure 2 the log of the rate of production of ETU is plotted vs. the inverse of the absolute temperature when compressed air (○) and when nitrogen (▲) was used to entrain volatile products into the absorption train (Figure 1). Results for the rate of production of carbon disulfide (■, compressed air; ●, nitrogen) were similar and are also included. For reasons of clarity the plotted values of the abscissa for points on carbon disulfide curves represent the experimental values plus 0.025 (■) and minus 0.025 (●). Linear regression analysis of the

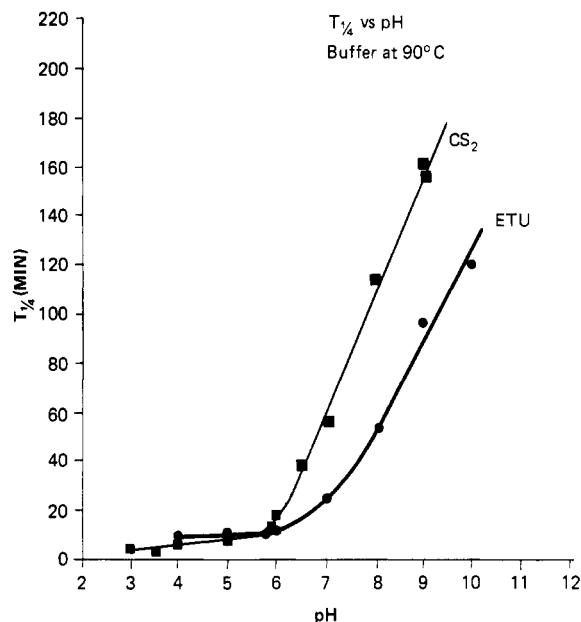


Figure 3. Variation in reaction rate with pH.

variation in the log of the reaction rate with the inverse of temperature resulted in curves having the following slopes:

	Compressed air	Nitrogen	F (variance ratio)
ETU	-2.857 (○)	-3.512 (▲)	46.82
CS ₂	-2.691 (■)	-3.633 (●)	43.20
F (variance ratio)	1.80	1.14	

The difference in these slopes when the same product is monitored under different experimental conditions (ETU = -2.857 vs. -3.512 and carbon disulfide = -2.691 vs. -3.633) reflects the dependence of the aqueous decomposition on oxygen availability. That these differences are significant is demonstrated by the variance ratio (F) for the ETU curves ○ and ▲ (F , variance ratio = 46.815 vs. 6.36 for 2 and 15 degrees of freedom (df) at 99% confidence limits) and for the carbon disulfide curves ■ and ● (F ratio = 43.203 vs. 6.36). When the same statistical test was applied to products generated under the same experimental conditions (curve ■ vs. curve ▲, F ratio = 1.797 vs. 3.49 for 2 and 20 df at 95% confidence limits) results were negative. Similarly, when nitrogen was used to entrain volatile products (curve ▲ vs. curve ●, F ratio = 1.141 vs. 4.10 for 2 and 10 df at 95% confidence limits) no evidence for a significant difference between these two curves was obtained. Confirmed by these plots are the observations of Hylin (1973) that at room temperature the decomposition is very slow. The pH of the system was found to vary only slightly over the course of the reaction (typically 9.3 to 9.8).

In order to study the effect of pH on the decompositions subsequent experiments were carried out in buffered media while the temperature was held constant at 90 °C. Each buffer system covers approximately 2 pH units and the total buffer concentration of each system was held constant (0.05 M). Figure 3 demonstrates the increase in the rate of ETU and carbon disulfide formation (as measured by the time in minutes to produce one-quarter of the theoretical equivalent of product) as the pH is lowered from 9 to 3. At pH below 4 less than one-quarter of the theoretical equivalent of ETU was generated although carbon disulfide generation suggested considerable decomposition

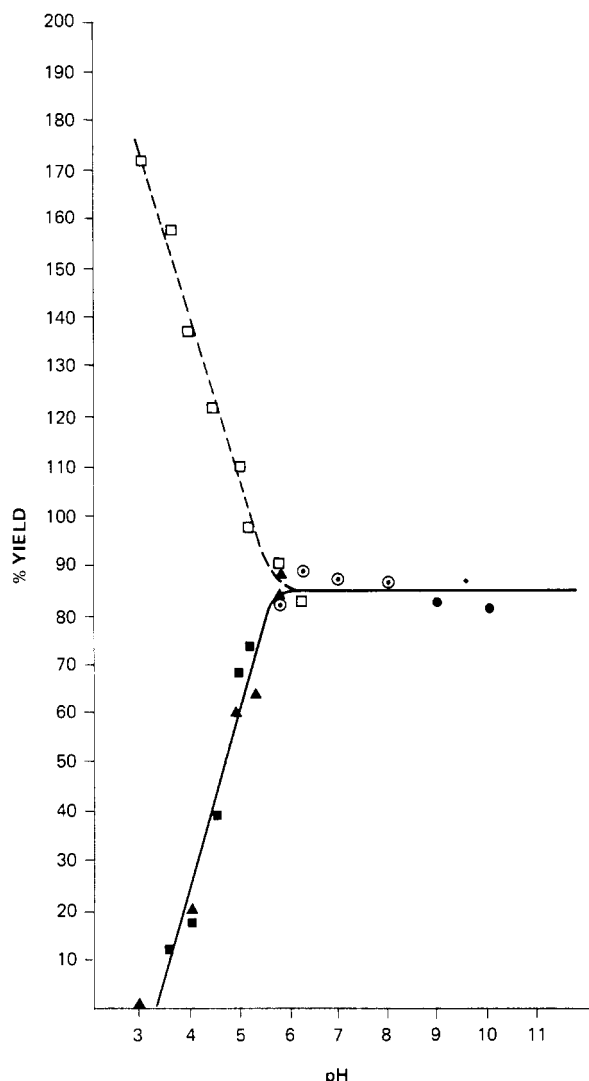
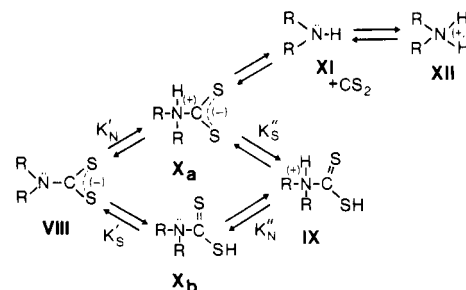


Figure 4. Variation in the yield of carbon disulfide (□) and of ETU with pH using borate (●), distilled water (○), phosphate (○), acetate (■), and phthalate (▲) buffer systems.

of the nabam. A discontinuity in the curves (particularly pronounced for the carbon disulfide curve) suggests a change in the mechanism of decomposition about pH 6. The discontinuity is more pronounced (Figure 4) when the total yield of ETU and of carbon disulfide for each kinetic run is plotted vs. the pH of the solution. The total yield of ETU (83–87%) was found to be independent of the pH in the range of 6 to 11. However, as the pH was lowered from 6 to 3 the total yield rapidly decreased to zero; at the same time the total yield of carbon disulfide rose from 0.9 equiv to 1.72 equiv. The yield of carbon disulfide at pH 3 (172%) agrees well with the yield (178%) obtained when nabam was decomposed in strong acid with stannous chloride according to the method of Keppel (1969).

Zahradnik and Zuman (1958) have proposed the following series of equilibria for the protonation of a dithiocarbamate group in acid media. Species VIII exists under alkaline conditions while form IX exists in strongly acid conditions. pK values for the monoprotonated forms X_a and X_b lie between 2 and 4. Activated species X_a may then lose carbon disulfide resulting in amine XI which is inactivated for recombination with carbon disulfide by further protonation resulting in amine salt XII. Thus, the overall reaction at pH values which are the same as or below the pK' value is the irreversible decomposition of the dithiocarbamate.



A possible degradation scheme which is consistent with the kinetic observations on nabam decomposition is diagrammed in Figure 5. Protonation of carbamate nitrogen of nabam, subsequent loss of carbon disulfide, and protonation of the liberated amine results in β -aminoethylthiocarbamate (inner salt) (VI). Protonation of VI would lead to ethylenediamine by loss of carbon disulfide or to ETU by loss of hydrogen sulfide. Table I provides a comparison of predicted and observed yields of carbon disulfide at pH in the range of 3–6. It is assumed that 1 mol of carbon disulfide is produced for each mole of ETU and 2 mol is produced for each mole of EDA.

Under less acidic conditions the predominant mode of decomposition is considered to be oxidation of the EBDC

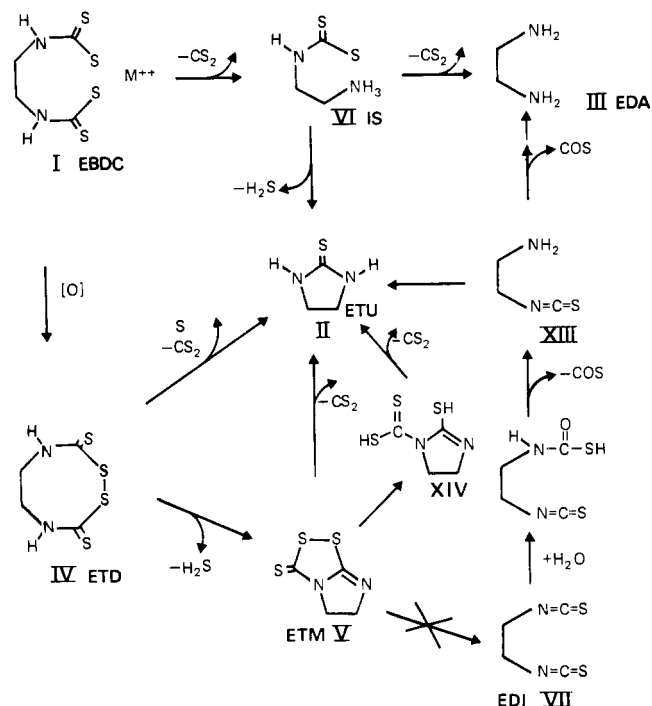


Figure 5. Decomposition scheme for nabam in aqueous medium at high temperature.

Table I. Percent Yield of Carbon Disulfide from the Decomposition of Nabam in Acid Medium in the Presence of Oxygen

pH	ETU	CS ₂ ^a (predicted)	CS ₂ (obsd)
5.85	85.8	85.8	90.1
5.25	73.9	97.1	98.0
5.0	60.5	106.5	110.0
4.5	42.5	125.5	128.5
4.0	20.5	141.8	136.8
3.6	12	156.9	157.4
3.0	0.0	171.0	173.4

^a Predicted CS₂ = ETU + 2(85.5 - ETU). 85.5 = average percent yield of ETU from decompositions in aqueous media, pH 6–11.

Table II. Percent Yield of Products from the Decomposition of Nabam in Acid Medium in the Absence of Oxygen

Reactant	pH	ETU	Products		
			CS ₂ (pre-dicted)	CS ₂ (obsd)	EDA
Nabam	5.5	83.5	87.5	85.1	nm ^a
Inner salt	5.5	84.4	15.6	16.3	
Nabam	5.0	39.5	131.5	128	nm ^a
Inner salt	5.0	39.4	60.6	58.5	
Nabam	4.5	21.3	149.7	152	nm ^a
Inner salt	4.5	22.8	77.2	82.8	
Nabam	4.0	10.9	160.1	151	76.6
Inner salt	4.0	8.2	91.8	86.0	88.7

^a nm = not measured.

to ETD (IV) (Hylin, 1973; Engst and Schnaak, 1970; Morehart and Crossan, 1965), which may subsequently decompose to ETM (V) or to ETU (Figure 5). As a further probe of the decomposition route, nabam, in acid solution, was decomposed under nitrogen and the product yields compared with those obtained when the inner salt was subjected to similar conditions. The results are given in Table II. Under conditions in which the normal oxidative mode of decomposition is suppressed the yield of ETU from nabam decreased more rapidly with decreasing pH (Table II vs. Table I). Excellent agreement was observed between the yields of ETU from the EBDC and from the inner salt. In all cases EDA (as measured by carbon disulfide evolution or directly) appears to be the only other decomposition product.

Efforts to trap the intermediate inner salt (in nabam decomposition studies) by reaction with fluorescamine were unsuccessful. Although the decomposition is rapid, it was felt that if the inner salt were present in appreciable concentrations, trappings would have been effective. Thus, it is suggested that decomposition of the inner salt to EDA or to ETU is more rapid than its formation from nabam. Alternatively, the acid dissociation constant is higher for the inner salt than for the ethylenebisdithiocarbamate. A similar conclusion was reached by Zahradnik and Zuman (1958) from a more detailed study of the acid decomposition of several monoalkyl- and dialkylidithiocarbamates.

When phthalate buffer was used as the decomposition medium the rapid formation of a white precipitate was observed. This product was isolated by filtration and recrystallized from chloroform (mp 240–241.5 °C). Spectroscopic studies [IR 1775, 1705 (phthalimide), 1070, 885, and 775 cm⁻¹ (aromatic); NMR τ 2.24 (aromatic protons, s, 4 H), 6.06 (NCH₂, s, 2 H)] suggested the product to be ethylenebisphthalimide. This was corroborated by mass spectrometry. Although no molecular ion was observed, prominent ions at *m/e* 174, 173, 161, and 160 (corresponding to β and α cleavage, respectively, of the bisphthalimide), at *m/e* 133 (loss of CO from *m/e* 161), 104 (C₆H₄CO), and 76 (benzyne) are evidence for this structure.

The decompositions were repeated using acetate buffer and no differences in the kinetics of decomposition or product distributions were observed between these media (Figure 4), nor was any evidence for the formation of ethylenebisacetimide obtained. It was concluded that the presence of phthalimide did not affect the kinetics of decomposition but reacted with the EDA once formed. Varying the ionic strength of the medium at pH 5.8 (0.05–0.1 M, compressed air) and at pH 4.0 (0.05–0.2 M, nitrogen) did not alter the kinetics or the product yield. When the decomposition (pH 5.25) was carried out at 60

Table III. Variation in the Percent Yield of ETU, Carbon Disulfide, and Ethylenediamine with pH from the Decomposition of Ethylene Diisothiocyanate in Aqueous Medium

Reactant	pH	Products		
		ETU	CS ₂	EDA
(1) Ethylene diisothiocyanate	8	12.6	21.4	nm ^a
(2) Ethylene diisothiocyanate + <i>p</i> -nitrothiophenol	8	13.4	23.5	nm ^a
(3) Ethylene diisothiocyanate	7	74.9; 76.5	26	6.5; 7.8
(4) Ethylene diisothiocyanate	6	94.7	27	<1.0

^a nm = not measured.

°C the rate of decomposition but not the product distribution was altered. These observations are included in Figure 4. Efforts to change the rate by adding 1 equiv of zinc metal (pH 9.0 and 5.0) or by adding 0.01 equiv of Mn²⁺ as manganese sulfate at pH 7.0 and 5.0 (Ludwig and Thorn, 1958) were not successful.

The role of ethylene diisothiocyanate (EDI) (VII) in the chemical decomposition of EBDC fungicides is unclear. The in situ conversion of EBDC's to this product may be responsible for their fungitoxic activity (Klopping, 1951). It was noted (Kaars Sijpesteijn and van der Kerk, 1954) that the fungistatic activity of nabam and ETM (V) was antagonized by thiols such as thioglycolic acid and cysteine. The in vitro conversion of EDI to ETU was suggested by Habrekke and Goksoyr (1970) who observed a pH dependence on the rate of cyclization to ETU. When EDI, suspended in phosphate buffer (pH 8.0), was heated to 90 °C using compressed air to entrain volatile products ETU was indeed formed as evidenced by co-chromatography of the product with standard on both thin-layer and column chromatography. The product also gave a positive test to Dragendorff reagent, Grote's reagent (1931), and to iodine-sodium azide sprays. However, carbon disulfide was also generated. In subsequent runs in which the pH of the medium was lowered to 7.0 and 6.0 the yield of carbon disulfide increased marginally while the yield of ETU increased dramatically. The product yields, shown in Table III, are very different from those obtained when nabam was decomposed under similar conditions. Thus, EDI does not appear to be an intermediate in the thermal decomposition of nabam to ETU. The addition of a nucleophilic thiol (*p*-nitrothiophenol) to the reaction mixture (experiment 2, Table III, vs. experiment 1) had no discernible effect upon the decomposition kinetics or on the product distribution. A possible decomposition mechanism for the conversion of EDI to ETU is included in Figure 5. Addition of water to the diisothiocyanate and subsequent decomposition of the thiocarbamate results in β -aminoethyl isothiocyanate (XIII) and liberates an equivalent of carbonyl sulfide. The aminoethyl isothiocyanate could cyclize to ETU or decompose to EDA by adding an equivalent of water and liberating a second equivalent of carbonyl sulfide. Hydrolysis of carbonyl sulfide results in hydrogen sulfide which could add to unreacted isothiocyanate resulting in the corresponding dithiocarbamate. Decomposition of the dithiocarbamate would result in carbon disulfide as demonstrated above.

To test the possibility that carbonyl sulfide was a decomposition product of EDI a gas trap containing absolute ethanol was placed between the condenser of the reaction flask and the first trap (Figure 1). The decomposition was repeated (pH 8.0, nitrogen) and the contents of the ethanol

Table IV. Variation in the Percent Yield of ETU and Carbon Disulfide with pH from the Decomposition of Ethylenethiuram Monosulfide in Aqueous Medium

Reactant	pH	Products	
		ETU ^c	CS ₂ ^d
(1) Ethylenethiuram monosulfide	8 ^a	53.5	48.1
(2) Ethylenethiuram monosulfide	8 ^b	51.9	52.6
(3) Ethylenethiuram monosulfide	7 ^a	55	54.2
(4) Ethylenethiuram monosulfide	6 ^a	20.5	22.3

^a Compressed air to entrain volatiles. ^b Nitrogen to entrain volatiles. ^c Measured after 22 h. ^d Cumulative total for 6 h.

Table V. Variation in the Percent Yield of ETU with pH from Ethylenebisdithiocarbamate Formulations

pH ^a	Reactant		
	Maneb	Mancozeb	Metiram
2.2	10.0	11.2	15.1
4.0	18.7	19.1	17.5
5.6	69.0	70.3	69.3
8.0	78.1	78.9	77.0

^a Citric acid/phosphate buffer.

trap analyzed by gas chromatography using a sulfur detector. Three products were observed with retention times of 0.28, 0.47, and 1.0 relative to carbon disulfide. The identity of each of the products as carbonyl sulfide, hydrogen sulfide, and carbon disulfide was confirmed by gas chromatography/mass spectrometry using a column of Deactigel.

Ethylenethiuram monosulfide (ETM) (V) is usually considered to be a stable end product of EBDC decomposition at room temperature. Under elevated temperature, however, this intermediate was also converted to ETU as summarized in Table IV. Good agreement between the yield of ETU and of carbon disulfide was observed. These results suggest that decomposition of ETM to ETU occurs via reduction of the disulfide linkage to form the corresponding dithiol (XIV) and not via the intermediacy of EDI (VII). Hydrolysis of the reduced ETM (XIV) results in ETU with the liberation of an equivalent of carbon disulfide. The same mechanism was recently proposed by Vonk and Kaars Sijpesteijn (1976) for the enzymatic and microbial conversion of ETM to ETU.

A study of the aqueous decomposition of three EBDC formulations (Maneb, Mancozeb, and Metiram) at several acid pH values demonstrated a similar behavior to that observed for nabam above. Formulations were refluxed for 2 h (to avoid differences in rates of reaction at different pH values), cooled, and filtered under suction, and the filtrate was assayed for ETU. The results are recorded in Table V. Within experimental error no differences in the yields of ETU were observed between the formulations at several different acid pH values. The pH dependence of ETU formation from the formulations is qualitatively

similar to the pH dependence observed for ETU formation from nabam decomposition.

These results suggest that it might be possible to control the conversion of EBDC residues to ETU by converting them instead to ethylenediamine. The incorporation into industrial processing of an acid cook followed by a readjustment of the pH provides a possible solution and is presently under investigation.

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