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Determination of Degradation Products and Pathways of Mancozeb and Ethylenethiourea (ETU) in Solutions Due to Ozone and Chlorine Dioxide Treatments

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The objective of the present study was to determine the degradation products of mancozeb and ethylenethiourea (ETU) and elucidate the possible degradation pathways in solution as a result of chemical oxidation using ozone and chlorine dioxide. This study was developed in a solution at 100 ppm of mancozeb and ETU concentration over the course of 60 min. Two different oxidizing agents used in this study were (1) ozone at 3 ppm and (2) chlorine dioxide at 20 ppm. Ozone was continuously provided throughout the course of the reaction. Degradation products were detected with high-resolution GC-MS. The total analysis time was 4 min per sample combined with rapid GC separation and time-of-flight mass spectrometry (TOFMS). Hydrolysis of mancozeb led to *m*/*z* 144 ion fragmentation, which is 5-imidazoledithiocarboxylic acid, as a major degradation product. ETU showed M^+ 102, which corresponds to its mass, indicating this compound was stable in distilled water and did not undergo hydrolysis during 60 min. The average retention times of mancozeb and ETU were approximately 181−189 and 210−230 s, respectively. Ozonation of mancozeb produced ETU as a major product. Treatment of ETU with ozone produced several degradation compounds. From prolonged ozonation, the CS_2 or CS group was removed. Overall, several byproducts identified were M^+ 60, M^+ 84, M^+ 163, M^+ 117, and M^+ 267 by ozone and M^+ 117, M^+ 86, and M^+ 163 by chlorine dioxide treatment. Several of these have been reported, but others have never been reported previously.

KEYWORDS: Mancozeb; ETU; ozone; chlorine dioxide; degradation

INTRODUCTION

Ethylenebis(dithiocarbamate)s (EBDCs) are one of the oldest and most widely used classes of organic fungicides in the world (*1*). The EBDCs registered for food uses in the United States are mancozeb, maneb, metiram, nabam, and zineb (*2*). They were first introduced during the 1940s and widely used. These compounds have low water solubility, which results in the pesticide remaining as superficial deposits on the surface of treated crops (*3*). The EBDCs are generally unstable in the presence of moisture or oxygen and in biological systems (*4*). They are easily degraded in these conditions, and several degradation products are formed, including ethylenethiourea (imidazolidine-2-thione, ETU) (*2*). It has been reported that ETU occurs as a result of metabolic (*5*) and chemical (*5*, *6*) alterations of the commercial fungicides. ETU has caused cancer in experimental animals and has been classified as a group B2 probable human carcinogen on the basis of evidence from animal studies performed by the U.S. EPA (*4*).

Chemical degradation occurs as a result of the various reactive agents in the formulations. Water is responsible for considerable breakdown of pesticides in solution, especially in conjunction with extremes of pH (*7*−*9*). Even slight variance from a neutral pH can cause rapid decomposition of pH-sensitive compounds. Molecular oxygen and its several more reactive forms (e.g., ozone, superoxide, and peroxides) are capable of reacting with many chemicals to generate oxidation products (*10*). Ozone and chlorine dioxide have been widely used for treating drinking water and processing food for many years in many countries (*11*). The use of ozone is particularly attractive because it can be applied as a gas or in water, and it dissipates quickly, so that no residue is left on foods (*11*, *12*). Like ozone, chlorine dioxide is a good disinfectant and can kill a large number of microorganisms, including some that are resistant to treatment with chlorine (*14*). Both of these compounds are also being explored for use in reducing pesticide residues on fruits and vegetables, and the results have shown them to be effective (*15*).

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However, there is also concern over the presence of chemical byproducts that are formed when chlorine, ozone, and chlorine dioxide are used for the reduction of pesticide residues. Many organic compounds present in water and foods treated with chlorine are subject to chlorination reactions. When chlorine is applied to organic molecules, they are changed to molecules with an increased hydrophobicity or hydrophilic nature. This in turn often increases the toxicity and bioaccumulation of these compounds. Chlorine treatment is known to produce some chemicals that cause cancer in laboratory animals (*16*). Use of ozone and chlorine dioxide as alternatives to chlorine for treatment of drinking water and food processing is increasing, mainly because they produce fewer disinfection byproducts. However, it is unknown whether they produce compounds as harmful or more harmful than those produced by chlorine. The EPA has therefore set out to identify all potentially harmful byproducts.

Gas chromatography (GC) is frequently interfaced with mass spectrometry (GC-MS) for confirmation and structural identification of pesticides (*17*). Chemical ionization mass spectrometry (CI/MS) is frequently used to generate molecular ions, as it provides the necessary empirical formula information for the molecular ion and fragments. It also helps to determine the number of possible structures for each unknown byproduct (*18*).

A time-of-flight mass spectrometer (TOFMS) is based on the elapsed time the ion takes to travel from the ion source to the detector. Ions that have been accelerated to equal energies move with velocities related to their mass-to-charge ratio; these characteristic velocities are used for mass analysis in TOFMS. Ions simultaneously accelerated out of an ion source separate into groups according to their velocities as they travel through an evacuated, field-free tube. The time elapsed between the extraction of an ion from the source and its detection at the end of the tube is measured and used to calculate mass. In a typical commercial TOFMS instrument, the energy applied for extraction is sufficient to cause ions up to about *m*/*z* 1000 to arrive at the detector within 100 μs of the extraction pulse (*19*). The instrument is therefore capable of producing a signal representing 10^4 complete mass spectra each second. This permits analysis of dozens of compounds in 1−3 min (*20*) due to the extremely rapid spectral acquisition capacity (up to 500 spectra/s) of the mass spectrometer. The use of TOFMS for detection allows compression of chromatography time by permitting significant overlap of eluting compounds without loss of analytical capacity as long as the mass spectra of overlapping compounds differ by a single *m*/*z* ratio. In addition, compression of chromatography time results in an increase in sensitivity in that the spectrometer response is concentrated over a shorter time interval than by conventional chromatography. Thus, sampling, chromatographic separation, detection, and analysis potentially can be completed in minutes per sample with enhanced sensitivity (*21*).

Among various oxidizing agents, ozone and chlorine dioxide were selected for this study because they are known to be relatively less toxic and would be good alternatives to chlorine treatment. The objective of this investigation was to determine the byproducts of mancozeb and ETU when treated with ozone and chlorine dioxide and elucidate possible degradation pathways of this pesticide.

MATERIALS AND METHODS

Materials. All organic solvents used for preparation of stock solution, sample extraction, and GC-MS were of distilled-in-glass grade. Hexane, xylene, chloroform, and methylene chloride were obtained from J. T. Baker Co. (Phillipsburg, NJ). Mancozeb standard (79.8%) was obtained from Rohm & Hass (Philadelphia, PA). Mancozeb is a complex polymeric, noncrystalline organometallic solid that does not exist in pure form. Standard product on material is ~80% pure and contains some stabilizers and formulation materials. Ethylenethiourea [ETU (2-imidazolidinethione), CAS Registry No. 96-45-7, 99.0%] and ethyleneurea [EU (2-imidazolidineone), CAS Registry No. 120-93-4, chemical purity 96.0%] standard were obtained from Aldrich Chemical Co. (Milwaukee, WI). Sodium sulfate (previously dried at 120 °C for at least 12 h), potassium fluoride, and ammonium chloride were all of reagent grade.

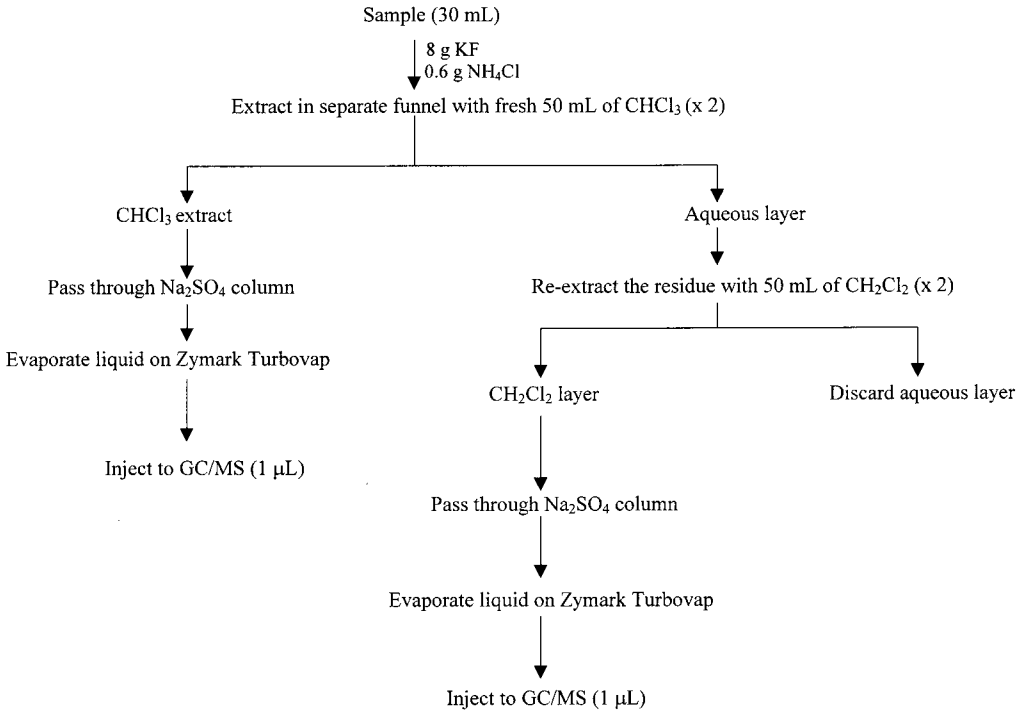
Methods. *A. Ozonation Procedure.* A laboratory research ozone generator (Allegheny Teledyne Inc., Enon Valley, PA) was used. Ozone (O_3) was bubbled through a glass sparger (produced bubbles of ~10 mm i.d.) into 500 mL of distilled water at ambient temperature and pH under 25 psi at 15 standard cubic feet per hour (SCFH) of oxygen until the desired ozone concentration (3 ppm) was attained. All ozone concentrations were determined according to the method published in *Standard Methods for Examination of Water and Wastewater*, 17th ed. (*22*) (4500-O_3 B indigo colorimetric method). Mancozeb was spiked to give a final concentration of 100 ppm. After the addition of the mancozeb, at the desired ozone concentration, the addition of ozone was continued at 25 psi and 15 SCFH of oxygen. A 30 mL sample was transferred at 1, 15, 30, and 60 min intervals into an Erlenmeyer flask. Two hundred microliters of 0.5% 0.1 M sodium thiosulfate solution was immediately added to the samples to quench the reaction.

B. Chlorination Procedure. Chlorine dioxide (ClO_2) was generated in the laboratory using the manufacturer's (S. C. Johnson Professional, Racine, WI) instructions as follows. One hundred milliliters of the stock 2% Oxine FP solution was added to a 200 mL volume French square screw-capped bottle. Twenty-five milliliters of 75% w/w food grade phosphoric acid was carefully but quickly added and the cap immediately tightened. Chlorine dioxide was allowed to be generated for 5 min of thorough mixing with a magnetic stirrer. At 5 min, the full concentrate volume was quickly decanted into a 5 gal polypropylene tote with a stopcock, and any remaining generated chlorine dioxide was flushed into the 5 gal tote. This served as a 100 ppm stock chlorine dioxide solution to achieve the final test concentration. For 20 ppm of chlorine dioxide, 8 L of stock solution was diluted to a total of 10 gal with distilled water. Mancozeb was spiked to give a final concentration of 100 ppm. All chlorine dioxide concentrations were determined using the Hach Co. (Loveland, CO) chlorine colorimeter (model 4670051) before and after each sampling run.

*C. Sample Extraction (**Scheme 1**).* Thirty milliliters of prepared sample, 8 g of potassium fluoride (KF), and 0.6 g of ammonium chloride (NH_4Cl) were extracted in a 250 mL separatory funnel. In the preliminary study, this mixture was extracted with five different solvents according to their polarity. The solvents included hexane (polarity = 7.3), xylene (polarity = 8.8), chloroform (polarity = 9.1), methylene chloride (polarity = 9.6), and water (polarity = 21.0). From these results, mancozeb and ETU residues were contained only in the chloroform and methylene chloride layer, so these two solvents were used for further extraction procedure. The mixture was extracted with 50 mL of chloroform and methylene chloride two times. Then, the solvent layer was passed through a bed of 25 g of sodium sulfate and collected in a Zymark Turbovap tube (Zymark Ind., Hopkin, MA). The extracted liquid was evaporated to 1 mL at 40 °C in a Zymark Turbovap evaporator using nitrogen gas. This reduced extract was analyzed by GC-MS. Byproducts of ozonation, chlorination, and possible degradation pathways were identified.

D. GC-MS Analysis. GC-MS analyses were performed on a mass spectrometer equipped with a Hewlett-Packard model 6890 gas chromatograph (Hewlett Packard Co., Wilmington, DE), and a Pegasus II version 1.4 computer workstation (LECO Corp., St. Joseph, MI, 1997) was used. Injections of 1 μL of the extract were introduced via a split injector onto a J&W Scientific (Palo Alto, CA) hp-5 chromatographic column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Ultrapurified helium (99.9%) was used as carrier gas at a flow rate of 1.5 mL/min. The GC temperature program consisted of an initial temperature of 40 °C, which was held for 1 min, followed by an increase at a rate of 55

Scheme 1. Summary of the Extraction Procedure for the Degradation of Mancozeb in Solution



°C/min to 300 °C, which was held for 1 min. Transfer lines were held at 250 °C, and the injection port was controlled at 280 °C. Sample detection was by TOFMS with an electron ionization source (FCD-650, LECO Corp.). Mass spectra were collected at a rate of 40/s over the mass range (*m*/*z*) 33−350. The electron ionization energy was 70 eV. The temperature of the ion source was 200 °C.

RESULTS AND DISCUSSION

Identification of fragment ions in this study was not conducted for unknown compounds but confirmed by comparison of published structural data with those of degradation of pesticides (*23*). Although mancozeb and ETU were degraded by chlorine dioxide, this oxidant was less effective than ozone at the concentration used in this study. However, it is anticipated that mancozeb and ETU would be completely degraded by the chlorine dioxide treatment if the concentration of chlorine dioxide was increased above the 20 ppm that was used in this study.

A. Byproducts Formed from Hydrolysis. *1. Degradation of Mancozeb.* Identification of fragment ions was confirmed by comparison of collected mass spectra with those of authenticated chemical standards and to reference spectra in a mass spectral library (National Institute for Standard Technology, search version 1.5, Gaithersburg, MD). A mass spectrum is a graph of ion abundance versus mass-to-charge ratio. The ions and their abundance serve to establish the molecular weight and structure of the compound being analyzed. Because the ionization process frequently breaks up or fragments the molecule, ions appear in the spectrum at lower *m*/*z* values than that which corresponds to the molecular mass of the molecule. **Figure 1A** shows a typical spectrum of mancozeb standard at a concentration of 100 ppm, whereas **Figure 1B** shows the mass spectrum of the chloroform extract of mancozeb obtained by GC-MS. These spectra corresponded to library search data for mancozeb. In the mass spectrum of the chloroform extract, mancozeb has a strong molecular cluster at *m*/*z* 144, both with and without computer background subtraction. The average retention time of this peak was ∼181−189 s. This corresponded to the

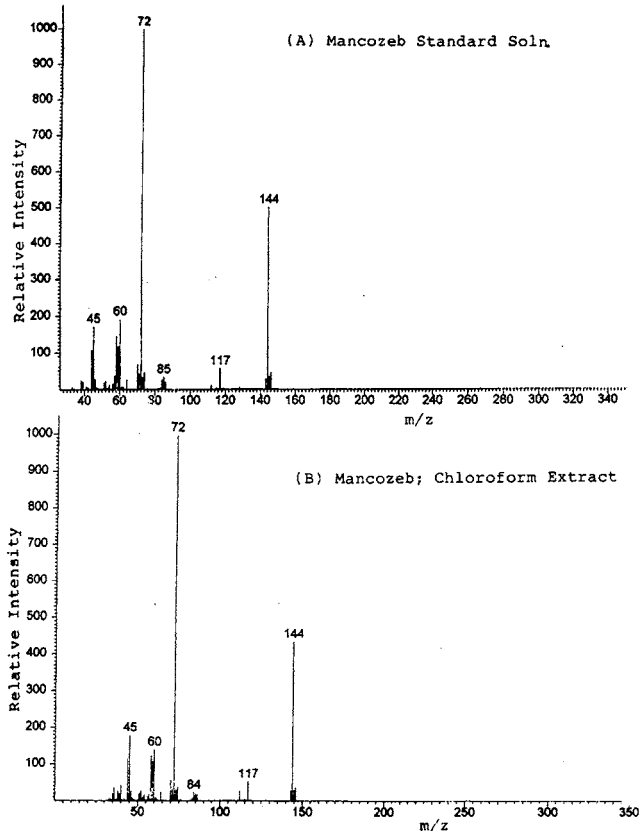


Figure 1. Typical spectrum of mancozeb from (A) standard solution at 100 ppm in distilled water and (B) chloroform extract.

ethylenebis(dithiocarbamic acid) compound minus manganese and zinc ion ($C_4H_4N_2S_2$; 5-imidazoledithiocarboxylic acid) (**Figure 2**). The metal ions are considered to be very unstable and are quickly lost when mancozeb is introduced into a high-temperature condition. This compound can be present as a linear or cyclic form. The major peak with the highest intensity was

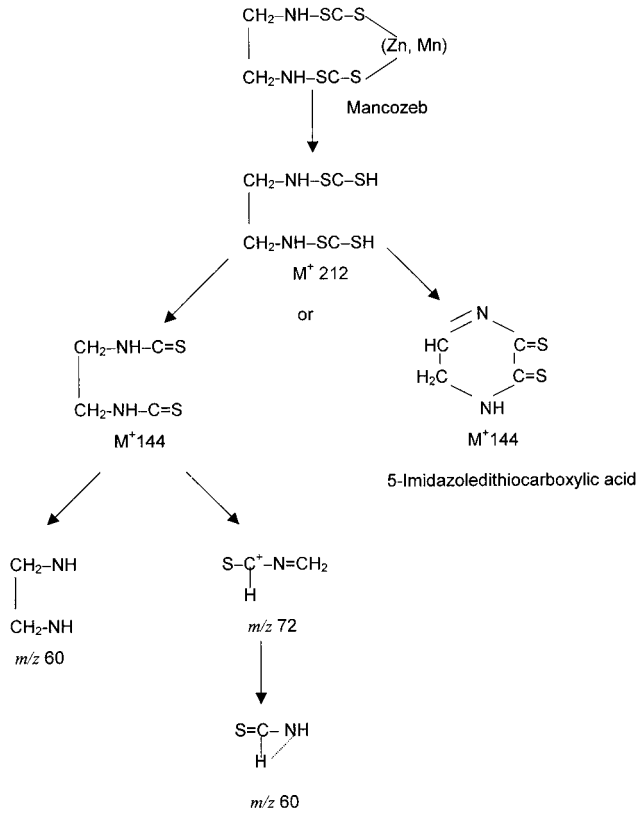


Figure 2. Possible fragmentation of mancozeb in aqueous solution by hydrolysis.

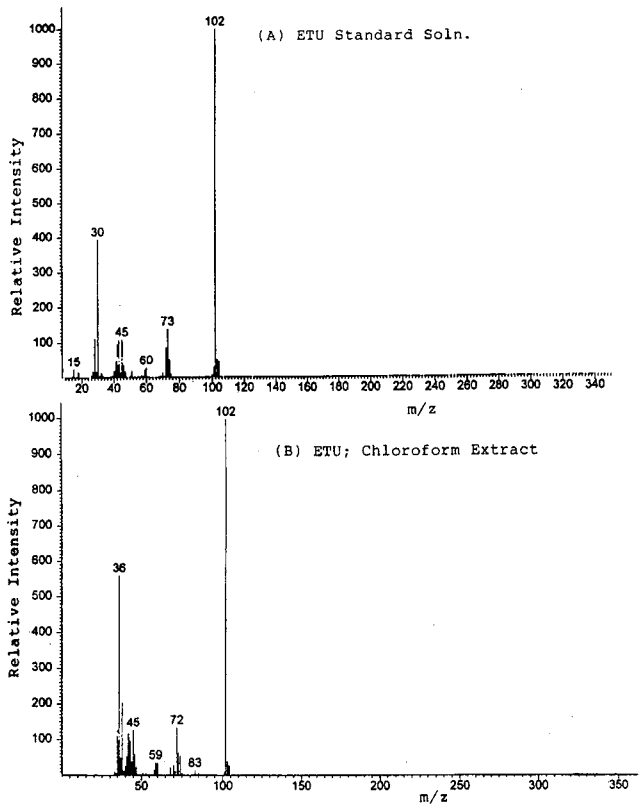


Figure 3. Typical spectrum of ETU from (A) standard solution at 100 ppm in distilled water and (B) chloroform extract.

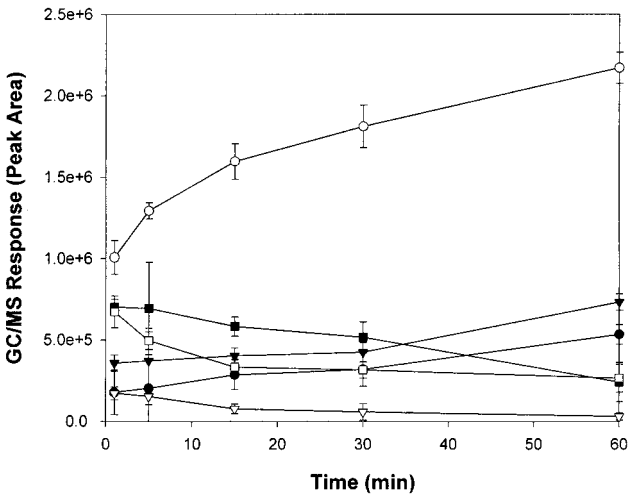


Figure 4. Effect of ozone on time dependence of the GC-MS response on the formation of molecular ion (M^+ 72), one of the major degradation compounds in solution: (●) control, pH 4.6; (○) O_3, pH 4.6; (▼) control, pH 7.0; (▽) O_3, pH 7.0; (■) control, pH 10.7; (□) O_3, pH 10.7.

m/*z* 72 at 181−181 s, and several other peaks, including *m*/*z* 60 and 45, appeared. The ion at *m*/*z* 85 represented a smaller portion of the total ion current. The fragment ions were used to determine molecular structure. The proposed structures of the fragment ions are illustrated in **Figure 2**.

2. Degradation of ETU. **Figure 3A** shows a typical spectrum of ETU standard at a concentration of 100 ppm, whereas **Figure 3B** shows the mass spectrum of the chloroform extract of ETU obtained by GC-MS. These spectra corresponded to library search data for ETU. After 60 min of reaction in distilled water, the spectrum showed patterns similar to that of 0 min and still had a strong molecular cluster at *m*/*z* 102. The M^+ (102) corresponded to the molecular weight of ETU. This indicates that ETU was stable in distilled water and did not undergo hydrolysis during 60 min. The average retention time of ETU was ∼210−230 s.

3. Effect of pH on the Formation of Mancozeb Degradation Product. The mass spectra of mancozeb in each pH solution were collected and monitored for a period of 60 min in both chloroform and methylene chloride layers. The chloroform layer showed a more intense GC-MS response to the mancozeb degradation products than the methylene chloride layer. This was due to the effect of serial extraction. Most mancozeb residues were extracted by chloroform, and only small amounts of mancozeb residues remained on the methylene chloride layer. In pure mancozeb standard solution, the most abundant ion was *m*/*z* 72. In **Figures 4** and **5**, the time dependence of the GC-MS response as the peak area of the molecular ion (M^+ 72) is shown. As time elapsed the relative response of the ion currents at *m*/*z* 72 increased in control treatment at three pH ranges. The formation of *m*/*z* 72 was greatest at pH 7.0 and decreased in pH 4.7 and 10.7. This result suggested that the *m*/*z* 72 ion was stable at neutral pH, and the formation of this ion increased as time elapsed.

Ozone treatment at pH 4.6 showed a preventative effect on the formation of *m*/*z* 72 ion (**Figure 4**). The ozone treatment at pH 10.7 was the least effective. No *m*/*z* 72 ion was detected at pH 4.6 or 7.0 after 60 min of reaction time. This was due to the instability of ozone at alkaline conditions. These results corresponded to the model system study. Chlorine dioxide also showed a preventative effect on the formation of *m*/*z* ion (**Figure 5**). pH 4.6 showed the most effectiveness, and pH 10.7 was the least effective. However, the effect was lower than ozone treatment. The *m*/*z* 72 ion remained at 20 ppm chlorine dioxide treatment after 60 min.

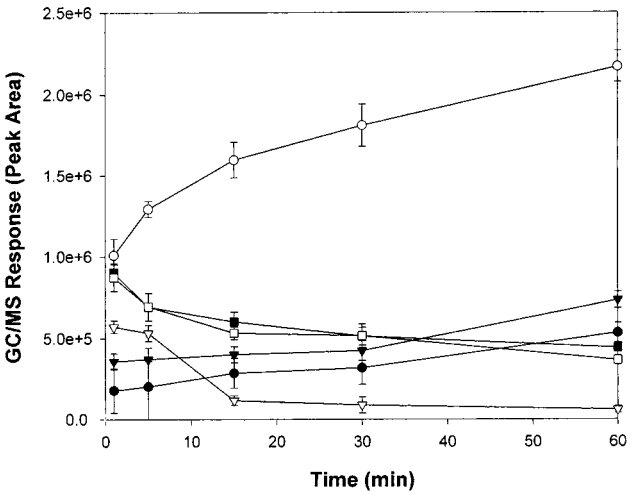


Figure 5. Effect of chlorine dioxide on time dependence of the GC-MS response on the formation of molecular ion (M^+ 72), one of the major degradation compounds in solution: (●) control, pH 4.6; (○) ClO_2, pH 4.6; (▼) control, pH 7.0; (▽) ClO_2, pH 7.0; (■) control, pH 10.7; (□) ClO_2, pH 10.7.

B. Byproducts Formed from Ozonation. *1. Degradation of Mancozeb.* Ozonation of mancozeb produced ETU, with a retention time of 206 s. When the reaction between mancozeb and ozone continued, degradation of mancozeb occurred. At 30 min of reaction time, the total amount of *m*/*z* 144 ion decreased compared to that at 1 min. After 60 min of ozone treatment, no *m*/*z* 144 was detected at 206 s. Oxidation due to ozonation or hydrolysis changes the byproducts into high-polarity hydrophilic compounds, such as ETU and others. Analysis of the aqueous ozonation of mancozeb and its degradation products demonstrated that metal groups, such as manganese and zinc, are the first site of attack and then the CS_2 or CS group was removed.

Usually, reference standards are pure compounds; however, the sample extracts are not, so they can introduce interfering ions into the mass spectrum, complicating the confirmation process. Standard mancozeb is ~80% pure and contains some stabilizers and formulation materials. Therefore, determination of some oxidation products was not possible because of matrix interference.

2. Degradation of ETU. Treatment of ETU with ozone yielded several degradation compounds. Prolonged ozonation (60 min) of ETU eventually gave rise to ethylenediamine (EDA) and several degradation products, but no ethyleneurea (EU) was detected in this study. The molecular ions found as ETU degradation products by ozone treatment were M^+ 60 at 42.77 s, M^+ 84 at 47.87 s, M^+ 163 at 61.37 s, M^+ 117 at 62.47 s, and M^+ 267 at 131.57 s. The proposed structures of the degradation products are illustrated in **Figure 6**. The degradation byproducts were confirmed with previous findings (*21*). The results suggest that ozonation increases the removal of mancozeb and produces several degradation products. These results, however, do not reveal the underlying mechanism(s) or toxicity. Hence, more detailed studies are required to identify these mechanisms and, subsequently, optimize the combined treatment process. Toxicity tests are also required.

C. Byproducts Formed from Chlorine Dioxide. *1. Degradation of Mancozeb.* Chlorination of mancozeb produced ETU, with a retention time of 206−218 s. When the reaction between mancozeb and ozone continued, the degradation of mancozeb occurred. At 30 min of reaction time, the total amount of *m*/*z* 144 ion decreased as compared to 0 min. After 60 min of chlorine treatment, a small peak of *m*/*z* 144 was still detected. This indicated that mancozeb residue did not completely degrade into other byproducts but remained. This was probably due to the high concentration of mancozeb (100 ppm) compared to the low chlorine dioxide concentration. It is anticipated that the *m*/*z* 144 peak would completely disappear with chlorine dioxide treatment if the concentration of chlorine dioxide was increased above the 20 ppm that was used in this study.

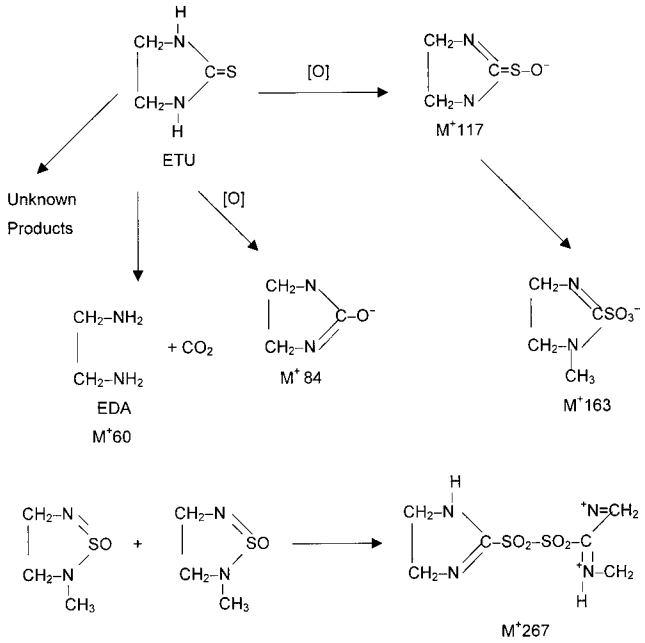


Figure 6. Proposed degradation pathway of ETU by ozonation.

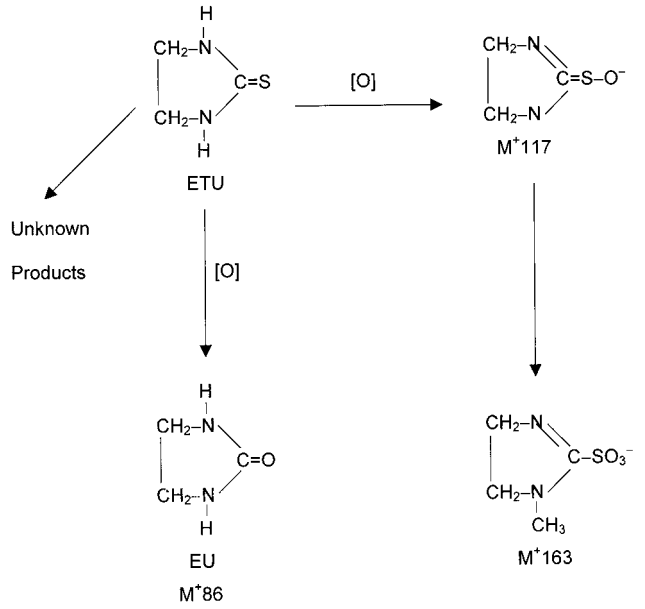


Figure 7. Proposed degradation pathway of ETU by chlorine dioxide.

2. Degradation of ETU. Treatment of ETU with chlorine dioxide yielded several degradation compounds. At prolonged ozonation (60 min), ETU was oxidized to ethyleneurea (EU) at a retention time of 162−180 s. However, ETU was still detected at 209−221 s in the spectra. This means that ETU did not completely degrade into other byproducts but remained in the reaction mixture. This was probably due to the high concentration of ETU (100 ppm) compared to low chlorine dioxide concentration. The molecular ions found as ETU degradation products were M^+ 117 at 62.72 s, M^+ 86 at 160.12 s, and M^+

163 at 61.37 s. Several unknown products are also present. The proposed structures of the degradation products are illustrated in **Figure 7**. Chlorine dioxide showed less effectiveness in the degradation of ETU compared to ozone treatment. ETU produced fewer degradation products compared to ozonation. This is probably due to the fact that ETU was not completely degraded by chlorine dioxide.

The results suggest that low-dose chlorine dioxide treatment does not significantly remove mancozeb and ETU. However, the effect of chlorine treatment may be expected to depend on the applied chlorine dioxide dosage and contact time, as well as the concentration of mancozeb present in solution. Consequently, further studies are required to assess these effects.

Overall, many byproducts were identified, several of which have never been reported previously. Many of the compounds were not present in any spectral library (NIST or Wiley), and many of the ones that were in the libraries did not give conclusive library matches (*14*). For many of the compounds, little information was provided by the mass spectra because of the absence of molecular ions, which provide molecular weight information.

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