



Experimental studies on ozonation of ethylenethiourea

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Abstract

The experimental study on ozonation of ethylenethiourea (ETU) is conducted. The reaction of gas-phase ETU with 0.63×10^{-6} mol/L ozone is carried out in a 200-L reaction chamber. The secondary organic aerosol (SOA) resulted from the ozonation of gas-phase ETU is observed with a scanning mobility particle size (SMPS). The rapid exponential growth of SOA reveals that the atmospheric lifetime of ETU vapor towards ozone reaction is less than four days. The ozonation of dry ETU particles, ETU-contained water droplets and ETU aqueous solution is investigated with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-AToFMS). The formation of 2-imidazoline is observed in the ozonation of dry ETU particles and ETU-contained water droplets. The formation of 2-imidazoline and ethyleneurea is observed in the ozonation of ETU aqueous solution.

Key words: ethylenethiourea; pesticide; ozonation; VUV photoionization; AMS

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Introduction

Ethylenethiourea (ETU) is one of the main degradation products of ethylenebis-(dithiocarbamate)s (EBDCs), which is one of the oldest and most widely used classes of organic fungicides all over the world, including mancozeb, maneb, metiram, nabam, and zineb (Hwang et al., 2003; Lentzarizos, 1990). ETU is the most toxic degradation product of EBDCs (Houeto et al., 1995). The EBDCs were first introduced in the 1940s and widely used for a long period of time. In the 1990s, the amount was 8–12 million pounds per year (Dearfield, 1994). Most of these pesticides have low water solubility, resulting the residual pesticide existed on the surface of treated crops (Hwang et al., 2003). They are unstable in the presence of either oxygen or in biological systems. ETU is also used as an accelerator in the rubber industry, where it is used for vulcanization of polyacrylate rubber and as an accelerator in the manufacture of neoprene rubber. Additionally, ETU is used in production of antioxidants and synthetic resins (Montelius, 2001). To the best of our knowledge, no data of the gas-phase or the particle-phase concentrations in the atmosphere are available.

Pure ETU is white to pale-green crystalline solid. The molecular formula of ETU is $C_3H_6N_2S$ and its molecular weight is 102. ETU has a solubility of 2 g in 100 g water at 303 K, which is relatively stable to hydrolysis but can be rapidly photolyzed in the presence of photosensitizers (Xu,

2000). The photolysis half-lives of ETU in natural water are reported as 1 to 4 days, the concentration of 1×10^{-7} mol/L ETU solution remained constant after 48 hr (Lyman and Lacoste, 1974). Through chemical and biological decompositions in soil, its half-life is 1 to 7 days, while its half-life in the air is 8–9 days (Xu, 2000). The degradation of ETU in solution or on the surface of crops oxidized by chlorine dioxide, hypochlorite, hydrogen peroxide, and ozone were reported and the main oxidation products were ethyleneurea, Jaffe's base, 2-imidazoline, and IM-SS-IM (Hwang et al., 2003; Houeto et al., 1995; IUPAC, 1977; Marshall, 1979; Marshall and Singh, 1977). The vapor pressure is 11 Pa at 293 K (GSI data base). This relative high vapor pressure indicates most of ETU in atmosphere should exist in gas-phase while some of them may attach to the surface of aerosols in the atmosphere (Whitby, 1978; Tsai et al., 1991; Millet et al., 1997; van den Berg et al., 1998; van Dijk and Guicherit, 1998). Because of the higher water-solubility of ETU, it would be easily adsorbed on moist particle surfaces, forming particulate ETU. Ozone is one of the most common atmospheric oxidants which plays an important role in the chemistry of the atmosphere (Adeniji et al., 1981). The annual average background ozone concentrations over the midlatitude of the Northern Hemisphere range $(0.89\text{--}2.01) \times 10^{-9}$ mol/L (Vingarzan, 2004). However, the studies on ozonation of gas-phase and particle-phase ETU have not been reported yet.

In this study, the ozonation of ETU is investigated using a scanning mobility particle sizer (SMPS) and a vacuum

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ultraviolet photoionization aerosol time of flight mass spectrometer (VUV-ATOFMS). The estimated atmospheric lifetime of ETU vapor towards ozone reaction is less than 4 days based on the measurement of the secondary organic aerosol (SOA) growth rate. The formation of 2-imidazoline is observed in the ozonation of dry ETU particles and ETU-contained water droplets. IM and EU are observed in the ozonation of ETU aqueous solution.

1 Materials and methods

1.1 Materials

Azelaic acid (99%, China North Region Special Chemical Reagent Development Center), and ethylenethiourea (99.5%, DIMA Technology, Inc., Beijing) were used in this experiment. Oxygen (99.99%) and nitrogen (99.99%) were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd., China.

1.2 Description of instruments

The diagram of the experimental setup is shown in Fig. 1. It has been described in detail elsewhere (Gao et al., 2009). Briefly, the aerosol reaction chamber works at the ambient pressure and temperature (1.01×10^5 Pa, 298 K). The volume of the chamber is 200 L. A hygrothermograph is used to measure the relative humidity. The size distribution and the concentration of the particles in the reaction chamber are measured using a scanning mobility particle sizer (SMPS, TSI 3080, USA) equipped with a long differential mobility analyzer electrode (DMA, TSI 3081, USA) and a condensation particle counter (CPC, TSI 3010, USA). The ozone denuder is employed to remove about 95% of ozone in the flow sampled by SMPS. Ozone is generated by an ozone generator (model NPF8W, Shandong NIPPON, China) with purified O_2 (99.9%). The VUV-ATOFMS utilized to analyze suspended particles is homemade and the detailed description has been given elsewhere (Shu et al., 2008).

1.3 ETU vapor experiment

ETU vapor used for the homogeneous reaction is generated by heating 0.1 g of ETU contained in a 3-cm (inner

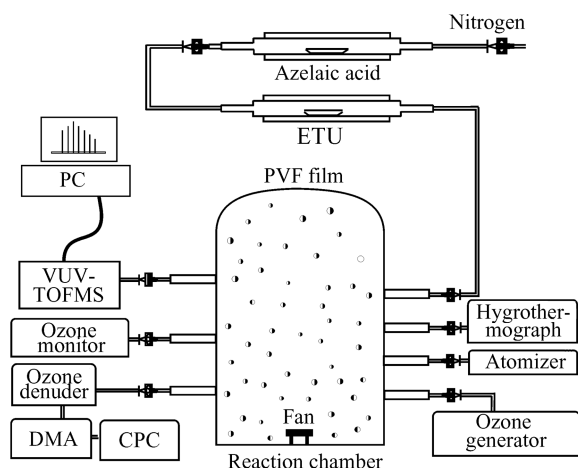


Fig. 1 Diagram of experimental setup.

diameter) \times 40-cm (length) quartz tube at (363 ± 2) K. ETU vapor is introduced into the chamber by flushing nitrogen at a flow rate of 0.5 L/min. The introduction lasted 180 min. The particles in the reaction chamber are monitored every 30 min before ozone is added. Then ozone is added into the chamber and its concentration reaches 0.63×10^{-6} mol/L. The size distributions of the SOA particles are measured with the SMPS continuously until the amount of SOA ceases increasing.

1.4 ETU particle experiment

The ETU particles are generated by the homogeneous nucleation method. The aerosol generator consists of two 3-cm (inner diameter) \times 40-cm (length) quartz tubes equipped with heating tapes and thermometers. Azelaic acid of 0.2 g used to generate nucleus is put in the first quartz tube. Pure nitrogen passes through the first tube with a flow rate of 0.5 L/min. Azelaic acid is chosen as the nucleus because it has little reactivity with ozone (Kwamena et al., 2007). The temperature of the quartz tube is set at (408 ± 2) K. Meanwhile, 0.1 g ETU used to coat the azelaic acid nucleus is placed in the second quartz tube. The temperature of the second tube is set at (375 ± 2) K. ETU-coated particles are introduced into the chamber for 30 min. The size distribution of the generated particles measured with the SMPS are shown in Fig. 2a. The size distribution of the pure azelaic acid particles has a mean diameter of 94 nm. The size distribution of the ETU-coated particles shift to the mean diameters of 220 nm and the mass concentration of ETU-coated particles is $2400 \mu\text{g}/\text{m}^3$ on the assumption of both the densities of azelaic acid and ETU particles equal to $1.2 \text{ g}/\text{cm}^3$.

1.5 ETU droplet experiment

ETU-contained water droplets are generated by atomizing 0.1 g ETU dissolved in 50 mL water. The droplets

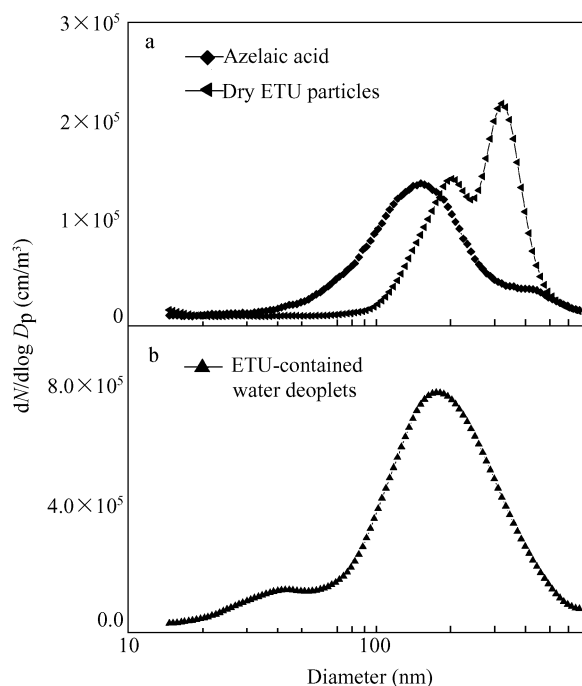


Fig. 2 Typical particle size distributions of azelaic acid and dry ETU particles (a), and ETU-contained water droplets (b) measured by SMPS.

are introduced into the reaction chamber by a nitrogen stream with flow rate 1.5 L/min. The introduction lasts 30 min. The size distributions of the droplets in the reaction chamber measured with SMPS are shown in Fig. 2b. The relative humidity in the reaction chamber is 50%.

1.6 Liquid phase experiment

In order to verify the time-of-flight mass spectra of the ozonation products of ETU in particle reaction, analysis of the ozonation products of ETU in liquid solution is carried out. A stream of oxygen containing ozone with a flow rate of 1.5 L/min bubbled through a beaker containing a solution of 50 mg ETU in 30 mL water. The bubbling takes 40 min. Then, the droplets generated by atomizing the solution are analyzed with VUV-ATOFMS.

2 Results and discussion

2.1 Ozonation of ETU vapor

The SOA formation is observed in ozonation of gas-phase ETU. Figure 3a shows the size distributions of the SOA measured with SMPS, which are 4, 12, 26 and 38 min after the ozone injection. There are very few residual particles in the chamber before the ozone injection. After the ozone injection, a large quantity of the SOA particles with diameters of 20 nm pops up. The number of the SOA particles decreases with reaction time whereas the sizes of those increase with that. This phenomenon indicates the formation of SOA from the ozonation of ETU vapor. On the assumption that the SOA particles are spheric and the densities of those are equal to 1.2 g/cm³, mass concentrations of the SOA particles can be calculated. Figure 3b

shows the calculated time-dependant mass concentrations of the SOA particles. After ozone is introduced into the reaction chamber, the mass concentrations of the SOA particles increase rapidly and reach a maximum at 20 min. By fitting the mass concentration of SOA as a function of time, the exponential growth rate of SOA obtained is 0.002 with the related coefficient (R^2) of 0.956. Since the concentration of ozone does not change apparently, thus we think that the amount of ozone is much more than that of ETU in the reaction chamber and the reaction can be processed as a pseudo first-order reaction. Additionally, the reaction of ETU vapor with ozone is prior to the formation of SOA. Hence, the pseudo first-order rate constant of ETU vapor with ozone should be larger than 0.002 which corresponds to a second order reactive rate constant $k_{O_3} = 5.3 \times 10^{-18}$ cm³/(mol·sec) in this experiment. Estimated by using the formula of $\tau_{O_3} = 1/(k_{O_3} \times [O_3])$ and $[O_3] = 7 \times 10^{11}$ mol/cm³ (Logan, 1985), the atmospheric lifetimes of gas-phase ETU towards ozone reaction should be less than 4 days. Nash and Beall reported that the half-lives of ETU in the air of microagroecosystem chambers were 8–9 days (Nash and Beall, 1980). This discrepancy might result from the lower concentration of the atmospheric oxidants in the microagroecosystem chambers.

2.2 Ozonation of ETU particles and droplets

The time-of-flight mass spectrum of ETU (C₃H₆N₂S, mol. wt 102) particles is shown in Fig. 4a. It is acquired before ozone is introduced into the reaction chamber. The acquisition time for the mass spectrum is 20 sec. The mass spectrum is normalized to the intensity of the mass peak at m/z 102 which is assigned to the molecular ion of ETU. The small mass peaks at m/z 103 and 104 shown in Fig. 4a are contributed from ¹³CC₂H₆N₂S (mol. wt 103) and C₃H₆N₂³⁴S (mol. wt 104). The time-of-flight mass spectrum of ETU is fragment free.

Figure 4b shows time-of-flight mass spectrum of the ozonation product of dry ETU particles. The mass spectrum is collected after the ETU particles react with ca. 2.23×10^{-6} mol/L ozone for 1 min. The acquisition time for the mass spectrum is 20 sec. The mass spectrum is normalized to the intensity of the mass peak at m/z 102 shown in Fig. 4a. Compared with the mass spectrum of ETU shown in Fig. 4a, the new mass peaks at m/z 69 and 70 arise in the mass spectrum. The mass peak at m/z 70 is assigned to 2-imidazoline, which was found to be one of the principle terminal oxidations produced by peroxide (Marshall, 1979). The mass peak at m/z 69 is assigned to the daughter ion of 2-imidazoline.

The time-of-flight mass spectrum of ETU water droplets is shown in Fig. 4c. The mass spectrum is normalized to the intensity of the mass peak at m/z 102. The mass spectrum of wet ETU particles is acquired before the ozone injection. Figure 4d shows time-of-flight mass spectrum of the ozonation products of ETU-contained water droplets. The mass spectrum is also collected after the droplets react with ca. 2.23×10^{-6} mol/L ozone for 1 min. The acquisition time for the mass spectrum is 20 sec. The mass spectrum is normalized to the intensity of the mass peak at

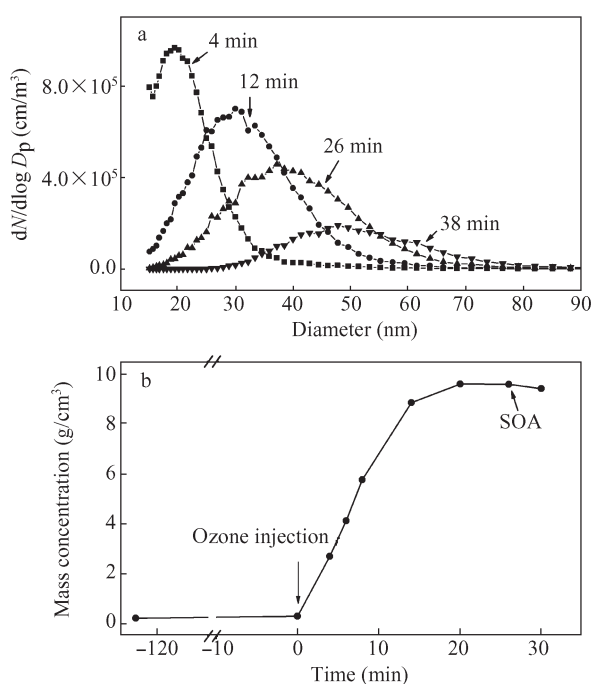


Fig. 3 Time-dependent size distributions of the secondary aerosol particles (a) and time-dependent mass concentrations of secondary aerosol particles (b) resulted from the ozonation of ETU vapor. SOA: secondary organic aerosol.

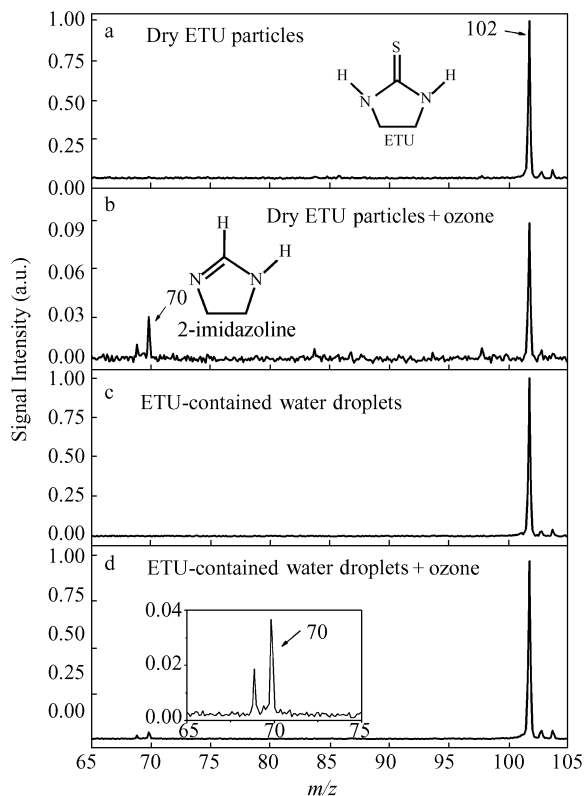


Fig. 4 TOF mass spectra of dry ETU particles (a), the ozonation products of dry ETU particles (b), ETU-contained water droplets (c), and the ozonation products of ETU-contained water droplets (d). The acquisition time for each mass spectrum is 20 sec. The mass spectra shown in Fig. 4a, c are acquired before ozone is injected. The mass spectra shown in Fig. 4b, d are acquired after ozone is injected.

m/z 102 shown in Fig. 4c. Compared to the mass spectrum of ETU shown in Fig. 4c, the new mass peaks at m/z 69 and 70 are observed in the mass spectrum shown in Fig. 4d. The mass peaks at m/z 69 and 70 are contributed from IM as discussed above.

2.3 Liquid phase reaction

Figure 5a and b shows the mass spectrum of the droplets atomized from the ETU water solution without exposure and exposure to ozone for 40 min, respectively. The mass spectra shown in Fig. 5 are normalized to the intensity of the mass peak at m/z 102 shown in Fig. 5a. The acquisition time for each mass spectrum is 20 sec. Compared with Fig. 5a, it can be seen that the new mass peaks at m/z 69, 70, and 86 arise in Fig. 5b. The mass peaks at m/z 69 and 70 are contributed from 2-imidazoline as discussed above. The mass peak at m/z 86 is assigned to ethyleneurea, which is one of the major oxidation products of ETU (Hwang et al., 2003; James et al., 1995).

2-Imidazoline was found in ETU metabolism by animals, plants, and soils (IUPAC, 1977; Iverson, 1977) and in the oxidation by oxidizers (Marshall, 1979). However, 2-imidazoline and ethyleneurea were not found in the aqueous solution oxidized with ozone (Hwang et al., 2003). In this experiment, 2-imidazoline is the solo observed solid-state ozonation product of dry ETU particles and ETU-contained water droplets. Ethyleneurea

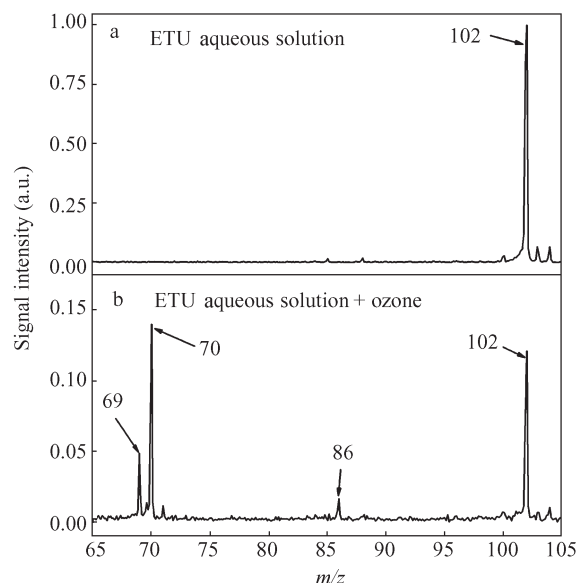


Fig. 5 TOF mass spectra of the ETU solution before ozone exposure (a) and after 40 min ozone exposure (b). The acquisition time for each mass spectrum is 20 sec. The peak intensities of the mass spectra are normalized to that of the mass peak at m/z 102 shown in Fig. 5a.

is not observed in the ozonation of ETU particles and droplets perhaps due to its lower product yield. Since VUV-ATOFMS is only capable of detecting particle-phase products, information about the gas-phase products is not obtained in the experiment. The oxidation mechanism of ETU has been proposed by many researchers (Hwang et al., 2003; Marshall, 1979; James et al., 1995). Generally, the oxidation of ETU takes place with continuous oxidation of S atom of the ETU molecule. Based on the references cited above, we suppose the oxidation is initiated by the insertion of ozone between the C=S bond, forming imidazoline-2-al. Imidazoline-2-al is subsequently oxidized by ozone and hydrolyzed to produce 2-imidazoline.

3 Conclusions

The ozonation of gas-phase and particle-phase ETU are investigated in the experiment. The atmospheric lifetime of ca. 4 days towards ozone reaction is derived from the rate of SOA formation resulted from the ozonation of gas-phase ETU. 2-Imidazoline is the solo solid-state products observed in ozonation of dry ETU particles and ETU-contained water droplet. 2-imidazoline and ethyleneurea are observed in the ozonation of ETU aqueous solution.

Acknowledgments

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