Products and Kinetics of the Heterogeneous Reaction of Suspended Vinclozolin Particles with Ozone

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Products and Kinetics of the Heterogeneous Reaction of Suspended Vinclozolin Particles with Ozone

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Vinclozolin is a widely used fungicide that can be released into the atmosphere via application and volatilization. This paper reports an experimental investigation on the heterogeneous ozonation of vinclozolin particles. The ozonation of vinclozolin adsorbed on azelaic acid particles under pseudo-first-order conditions is investigated online with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). The ozonation products are analyzed with a combination of VUV-ATOFMS and GC/MS. Two main ozonation products are observed. The formation of the ozonation products results from addition of O_3 on the C−C double bond of the vinyl group. The heterogeneous reactive rate constant of vinclozolin particles under room temperature is $(2.4 \pm 0.4) \times 10^{-17}$ cm^3 molecules^{-1} s^{-1}, with a corresponding lifetime at 100 ppbv O_3 of 4.3 ± 0.7 h, which is almost comparable with the estimated lifetime due to the reaction with atmospheric OH radicals (∼1.7 h). The reactive uptake coefficient for O_3 on vinclozolin particles is $(6.1 \pm 1.0) \times 10^{-4}$.

1. Introduction

Fungicides are a class of pesticides with extensive use for the purpose of killing or inhibiting the growth of fungi which cause economic damage to crops and ornamental plants. Wide application of the chemicals has been become a large anthropologic source of air pollution.[1] Concern about the transportation and degradation of the chemicals in the atmosphere has been arising. As organic compounds, fungicides in the atmosphere are supposed to undergo the chemical process of photolysis and reaction with hydroxyl radicals, nitrate radicals, and O_3.[2] Much effort has been made to understand the degradation behaviors of fungicides in water, in soil, and on the plants.[3−5] However, data about the atmospheric transportation, transformation, and lifetime of fungicides are sparse, particularly for the particulate fungicides.

Vinclozolin (3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2, 4-dione) is a general use fungicide marketed by BASF in 1975, which aims at controlling diseases of grapevines, fruit trees, and vegetable crops caused by *Botrytis* spp. (species), *Sclerotinia* spp., and *Monilinia* spp.[6] This cyclic imide fungicide has been widely used to treat fungal diseases in plants and plant-derived foodstuffs. It is well-known that vinclozolin acts as an androgen receptor antagonist in vitro and in vivo,[7−11] with a complex influence on cytochrome P450-dependent enzymes, referring to the reduced expression of various monooxygenases depending upon dose, sex, and organ of the mammals studied.[12,13] Embryonic exposure to vinclozolin can influence sexual differentiation and reproductive functions in the F1 generation.[9,14−16]

Since the introduction of vinclozolin into the market, the concerns of its environmental behavior have mainly focused on photochemistry, hydrolysis, and biodegradation. The stability of vinclozolin in the presence of ethanol, methanol, and water was tested, with the identified hydrolysis products of no antifungal activity.[17] Research on the kinetics of hydrolysis of vinclozolin was conducted.[18] The degradation pathway of hydrolysis underwent the opening of 2,4-oxazolidine ring to yield either butenoic acid or enanilide.[19] The degradation products of photolysis of vinclozolin in the liquid medium have been also reported.[20−22] Schick et al. (1999) suggested the photolysis pathways for opening of 2,4-oxazolidine ring, dechlorination, and elimination of the $CHCH_2$ moiety. Of all investigations, biodegradation related to the reproductive toxicity has always attracted scientists' attention, partially due to its metabolites (2-[[(3,5-dichlorophenyl)carbamoyl]oxy]-2-methyl-3-butenoic acid and 3′,5′-dichloro-2-hydroxy-2-methylbut-3-enanilide) which also act as endocrine disruptor compounds.[14,23] Investigations of the decay of vinclozolin on grapevines, and in soil, thatch, and grass clippings were conducted.[24−27] Vinclozolin exists in the atmosphere mainly in the form of the particle phase with a vapor pressure of 1.6×10^{-8} kPa at 20 °C.[28] Therefore, the heterogeneous reaction of vinclozolin may affect its degradation behavior in the environment. It is demonstrated that vinclozolin is susceptible to O_3 in water;[29] however, the heterogeneous oxidation of suspended vinclozolin by gaseous O_3 has not been carried out yet.

The experiments described in the paper are designed to investigate the behavior of heterogeneous ozonation of vinclozolin. The vinclozolin particles and their particle-phase ozonation products are analyzed online with a laboratory-built VUV-ATOFMS. After the reaction, the particles are collected with glass fiber filters, followed by extraction and GC/MS analysis. To further identify ozonation products, the compounds formed in the liquid-phase reaction are eluted out for VUV-ATOFMS detection.

2. Experimental Section

2.1. Description of Instruments. A diagram of the experimental setup is shown elsewhere,[30] basically consisting of an aerosol generator, a reaction chamber, and analytic instruments.

The aerosol generator is an electric tube furnace with two tandem 50 cm (length) × 4 cm (outer diameter) quartz tubes, each with an independent temperature controller. The homogeneous nucleation method is adopted to produce aerosol particles. About 100 mg of azelaic acid located at the center of

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the first tube is used to generate a nuclei. The generated particles are carried out with a nitrogen stream of 0.5 L min^{-1}. In the meantime, ~70 mg of vinclozolin placed in the second tube is used to coat azelaic acid particles entrained on the nitrogen flow. The corresponding temperatures of two tubes are 408 ± 1 and 393 ± 1 K for azelaic acid and vinclozolin, respectively. The nitrogen stream is controlled by a mass flow meter (D08-2F, Beijing Sevenstar Electronics Co.).

The reaction chamber with a volume of ~180 L is a thin-walled open head stainless steel drum (50 cm (outer diameter) × 60 cm (height)) coated with Teflon, covered with a Tedlar poly(vinyl fluoride) (TVF) film bag (50 cm (length) × 50 cm (diameter)) in order to maintain a constant atmospheric pressure during experiments. A small fan is positioned at the center of the chamber bottom with the purpose of mixing reactants rapidly. The experiments are conducted at ambient conditions of the laboratory, with a room temperature of 295−298 K and relative humidity of 23−25%. The relative humidity in the chamber is estimated to be ~5%, as the air in the chamber is filtered by silica gel following activated carbon. O_3 is produced by an ozone generator (NPF8W, NIPPON), with a pure oxygen stream of 2.5 L min^{-1} as discharging gas.

A laboratory-built VUV-ATOFMS[31] is employed to analyze particles online. A nozzle of ~0.15 mm orifice combined with an aerodynamic lens assembly and a three-stage differential pumping system is used to sample particles at atmospheric pressure. The sample rate is 1.3 cm^3 s^{-1}. The organic particles are vaporized by a heated tip in the detection chamber. The temperature of the heated tip is ~410 K. The nasent organic vapor is photoionized with VUV light emitted from a home-assembled VUV light lamp with a photoflux of 5×10^{14} photon s^{-1} and the wavelength of the main emission at 123.6 nm. The ions produced by VUV photoionization are detected with a reflectron time-of-flight mass spectrometer characterized with a field free flight distance of 1.4 m, an ion mirror, and a chevron multichannel plate detector. A scanning mobility particle size (SMPS), comprising a long differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010), is used to measure the size distribution of particles. The O_3 concentration is measured by an ozone monitor (model 202, 2B Tecnologies, Inc.). An Agilent 6890 GC/MS is used to identify the ozonation products. Samples are injected (splitless) onto an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The injector temperature and transfer line temperature are set at 280 and 250 °C, respectively. The capillary column is set for 2 min at 70 °C with an increase of 25 °C min^{-1} to 150 °C, 3 °C min^{-1} up to 200 °C, and 8 °C min^{-1} up to 280 °C. The temperature is held at 280 °C for 10 min.[32]

2.2. Particle-Phase Reaction. The mass concentration of background particles in the reaction chamber due to the residual ambient particles in the filtered air is below 0.5 μg m^{-3} before the addition of vinclozolin particles. During the operation of the experiments, the filling time for vinclozolin particles is ~40 min for each reaction. The azelaic acid nuclei have a mean diameter of ~269 nm, with a density of 1.2 g cm^{-3}. The vinclozolin particles with azelaic acid nucleus have a mean diameter of ~335 nm. The density of pure vinclozolin is 1.51 g cm^{-3}.[26] The total mass concentration of vinclozolin particles is 238 ± 33 μg m^{-3}. Then O_3 is introduced into the chamber. The O_3 monitor is stabilized after about half a minute. The ozonation products are analyzed with VUV-ATOFMS online. After the reaction, particles in the reaction chamber are collected with two layers of glass fiber filters (Whatman, annealed at 723 K for 4 h) previously cleaned by hexane. Filters with particles are extracted with three 15 mL portions of hexane, and each lasts 10 min. The extracts are mixed together and concentrated with a rotary evaporator (bath temperature 313 K). About 5 mL of the concentrated extract is used for off-line analysis with GC/MS.

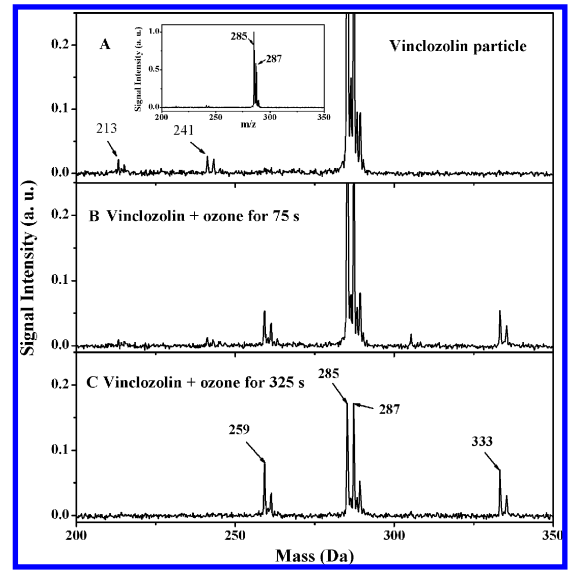

Figure 1. VUV-TOF mass spectra of the vinclozolin particles (A) and its ozonation products (B and C). The mass spectra shown in (B and C) are acquired at 75 and 325 s after O_3 is injected into the chamber. The acquisition time for each mass spectrum is 20 s. The intensities of all mass peaks are normalized to that of the mass peak at *m*/*z* 285 shown in (A).

2.3. Liquid-Phase Reaction. An oxygen stream containing 150 ppmv O_3 bubbles through a solution of 50 mg of vinclozolin in 50 mL of hexane. The bubbling takes ~1 min with a flow rate of 1.5 L min^{-1}. The solution is analyzed with GC/MS. The bubbling for the ozonation of 250 mg of vinclozolin in 50 mL dichloromethane lasts 20 min in order to obtain a complete transformation. The solution is concentrated with a rotary evaporator and reduced to ~5 mL. Compounds are eluted out by flush chromatography on silica gel using dichloromethane and a mixture of dichloromethane and methanol (40:1, v/v) in sequence. The isolated ozonation products are analyzed with VUV-ATOFMS.

2.4. Chemicals. Vinclozolin (Sigma-Aldrich, 99.5%) and azelaic acid (HT, China, 99%) are used in the experiments. Oxygen (99.99%) and nitrogen (99.99%) were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd. All solvents are of chromatographic grade, from J.T. Baker Co. The silica gel (200−300 mesh) is purchased from Qingdao Haiyang Chemical Co., Ltd.

3. Results and Discussion

3.1. Ozonation Products of Vinclozolin Particles. The VUV-TOF mass spectra of vinclozolin ($C_{12}H_9Cl_2NO_3$, mol wt 285) particles and ozonation products are shown in Figure 1, with each acquisition time of 20 s. Figure 1 is zoomed in a small scale, exhibiting small peaks clearly. The mass spectra of ozonation products shown in parts B and C of Figure 1 are acquired at 75 and 325 s after the injection of O_3. All the peak intensities are normalized to that of the mass peak at *m*/*z* 285 shown in Figure 1A. The dominant mass peaks at *m*/*z* 285 and 287 shown in the inset of Figure 1A correspond to the molecular ions of ^{35}Cl and ^{37}Cl vinclozolin, respectively. The very small mass peaks at *m*/*z* 213 and 241 are assigned to the daughter

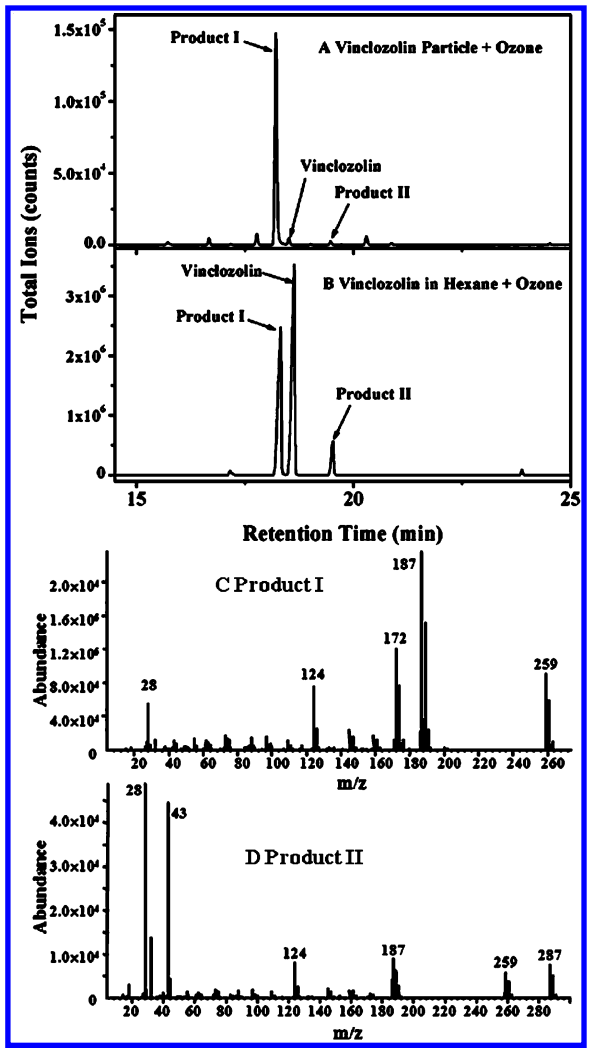

Figure 2. GC/MS total ion chromatograms of the ozonation products of vinclozolin particles collected with glass fiber filters (A) and those formed in the liquid-phase reaction in hexane solution (B). The EI mass spectra of products I (C) and II (D).

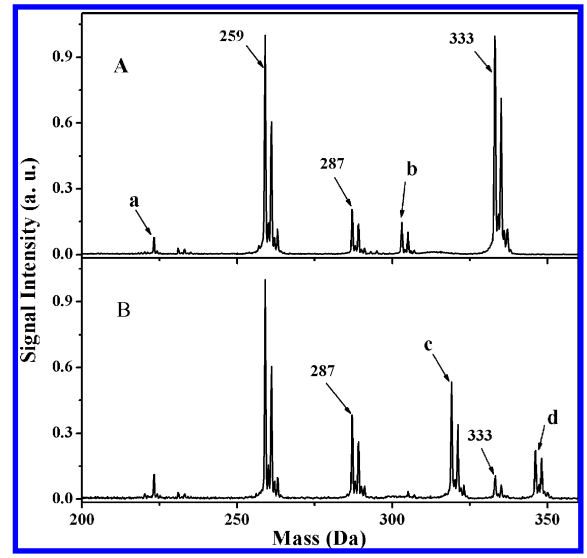

Figure 3. VUV-TOF mass spectrum of products II (A) and I (B) isolated with dichloromethane and a mixture of dichloromethane and methanol (40:1, v/v) as eluants. The acquisition time for each mass spectrum is 10 s. The mass peaks labled with a, b, c, and d are byproducts during eluation.

ions of vinclozolin. As shown in Figure 1, the signal of vinclozolin (*m*/*z* 285) decreases with the reaction time, whereas the new mass peaks at *m*/*z* 259 and 333 appear and rise as the reaction time increases. Besides, the intensity ratios of *m*/*z* 287 vs *m*/*z* 285 change from 0.59 (Figure 1A) to 1.0 (Figure 1C). The intensity ratio of *m*/*z* 287 vs *m*/*z* 285 before the reaction results from the natural isotopic abundances of ^{35}Cl and ^{37}Cl. The increase of the relative intensity of mass peak at *m*/*z* 287 indicates a new product or a fragment ion with *m*/*z* 287.

The identification of ozonation products is assisted with GC/MS analysis. The total ion chromatograms of ozonation products of vinclozolin particles and vinclozolin in hexane are shown in parts A and B of Figure 2. Parts A and B of Figure 2 reveal two main ozonation products with retention times at 18.3 (product I) and 19.5 min (product II). Smaller peaks in the GC/MS cannot be indentified and assigned due to lack of the EI mass spectra of the standard compounds. Compared with three new mass peaks in Figure 1, the mass peak at *m*/*z* 333 is assigned to a molecular ion of one of the two ozonation products, while one of the other two mass peaks is assigned to a daughter ion of ozonation products. The EI mass spectra of products I and II are shown in parts C and D of Figure 2, with maximum mass peaks of *m*/*z* 259 and 287, respectively. However, the maximum mass peaks of products I and II observed with electron impact ionization are not consistent with the mass peaks observed with VUV photoionization. We speculate that the molecular ions of ozonation products do not survive in the process of electron impact ionization. In order to identify the ozonation products further, products I and II isolated by flush chromatography are detected with VUV-ATOFMS. Parts A and B of Figure 3 show the VUV-TOF mass spectra of products II and I, respectively, isolated by dichloromethane and a mixture of dichloromethane and methanol (40:1, v/v). Compared with Figure 3A, the relative intensity of the mass peak at *m*/*z* 333 shown in Figure 3B greatly decreases and that of mass peak at *m*/*z* 287 slightly increases. Therefore, the mass peak at *m*/*z* 287 is assigned to a molecular ion of a ozonation product, whereas the mass peak at *m*/*z* 259 is deemed to be a daughter ion mainly contributed from the product with a molecular weight of 287. It is difficult to isolate products I and II completely by flush chromatography, due to their similar polarity. We speculate that product II with a longer retention time should correspond to the mass peak at *m*/*z* 333 shown in Figure 1C and product I with the shorter retention time should correspond to the mass peak at *m*/*z* 287. According to the GC/MS measurement shown in Figure 2A, product I is the main product of the heterogeneous ozonation of vinclozolin particles.

Vinclozolin has a vinyl group. It is well-known that the ozonation of alkene usually produces the carbonyl and diradical products. The formation of the diradical product can lead to the secondary reaction. The carbonyl ozonation product of vinclozolin should be 3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxo-oxazolidine-5-carbaldehyde (mol wt 287), which matches product I observed in the experiment. Product II has a molecular weight of 333, which is equal to the molecular weight of vinclozolin (mol wt 285) plus the molecular weight of O_3 (mol wt 48). Therefore, product II is tentatively assigned to the trioxane-like ozonation product, 3-(3,5-dichlorophenyl)-5-methyl-5-(1,2,4-trioxane)-1,3-oxazolidine-2,4-dione (mol wt 333). The ozonation pathway is proposed in Figure 4A.

The accepted mechanism for ozone−alkene reactions is based on the mechanism developed by Criegee.[33] The reaction is initiated by the formation of a primary ozonide (POZ), followed by a rapid unimolecular decomposition into two different

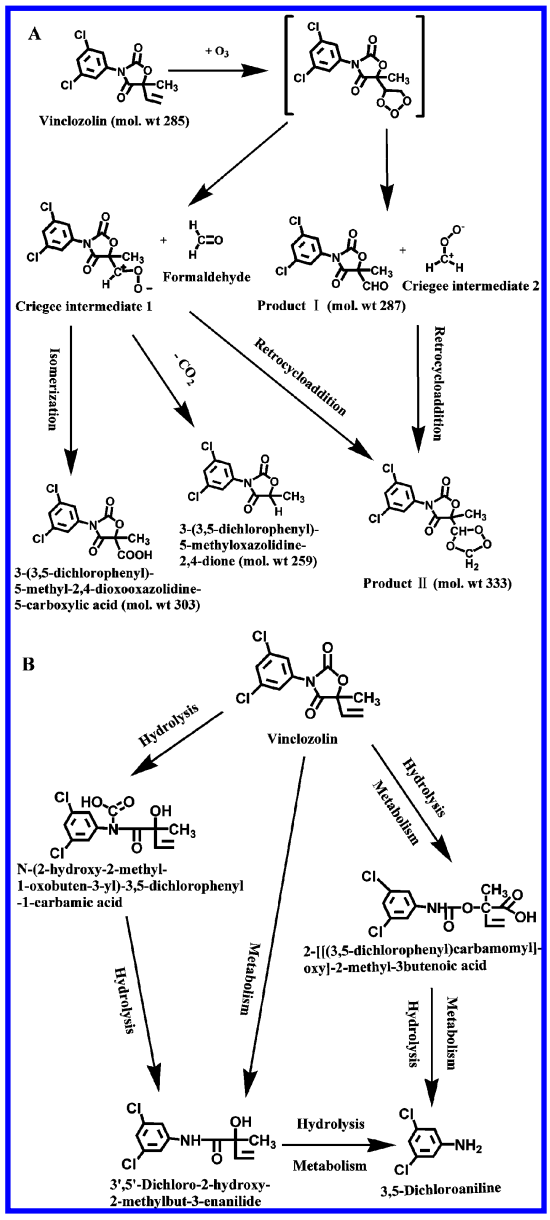

Figure 4. Proposed pathways for the ozonation of vinclozolin particles (A). Degradation pathways of vinclozolin by chemical hydrolysis and metabolism in bacterial and mammalian systems (B).

Criegee intermediates (CIs) and two corresponding primary carbonyl compounds via two competing pathways, respectively. The formation of product I observes the classical mechanism. In recent theoretical work,[34] the secondary ozonides (SOZs) of 1,2,4-trioxane form as the primary ozonide rearranges and generates the dipole complex. The retrocycloaddition of the CIs and their counterparts may result in the formation of secondary ozonides. Product II observed in the experiment is assigned to the product resulted from this retrocycloaddition. The secondary ozonides have been reported both in the gas-phase and liquid-phase ozonations of the organics containing the C−C double bond.[35−40] In smog chamber experiments, especially at the low water vapor concentration and at the high reactant concentrations, the formation of secondary ozonides through reaction of RCHOO biradical with acetaldehyde was observed.[2] 1,2,4-Trioxane has been thought to be an unstable chemical substance, even though many SOZs have been successfully detected by some analytical techniques (GC/MS and ESI/MS) which require heating the sample.[41,42] Fajgar et al. (1999) reported that the secondary ethene ozonide might decompose at about 150 °C, with HCOOH and H_2CO as two major products. In this experiment, the difference between the molecular weight of product II (mol wt 333) and the maximum ion peak at 287 shown in Figure 2D is 46, which could be assigned to HCOOH. However, it is not clear whether product II detected with GC/MS is 1,2,4-trioxane which survives through the capillary column with a temperature of 190 °C or a pyrolysis product of 1,2,4-trioxane. CI 1 can produce 3-(3,5-dichlorophenyl)-5-methyloxazolidione-2,4-dione (mol wt 259) via a unimolecular reaction by losing CO_2 as shown in Figure 4A. However, the VUV-TOF mass spectra obtained cannot reveal it clearly because of the overlap of the molecular ion of this product with the daughter ions of product I. Nevertheless, if any of this product is generated in the reaction, the pathway should be very minor based on the GC/MS analysis. 3-(3,5-Dichlorophenyl)-5-methyloxazolidione-5-carboxylic acid (mol wt 303) and the products resulting from the reactions between the CIs and vinclozolin are not observed in the experiment.

The main ozonation route of vinclozolin in this paper involves only the ozone−alkene mechanism, which differs from the degradation pathways of both hydrolysis and metabolism[19,43,44] shown in Figure 4B. The opening of the 2,4-oxazolidine ring in hydrolysis and metabolism is not observed in this research.

3.2. Heterogeneous Reactive Rate Studies. The pseudo-first-order reaction rate constant of particle-phase vinclozolin ozonation is acquired by analyzing the time-dependent intensities of the mass peak of vinclozolin particles. The decay of vinclozolin particles with O_3 concentrations of 4.2, 8.6, 27.5, 35.5, and 54.5 ppmv (9.0, 18.4, 58.9, 76.1, and 116.8 mg m^{-3}) is presented in Figure 5A. The signal intensities of vinclozolin particles in Figure 5A are normalized to their initial intensities. The molar ratio of the lowest O_3 concentration (4.2 ppmv) to the concentration of vinclozolin is about 225 to guarantee the pseudo-first-order condition. The decay rate of the vinclozolin particles is obtained by fitting the data points shown in Figure 5A with an exponential decay to a minimum function. Given the linear relation of the signal intensity of particles and their concentration, the decay rate of the concentration of vinclozolin particles is equal to that of the signal intensity. The results of fitting data are shown in Figure 5B, in which the pseudo-first-order rate coefficient acquired is linear with the O_3 concentration. The linear regression indicates that the reaction between the surface-adsorbed reactants and gas-phase O_3 is a simple bimolecular reaction following the Eley−Rideal gas−surface reaction mechanism.[45] The second-order rate constant is calculated by dividing the pseudo-first-order rate constants by the O_3 concentration,[46] which is $(2.4 \pm 0.4) \times 10^{-17}$ cm^3 $molecules^{-1}$ s^{-1}. The uncertainty here is obtained with the standard deviation of five experiments, which is also applied in the estimation of the following uptake coefficient and the atmosphere lifetime. The second-order rate constant calculated here is similar to that of ozonation of 1-tetradecene, with a rate constant of $(2.44 \pm 0.24) \times 10^{-17}$ cm^3 $molecules^{-1}$ s^{-1}.[47]

3.3. Atmospheric Implications. The lifetime of particle-phase vinclozolin at 100 ppbv O_3 is 4.3 ± 0.7 h, which is estimated with the second-order rate constant calculated above. By comparing the lifetime of vinclozolin toward O_3 with those due to the degradation in soil, thatch, and grass clippings, as well as on grapevines,[24−27] vinclozolin is more vulnerable to O_3. Consequently, the ozonation process plays an important role in the degradation of vinclozolin under the natural environmental conditions. To the best our knowledge, there are no data on the lifetime of gas-phase or particle-phase vinclozolin due to reaction with atmospheric OH radicals reported yet. With

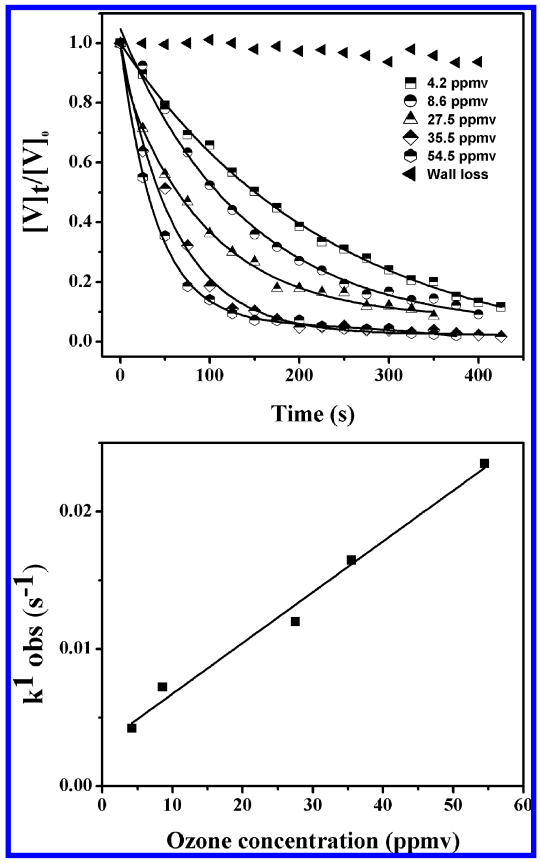

Figure 5. Decay curves of vinclozolin particles with different O_3 concentrations (A) and the linear regressions of the pseudo-first-order rate constants as a function of the O_3 concentration (B). The data points shown in (A) are the normalized signal intensities of vinclozolin particles.

reference to the concentration of the atmospheric OH radicals (1.6×10^6 molecules cm^{-3})[48] and the rate coefficient for the reaction of ethylene glycol monovinyl ether and OH radicals ($(1.04 \pm 0.22) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}),[49] the lifetime of gas-phase vinclozolin due to reaction with atmospheric OH radicals is estimated to be ~1.7 h. So the lifetime of vinclozolin toward 100 ppbv O_3 is comparable with that toward atmospheric OH radicals. The reactive uptake coefficient (γ) for the ozonation of particle-phase vinclozolin is calculated to be (6.1 ± 1.0) $\times 10^{-4}$ according to the method reported in the literature.[50] The uptake coefficients of the alkene-containing samples coated on glass were $(1.2-2.7) \times 10^{-4}$, depending on the length of the olefin chain and the reaction condition.[51] The reactive uptake coefficients of the aerosol-associated unsaturated fatty acids toward O_3 have been determined to be between (5.2 ± 0.1) $\times 10^{-5}$ and (1.4 ± 0.1) $\times 10^{-4}$.[52] The reactive uptake coefficient of vinclozin to O_3 is slightly higher than those of unsaturated fatty acids.

On the basis of the experimental results, the ozonation products of vinclozolin contain the intact 3,5-dichloroaniline moiety, which is a chlorinated aromatic amine. It is believed that this functional group gives rise to a health hazard with human exposure.[53,54] Therefore, the ozonation products of vinclozolin should be of the same concern as its metabolites. Furthermore, the ozonation of the C−C double bond leads to the release of aldehydes. The tropospheric reaction of vinclozolin with O_3 can thus contribute to the oxidative capacity of the atmosphere via the aldehyde photolysis to HCO and subsequent generation of HO_2.[52] Those radicals might trigger chain reactions due to reaction with other organic compounds in the atmosphere.

4. Conclusion

This paper reports an investigation of the heterogeneous reaction of vinclozolin and O_3 with VUV-ATOFMS and GC/MS for both online and off-line analysis. Two main ozonation products are observed, which are tentatively assigned to be 3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxo-oxazolidine-5-carbaldehyde and 3-(3,5-dichlorophenyl)-5-methyl-5-(1,2,4-trioxane)-1,3-oxazolidine-2,4-dione. Vinclozolin adsorbed on azelaic acid particles reacts with gas-phase O_3 following a simple bimolecular mechanism, with a second-order rate constant of (2.4 ± 0.4) $\times 10^{-17}$ cm^3 $molecules^{-1}$ s^{-1}. The reactive uptake coefficient of vinclozin to O_3 is slightly higher than those of unsaturated fatty acids.

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