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Products and kinetics of the heterogeneous reaction of particulate ametryn with NO₃ radicals

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As a renowned *s*-triazine herbicide, ametryn is worldwide emitted into the atmosphere in both gaseous and particulate phases via spray drifts from treatments and post application emissions, but its chemical degradation in the atmosphere has not been well characterized. In this study, the heterogeneous kinetics of particulate ametryn with NO₃ radicals were investigated with a mixed-phase relative rate method. A vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an atmospheric gas analysis mass spectrometer were synchronously used to online monitor the decays of particulate ametryn and gas-phase isoprene. The reactive uptake coefficient of NO₃ radicals on ametryn particles was calculated to be 2.9×10^{-2} , according to the measured ametryn loss ratio and the average NO₃ concentration. The effective rate constant for the heterogeneous reaction of particulate ametryn with NO₃ radicals measured under experimental conditions was $8.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition, atraton, ametryn sulfoxide and ametryn sulfone were identified as the reaction products by gas-chromatography-mass spectrometry (GC-MS) analysis. The experimental results might shed light on the chemical behavior of atmospheric ametryn at night-time.

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Environmental impact

Ametryn is highly persistent and bio-accumulating in the environment, having a significant impact on the environment and public health. Therefore, comprehensive knowledge of its behavior in the environment is very important for toxicity and safety assessments. To date, few studies on its chemical degradation in the atmosphere have been performed. In this study, heterogeneous kinetics of particulate ametryn with NO₃ radicals was investigated with a mixed-phase relative rate method, and the reaction products were also determined by GC-MS. The results demonstrated that ametryn could be effectively degraded by NO₃ radicals. This investigation might shed light on the chemical behavior of atmospheric ametryn at night. In addition, the results can provide fundamental data for its health effects in the atmosphere.

1. Introduction

Ametryn [*N*-ethyl-*N'*-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine] is a globally used *s*-triazine herbicide, mainly applied to control the pre and post emergence of broadleaf and grass weeds in fields planted with maize, pineapple, popcorn, and sugarcane.¹ It is highly persistent and bio-accumulating in the environment, having a significant impact on ecosystems. The Environmental Protection Agency (EPA) has included triazines and their degradation products as a group of the Contaminant Candidate List, and classified ametryn as a Class III herbicide.² Ametryn is embryotoxic and genotoxic,^{3,4} and highly toxic to crustaceans and molluscs.⁵ Farré *et al.* reported that ametryn and its four biodegradation metabolites exhibited high toxicity to *Vibrio fischeri*.⁶ In addition, it could cause DNA damage to human

peripheral lymphocytes after being metabolized by *Vicia faba* roots.⁷ Therefore, a comprehensive knowledge of its behavior in the environment is very important for toxicity and safety assessment.

As a result of the widespread use of ametryn in agriculture, not only water and soil, but the air is also contaminated with it.^{8–12} This is due to spray drift from the application and the post-application emission, including volatilization and wind erosion.^{13–15} Therefore, the atmosphere becomes a major receptacle and transport medium of pesticides.¹⁵ Once emitted into the atmosphere, ametryn may undergo photolysis or chemical transformation by the reactions with atmospheric gas-phase species. These oxidation processes lead to the chemical modification of the particle with subsequent effects on air quality, health-related issues and climate.¹⁶ To the best of our knowledge, significant efforts have been made to study ametryn in the past decades, most of which were focused on detection methods, toxic effects, environmental monitoring, and treatment technologies in aqueous conditions.^{1,3,6,8,10,17–22} However, to date, the chemical behavior of ametryn toward trace gas-phase oxidants in the atmosphere has not been well characterized.

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The NO_3 radical plays an important role in the night-time atmosphere, and its reactivity is comparable to that of hydroxyl (OH) radicals in the daytime atmosphere.²³ Due to rapid photolysis by sunlight, NO_3 radicals can only accumulate at night-time with a concentration ranging from $\sim 5 \times 10^7$ to $\sim 1 \times 10^{10}$ molecules cm^{-3} .^{24,25} Considering its high concentration at night-time, NO_3 radicals may play an important role in controlling the lifetime of atmospheric ametryn. To improve our understanding of the importance of NO_3 radicals to the fate of particle-associated ametryn in the atmosphere, the heterogeneous kinetics of reaction of NO_3 radicals with ametryn adsorbed on suspended azelaic acid particles was investigated in this study with a mixed-phase relative rate method. In addition, the products formed in the heterogeneous reaction of surface-bound ametryn with NO_3 radicals were determined by GC-MS.

2. Experimental section

2.1 Chemicals

Ametryn (Dikma, 98.8%), isoprene (Alfa Aesar, 99%), azelaic acid (Sinopharm Chemical Reagent Co., Ltd., 99%), fuming nitric acid (Beijing Lisui Chemical Factory, 95%), P_2O_5 (Sinopharm Chemical Reagent Co., Ltd., 98%), absolute ethyl alcohol (Sinopharm Chemical Reagent Co., Ltd., 99.7%), and dichloromethane (J. T. Baker Co., chromatographic grade) were used in the experiment. Nitrogen (99.99%) and nitrogen dioxide (15.9%) were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd.

2.2 Experimental setup

A diagram of the experimental setup has been shown elsewhere,²⁶ basically consisting of an aerosol generator, a reaction chamber and analytical instruments.

Ametryn particles were generated through homogeneous nucleation. The aerosol generator was an electric tube furnace equipped with two tandem quartz tubes [50 cm (length) $\times$ 3 cm (inner diameter)], each with an independent temperature controller. Azelaic acid was used to form nuclei because of its limited reactivity toward NO_3 radicals.²⁷ Azelaic acid was vaporized in the first tube and then nucleated in a N_2 stream to generate nuclei through a temperature gradient. A N_2 stream with a volumetric flow rate of 0.8 L min^{-1} flowed through the first tube, carrying the nuclei into the second tube, where azelaic acid nuclei were coated with ametryn vapor. The size and concentration of particles were monitored by a scanning mobility particle sizer (SMPS), which consisted of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The measured mean diameter of ametryn particles was 293 nm, and its corresponding mass concentration was $223 \pm 18 \mu\text{g m}^{-3}$. The thickness of the coating was 29 nm for ametryn, calculated according to the size distributions of the particles before and after being coated by the ametryn sample.

The reaction chamber, with a volume of ~ 180 L, was composed of a thin-walled open head stainless steel drum and a

thin Tedlar poly(vinyl fluoride) (PVF) film bag. A magnetic-driven fan was set at the bottom of the chamber to rapidly and sufficiently mix the reactants. The experiments were performed under atmospheric pressure at room temperature (~ 298 K). The relative humidity in the chamber was approximately 5%, estimated from the residual filtered air in the chamber. After the concentration of ametryn particles within the reaction chamber reached the desired value, isoprene was injected into the reaction chamber. The initial concentration of isoprene in the chamber was $\sim 1.0 \times 10^{14}$ molecules cm^{-3} measured with an atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden) *via* detection of the mass peak at m/z 67 (C_5H_7^+). Subsequently, a N_2 stream with a volumetric flow rate of 0.8 L min^{-1} was passed through a flask containing N_2O_5 powder that brings gaseous N_2O_5 into the chamber. NO_3 radicals were generated by the thermal decomposition of N_2O_5 at room temperature (~ 298 K). The concentrations of NO_3 radicals in the experiment were $(0.7\text{--}7.9) \times 10^{10}$ molecules cm^{-3} , calculated according to the loss rates of isoprene ($\sim 10^{-3} \text{ s}^{-1}$). The 300 s wall losses of ametryn and isoprene in the absence of oxidants were $\sim 5\%$, measured with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and the atmospheric gas analysis mass spectrometer, respectively.

The concentration of ametryn particles was measured in real-time with the VUV-ATOFMS *via* the detection of its molecular ion mass peak. Detailed descriptions of the VUV-ATOFMS have been presented elsewhere.²⁸ The concentration of ametryn particles is linear to the signal intensity of the molecular ion mass peak measured by the VUV-ATOFMS. Thus, the decay rate of signal intensity is equal to the decay rate of the ametryn concentration.²⁸

2.3 Gas chromatography-mass spectrometry (GC-MS)

In order to assign the TOF mass spectra of reaction products, GC-MS analysis was performed to identify the products produced in the reactions of surface-bound ametryn with NO_3 radicals. The detailed description of sample preparation for GC-MS analysis has been presented elsewhere.²⁹ An Agilent 6890 GC-MS equipped with a 30 m $\times$ 0.25 mm $\times$ 0.25 μm HP-5 capillary and an HP-5973 quadrupole mass filter with a 70 eV electron impact ionizer was used to identify the products. 1 μL of sample was injected *via* the pulsed splitless mode. The GC temperature was set to 353 K for 1 min, followed by an increase rate of 15 K min^{-1} up to 493 K, finally to 573 K at 25 K min^{-1} , and held for 15 min. The reaction products were analyzed by GC-MS in total ion chromatogram (TIC) mode and identified by comparing their electron ionization (EI) mass spectra with those from a Mass Spectral Library [The National Institute of Standards and Technology (NIST) 2005]. Moreover, because no standard samples of some products are available, they were tentatively identified by comparing their EI mass spectra with those of their parent chemicals. The mass range from 50 to 500 amu was used in the process of data acquisition.

3. Results and discussion

From the maximum loss of isoprene and the thermal decomposition rate of N_2O_5 at 298 K,³⁰ the maximum average concentrations of NO_2 and N_2O_5 in this study were estimated to be $\sim 4.3 \times 10^{13}$ and $\sim 7.5 \times 10^{12}$ molecules cm^{-3} , respectively. To evaluate the possible effects of the reactions with NO_2 , air and N_2 on the decay of ametryn in the experiment, particulate ametryn exposed to NO_2 ($\sim 4.9 \times 10^{14}$ molecules cm^{-3}), air and N_2 were investigated. The results showed that there was no product formed after the ametryn particles were exposed to NO_2 , air and N_2 for 600 s, respectively. Considering that the reaction time in the experiment was less than 300 s, the direct reactions of particulate ametryn with NO_2 , air and N_2 were neglected in this study. In addition, it was reported that the reactive uptake coefficient of NO_3 radicals on organic substrate surfaces was ~ 3 –4 orders of magnitude greater than those of NO_2 and N_2O_5 .^{16,31} Therefore, the effects of N_2O_5 on the loss of particulate ametryn was also neglected in the experiment. From the previous studies, it was well known that OH radicals could be formed by the NO_3 -initiated oxidation of volatile organic compounds in the presence of O_2 .^{32,33} In this study, the NO_3 -initiated reaction was performed in the absence of O_2 because the chamber was filled with N_2 and ametryn particles. Therefore, OH radicals were hardly produced and OH chemistry was neglected in the chamber.

3.1 Reaction products

The TOF mass spectrum of ametryn particles shown in Fig. 1A was obtained before exposure to NO_3 radicals, with an acquisition time of 10 s. The most intense mass peak at m/z 227 corresponds to the molecular ion peak of ametryn. The intensities of all other mass peaks were normalized to that at m/z 227. The TOF mass spectrum shown in Fig. 1B was acquired 120 s after the injection of NO_3 radicals. Compared with Fig. 1A, there were three new mass peaks appearing at m/z 211, 243 and 259. According to the GC-MS analysis (see Fig. 2), Product I of ametryn [retention time (R_T) = 7.0 min, see Fig. 3A] was identified to be atraton ($\text{C}_9\text{H}_{17}\text{N}_5\text{O}$, mol. wt 211), formed by the transformation of $-\text{S}-$ into $-\text{O}-$.³⁴ Its molecular ion peak was located at m/z 211, which was smaller than that of ametryn by m/z of 16. The mass spacing of 16 amu between ametryn and Product I suggests the loss of a sulfur atom (-32 amu) and the addition of an oxygen atom ($+16$ amu).³⁴ The mass peaks at 243 and 259 were assigned to the molecular ions of ametryn sulfoxide (Product II, $\text{C}_9\text{H}_{17}\text{N}_5\text{OS}$, mol. wt 243, R_T = 8.6 min, see Fig. 3B), and ametryn sulfone (Product III, $\text{C}_9\text{H}_{17}\text{N}_5\text{O}_2\text{S}$, mol. wt 259, R_T = 10.4 min, see Fig. 3C), respectively. The mass spacing of 16 amu between ametryn and Product II could be a result of the addition of an oxygen atom ($+16$ amu) to the sulfur atom, the subsequent addition of an oxygen atom to the sulfur atom would produce Product III.^{21,22,35}

In the previous studies, these three products have been identified as the degradation products of ametryn under aqueous conditions treated by hypochlorite ion or metalloporphyrins.^{21,22,35} Moreover, these products show more

Fig. 1 TOF mass spectra of ametryn particles (A) and its oxidation products in the reaction with NO_3 radicals (B). The spectrum shown in Fig. 1B was acquired 120 s after NO_3 radicals were introduced into the reaction chamber. The acquisition time for each mass spectrum was 10 s. The TOF mass spectra were normalized to their most intense peaks at m/z 227.

Fig. 2 GC-MS total ion chromatograms of the oxidation products in the reaction between NO_3 radicals and surface-bound ametryn.

hydrophilic structures than ametryn.²¹ This indicates that the hygroscopicity of ametryn particles after being oxidized is improved. The hygroscopic growth could have significant effects on the particle properties, atmospheric visibility, climate and human health.

Fig. 3 EI mass spectra of the reaction products with retention times at 7.0 (A), 8.6 (B) and 10.4 min (C) obtained in the experiments.

3.2 Reaction mechanism

The reaction mechanism of particulate ametryn with NO_3 radicals is illustrated in Scheme 1. The NO_3 radical is a strong electrophilic oxidant, and it usually undergoes addition to an unsaturated bond when reacting with unsaturated organic compounds, forming one or more unstable intermediates.²⁴ Therefore, Intermediate I was speculated to be formed by the addition of NO_3 radicals to the sulfur atom on the methylthio group. In a previous study, Cabañas *et al.* reported that sulfur dioxide (SO_2) and carbonylic compounds were identified as the secondary products of thiophene, which were produced by the attack of NO_3 radicals on the sulfur atom.³⁴ Therefore, Product I and SO_2 were speculated to be produced by Intermediate I oxidized by NO_3 radicals. Moreover, Product II was formed through Intermediate I by losing a NO_2 molecule, which could

be converted to Product III by the subsequent oxidation of a sulfur atom on the methylthio group.^{21,22,35} The similar mechanism was reported in the reaction between fenthion particles and NO_3 radicals.³⁶

3.3 Heterogeneous kinetics

In this study, the heterogeneous kinetics of particulate ametryn with NO_3 radicals was investigated using a mixed-phase relative rate method. The average concentration of NO_3 radicals ($\bar{C}_{\text{NO}_3}$) was determined from the observed loss rate of gas-phase isoprene. The preferred rate constant of the reaction of isoprene with NO_3 radicals is $7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³⁷ The average NO_3 exposure ($\bar{C}_{\text{NO}_3}t$) can be typically represented as follows:³⁸

$$\bar{C}_{\text{NO}_3}t = \ln(C_{\text{R}0}/C_{\text{R}})/k_{\text{R}} \quad (1)$$

where $C_{\text{R}0}$ and C_{R} are the initial and real-time concentrations of gas-phase isoprene after NO_3 radicals were introduced into the chamber, k_{R} is the reaction rate constant of the reference compound with NO_3 radicals ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and t is the reaction time. Calculated from the eqn (1), the average concentration of NO_3 radicals for the reaction of ametryn was $\sim 2.2 \times 10^{10} \text{ molecules cm}^{-3}$.

It was assumed that the particles generated in the experiment were spherical and the loss of one ametryn molecule was caused by the attack of one single NO_3 radical. The reactive uptake coefficient (γ) of NO_3 radicals on ametryn particles can be expressed as the ratio between the number of ametryn molecules on a single particle consumed in the reaction and the number of NO_3 radicals diffusing to the particle. With the loss ratios of particulate ametryn and the average concentration of NO_3 radicals measured in the experiment, the uptake coefficient of NO_3 radicals can be obtained using the following equation:²⁷

$$\gamma = \frac{(R_{\text{p}}^3 - R_{\text{c}}^3)\rho N_{\text{A}}\eta}{3MR_{\text{p}}D_{\text{NO}_3}\bar{C}_{\text{NO}_3}t} \quad (2)$$

where R_{p} is the particle radius (cm), R_{c} is the radius of the inner core (cm), ρ is the densities of ametryn (1.2 g cm^{-3}), N_{A} is the Avogadro's number, η is the ratio of consumption (~ 0.96), M is the molecular weight of ametryn (227 g mol^{-1}), D_{NO_3} is the diffusion coefficient of NO_3 radicals under forced diffusion in the experiment ($\sim 1 \text{ cm}^2 \text{ s}^{-1}$),²⁷ and $\bar{C}_{\text{NO}_3}$ is the average concentration of NO_3 radicals.

Calculated using eqn (2), the reactive uptake coefficient for NO_3 radicals on ametryn particles was 2.9×10^{-2} , indicating that 2.9% of the NO_3 collisions with ametryn result into reactions. The concentrations of NO_3 radicals employed in the experiment were close to the concentration of NO_3 radicals in the night-time atmosphere.²⁴ Therefore, we could directly use the obtained uptake coefficient to estimate the atmospheric lifetime of ametryn particles. With a typical NO_3 concentration of $5 \times 10^8 \text{ molecules cm}^{-3}$ at night-time,²⁴ the atmospheric lifetime of ametryn was $\sim 17.5 \text{ h}$, calculated using a NO_3 diffusion coefficient of $0.12 \text{ cm}^2 \text{ s}^{-1}$ in air.³⁹ The detailed description of the lifetime calculation has been presented elsewhere.²⁹

Scheme 1 Proposed pathways of particulate ametryn with NO_3 radicals.

According to the mixed-phase relative rate expression represented in the previous studies, the effective rate constant can be calculated using the following equation:^{40,41}

$$\ln(C_A/C_{A0}) = -(k_A)_{\text{eff}} \bar{C}_{\text{NO}_3} t \quad (3)$$

where C_A and C_{A0} are the initial and real-time concentrations of ametryn particles after the NO_3 radicals were introduced into the chamber, and $(k_A)_{\text{eff}}$ is the effective reaction rate constant of particulate ametryn.

Fig. 4 shows a plot of $\ln(C_A/C_{A0})$ versus $\bar{C}_{\text{NO}_3} t$ for ametryn particles. The wall loss ($\sim 5\%$) of the ametryn particles was neglected in data processing. The error bars represent the standard deviation of four duplicate experiments. The plot shown in Fig. 4 was efficiently fitted using the linear least-square function ($R^2 > 0.99$). The obtained slope of linear regression corresponds to the effective reaction rate constant (k_{eff}) for particulate ametryn in the reaction with NO_3 radicals. The obtained effective reaction rate constant for particulate ametryn was $8.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with isoprene as the reference compound.

Fig. 4 Plot of $\ln(C_A/C_{A0})$ vs. NO_3 radical exposure for ametryn particles. The time-averaged concentration of NO_3 radicals was $\sim 2.2 \times 10^{10} \text{ molecules cm}^{-3}$.

In the previous studies, the heterogeneous reaction rates of pesticides with O_3 were reported to be in the order of $\sim 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{42,43} Compared to the results obtained in this study, the effective rate constant of ametryn with NO_3 radicals was ~ 5 orders of magnitude faster than those of particulate pesticides with O_3 . Compared with NO_3 radicals, the effect of OH radicals on the degradation of atmospheric particulate organic compounds may not be remarkable due to its lower concentration in the atmosphere.³⁴ Therefore, under typical atmospheric conditions at night, NO_3 radicals might be the most important oxidant for the degradation of atmospheric ametryn. The calculated atmospheric lifetime of ametryn was $\sim 17.5 \text{ h}$. This reveals that ametryn can be effectively degraded by NO_3 radicals. Under real atmospheric conditions, the phase and morphology of ametryn particles might be complex, and those distributed in the particle bulk may not be accessible for oxidation by NO_3 radicals. In addition, other factors such as the atmospheric relative humidity,⁴⁴ particle size⁴⁵ and the concentrations of particulate reactants and gas-phase oxidants⁴⁶ can affect the heterogeneous reaction. Consequently, the lifetimes of ametryn particles may vary under different atmospheric conditions.

4. Conclusions

In this study, the VUV-ATOFMS and an atmospheric gas analysis mass spectrometer were used to investigate the heterogeneous kinetics of particulate ametryn with NO_3 radicals by a mixed-phase relative rate method. Based on the measured ametryn loss ratio and the average NO_3 concentration, the reactive uptake coefficient of NO_3 radicals on ametryn particles was calculated to be 2.9×10^{-2} , and its corresponding atmospheric lifetime was $\sim 17.5 \text{ h}$ at a typical NO_3 concentration of $5 \times 10^8 \text{ molecules cm}^{-3}$ at night. The effective rate constant for the heterogeneous reaction of particulate ametryn with NO_3 radicals measured under experimental conditions was $8.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition, atraton, ametryn sulfoxide, and ametryn sulfone were identified as the reaction products by GC-MS analysis. These experimental results might help improve our understanding of the chemical transformation of atmospheric ametryn at night.

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