

Impact of the Ultraviolet Photolysis of Monochloramine on 1,4-Dioxane Removal: New Insights into Potable Water Reuse

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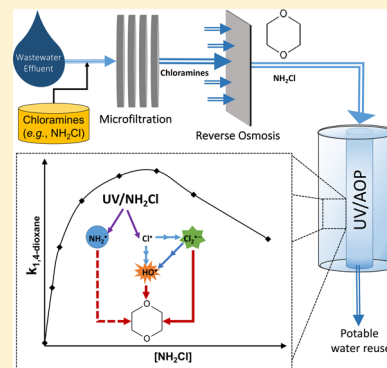
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S Supporting Information

ABSTRACT: Although chloramines are ubiquitously present during ultraviolet-driven advanced oxidation processes (UV/AOP) that are becoming increasingly important for potable water reuse, the photochemistry of chloramines in treated wastewater, and the associated effects on trace chemical contaminant degradation, are unknown. This study investigated the fundamental radical chemistry involved in monochloramine (NH_2Cl) photolysis and its efficiency in degrading 1,4-dioxane using a low-pressure Hg lamp ($\lambda = 254 \text{ nm}$). These results showed that the UV fluence-normalized rate of 1,4-dioxane degradation in UV/ NH_2Cl ranged between 1.1×10^{-4} and $2.9 \times 10^{-4} \text{ cm}^2 \cdot \text{mJ}^{-1}$. The photolysis of NH_2Cl produced NH_2^\bullet and Cl^\bullet , which further transformed to a series of reactive radical species. An optimal NH_2Cl dosage for 1,4-dioxane degradation was observed at a NH_2Cl /1,4-dioxane concentration ratio of 8.0, while excess NH_2Cl scavenged reactive radicals and decreased the treatment efficiency. Scavenging experiments and probe compound calculations showed that both $\text{Cl}_2^{\bullet-}$ and HO^\bullet contributed significantly to 1,4-dioxane removal, while the NH_2^\bullet radical reacted slowly with 1,4-dioxane. The presence of dissolved oxygen further decreased NH_2^\bullet reactivity. This study generated critical knowledge of the photochemistry of NH_2Cl and will allow for future optimization of the UV/AOP for more efficient water reuse treatments.



INTRODUCTION

Potable water reuse offers a sustainable approach to addressing water scarcity and mitigating the long-term impacts of climate change.^{1,2} The ultraviolet-based advanced oxidation process (UV/AOP) is integral to potable water reuse treatments. Typically, an oxidant, e.g., hydrogen peroxide (H_2O_2), persulfate ($\text{S}_2\text{O}_8^{2-}$), or free chlorine (HOCl), is added and photolyzed to generate reactive radical species that degrade trace organic contaminants in the recycled water.^{3–13} However, membrane treatment processes, including microfiltration (MF) and reverse osmosis (RO), are employed prior to any UV/AOP. Chloramines, especially monochloramine (NH_2Cl), are deliberately generated in the feedwater to minimize membrane biological fouling.^{14,15} Because of their small molecular size and neutral charge, chloramines easily diffuse through RO membranes and subsequently will undergo photolysis in the UV/AOP.¹⁶

Neutral and low-molecular weight trace organic contaminants are also poorly removed by the RO membrane and carried over to the UV/AOP.¹⁷ For example, 1,4-dioxane (1,4-D), a solvent stabilizer used in many industrial and personal care products, is persistent in RO permeate.¹⁸ 1,4-D is classified as a probable Class 2B human carcinogen.¹⁹ It has served as a surrogate contaminant for the validation of AOPs as

it is water-soluble, is not photolyzed at 254 nm, and requires oxidation to be removed from the recycled water.²⁰ Because of its significant implications on the quality of recycled water, regulatory standards in California require at least 0.5 log of removal for 1,4-D by the UV/AOP.²¹

As more water utilities adopt UV/AOPs as part of their wastewater treatment, the nature of chloramine photochemistry in recycled water of RO permeate needs to be better understood, as this can potentially provide additional removal of trace organic contaminants and enhance the UV/AOP performance for potable water reuse. Prior studies of chloramine photochemistry have mainly examined its reactivity as a disinfectant in swimming pools,^{22,23} formation of disinfection byproducts during drinking water treatment,^{24,25} solar irradiation in ballast water,²⁶ and its photolysis under organic-free conditions.^{27,28} The chemical condition of recycled water during the UV/AOP treatment step is characteristic of low natural organic matter content, acidic pH, and the presence of neutral and small trace organic contaminants. The nature of

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NH₂Cl photolysis after membrane treatment during the UV/AOP in recycled water has not been systematically explored. Currently, little is known about the nature and reactivity of NH₂Cl photochemistry with 1,4-dioxane in the unique water chemistry relevant to water reuse.

It was previously reported that the photolysis of NH₂Cl generates the amine radical (NH₂•) and the chlorine atom (Cl•).^{23,28,29} The Cl• atom can be converted to the hydroxyl radical (HO•) via its reaction with hydroxide, followed by the dissociation of ClOH•⁻, or generate the chlorine dimer, Cl₂•⁻.^{30–33} The fate of NH₂• in water is largely unknown. Although its redox potential is estimated to be lower than that of HO•,^{34–37} prior studies have shown that NH₂• is capable of oxidizing antibiotics in wastewater and generating NH₂-adduct products.^{38–40} However, the equivalent monochloramine photochemistry with 1,4-dioxane and the associated radical reactivity have not yet been established.

The objectives of this study were to investigate the photochemistry of NH₂Cl under RO permeate chemical conditions, to examine the distribution and reactivity of the radical species generated, and to elucidate the mechanisms associated with the oxidation of 1,4-dioxane in a water reuse scenario.

MATERIALS AND METHODS

All chemicals used in this study were reagent grade or higher. Solutions were prepared using deionized (DI) water (resistivity of >18.2 MΩ, Millipore System) purged with ambient air to achieve air-saturated conditions. In some experiments, the DI water was purged with N₂ for 30 min prior to use to remove the dissolved O₂. A 50 mM NH₂Cl working solution was prepared daily by adding a HOCl stock solution to (NH₄)₂SO₄ with a N:Cl molar ratio of 1.2:1 buffered at pH 8 using borate. The chloride residual in NH₂Cl was quantified by ion chromatography (Dionex Inc.). There was an equimolar concentration of chloride with NH₂Cl due to its equilibrium with the HOCl stock solution (Figure S1).⁴¹ The targeted NH₂Cl concentration ranged between 0.2 and 6 mM, and the concentration of 1,4-D was 0.25 mM. The final solution pH was controlled at 5.8 (i.e., the typical pH of RO permeate) with 40 mM phosphate buffer. To examine the reactivity of NH₂• and other reactive amine species formed in the UV/NH₂Cl experiments, additional UV/H₂O₂ experiments were conducted in the presence of NH₃ at pH 5.8 and 11.⁴² The ionic strength was controlled at 35 mM in UV/NH₂Cl experiments and 120 mM in UV/H₂O₂ experiments. The choice of NH₂Cl and 1,4-dioxane concentrations that were higher than those under RO permeate conditions (typically ~0.05 mM and ~0.05 μM, respectively) provides useful insight into the reaction kinetics and fundamental radical pathways in the UV/NH₂Cl experiment.

Prepared solutions were transferred to multiple 8 mL sealed quartz tubes without headspace. The tubes were then placed in a carousel UV chamber illuminated with a low-pressure monochromatic Hg lamp (λ = 254 nm) at an intensity of 2.1 mW/cm² (Phillips TUV6T5). At targeted time intervals, reaction tubes were taken out of the carousel chamber and analyzed for chemical compositions. All experiments were conducted in duplicate or triplicate at room temperature (23 ± 2 °C).

Concentrations of NH₂Cl were determined using the standard DPD method.⁴³ Concentrations of 1,4-D were analyzed with an Agilent 1200 liquid chromatograph equipped with a diode array detector (details provided as Text S1 in the

Supporting Information). Dissolved O₂ was measured using a dissolved O₂ probe (Mettler Toledo). Nitrobenzene (20 μM) and benzoic acid (10 μM) were added simultaneously as probe compounds to quantify the steady-state concentrations of reactive radicals in the UV/NH₂Cl experiments using competition kinetics. *tert*-Butanol (TBA) was employed as a radical scavenger in some experiments. The second-order rate constants of reactive chlorine species (Cl• and Cl₂•⁻) reacting with 1,4-D were determined by electron pulse radiolysis experiments conducted at Notre Dame Radiation Laboratory in Notre Dame, IN. In short, the electron pulse radiolysis of water in the presence of chloride and persulfate was conducted and the production of Cl₂•⁻ that absorbed strongly at 340 nm was monitored to measure the rate constants. Details about the radiolysis experiments and data analysis are provided as Text S2 and Figures S2 and S3 in the Supporting Information.

RESULTS AND DISCUSSION

1,4-Dioxane Degradation in UV/NH₂Cl. 1,4-D degradation took place in UV/NH₂Cl under RO permeate chemical conditions (Figure 1A). The UV fluence-normalized pseudo-first-order rate constant of 1,4-D degradation ($k_{1,4\text{-dioxane}}$)

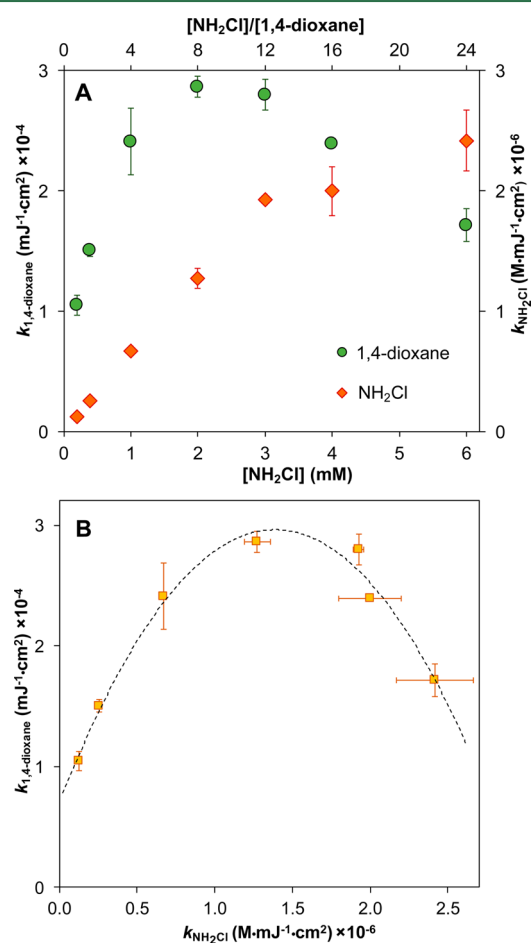
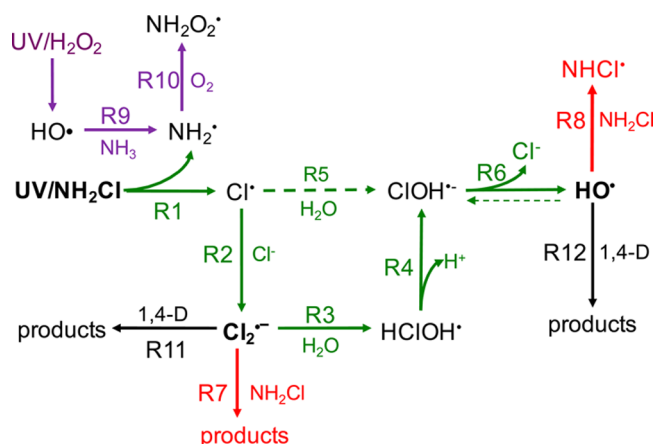


Figure 1. Treatment of 1,4-dioxane with UV/NH₂Cl at varying NH₂Cl doses. (A) Dose response of 1,4-dioxane treatment to NH₂Cl concentration. (B) Correlation between UV fluence-normalized rates of 1,4-dioxane decay and NH₂Cl consumption at varying NH₂Cl doses. [1,4-D] = 250 μM, [NH₂Cl] = 0.8–6 mM, pH = 5.8, and a N₂-purged solution. The dashed line is the polynomial trend line fitting of the experimental data.

initially increased with NH_2Cl dosage, peaking at approximately $2.9 \times 10^{-4} \text{ cm}^2 \cdot \text{mJ}^{-1}$ with 2 mM NH_2Cl . This corresponded to a $\text{NH}_2\text{Cl}/1,4\text{-D}$ concentration molar ratio of 8. The degradation rate decreased by nearly 40% as the NH_2Cl dosage further increased from 2 to 6 mM. Meanwhile, the rate of NH_2Cl consumption ($k_{\text{NH}_2\text{Cl}}$) increased with NH_2Cl dosage. The direct photolysis of 1,4-D was negligible in the absence of NH_2Cl . Both NH_2Cl and 1,4-D exhibited pseudo-first-order decay kinetics (Figures S4 and S5).

The incipient increase in NH_2Cl dosage enhanced the generation of NH_2^\bullet and Cl^\bullet (reaction 1 in Scheme 1; all

Scheme 1. Illustration of the Radical Reaction Pathways Involved in the UV/ NH_2Cl -Based Degradation of 1,4-Dioxane (1,4-D)^a



^a[1,4-D] = 0.25 mM, [NH_2Cl] = 0.2–6 mM, and pH 5.8.

subsequent reactions refer to Scheme 1). On the basis of the rate constants of radical reactions, Cl^\bullet was transformed to HO^\bullet mainly via the $\text{Cl}_2^{\bullet-}$ and ClOH^\bullet pathways (reactions 2–6). Detailed calculations on the fate of Cl^\bullet , $\text{Cl}_2^{\bullet-}$, and HO^\bullet are provided in Texts S3–S5. Essentially, the increase in NH_2Cl dosage promoted HO^\bullet and $\text{Cl}_2^{\bullet-}$ formation and enhanced 1,4-D degradation. The subsequent decrease in the 1,4-D degradation rate at NH_2Cl concentrations of >2 mM was due to the scavenging of HO^\bullet and $\text{Cl}_2^{\bullet-}$ by NH_2Cl (reactions 7 and 8). The scavenging reactions produced NHCl^\bullet that did not significantly contribute to the oxidation of 1,4-D. The correlation between the rates of 1,4-D degradation and NH_2Cl consumption exhibited bell-shaped behavior (Figure 1B). Lower NH_2Cl consumption rates corresponded to the desirable conditions under which HO^\bullet and $\text{Cl}_2^{\bullet-}$ generated from NH_2Cl photolysis effectively reacted with 1,4-D. Higher NH_2Cl consumption rates were dominated by scavenging reactions that decreased the yields of Cl^\bullet , OH^\bullet , and $\text{Cl}_2^{\bullet-}$. In addition, higher concentrations of NH_2Cl were associated with higher Cl^- concentrations, contributing to higher steady-state concentrations of $\text{Cl}_2^{\bullet-}$ and a larger contribution of $\text{Cl}_2^{\bullet-}$ to 1,4-D oxidation.

Nature of Reactive Amine Radicals in UV/ NH_2Cl . To understand the reactivities of radical species with 1,4-D in UV/ NH_2Cl , especially reactive amine radicals, including NH_2^\bullet , additional UV/ H_2O_2 experiments were conducted in the presence of varying concentrations of NH_3 at different levels of pH and dissolved O_2 . The generation of NH_2^\bullet was controlled via the addition of NH_3 , which scavenged HO^\bullet

during H_2O_2 photolysis (reaction 9). Experiments showed that in N_2 -purged solutions and at pH 11, as the branching ratio of HO^\bullet reacting with NH_3 increased from 0 to 90% (i.e., the percentage of HO^\bullet reacting with NH_3 over HO^\bullet reacting with NH_3 and 1,4-D combined, which is indicative of the extent of NH_2^\bullet formation via HO^\bullet), the rate of 1,4-D degradation decreased by 80% (Figure 2). NH_2^\bullet was reported not to react

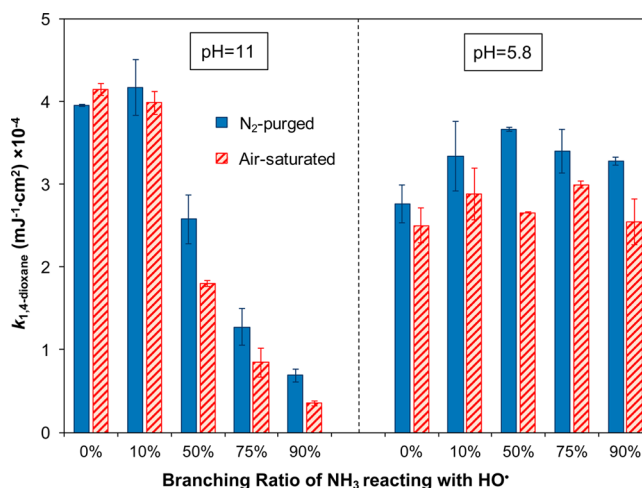


Figure 2. Degradation of 1,4-dioxane in UV and H_2O_2 with NH_3 . Initial $[\text{H}_2\text{O}_2] = 2 \text{ mM}$, initial $[1,4\text{-D}] = 250 \mu\text{M}$, and ionic strength = 120 mM. The branching ratio refers to the ratio of HO^\bullet reacting with NH_3 instead of with 1,4-dioxane. Experiments were conducted in either a N_2 -purged solution or an air-saturated solution.

quickly with organic compounds in general.⁴⁴ For example, a prior study showed that NH_2^\bullet had a low reactivity with primary amines ($<10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$) and phenolate ($10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$).⁴⁵ The NH_3 scavenging trend also suggested NH_2^\bullet had very limited reactivity with 1,4-D. When the pH of the N_2 -purged solution was decreased to 5.8, the rate of 1,4-D degradation remained high and stable at varying NH_3 branching ratios (Figure 2). This indicated that the NH_2^\bullet was not generated via HO^\bullet at the acidic pH when NH_4^+ was the predominant ammonium species ($\text{pK} = 9.6$).

When similar experiments were conducted in air-saturated solutions, the rate of 1,4-D degradation also decreased with increasing NH_3 branching ratios at pH 11; however, these rates were nearly 40% lower in the air-saturated solution than under N_2 -purged conditions for a NH_3 branching ratio of >50% (Figure 2). It has been reported that NH_2^\bullet reacts with dissolved O_2 to yield $\text{NH}_2\text{O}_2^\bullet$ (reaction 10).^{46,47} It is likely that $\text{NH}_2\text{O}_2^\bullet$ further decayed to less oxidative species that negligibly impacted 1,4-D degradation (Text S6). In addition, when the pH of the air-saturated solution decreased to 5.8, the rate of 1,4-D degradation also remained stably high regardless of the NH_3 branching ratio (Figure 2). It is noticeable that there was only a trace level of carbonate species in the solution, and the generation of carbonate radical $\text{CO}_3^{\bullet-}$ was negligible (Text S7).

Nature of Reactive Chlorine Radicals in UV/ NH_2Cl . $\text{Cl}_2^{\bullet-}$ was the predominant chlorine radical species that contributed to 1,4-dioxane degradation in UV/ NH_2Cl . On the basis of the decay of radical probe compounds (calculations provided in Text S8), the steady-state concentrations of $\text{Cl}_2^{\bullet-}$, HO^\bullet , and NH_2^\bullet were calculated as 4.9×10^{-11} , 1.6×10^{-13} , and $8.7 \times 10^{-9} \text{ M}$, respectively, in UV/ NH_2Cl with 2 mM NH_2Cl and 250 μM 1,4-dioxane. Because of the low reactivity of NH_2^\bullet

with 1,4-D, HO^\bullet and $\text{Cl}_2^{\bullet-}$ contributed 76 and 24%, respectively, to 1,4-D degradation (reactions 11 and 12, respectively).

Additional TBA scavenging experiments were performed to further confirm the importance of $\text{Cl}_2^{\bullet-}$. 1,4-D degradation was suppressed by approximately 30% with 5 mM TBA (Figure 3).

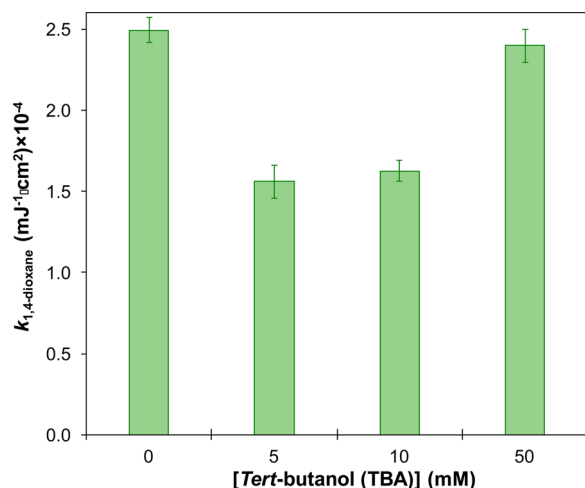


Figure 3. Impacts of *tert*-butanol (TBA) on 1,4-dioxane degradation in UV/ NH_2Cl with a N_2 -purged solution. Initial [1,4-D] = 250 μM , initial [NH_2Cl] = 2 mM, pH 5.8, and ionic strength = 35 mM.

This decrease in reaction rate resulted from the TBA scavenging of Cl^\bullet , $\text{Cl}_2^{\bullet-}$, and HO^\bullet . TBA reacted quickly with HO^\bullet and Cl^\bullet yet quite slowly with $\text{Cl}_2^{\bullet-}$ (Table S1). The scavenging of Cl^\bullet by 5 mM TBA decreased the steady-state concentrations of $\text{Cl}_2^{\bullet-}$ and HO^\bullet by 8 and 34%, respectively (detailed calculations in Text S9). The combined predicted scavenging effects on $\text{Cl}_2^{\bullet-}$ and HO^\bullet by 5 mM TBA decreased the degradation rate of 1,4-D by approximately 30% (Text S9), which was consistent with the experimental observation (Figure 3). The consistency between the calculated steady-state radical concentrations and the experimental data strongly suggested that both $\text{Cl}_2^{\bullet-}$ and HO^\bullet significantly contributed to 1,4-D degradation in UV/ NH_2Cl . Furthermore, an increase of TBA concentration from 5 to 50 mM increased the decay rate of 1,4-D (Figure 3). This was likely contributed by a significant generation of intermediate reactive TBA oxidation products. Previous studies showed that an intermediate radical from TBA oxidation, $^\bullet\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, also possibly reacted with 1,4-dioxane.^{44,48,49}

Environmental Implications. The presence of chloramines in the UV/AOP as carryover chemical residuals from membrane treatment processes can also be harnessed as an oxidant beneficial to water reuse. To maximize the efficiency of UV/ NH_2Cl in trace organic contaminant removal, an optimal chloramine dosage is required, as higher NH_2Cl concentrations act as self-scavengers to decrease the yields of reactive radicals, i.e., HO^\bullet and $\text{Cl}_2^{\bullet-}$. It should be noted that the NH_2Cl dose in our experiments promoted the production of $\text{Cl}_2^{\bullet-}$, which would have a yield lower than that of Cl^\bullet under applied RO permeate conditions. Considering the long-term impacts of climate change and drought, an efficient utilization of chloramine photolysis will lead to more sustainable water management. The generation of amine and halide radicals in UV/ NH_2Cl may affect the formation of nitrogenous

disinfection byproducts (N-DBPs) and will be investigated in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00444.

Additional text, figures, and tables (PDF)

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Notes

The authors declare no competing financial interest.

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