Mechanism of Cu(II)-catalyzed monochloramine decomposition in aqueous solution

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ABSTRACT

The decomposition of monochloramine, which is commonly used as a secondary disinfectant at water treatment plants to reduce the formation of disinfection byproducts, always occurs in water and can be accelerated by certain catalytic substances. This work was to investigate the mechanism of monochloramine decomposition catalyzed by Cu(II) in aqueous solution. Ultraviolet (UV) spectral results showed that either Cu(II) addition or pH decrease would significantly promote the transformation of monochloramine to dichloramine. A copper intermediate, Cu(I), was extracted from the NH_2Cl –Cu(II) solution by solid-phase extraction and identified by X-ray photoelectron spectroscopy (XPS). Electron spin resonance (ESR) results showed that hydroxyl radical ($\cdot\text{OH}$) and amidogen radical ($\cdot\text{NH}_2$) were generated in the reaction between monochloramine and Cu(II). These radical intermediates also contributed to monochloramine decomposition. Based on the experimental results, the reaction mechanism for Cu(II)-catalyzed monochloramine decomposition was proposed which consisted of two pathways: 1) direct catalysis in which Cu(II) acts as a Lewis acid to accelerate monochloramine decomposition to dichloramine (major pathway); and 2) indirect catalysis in which the active radical intermediates ($\cdot\text{OH}$ and $\cdot\text{NH}_2$) react with monochloramine and lead to its decomposition (minor pathway).

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1. Introduction

In response to the stringent health regulations regarding disinfection byproducts, monochloramine has been utilized as a secondary disinfectant more and more extensively in water treatment (Howard and Inglis, 2005; Duirk and Valentine, 2006; Liu et al., 2006). Monochloramine is nonetheless inherently unstable even without any reactive substance, and decomposes through a complex set of reactions. These reactions ultimately result in the oxidation of ammonia and the reduction of active chlorine (Jafvert and Valentine, 1992). Among these reactions, the transformation of monochloramine into dichloramine, which significantly depends on solution pH, governs the overall rate of monochloramine decomposition. These processes are described in the following proton-catalyzed reactions (Valentine, 1988):

Many efforts have been made to investigate the reactions between monochloramine and organic/inorganic constituents during water

disinfection (Wistrom et al., 1996; Vikesland et al., 1998; Brown and Emmert, 2006). Vikesland and Valentine (2000) found that monochloramine can be decomposed by both redox and autocatalytic reductions in the presence of Fe(II). The autocatalytic mechanism involves the formation of amidogen radical ($\cdot\text{NH}_2$) as an intermediate. Previous studies also showed that electron transfer processes may produce some radicals (e.g., $\cdot\text{OH}$ and $\cdot\text{NH}_2$) along with hydrated electrons and various other intermediate species (Johnson et al., 2002). The reaction mechanisms of monochloramine with these intermediates have been specifically investigated (Johnson et al., 2002; Poskrebyshev et al., 2003). Monochloramine can react with hydrated electrons very rapidly via single electron reduction to produce $\cdot\text{NH}_2$ (Eq. (4)). Monochloramine can also react with $\cdot\text{OH}$ to produce $\cdot\text{NHCl}$ and $\cdot\text{NH}_2$ (Eqs. (5)–(7)). Both $\cdot\text{NH}_2$ and $\cdot\text{NHCl}$ extinguish in radical–radical merging reactions. These processes occur concurrently and may involve complex and interrelated pathways.

Copper, mainly presents as Cu(II), can act as heterogeneous or homogeneous catalyst in many reactions. It was reported that Cu(II) could catalyze sodium hypochlorite decomposition in alkaline solutions (Gray et al., 1977; Church, 1994). Cu(II) could also catalyze the decomposition of monochloramine in drinking water, and its catalytic

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effect increased as the solution pH decreased (Fu et al., 2009). However, the catalytic mechanism of Cu(II) on monochloramine decomposition still remains largely unknown.

Similar to the catalytic effect of Fe(II) on monochloramine decomposition, it is hypothesized that Cu(II) may also react with monochloramine via electron transfer to produce $\cdot\text{NH}_2$. Meanwhile, the oxidation state of copper may vary from Cu(II) to Cu(I) or Cu(III) correspondingly. The objective of this work was to elucidate the reaction mechanism of monochloramine decomposition catalyzed by Cu(II). The transformation of Cu(II) species was examined by X-ray photoelectron spectroscopy (XPS), and the generation of radical intermediates was detected by electron spin resonance (ESR).

2. Materials and methods

2.1. Chemicals

Reaction solutions were all prepared with deionized water produced by a Barnstead ULTRO pure water system with a resistivity greater than 18 M Ω cm. CuBr ($\geq 98.5\%$) was stored in a nitrogen-filled exsiccator in the dark to prevent moisture and light. Ethylenediamine ($\geq 99\%$), NaCl ($\geq 99.5\%$ Suprapur), borate ($\geq 99.99\%$, Suprapur), and HCl (30%, Suprapur) were purchased from Beijing Chemical Co. (Beijing, China). Bathocuproine disulfonic acid disodium salt (2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline disulfonic acid disodium salt, 97%) was obtained from Acros (NJ, USA). All glassware was soaked in a concentrated chlorine solution (about 5000 mg L $^{-1}$ as Cl $_2$) for at least 24 h, rinsed with deionized water, and dried at 105 °C before use.

2.2. Preparation of NH $_2$ Cl solution

The stock solution of monochloramine was prepared by adding sodium hypochlorite solution to a well-stirred solution of ammonium chloride at a Cl $_2$ /N molar ratio of 0.65, and its pH was immediately adjusted to 8.0 by NaOH. The working solutions of monochloramine were prepared by diluting the stock to desired concentrations. The concentration of monochloramine was measured with the DPD-FAS titrimetric method. KH $_2$ PO $_4$ of 10 mM was used to buffer all the reaction solutions. All reactions were carried out at a constant temperature of 25 °C.

2.3. Solid phase extraction (SPE) of Cu(I)

Following the previous studies (Moffett et al., 1985; Buerge-Weirich and Sulzberger, 2004), bathocuproine was selected as a chelator for Cu(I) and ethylenediamine as a masking ligand for Cu(II). The NH $_2$ Cl–Cu(II) solution (1000 mL) was mixed with the bathocuproine/ethylenediamine/borate (BEB) solution (1000 mL) that approximately contained 1 μM bathocuproine, 1 μM ethylenediamine, and 10 mM borate. The resulting Cu(I)–BEB solution was allowed to equilibrate for 3 h in the dark for sufficient exchange of Cu(I) between bathocuproine and other ligands. The stock solution of bathocuproine disulfonic acid disodium salt (10 mM) was freshly prepared prior to preparing the BEB solution.

Cu(I)–bathocuproine complex was solid-phase extracted with C18 column. The appearance of a single, narrow and orange-colored band in the C18 column, through which the sample passed, would denote the successful extraction of Cu(I) (Moffett et al., 1985).

2.4. XPS analysis

XPS analysis was performed using a PHI Quantera SXM spectrometer with monochromatic Al K α radiation. The C1s peak was selected as an inner standard calibration peak at 284.8 eV. XPS data were processed using a nonlinear least-square fitting program (XPSpeak software 4.1, Raymund W. M. K. Work).

2.5. ESR analysis

Radical intermediates were detected using a Bruker ESP-300E ESR spectrometer which was operated at 9.79 GHz with 100 kHz modulation, 0.5 G modulation amplitude, 2.5×10^5 gain, 39.9 mW microwave power, 40.96 ms time constant, 80 G/84 s sweep rate and 80 G sweep width. The solution of 5,5-dimethylpyrroline-N-oxide (DMPO, 50 mM) was used as spin trap for radicals. After the DMPO solution was mixed with monochloramine solution, Cu(II) was added to initiate the reaction. The time between the reaction initiation and the onset of ESR scanning was controlled for less than 2 min.

The effect of solution pH on radical intensity was investigated according to the following procedures: 1) prepare a working solution containing 0.9 mM NH $_2$ Cl, 50 mM DMPO and 10 mM phosphate as buffer; 2) adjust the solution pH to a desired value (i.e., 5.8, 6.6, 7.9); 3) add 0.1 mM Cu(II) into the working solution to initiate the reaction; and 4) immediately analyze the radical intensity with ESR.

The effect of Cu(II)/NH $_2$ Cl molar ratio on radical intensity was examined following the procedures: 1) prepare a working solution containing 0.9 mM NH $_2$ Cl, 50 mM DMPO and 10 mM phosphate as buffer; 2) adjust its pH to 6.0; 3) add a desired amount of Cu(II) (i.e., 0, 0.09, 0.54, 0.90 and 1.35 mM) into the working solution to initiate the reaction; and 4) immediately analyze the radical intensity with ESR.

3. Results and discussion

3.1. Ultraviolet (UV) spectral characteristics

UV spectral experiments were conducted to investigate the effects of solution pH and Cu(II) on the decomposition of monochloramine. Monochloramine and dichloramine have a characteristic absorption peak at 245 nm and 294 nm, respectively (Hand and Margerum, 1983; Valentine et al., 1986).

Fig. 1a showed the variation of UV spectra of 1 mM monochloramine solution as pH was continuously adjusted downward from 7.3 to 3.5. The pH adjustment and UV scan were finished within 5 min. Results indicated that as the solution pH decreased, the 245-nm peak (denoting monochloramine) intensity gradually decreased while the 294-nm peak (denoting dichloramine) intensity increased accordingly. It implies that the decrease of pH would accelerate the decomposition of monochloramine to dichloramine. This result agrees well with the literature information (Qiang and Adams, 2004).

Fig. 1b showed the variation of UV spectra of the NH $_2$ Cl–Cu(II) reaction system as a function of reaction time. The concentration of monochloramine was prepared at 1 mM with solution pH maintained at 6.0×10^{-3} M phosphate buffer, then 10 mg L $^{-1}$ Cu(II) was introduced. Results indicated that the intensity of the monochloramine peak (245 nm) notably decreased and the dichloramine peak emerged at 294 nm upon the addition of Cu(II). As the reaction proceeded, the intensities of both monochloramine and dichloramine peaks attenuated. It is seen that although dichloramine was continuously produced from monochloramine decomposition, its own decomposition rate outweighed its formation rate.

Valentine (1988) reported that the disproportionation of monochloramine, which resulted in the formation of dichloramine, was a general acid-catalyzed process. The resulting dichloramine decomposed rapidly via a series of redox reactions, leading to more monochloramine decomposition in turn. The UV spectral results clearly indicated that Cu(II) could serve as a Lewis acid, similar to H $^+$, to catalytically promote the disproportionative decomposition of monochloramine.

3.2. Copper species transformation

SPE and XPS methods were utilized together to investigate copper species transformation during the reaction between monochloramine

Fig. 1. Variation of UV spectra of: (a) NH_2Cl solution as pH was adjusted downward in the absence of Cu(II) ; and (b) the NH_2Cl – Cu(II) reaction system at pH 6.0 as reaction time extended, $[\text{NH}_2\text{Cl}]_0 = 1.0 \text{ mM}$, $[\text{Cu(II)}]_0 = 10 \text{ mg L}^{-1}$.

and Cu(II) . After the sample passed through the C18 column, a small fraction of the orange-colored band was sliced, freeze-dried, and analyzed by XPS. Fig. 2 compared the XPS spectra of a $\text{Cu}^{\text{I}}\text{Br}$ standard and the Cu –bathocuproine complex extracted from the sample. Results indicated that both spectra had two peaks at the same binding energies of 932.3 and 952.2 eV. It was thus confirmed that Cu(I) was generated via electron transfer step during the reaction between monochloramine and Cu(II) .

Fig. 2. $\text{Cu}2\text{p}$ core level photoelectron spectra of $\text{Cu}^{\text{I}}\text{Br}$ standard and Cu –bathocuproine complex extracted from the NH_2Cl – Cu(II) reaction system.

Fig. 3. Comparison of ESR spectra of different reaction systems: (a) NH_2Cl + DMPO ; (b) Cu(II) + NH_2Cl + DMPO (at 0 min); (c) Cu(II) + NH_2Cl + DMPO (at 40 min); and (d) Cu(II) + HClO + DMPO . Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.9 \text{ mM}$, $[\text{Cu(II)}]_0 = 0.9 \text{ mM}$, $[\text{HClO}]_0 = 0.9 \text{ mM}$, $[\text{DMPO}]_0 = 50 \text{ mM}$, pH = 6.0.

3.3. Detection of active radical intermediates

ESR was employed to detect the active radical intermediates produced in the reaction system of NH_2Cl – Cu(II) . Results indicated that in the absence of Cu(II) , no radical signal was detected in the NH_2Cl solution (Fig. 3a). Right after Cu(II) addition, however, radical signals appeared and a part of which was identified to result from $\cdot\text{OH}$ according to Paciolla et al. (1999) (Fig. 3b). Moreover, there existed other radical signals (Fig. 3b) which eventually disappeared after the NH_2Cl – Cu(II) reaction was allowed to proceed for 40 min (Fig. 3c). It was suspected that these signals might come from a radical intermediate generated from the reaction between Cu(II) and hypochlorous acid (HClO), a trace byproduct produced from the reaction of monochloramine with $\cdot\text{OH}$ (Eq. (5)) or from monochloramine hydrolysis (Eq. (7)). However, the experimental results showed that only $\cdot\text{OH}$ signals were detected with a much lower intensity in the reaction system of HClO – Cu(II) (Fig. 3d). It was reported that the reaction between hypochlorous acid and metal ions may produce $\cdot\text{OH}$ (Koppenol and Butler, 1985; Folkes et al., 1995).

To identify the unknown signals above, a standard $\cdot\text{NH}_2$ radical was generated by the reaction system of NH_2Cl – Fe(II) (0.9 mM each) according to Vikesland and Valentine (2000) and its signals were recorded by ESR (Fig. 4a). In addition, the $\cdot\text{OH}$ signals were eliminated by subtracting the ESR spectrum of Fig. 3c from that of Fig. 3b. The resulting spectrum (Fig. 4b), compared to that of the standard $\cdot\text{NH}_2$ radical (Fig. 4a), confirmed the formation of $\cdot\text{NH}_2$ in the reaction system of NH_2Cl – Cu(II) (Fig. 3b). Therefore, two active radical intermediates, $\cdot\text{OH}$ and $\cdot\text{NH}_2$, were generated when monochloramine reacted with Cu(II) . Upon formation, $\cdot\text{OH}$ could maintain a strong intensity for a longer time than $\cdot\text{NH}_2$ in the reaction solution (Fig. 3b and c).

The effect of solution pH on the intensity of active radical intermediates was studied in the pH range from 5.8 to 7.9. Results indicate that the radical intensity significantly decreased with the increase of pH (Fig. 5a). More than 80% of the radical intermediates disappeared in the NH_2Cl – Cu(II) reaction system as the solution pH was raised from 5.8 to 7.9. It is seen that the formation of active radical

Fig. 4. Identification of $\cdot\text{NH}_2$ intermediate: (a) ESR spectrum of the standard $\cdot\text{NH}_2$ generated in the reaction system of 0.9 mM Fe(II) + 0.9 mM NH_2Cl + 50 mM DMPO; and (b) derived ESR spectrum (Fig. 3b–c).

intermediates was highly pH dependent. Fig. 5b showed the effect of Cu(II)/ NH_2Cl molar ratio on the intensity of active radical intermediates at pH 6.0. The initial concentration of monochloramine was maintained constant at 0.9 mM, while the Cu(II)/ NH_2Cl molar ratio ranged from 0 to 1.5 by varying the initial concentration of Cu(II). Results indicated that the radical intensity reached maximum at the molar ratio of Cu(II)/ NH_2Cl equaling 1.0, and either decreasing or increasing this molar ratio would reduce the formation of active radicals.

Fig. 5. Initial intensity of active radical intermediates as a function of: (a) solution pH in the reaction system of 0.1 mM Cu(II) + 0.9 mM NH_2Cl + 50 mM DMPO; (b) molar ratio of $[\text{Cu(II)}]/[\text{NH}_2\text{Cl}]$ at pH 6.0, $[\text{NH}_2\text{Cl}]_0 = 0.9$ mM.

Fig. 6. Effect of tert-butanol on monochloramine decomposition in the absence or presence of Cu(II). Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.5$ mM, $[\text{Cu}^{2+}]_0 = 10$ mg L^{-1} , $[\text{tert-butanol}] = 5$ mM, pH = 6.0.

3.4. Effect of radicals on monochloramine decomposition

To assess the effect of active radical intermediates on Cu(II)-catalyzed monochloramine decomposition, tert-butanol was selected as the radical scavenger. Tert-butanol can react rapidly with radicals to generate inert intermediates, thus terminating radical chain reactions (Ma and Graham, 2000).

Fig. 6 showed that monochloramine attenuated naturally in water with about 50% loss after a reaction time of 50 h. The addition of tert-butanol into monochloramine solution had no effect on the monochloramine decomposition rate. In the reaction system of NH_2Cl –Cu(II), Cu(II) significantly enhanced the decomposition rate of monochloramine as compared to the natural attenuation curve above. If tert-butanol was added into the NH_2Cl –Cu(II) system to scavenge the active radical intermediates (i.e., $\cdot\text{OH}$ and $\cdot\text{NH}_2$), the monochloramine decomposition rate was decreased but still much faster than its natural attenuation rate. The applied concentration of tert-butanol was 5 mM that was enough to scavenge all the active radical intermediates produced in the reaction system. Results indicated that 85% of monochloramine was lost in the NH_2Cl –Cu(II) system as compared to the 77% loss in the presence of tert-butanol. It is noted that all the reaction curves approached parallel after approximately 10 h, implying that both Cu(II) and the radical intermediates promoted monochloramine decomposition only in the early period of reaction. Thereafter, the natural attenuation started to govern monochloramine decomposition. Results also revealed that the direct catalysis induced by Cu(II) on monochloramine decomposition

Fig. 7. Proposed reaction mechanism for Cu(II)-catalyzed monochloramine decomposition.

significantly outweighed the indirect catalysis induced by the active radical intermediates.

3.5. Proposed reaction mechanism

Based on the experimental results described above, the decomposition of monochloramine in the presence of Cu(II) was accelerated by the direct catalysis of Cu(II) and the indirect catalysis of the active radical intermediates, $\cdot\text{OH}$ and $\cdot\text{NH}_2$. The proposed reaction mechanism is illustrated in Fig. 7 and detailed below.

The direct catalysis of Cu(II) made a major contribution to monochloramine decomposition. Similar to the proton-catalyzed process, in which monochloramine auto-decomposes through disproportionation to form dichloramine (Valentine, 1988), Cu(II) could act as a Lewis acid to enhance monochloramine decomposition to dichloramine (Eqs. (8)–(9)). Dichloramine further reacted with monochloramine to the end products such as N_2 , Cl^- , NH_3 , and H^+ (Eq. (3)).

The indirect catalysis of active radical intermediates made a comparatively minor contribution to monochloramine decomposition (as shown in Fig. 6). The addition of Cu(II) into the monochloramine solution would initiate a series of redox reactions in which the active radical intermediates, mainly including $\cdot\text{OH}$ and $\cdot\text{NH}_2$, were generated. Both $\cdot\text{OH}$ and $\cdot\text{NH}_2$ were identified by ESR in this study. These radical intermediates further reacted with monochloramine to eventually produce the end products (Eqs. (5)–(6)).

In addition, our previous study (Fu et al., 2009) has shown that the complexation between Cu(II) and monochloramine led to the formation of Cu(I) (Eq. (10)), which was identified by the integrated method of SPE and XPS in this work. Cu(I) could in turn react with NH_2Cl to form $\cdot\text{NH}_2$ and Cu(II) was regenerated (Eq. (10)). Disintegration of the $[\text{Cu}^{\text{II}}\text{NH}_2\text{Cl}]^{2+}$ complex also yielded another product, $\cdot\text{NHCl}$ radical, which could hydrolyze to form $\cdot\text{OH}$ (Eq. (6)).

It was reported that $\cdot\text{NH}_2$ was generated in the reaction system of NH_2Cl –Fe(II) (Vikesland and Valentine, 2000). Therefore, it is reasonable to expect that $\cdot\text{NH}_2$ was generated, analogously, in the reaction system of NH_2Cl –Cu(I) (Eq. (11)). The $\cdot\text{NH}_2$ radical could also be generated from the reaction between monochloramine and $\cdot\text{OH}$ (Eq. (5)). The self-merging reaction between the $\cdot\text{NH}_2$ radicals led to the production of hydrazine (Eq. (12)) (Neta et al., 1988). Upon formation, hydrazine would react rapidly with monochloramine to produce nitrogen gas and ammonium chloride (Sisler et al., 1954; Sanftner et al., 1955):

4. Conclusions

This work investigated the mechanism of monochloramine decomposition catalyzed by Cu(II) in water. The experimental results indicated that both Cu(II) addition and pH decrease would enhance the decomposition of monochloramine to dichloramine. Cu(I), which was identified by XPS, and two active radicals ($\cdot\text{OH}$ and $\cdot\text{NH}_2$), which were identified by ESR, were major intermediates in the reaction system of NH_2Cl –Cu(II). In addition, the radical scavenging experiments indicated that Cu(II) contributed more to monochloramine

decomposition than the active radicals. Thus, the catalytic mechanism of Cu(II) on monochloramine decomposition was proposed to consist of a major direct catalysis pathway, in which Cu(II) acts as a Lewis acid to enhance monochloramine transformation to dichloramine, and a minor indirect catalysis pathway, in which the active radical intermediates ($\cdot\text{OH}$ and $\cdot\text{NH}_2$) react with monochloramine thus resulting in more monochloramine loss.

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