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Cu(II)-catalyzed THM formation during water chlorination and monochloramination: A comparison study

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ABSTRACT

The catalytic effect of Cu(II) on trihalomethane (THM) formation during chlorination and monochloramination of humic acid (HA) containing water was comparatively investigated under various pH conditions. Results indicate that in the presence of Cu(II), the formation of THMs was significantly promoted as pH decreased in both chlorination and monochloramination. More THMs were formed during Cu(II)-catalyzed monochloramination which was partially due to enhanced hydroxyl radical (•OH) generation as demonstrated by electron spin resonance (ESR) analysis. To discriminate the reactive moieties of HA, nine model compounds, which approximately represented the chemical structure of HA, were individually oxidized by chlorine or monochloramine. Results show that Cu(II) could promote THM formation through reacting with citric acid and similar structures in HA. During chlorination and monochloramination of citric acid in the absence of Cu(II), major intermediates including chlorocarboxylic acid, chloroacetone and chloroacetic anhydride were identified. However, the catalysis of Cu(II) did not produce any new intermediate. The complexation of Cu(II) with model compounds was characterized via FTIR analysis. The reaction mechanism for Cu(II)-catalyzed THM formation was proposed to comprise two pathways: (1) indirect catalysis in which •OH oxidizes the large molecules of HA into small ones to enhance THM formation; and (2) direct catalysis in which Cu(II) complexes with HA to accelerate the decarboxylation steps for THM formation.

1. Introduction

The formation of disinfection byproducts (DBPs) during chlorination, such as trihalomethanes (THMs) and haloacetic acids (HAAs), has received great concern in the past several decades. Monochloramine has been utilized more and more extensively to minimize DBPs formation [1–3].

Dissolved copper, a catalyst in many reactions including oxidation of phenol [4], methanol production, and dehydrogenation [5,6], is persistent and frequently detected in water. It comes from many sources such as corrosion of copper pipes and algicidal applications to water supplies. Limited studies have reported the catalytic effect of copper on THM formation during water chlorination. Some experiments were conducted to study the influence of copper on the reactions of humic acid (HA) with chlorine [7]. Blatchley et al. [8] investigated the catalysis of Cu(II) on chorination of some known THM precursors, and found that the THM yield was strongly influenced. However, these studies were only focused on chlorination of water, while much less information was available with respect to monochloramination.

Chlorination is always involved in monochloramination because the hydrolysis of monochloramine produces hypochlorous acid as follows:

$$NH_2Cl + H_2O \rightleftharpoons HClO + NH_3$$

Both monochloramine and hypochlorous acid can react with organic molecules to form DBPs through oxidation of electron-rich moieties, or substitution/addition of chlorine atom(s) into unsaturated structures [9].

A number of organics have been identified as THM precursors, such as HA [10], organic nitrogen compounds [11], citric acid [12], methyl ketones [13], algal cells [14], and hydroxybenzene [15]. HA is a main precursor with a complex macromolecule containing aromatic heterocyclic rings that are commonly substituted with methoxy (OMe), hydroxyl (OH), carboxylic (COOH), and other functional groups [16]. Due to the complex structure of HA, many studies have focused on the reactions of chlorine with simple alternative model compounds which are believed to approximate the chemical structure of HA. The main pathway for THM formation from these model compounds was reported to be a haloform reaction in

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which the hydrogen atoms of α-carbon, which connect to the carbonyl group of a methyl ketone, are substituted by halogens to form haloforms [12,17].

Based on the studies described above as well as our previous work [18,19], it is reasonably expected that copper tends to play an important role in THM formation upon water chlorination and monochloramination. Therefore, this study was to comparatively investigate the catalytic effect of Cu(II) on THM formation during chlorination and monochloramination of HA and simple model compounds, and further clarify the reaction mechanism through identification of reaction intermediates.

2. Materials and methods

2.1. Chemicals

HA was purchased from Aldrich in sodium salt form. The selected organic precursors consisted of six aromatic compounds and three non-aromatic compounds which included pyrocatechol (99%), 2,6-dihydroxybenzoic acid (98%), 3,5-dihydroxybenzoic acid (97%) and 2-methyl resorcinol (98%) from Aldrich, and resorcinol (99%), salicylic acid (99%), malonic acid (98%), aminoacetic acid (reagent grade) and citric acid (99.8%) from Beijing Chemical Co. Copper was added in the form of sulfate salt ($CuSO_4{\cdot}5H_2O$, reagent grade). Sodium hypochlorite (Beijing Chemical Co., >9% available chlorine) was used as the source of chlorine. Monochloramine stock solution was prepared by the addition of sodium hypochlorite into a well-stirred solution of ammonium chloride, and its pH was immediately adjusted to 8.0 by NaOH. The actual concentrations of chlorine and monochloramine in stock solutions were measured prior to each experiment.

2.2. Chlorination and monochloramination procedures

The Cu(II)-catalyzed chlorination and monochloramination experiments were carried out in a series of sealed 3-L glass reactors at room temperature (25 °C). The reactors were covered with aluminum foil to prevent light. All reaction solutions were buffered with 10 mM phosphate and the pH was adjusted with H_2SO_4 and NaOH solutions. The reactants were added in the following order: organic precursor, phosphate buffer, copper (if applicable), and finally monochloramine or chlorine. After all the reactants were added, the reaction was allowed to proceed under magnetic stirring condition. Samples were withdrawn from an outlet at regular time intervals and the reaction was terminated immediately by the addition of sodium thiosulfate.

2.3. Analytical methods

The concentrations of chlorine and monochloramine were determined using the N,N-diethyl-p-phenyl-enediamine (DPD) titration method by a UV–vis spectrophotometer (Hitachi U-3010, Japan).

A gas chromatography (Model 6890N, Agilent) with an electron capture detector was used to determine the concentrations of THMs following the USEPA method 552.1. The separation of THMs was achieved with an HP-5 fused silica capillary column (30 m × 0.32 mm, 0.25 μm film thickness) using the temperature program: initial temperature 35 °C for 4 min, ramp to 100 °C at 10 °C min^{-1} and hold for 3 min. Nitrogen gas of extra purity (>99.999%) was used as carrier gas.

Reaction intermediates were identified by an Agilent 7890GC/5975MSD with an HP-5 MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The temperature program was set as follows: initial temperature 70 °C for 2 min, ramp at 10 °C min^{-1} to 230 °C and hold for 10 min. The injector temperature was set at 280 °C, and high purity helium gas was used as carrier gas.

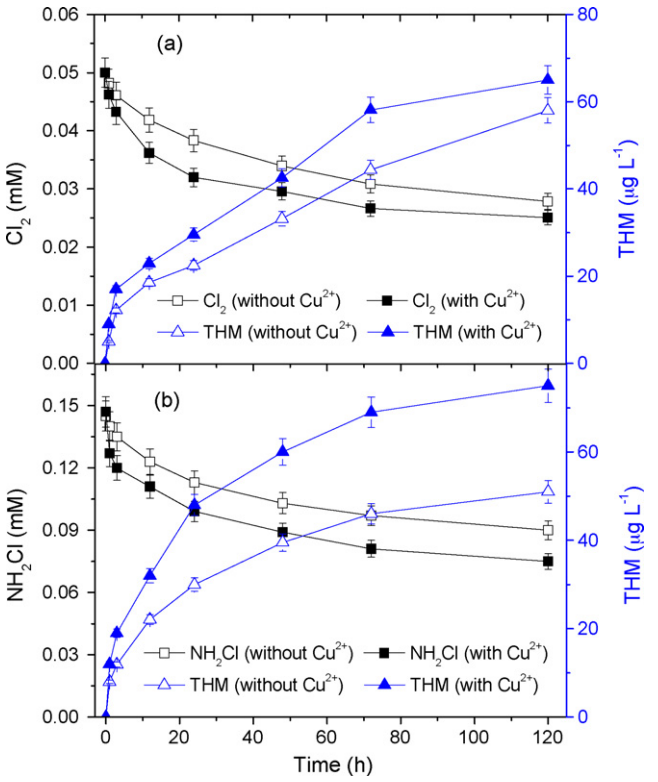


Fig. 1. Effect of Cu(II) on THM formation during (a) chlorination and (b) monochloramination of HA. Experimental conditions: 0.05 mM Cl_2, 0.15 mM NH_2Cl, 5.0 mg L^{-1} HA, 1.0 mg L^{-1} Cu(II), pH 7.0.

Hydroxyl radicals (•OH) 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, 5.0 mM) was used as spin trap for radicals. After the DMPO was mixed with the reaction 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.

FTIR spectra were collected on a Nicolet 5700 spectrometer in transmission mode. Samples were ground with spectral grade KBr in an agate mortar. A fixed amount of sample (1% w/w) in KBr was used to prepare the pellet.

3. Results and discussion

3.1. Chlorination and monochloramination of HA

3.1.1. Catalytic effect of Cu(II) on THM formation

It was reported that the use of monochloramine for disinfection instead of chlorine reduced the formation of THM often by as much as 40–80% [20]. Our preliminary experiments showed that 0.05 mM chlorine and 0.15 mM monochloramine generated a similar level of THM at neutral pH, which agrees well with the literature information [20]. Accordingly, the initial doses of chlorine and monochloramine were chosen to be 0.05 and 0.15 mM, respectively, in this study for comparison purpose.

The catalytic effect of Cu(II) on THM formation during chlorination (Fig. 1a) and monochloramination (Fig. 1b) of HA-containing water was separately examined. Results clearly indicate that both THM formation and chlorine/monochloramine decay were significantly promoted in the presence of Cu(II). When Cu(II) was added, the THM concentration was increased from 59 to 66 μg L^{-1}

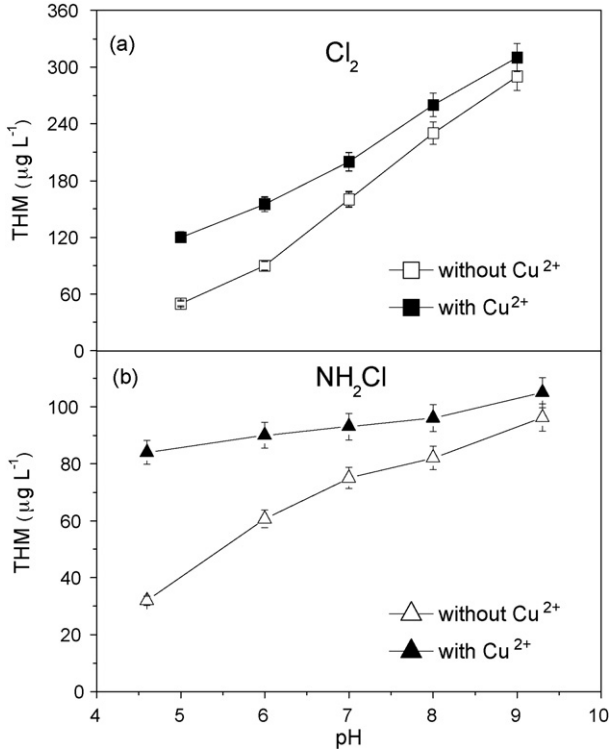


Fig. 2. Effect of pH on THM formation during (a) chlorination and (b) monochloramination of HA in the presence and absence of Cu(II). Experimental conditions: 0.1 mM Cl_2, 0.3 mM NH_2Cl, 5.0 mg L^{-1} HA, 1.0 mg L^{-1} Cu(II), reaction time 3 d.

in chlorination and from 52 to 75 μg L^{-1} in monochloramination, respectively. It is seen that Cu(II) was able to catalyze the decomposition of chlorine and monochloramine, and consequently enhancing THM formation. Moreover, the catalytic effect of Cu(II) on monochloramine was more distinguishable than on chlorine.

3.1.2. Effect of pH on Cu(II) catalysis

The effect of pH on THM formation was investigated during Cu(II)-catalyzed chlorination (Fig. 2a) and monochloramination (Fig. 2b) of HA. Results indicate that in spite of Cu(II), the THM concentration increased with the increasing pH value in both chlorination and monochloramination. The addition of Cu(II) notably enhanced THM formation, particularly under low pH conditions. The pH increase gradually diminished the catalytic effect of Cu(II) on THM formation. In terms of percent enhancement in THM formation, Cu(II)-catalyzed monochloramination is more significant than chlorination.

3.1.3. Involved active radicals

ESR was utilized to detect the active radicals produced during the Cu(II)-catalyzed chlorination and monochloramination of HA. As shown in Fig. 3, without Cu(II), no ESR signal was detected in monochloramination of HA (Insert a). Right after the addition of Cu(II), a strong ESR signal of •OH [21] appeared (Insert c). The •OH signal was also detected in the catalytic chlorination (Insert b), exhibiting a comparatively weaker intensity, however. Hua and Reckhow [22] found that •OH could oxidize the large molecules of HA to small molecules and thus enhance THM formation.

To assess the effect of •OH on THM formation during the catalytic monochloramination, carbonate was selected as the radical scavenger. Carbonate could react rapidly with radicals to terminate radical chain reactions [23]. Fig. 4a shows that if 0.2 mM carbonate was added into the catalytic monochloramination process, the formation rate of THMs was notably decreased but still higher than that in the non-catalytic monochloramination. It is seen that •OH played an important role in THM formation during Cu(II)-catalyzed monochloramination of HA. Fig. 4b shows that the addition of carbonate had little effect on monochloramine decay in the catalytic monochloramination. It implies that •OH, once generated during the catalytic monochloramination, was rapidly consumed by HA, rather than by monochloramine, to enhance THM formation.

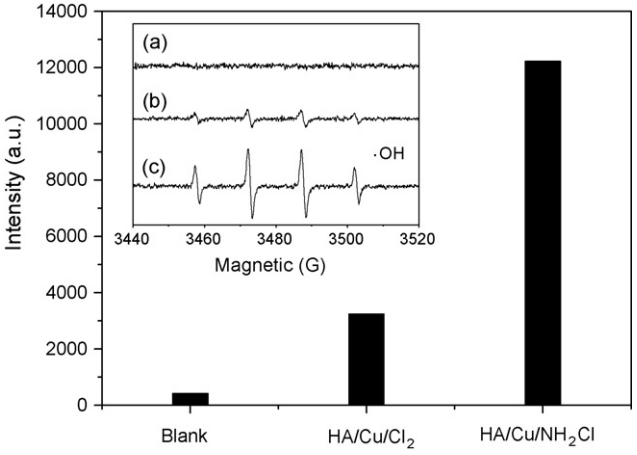


Fig. 3. ESR spectra of (a) blank, (b) catalytic chlorination, and (c) catalytic monochloramination. Experimental conditions: 0.5 mM Cl_2/NH_2Cl, 5.0 mg L^{-1} HA, 10 mg L^{-1} Cu(II), 5.0 mM DMPO, pH 6.0.

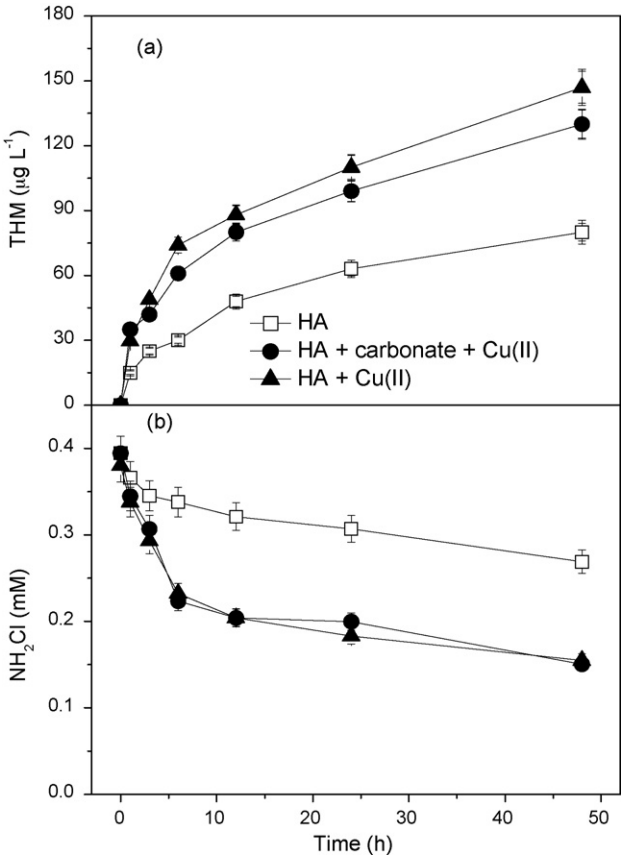
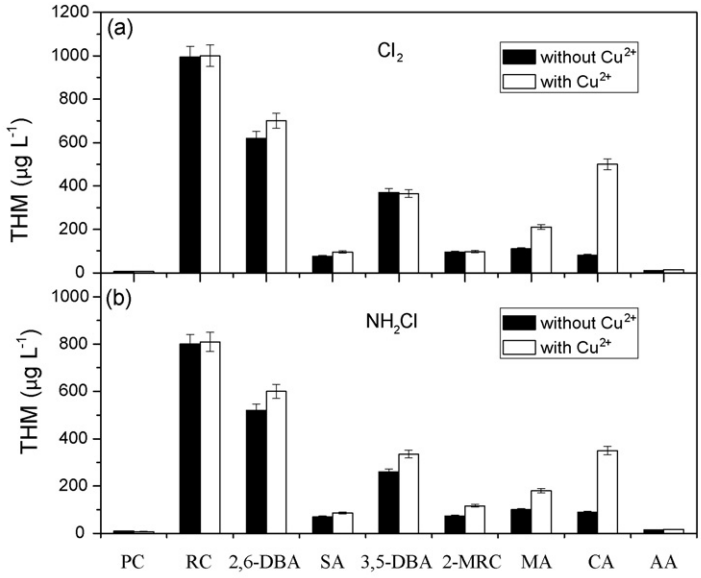


Fig. 4. Effect of carbonate on (a) THM formation and (b) monochloramine decay during Cu(II)-catalyzed monochloramination of HA. Experimental conditions: 0.4 mM NH_2Cl, 5.0 mg L^{-1} Cu(II), 0.2 mM carbonate.



Notes:

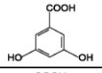
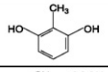
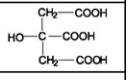
Abbreviation	Chemical name	Molecular structure	Abbreviation	Chemical name	Molecular structure
PC	Pyrocatechol		RC	Resorcinol	
2,6-DBA	2,6-Dihydroxybenzoic acid		SA	Salicylic acid	
3,5-DBA	3,5-Dihydroxybenzoic acid		2-MRC	2-Methyl resorcinol	
MA	Malonic acid		CA	Citric acid	
AA	Aminoacetic acid				

Fig. 5. Effect of Cu(II) on THM formation during (a) chlorination and (b) monochloramination of nine model compounds. Experimental conditions: 2.0 mg L^{-1} individual organic precursor, 0.2 mM Cl_2, 0.5 mM NH_2Cl, 1.0 mg L^{-1} Cu(II), pH 7.0, reaction time 1 d.

3.2. Chlorination and monochloramination of model compounds

3.2.1. Effect of Cu(II) on THM formation

Similar experiments were conducted with nine model compounds with varied functional groups which were selected according to the literatures [10,16,17]. The THM concentrations formed during the catalytic and non-catalytic chlorination were compared in Fig. 5a. Results indicate that in the non-catalytic chlorination, resorcinol, 2,6-dihydroxybenzoic acid and 3,5-dihydroxybenzoic acid yielded a high level of THMs; salicylic acid, 2-methyl resorcinol, malonic acid and citric acid yielded a moderate level of THMs; while pyrocatechol and aminoacetic acid contributed little to THM formation. Under the catalysis of Cu(II), the THM formation was significantly enhanced from malonic acid and citric acid, and was enhanced to some extent from 2,6-dihydroxybenzoic acid and salicylic acid. However, the catalysis of Cu(II) did not enhance the THM formation from pyrocatechol, resorcinol, 3,5-dihydroxybenzoic acid and aminoacetic acid at all. The most prominent promotion in THM formation by the catalysis of Cu(II) was observed from citric acid, i.e., from 94 to 500 μg L^{-1}. Larson and Rock reported that citric acid and other similar structures were present in HA [12]. Our results demonstrate that citric acid and malonic acid could be important precursors of THMs, particularly under the catalysis of Cu(II). In addition, by comparing the THM concentrations formed from resorcinol and 2-methyl resorcinol, it is seen that the electron-donating group "$-CH_3$" significantly suppressed THM formation.

The catalysis of Cu(II) exerted quite similar effect on THM formation during monochloramination of the selected model compounds (Fig. 5b). The only difference is that Cu(II) enhanced the THM formation from 3,5-dihydroxybenzoic acid and 2-methyl resorcinol during monochloramination, which was not observed during chlorination. It suggests that Cu(II) could catalyze more model compounds (or similar structures in HA) to form THMs during monochloramination than during chlorination.

3.2.2. Effect of pH on THM formation from citric acid

According to the above experiments, the catalytic effect of Cu(II) on THM formation during chlorination and monochloramination of HA was largely attributable to citric acid and similar chemical structures. To further investigate the effect of pH on Cu(II)-catalyzed THM formation from citric acid, chlorination experiments were comparatively conducted in the absence and presence of Cu(II). Monochloramination experiments were not purposely examined because Cu(II) yielded a similar catalytic effect on THM formation during chlorination and monochloramination of citric acid (see

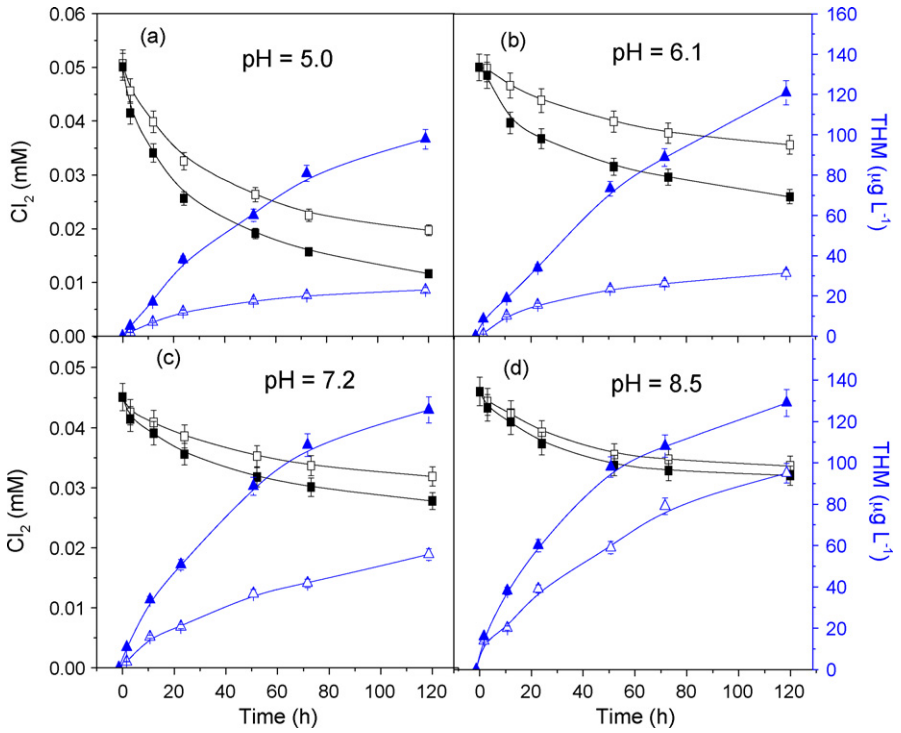
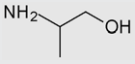
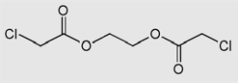
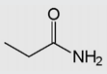
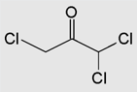
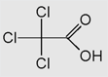
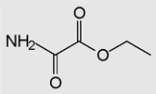
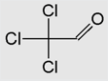
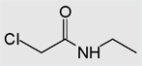
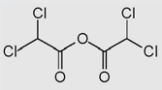
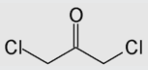
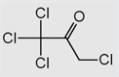
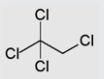
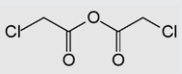
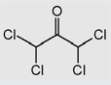


Fig. 6. Effect of Cu(II) on THM formation during chlorination of citric acid at different pH values. Experimental conditions: 1.0 mg L^{-1} citric acid, 0.05 mM Cl_2, 1.0 mg L^{-1} Cu(II).

Table 1
Major intermediates formed during chlorination and monochloramination of citric acid detected by GC–MS.

RT (min)	Intermediates	Molecular structure	RT (min)	Intermediates	Molecular structure
4.84[a,b]	Chloroacetyl chloride		8.88[a,b]	Trichloromethane	
4.89[b]	2-Aminopropanol		9.12[a,b]	Ethyleneglycol bischloro acetate	
5.04[b]	Propanamide		9.92[a,b]	1,1,3-Trichloroacetone	
5.92[a,b]	Dichloroacetic acid		9.97[a,b]	Trichloroacetic acid	
6.3[b]	Ethyl oxamate		10.01[a,b]	Trichloroacetaldehyde	
6.88[b]	2-chloro-N-ethylacetamide		10.803[a,b]	Dichloroacetic anhydride	
7.55[a,b]	1,3-Dichloroacetone		12.45[a,b]	1,1,1,3-Tetrachloroacetone	
8.67[a,b]	Dichloro-acetyl chloride		12.653[a,b]	1,1,1,2-Tetrachloro-ethane	
8.69[a,b]	Chloroacetic anhydride		12.85[a,b]	1,1,3,3-Tetrachlorophthalic acetone	

[a] Chlorination of citric acid: 0.15 mM chlorine, 10 mg L^{-1} citric acid, reaction time 24 h.
[b] Monochloramination of citric acid: 0.2 mM monochloramine, 10 mg L^{-1} citric acid, reaction time 24 h.

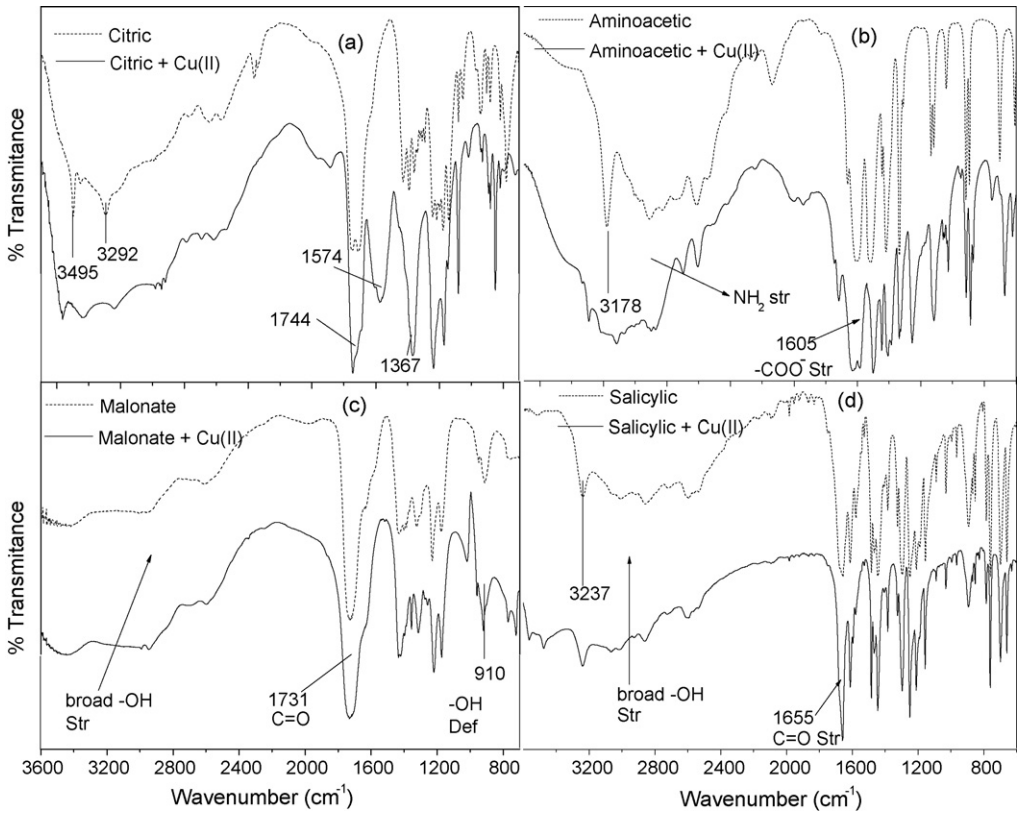


Fig. 7. FTIR spectra of (a) citric acid, (b) aminoacetic acid, (c) malonic acid, and (d) salicylic acid in the presence or absence of Cu(II). Experimental conditions: 5.0 mg L^{-1} individual organic precursor, 5.0 mg L^{-1} Cu(II), pH 6.0.

Fig. 5). Fig. 6 shows that as the solution pH increased from 5.0 to 8.5, the THM formation was enhanced notably in the absence of Cu(II), while to a relatively lesser extent in the presence of Cu(II). At a fixed pH, the catalysis of Cu(II) greatly promoted THM formation and chlorine decay as well. For example, at pH 7.2 which is common in water treatment plants, the THM concentration formed in chlorination of citric acid could be increased by two-fold under the catalysis of Cu(II) at a reaction time of 120 h.

3.2.3. *Identification of intermediates from citric acid*

The major intermediates produced during chlorination and monochloramination of citric acid in the absence and presence of Cu(II) are listed in Table 1. In the non-catalytic chlorination, many chlorine-substituted compounds, such as chloroacetyl acid, dichloroacetic acid, 1,3-dichloroacetone, dichloro-acetyl chloride, chloroacetic anhydride, trichlormethane and etc., were detected. Since citric acid has three carboxylic groups, the decarboxylation of citric acid yielded methyl ketone structures which could be substituted by chlorine to form the detected intermediates.

In addition to these chlorine substitutes, new intermediates such as 2-aminopropanol, propanamide, ethyl oxamate and 2-chloro-N-ethylacetamide were observed in the non-catalytic monochloramination. These nitrogenous intermediates indicate that monochloramine could directly react with citric acid to generate some new DBPs. Furthermore, as chlorine always exists in monochloramine solution, it is reasonable that the intermediates generated in chlorination would also appear in monochloramination.

Compared with the non-catalytic chlorination and monochloramination, no new intermediate was detected under the catalysis of Cu(II). It suggests that the addition of Cu(II) could change the reaction rates but not the major pathways of THM formation during chlorination or monochloramination of citric acid.

3.3. *FTIR spectroscopy for Cu(II) complexation with model compounds*

Cu(II) tends to complex with HA, which is essential for copper to act as a catalyst [24]. Cu(II) was reported to always bind to HA via carboxylate, amine and hydroxyl groups [25]. To examine the complexation of Cu(II) with HA, the FTIR spectra of four model compounds containing the above specific groups (i.e., citric acid, aminoacetic acid, malonic acid, and salicylic acid) and their complexes with HA were comparatively studied, as shown in Fig. 7. Results indicate that after complexing with Cu(II), the absorption peaks of citric acid at 3495 and 3292 cm^{-1} which were assigned to the stretching of hydroxyl [26] significantly decreased (Fig. 7a). For the other three model compounds, the bands assigned to the stretching of broad –OH also showed similar changes. For aminoacetic acid, the sharp peak at 3178 cm^{-1} was assigned to the stretching of $–NH_2$ group (Fig. 7b). In the presence of Cu(II), the percent transmittance of this peak decreased greatly, indicating the complexation of Cu(II) with $–NH_2$ group (Fig. 7b). Moreover, the carbonyl stretching of the keto group (1605 cm^{-1} in Fig. 7b; 1731 cm^{-1} in Fig. 7c; and 1655 cm^{-1} in Fig. 7d) was shifted to relatively lower frequencies due to the charge transfer from the carbonyl oxygen to the Cu^{2+} ion [27]. FTIR results have confirmed that the carboxylate, amine and hydroxyls groups in HA were active sites for Cu(II) complexation.

3.4. *Proposed catalytic mechanism*

Based on the above results, the THM formation during chlorination and monochloramination of HA under the catalysis of Cu(II) was promoted by both indirect catalysis of •OH and direct catalysis of Cu(II). The reaction mechanism is thus illustratively proposed in Fig. 8.

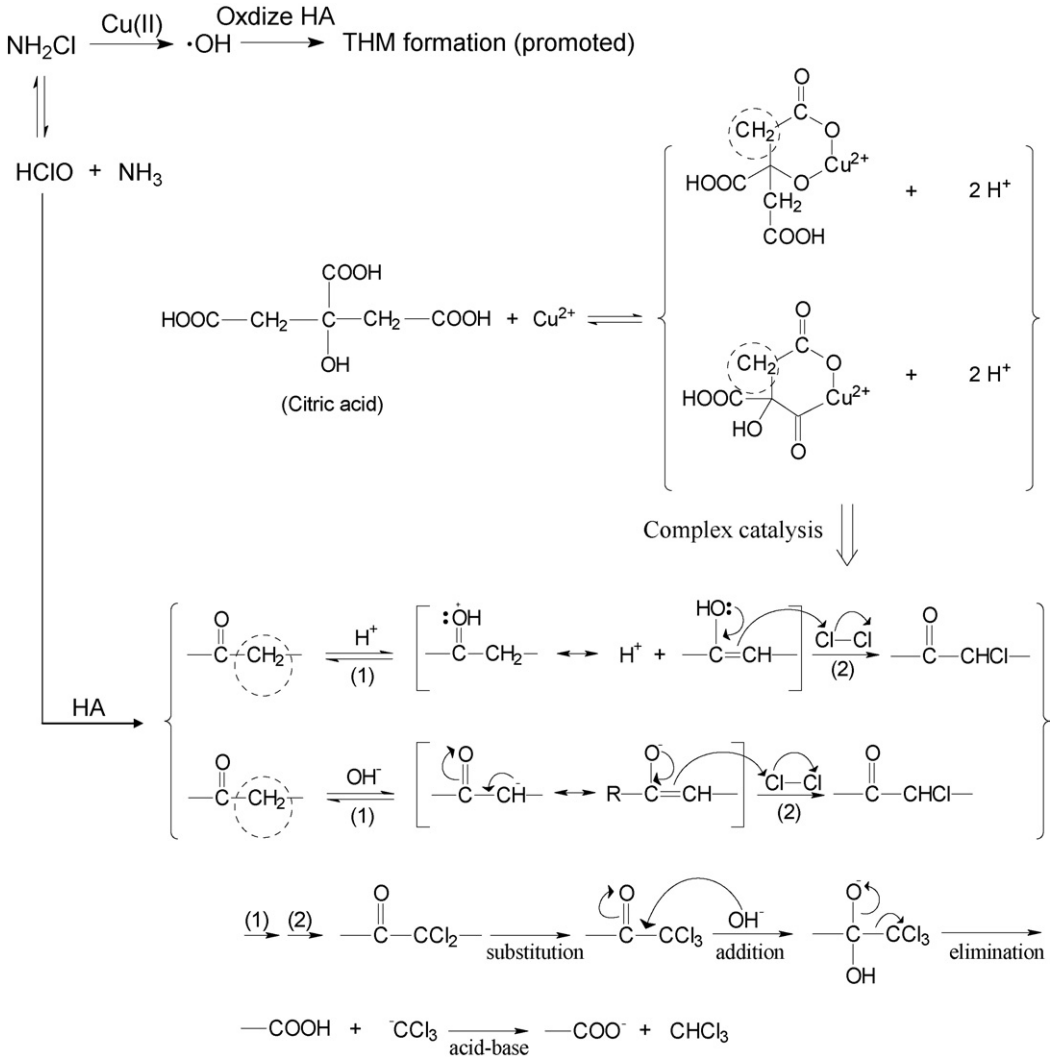


Fig. 8. Proposed reaction mechanism for Cu(II)-catalyzed THM formation during chlorination and monochloramination of HA.

In the indirect catalysis, •OH oxidized the large molecules of HA into small ones, thus promoting the THM formation. Under the catalysis of Cu(II), more •OH radicals were generated in monochloramination than in chlorination, leading to comparatively more THM formation. In the direct catalysis of Cu(II), Cu(II) could complex with citric acid and similar chemical structures in HA to enhance THM formation. Cu(II) did not change the major pathways of THM formation, but complexed with citric acid to accelerate the decarboxylation steps that governed the overall rate of THM formation [28].

4. Conclusions

This work comparatively investigated the catalytic effect of Cu(II) on THM formation during chlorination and monochloramination of HA. The experimental results indicate that in the presence of Cu(II), the formation of THMs was significantly promoted as pH decreased in both chlorination and monochloramination. The enhanced THM formation during the Cu(II)-catalyzed monochloramination could be partially ascribed to the fortified generation of •OH, as demonstrated by ESR analysis. Chlorination and monochloramination of nine structurally pertinent model compounds indicate that the catalysis of Cu(II) was largely attributable to citric acid and similar chemical structures in HA. FTIR analysis revealed the complexation of Cu(II) with four selected model compounds. Major reaction intermediates were determined during chlorination and monochloramination of citric acid in the absence and presence of Cu(II) by GC–MS. Results show that Cu(II) could change the reaction rates but not the major pathways of THM formation. Based on the above findings, it is proposed that the catalysis of Cu(II) on THM formation was caused by the indirect catalysis of •OH which broke down the large HA molecules as well as the direct catalysis of Cu(II) which formed complexes with HA to accelerate the decarboxylation steps.

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