



Oxidation of 4-chlorophenol catalyzed by Cu(II) complexes under mild conditions: Kinetics and mechanism

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ABSTRACT

Three synthetic copper(II) complexes exhibited remarkable catalytic activity for 4-chlorophenol (4-CP) oxidation by H_2O_2 in neutral and weak alkaline solution at 25 °C. The decomposition of H_2O_2 catalyzed by copper(II) complexes was investigated. The studies by fluorescence and UV–vis measurements proved that free hydroxyl radical was not the primary reactive species for the oxidation of 4-CP. “Associative radical” $LCu^{I-\bullet}OOH$ was suggested as the possible predominant reactive species in this work. The reaction kinetics of 4-CP oxidation catalyzed by copper(II) complexes was studied in detail. The pH effect was explicated by the catalytic kinetics model proposed in this paper. The catalysis involved not only the activation of H_2O_2 by copper(II) complex to yield more reactive species $LCu^{I-\bullet}OOH$, but also the formation of 4-chlorophenolate anion. A possible catalytic reaction mechanism of 4-CP oxidation was proposed.

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1. Introduction

Chlorophenols are found widely in pesticides, disinfectants and wood preservatives. They are also substantial by-products of wood pulp bleaching [1]. Due to chlorophenols' toxicity and the difficulty of microbial degradation in nature, it is a urgent demand to remove chlorophenols [2–4]. Recently, many chemical methods for the oxidation of chlorophenol have been developed [5–8]. Unfortunately, the most of reported catalysts exhibited high catalytic activity for the oxidation of chlorophenol only in acidic or strong alkaline solution [9–13]. Effective catalysts for chlorophenol oxidation in neutral or weak alkaline solution at room temperature were seldom reported.

Masarwa et al. pointed out that copper(II) complex/ H_2O_2 system in aqueous solution could be considered as “Fenton-like” reagent [14]. H_2O_2 could be activated by copper(II) complexes to generate active oxygen species [15], but the exact active oxygen species and their catalytic mechanisms were not clear yet [16]. The catalytic mechanism involved many factors including substrates, catalysts, pH of solution, solvent and temperature. A commonly acceptable mechanism for this kind of catalysis was originally proposed by Barb et al. [17], which involved a series of radical species including $\bullet OH$ and $O_2\bullet^-/\bullet OOH$. Haber–Weiss Fenton reaction indicated that H_2O_2 could be activated by metal ions to reactive radical species through one-electron redox reactions [18]. Passoni et al. [19] con-

sidered metal peroxo complexes (MOOH) as the early intermediates and no radical species formed in his reaction system. Hydroxyl radical was commonly recognized as the predominant reactive species in “Fenton reagent” reaction. However, was hydroxyl radical the predominant reactive species in copper(II) complex/ H_2O_2 system? If it was not, what kinds of reactive species could generate when H_2O_2 was added into copper(II) complex solution? Was reactive species free in solution? For these questions, there are no clear answers in literatures. In previous reports [20,21], reaction kinetics for the catalytic oxidation of chlorophenol was discussed and some kinetic constants were calculated. However, the further investigations of reaction kinetics and catalytic reaction mechanism were seldom reported.

We previously reported the efficient oxidation of phenols by H_2O_2 catalyzed by several copper(II) complexes in neutral aqueous solution [22,23]. In this work, three different copper(II) complexes were synthesized as catalysts to catalyze the oxidation of 4-CP by environmentally friendly hydrogen peroxide in neutral or weak alkaline solution under mild conditions. The goal of this study is to investigate the exact reactive species formed by mixing catalyst with H_2O_2 , and to deeply understand the catalytic reaction mechanism of 4-CP oxidation.

2. Experimental

2.1. Materials and synthesis

4-Chlorophenol, 30% hydrogen peroxide, hydroquinone, maleic acid, fumaric acid, malonic acid, propiolic acid, oxalic acid, acetic

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acid and formic acid were used from commercial sources without further purification. All reagents, unless otherwise indicated, were analytical or HPLC pure grade.

The complex *N,N'*-bis(2-pyridinecarboxamide)-1,2-ethane copper(II) (L^1Cu) was prepared according to the method in literature [24]. *Anal. Calcd.* for $C_{14}H_{14}O_2N_4Cu$: C, 50.37; H, 4.20; N, 16.79%; Found: C, 50.21; H, 4.23; N, 16.52%. The Cu loading was determined to be 3.06 mmol/g by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The ligand L_2 (4,9-di-methyl-2,11-dioxy-5,8-diazacyclododeca-2,4,8,10-tetraene) $C_{12}H_{20}N_2O_2$ and complex of copper(II) (L^2Cu) were synthesized according to the literature procedures [25]. *Anal. Calcd.* for $C_{12}H_{20}N_2O_2Cu$: C, 50.09; H, 6.95; N, 9.74%. Found: C, 49.98; H, 6.62; N, 9.78%. The Cu loading was determined to be 3.53 mmol/g by ICP-AES.

The complex 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene copper(II) (L^3Cu) was synthesized according to Chandra [26]. *Anal. Calcd.* for $C_{14}H_{24}N_4CuCl_2$: C, 43.92; H, 6.28; N, 14.64; Cl, 18.56%. Found: C, 43.80; H, 6.19; N, 14.50; Cl, 19.01%. The Cu loading was determined to be 2.61 mmol/g by ICP-AES.

2.2. Methods

Ultraviolet–visible absorbance measurements were implemented with a TU-1901 UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Fluorescence measurements were performed with a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan) equipped with a plotter unit and a 1-cm quartz cell.

The concentration of 4-CP was determined by means of 4-AAP method which was based on the measurement of the developed color resulting from the reaction of phenol with 4-aminoantipyrine at 510 nm [27]. Preliminary experiment involving the detection of 4-CP concentration was also carried out with HPLC method. Two methods were proved to be in accord for the measurement of 4-CP concentration under this work's conditions. The concentration of hydrogen peroxide was examined by titrating a standardized ceric sulfate solution to pale blue endpoint with a ferroin indicator. All buffer solutions were prepared with 50 mM NaH_2PO_4 -NaOH. Intermediates and ultimate products were analyzed by HPLC (Waters 254 Inc., Waters 1525 system) and GC-MS (Agilent Technologies 68900 GC System) [28].

The typical reaction solution, containing 5.0×10^{-5} M catalyst, 0.02 M hydrogen peroxide and desired concentration of 4-CP, was kept at constant 25 °C in a closed glass reactor. Reaction sample was periodically drawn from the reactor. The initial rate r_0 was calculated from the oxidation of 4-CP during the initial 30 min. Kinetic runs carried out in triplicate gave r_0 with uncertainty of less than 5%.

3. Results and discussions

3.1. Oxidation of 4-CP at pH 7.0

Reaction of 4-CP with H_2O_2 catalyzed by LCu (L^1Cu , L^2Cu or L^3Cu) was conducted at pH 7.0 and 25 °C. Result was shown in Fig. 1. From Fig. 1, it could be seen that three complexes all exhibited outstanding catalytic activity for the oxidation of 4-CP in neutral solution at 25 °C, and L^3Cu exhibited the best catalytic efficient, followed by L^2Cu and L^1Cu , respectively. From Fig. 1, it could be also observed that the oxidation of 4-CP catalyzed by LCu was very fast during the initial 2 h, then declined gradually.

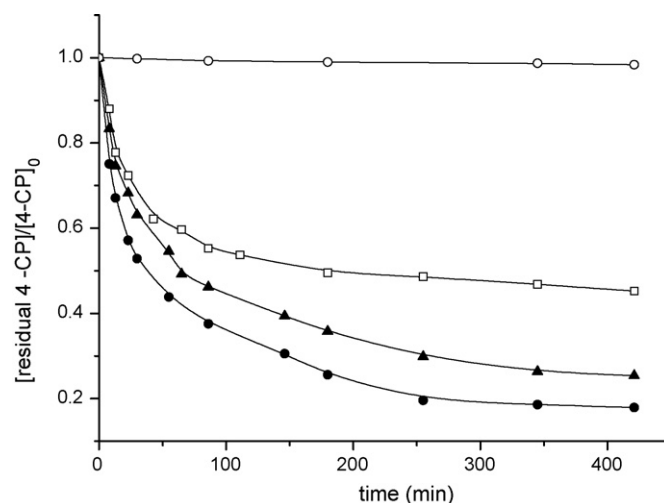


Fig. 1. Oxidation of 4-CP catalyzed by $\square L^1Cu$, $\triangle L^2Cu$, $\bullet L^3Cu$, \circ without catalyst at pH 7.0 and 25 °C; $[4-CP]_0 = 1.0$ mM, $[H_2O_2]_0 = 0.02$ M, $[catalyst] = 0.05$ mM.

3.2. Investigation of reactive species

In order to clarify the active oxygen species formed in this work, the effect of H_2O_2 concentration on the catalytic oxidation of 4-CP by LCu was studied. Results indicated that the reaction rate of 4-CP oxidation was very slow at a low concentration of H_2O_2 . With increasing concentration of H_2O_2 , the reaction rate increased gradually and attained saturation at a high concentration of H_2O_2 about 0.02 M. This implied that H_2O_2 played an important role in 4-CP oxidation. In addition, the decomposition of H_2O_2 catalyzed by LCu in buffer solution was studied at pH 7.0 and 25 °C, and results were shown in Fig. 2. From Fig. 2, it could be found that the decomposition of H_2O_2 was faster in the presence of catalyst than that in the absence of it, and the order of catalytic activity of three copper(II) complexes to decompose H_2O_2 was in accordance with that to oxidize 4-CP, i.e. $L^3Cu > L^2Cu > L^1Cu$. When the pH of buffer solution varied from 6.0 to 8.0, the decomposition rate of H_2O_2 catalyzed by LCu increased with increasing pH (which was not shown here). Based on all of these experimental results, we concluded that some active oxygen species must generate by mixing H_2O_2 with LCu. And it was favorable for the formation of active oxygen species in neutral or weak alkaline solution.

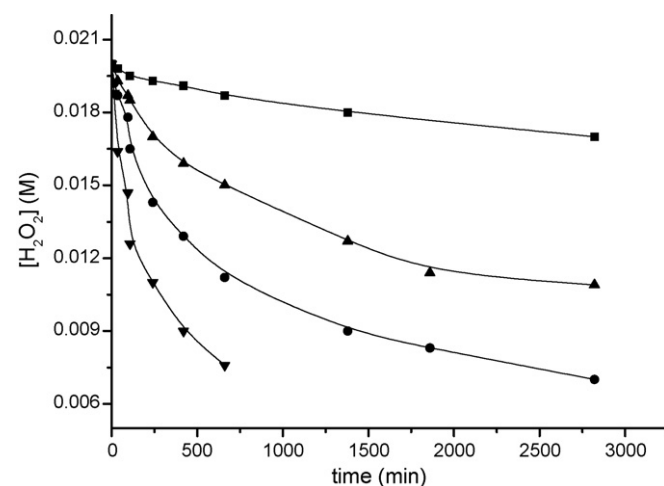


Fig. 2. Decomposition of H_2O_2 catalyzed by LCu at pH 7.0 and 25 °C, $\triangle L^1Cu$, $\bullet L^2Cu$, $\blacktriangledown L^3Cu$, \blacksquare buffer without catalyst; $[H_2O_2]_0 = 0.02$ M, $[catalyst] = 0.05$ mM.

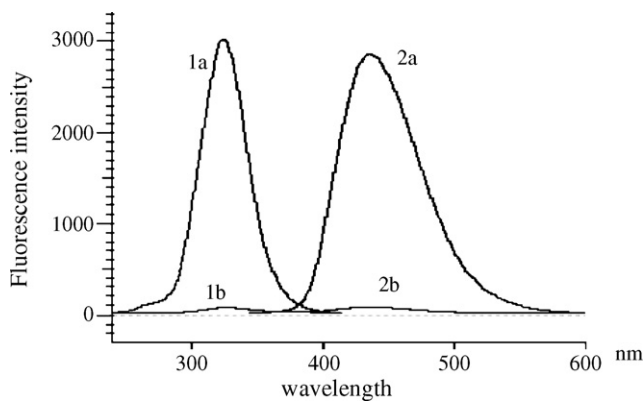


Fig. 3. Excitation and emission spectra of reaction solution, 1a: excitation spectra of solution including NaTA, copper(II) complex and H_2O_2 ; 2a: emission spectra of solution including NaTA, copper(II) complex and H_2O_2 ; 1b: excitation spectra of solution including NaTA, copper(II) complex, H_2O_2 and *tert*-butyl alcohol; 2b: emission spectra of solution including NaTA, copper(II) complex, H_2O_2 and *tert*-butyl alcohol.

Barb et al. [17] considered $\cdot\text{OH}$, $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ and superoxide as the reactive species in “Fenton-like” system. Similarly, a mixture of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ in $\text{Cu(II)}/\text{H}_2\text{O}_2$ system at pH 7.4 was observed by Kadiiska et al. [29]. In order to identify the reactive species formed in this work, fluorescence and UV–vis measurements were carried out. The probe selected for the fluorescence experiment was disodium salt of terephthalic acid (NaTA). According to Sahni and Locke [30], NaTA could react with $\cdot\text{OH}$ or $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ to give 2-hydroxyterephthalic acid (HTA). HTA could produce a bright stable fluorescence ($\lambda_{\text{analyzing}} = 425 \text{ nm}$, $\lambda_{\text{excitation}} = 315 \text{ nm}$). The similar experimental condition as Sahni’s [30] was used in this work, and result was shown in Fig. 3. When NaTA was added into the buffer solution containing H_2O_2 and LCu, the solution exhibited high fluorescence intensity. Further, when the same concentration of *tert*-butyl alcohol [31] and NaTA were simultaneously added into this solution, fluorescence intensity of solution decreased dramatically from 3000 to 75. This result implied that the most of active oxygen species reacted rapidly with *tert*-butyl alcohol other than NaTA. Shah et al. [32] pointed out that $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ were generated simultaneously in copper(II)/organic acid/hydrogen peroxide system and these radicals could not only diffuse into the solution but also associate with the ligand to form peroxy or hydroperoxide complex. Thus, we proposed a new concept called “associative radical” in this paper, i.e., radicals $\cdot\text{OH}$ or $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ could associate with copper(II) complex to form steady reactive species- “associative radical” which had bigger volume. Due to the steric effect, the most of active oxygen species reacted with *tert*-butyl alcohol other than NaTA.

Methylene blue dye test, which could quantify hydroxyl radical [33], was also performed. In this test, addition of a sample with hydroxyl radicals into methylene blue dye would result in a change of color from dark blue to colorless. Thus, the concentration of methylene blue could be detected by UV–vis spectrophotometer at $\lambda = 660 \text{ nm}$. When copper(II) complex and hydrogen peroxide were added into the methylene blue solution, the absorbance of methylene blue at $\lambda = 660 \text{ nm}$ had no change. Ethanol, an effective scavenger of $\cdot\text{OH}$ [34], was widely used to discern reactions with $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}/\cdot\text{OOH}$ when both species were present. When ethanol was added, the absorbance of methylene blue at $\lambda = 660 \text{ nm}$ had still no change. This indicated that ethanol had no effect on our system, and there was little hydroxyl radical formed in this work. All these experimental results suggested that $\cdot\text{OH}$ was not the predominant oxidant for the catalytic oxidation of 4-CP.

Lin and Wu [35] pointed out that the association of peroxide with Cu(II) could change the oxidation state of Cu(II) to yield Cu(I) in copper(II)/amino acid/ H_2O_2 system. Though the amount of $\text{O}_2^{\cdot-}$ in alkaline solution was much larger than that of $\cdot\text{OOH}$, $\cdot\text{OOH}$ showed higher redox potential than $\text{O}_2^{\cdot-}$ [18]. Based on the discussions above-mentioned, “associative radical” $\text{LCu}^{\text{I}}-\cdot\text{OOH}$ was suggested as the possible reactive species to oxidize 4-CP under this work’s conditions. The possible interaction pathway between LCu and H_2O_2 was proposed as follows: first, H_2O_2 exhibited a dissociated equilibrium in neutral or weak alkaline solution [36].



Then, the association of anion HO_2^- with LCu yielded $\text{LCu}^{\text{II}}-\text{OOH}^-$ [35].



Further, electron transfer from HO_2^- to LCu would lead to form $\text{LCu}^{\text{I}}-\cdot\text{OOH}$ [37]. $\text{LCu}^{\text{I}}-\cdot\text{OOH}$ reacted rapidly with substrate 4-CP, consequently, the decomposition of H_2O_2 (Eqs. (5) and (6)) was inhibited. This was proved by the experimental result that the decomposition rate of H_2O_2 in the presence of 4-CP was lower than that of absence of it. If substrate was absent, $\text{LCu}^{\text{I}}-\cdot\text{OOH}$ would dissociate to LCu^{I} and $\cdot\text{O}_2\text{H}$, then reactions (Eqs. (5) and (6)) would take place, resulting in the rapid decomposition of H_2O_2 . According to discussions above-mentioned, $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ were not the predominant reactive species. Therefore, the amount of oxidation products in Eqs. (8) and (9) was very low.

3.3. pH effect and kinetic analyses

From Fig. 1, it could be found that the oxidation of 4-CP did not obey the first-order kinetics during the whole oxidation process. However, when the concentration of H_2O_2 in reaction solution was kept constant, the oxidation of 4-CP obeyed the first-order kinetics indeed. Thus, for the following kinetic experiments, the desired concentration of H_2O_2 was added periodically into reaction solution to keep its concentration constant.

The pH of solution could affect the reaction mechanism and rate of 4-CP oxidation [5–8]. In this work, the initial processes of 4-CP oxidation at various concentrations of 4-CP were studied in the pH range of 6.0–8.0. Experimental results indicated that the reaction kinetics of 4-CP oxidation was similar to that of enzyme–catalysis reaction. Michaelis–Menten (M–M) kinetics model was often used for the enzyme–catalysis reaction, which was characterized in the reversible formation of a catalyst–substrate complex prior to the rate-determining step. In this paper, we suggest a similar catalytic reaction mechanism shown as Eq. (10).

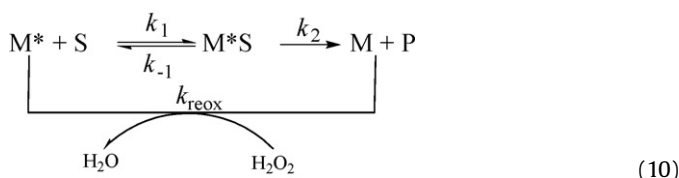


Table 1The initial rate r_0 (10^{-6} M s^{-1}) of the catalytic oxidation of 4-CP at various initial concentrations of 4-CP in the pH range of 6.0–8.0 at 25 °C.

[S] ₀ (mM)	L ¹ Cu					L ² Cu					L ³ Cu				
	6.0	6.5	7.0	7.5	8.0	6.0	6.5	7.0	7.5	8.0	6.0	6.5	7.0	7.5	8.0
0.2	0.24	0.45	0.73	0.94	1.01	0.585	0.897	1.47	2.38	4.48	2.09	4.50	6.38	8.54	10.5
0.4	0.32	0.71	1.22	1.56	1.79	0.811	1.42	2.44	4.48	6.86	2.36	5.59	8.83	12.1	15.5
0.6	0.38	0.80	1.60	2.07	2.40	0.934	1.80	3.09	5.10	8.36	2.52	6.10	10.2	14.3	19.3
0.8	0.42	0.91	1.68	2.45	2.68	0.981	1.88	3.42	5.89	9.18	2.61	6.58	11.6	16.9	20.9
1	0.43	0.95	1.84	2.58	2.87	1.03	2.09	4.03	6.40	9.40	2.65	6.74	12.1	18.0	22.6

where M^* represents the possible reactive species $\text{LCu}^{\text{I}}-\text{OOH}$. Once H_2O_2 was added into copper(II) complex solution, M^* produced. This was a very fast process. M^* could associate with substrate S (4-CP) reversibly to form an active intermediate complex M^*S with rate constants of k_1 and k_{-1} . Then, an irreversible oxidation of substrate gave free catalyst M and product P. k_2 is the rate constant of oxidation reaction, which is regarded as the rate-limiting step.

The Michaelis constant K_m could be expressed as

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (11)$$

In this work, the concentration of H_2O_2 is far excessive over that of catalyst, so we think that M can be almost oxidized into active state M^* . Thus, Eq. (12) can be obtained:

$$\frac{1}{r_0} = \frac{1}{k_2[M]_{\text{T}}} + \frac{K_m}{k_2[M]_{\text{T}}[S]_0} \quad (12)$$

where r_0 is the initial rate of 4-CP oxidation. $[M]_{\text{T}}$ is the total concentration of catalyst, and $[S]_0$ is the initial concentration of 4-CP.

Values of r_0 for the catalytic oxidation of 4-CP by LCu at various initial concentration of 4-CP in the pH range of 6.0–8.0 were listed in Table 1. From Table 1, we found that r_0 increased with increasing initial concentration of 4-CP at the same pH, and for the same initial concentration of 4-CP, r_0 increased with increasing pH. According to Eq. (12), the plot of $1/r_0$ vs. $1/[S]_0$ should be a straight line, and values of k_2 and K_m could be evaluated from the slopes and intercepts. According to the data in Table 1, $1/r_0$ vs. $1/[4\text{-CP}]_0$ displayed good linear relationship indeed and all linear correlation coefficients were no less than 0.99, which indicated that the proposed kinetic model for the catalytic oxidation of 4-CP was reasonable. The calculated values of k_2 and K_m were listed in Table 2. From Table 2, it was observed that the catalytic rate constant k_2 was far greater than the uncatalyzed value $1.95 \times 10^{-6} \text{ s}^{-1}$. From Table 2, it could be also found that k_2 ($10.5 \times 10^{-4} \text{ s}^{-1}$, pH 8.0) of 4-CP oxidation catalyzed by L³Cu was the greatest.

3.4. Catalytic reaction mechanism

From Table 2, it could be found that the pH of solution could greatly influence the catalytic oxidation of 4-CP, and k_2 increased with increasing pH. From the pH effects on the 4-CP oxidation and on the decomposition of H_2O_2 , we consider that the pH of solution influences not only the formation of reactive species but also the substrate 4-CP. Here, we assume that 4-CP associating with reactive species can dissociate to chlorophenolate anion complex, as follows:



$$K_a = \frac{[M^*S^-][H^+]}{[M^*S]} \quad (14)$$

where M^*S^- is the dissociated 4-chlorophenolate anion complex, which has lower redox potential by around 0.5V than that of 4-

CP [38]. K_a the acidic dissociate constant of M^*S . According to the material balance, we have

$$[M^*S]_{\text{T}} = [M^*S] + [M^*S^-] \quad (15)$$

where $[M^*S]_{\text{T}}$ is the total concentration of M^*S . Therefore, the rate equation can be rewritten as

$$r_0 = k_2[M^*S]_{\text{T}} = k'_2[M^*S^-] \quad (16)$$

Combination of Eqs. (14)–(16) and arrangement yield

$$\frac{1}{k_2} = \frac{1}{k'_2} + \frac{[H^+]}{k'_2 K_a} \quad (17)$$

where k'_2 is the real catalytic reaction rate constant, which is pH independent.

The plot of $1/k_2$ vs. $[H^+]$, illustrated in Fig. 4, yielded a straight line. All linear correlation coefficients were no less than 0.98, which indicated that the proposed kinetic model for the catalytic oxidation of 4-CP was reasonable. Values of k'_2 and K_a can be evaluated from the slope and intercept of line, which were listed in Table 3.

Based on the above-mentioned discussions, a possible catalytic reaction mechanism of 4-CP oxidation was proposed as shown in Scheme 1. Cu(II) ion in complex was found to coordinate with four N or O atoms and two water molecules as axial ligands, which exhibited a distorted octahedral structure. Due to the dynamic Jahn–Teller effect [39,40], the copper(II) complex associating with Cu(II) ion was unstable. Normally, the water exchange rate constant for solvated Cu(II) was very fast ($4.4 \times 10^9 \text{ s}^{-1}$), and the lifetime of the complex was in the picosecond's time scale with an activation energy of 3.5 kJ mol⁻¹. Therefore, the reversible dissociation of a water molecule from a distorted octahedral Cu(II) complex was reasonably easy. Once one water molecule dissociated from

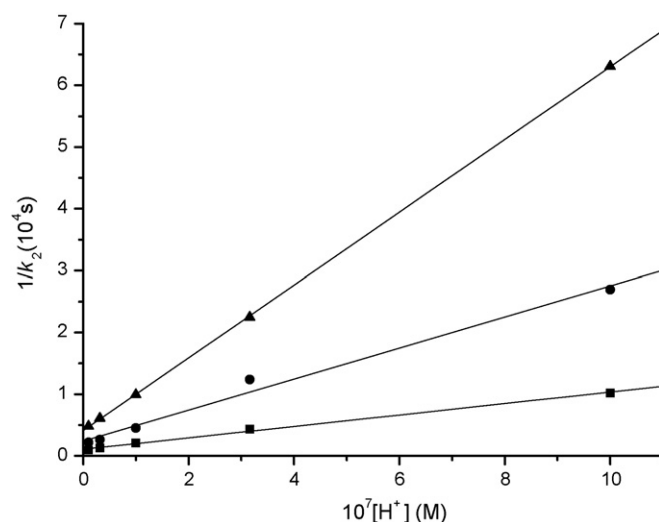


Fig. 4. Plots of $1/k_2$ vs. $[H^+]$, \blacktriangle L¹Cu, \bullet L²Cu, \blacksquare L³Cu.

Table 2The calculated values of k_2 and K_m of the catalytic oxidation of 4-CP at 25 °C.

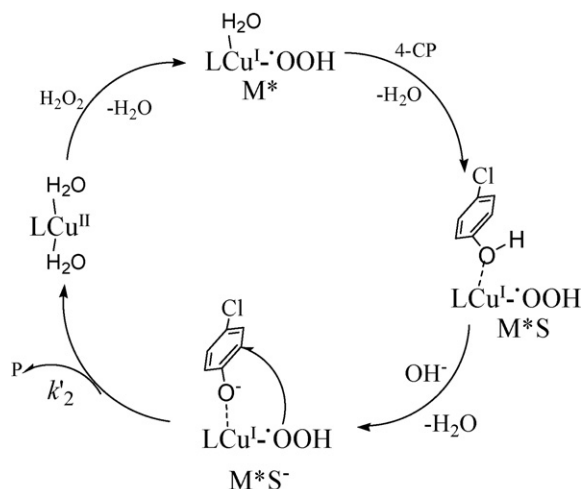
pH	L ¹ Cu		L ² Cu		L ³ Cu	
	10 ⁴ k_2 (s ⁻¹)	10 ⁴ K_m (M)	10 ⁴ k_2 (s ⁻¹)	10 ⁴ K_m (M)	10 ⁴ k_2 (s ⁻¹)	10 ⁴ K_m (M)
6.0	0.159	2.18	0.371	2.06	0.977	0.735
6.5	0.445	3.91	0.809	3.86	2.31	1.28
7.0	1.01	6.35	2.22	7.08	4.84	2.67
7.5	1.64	8.40	3.83	7.54	7.94	3.64
8.0	2.08	10.2	4.54	4.08	10.5	4.03

copper(II) complex, hydrogen peroxide could directly associate with Cu(II) complex, consequently electron transfer from hydrogen peroxide to Cu(II) might happen. Thus, the possible reactive species LCu^I-•OOH (M^{*}) formed. Then, the other water molecule on M^{*} could be replaced by substrate 4-CP to give M^{*}S. The association of S with M^{*} resulted in O–H bond of 4-CP weakening, so that H atom could dissociate from 4-CP easily. In weak alkaline solution, OH⁻ could attack H atom of hydroxyl in 4-CP to yield 4-chlorophenolate anion. Finally, associative radical might attack the *ortho*, *para* carbon atoms of 4-chlorophenolate anion to give products, which was a rate-limiting step [41].

In order to better understand the reaction paths, the reaction intermediates and final products in whole reaction process were detected by HPLC and GC–MS analyses. After 1 h, a large quantity of hydroquinone was detected, which indicated that the most of Cl atom had left off from 4-CP. During the oxidation process, it could be observed that the color of reaction solution became light yellowish initially, which was possibly owed to the formation of aromatic intermediates, then turned a little brown because of the formation of *p*-benzoquinone, and finally became colorless resulting from the oxidation of *p*-benzoquinone. After 8 h, reaction products were detected again and many short-chain acids including maleic acid, fumaric acid, malonic acid, propionic acid, oxalic acid, acetic acid and formic acid were found. The dimeric intermediate was not found, which also indicated that free •OH was not the predominant reactive species [18].

Table 3The calculated values of k'_2 and pK_a of the catalytic oxidation of 4-CP at 25 °C.

Complex	10 ⁴ k'_2 (s ⁻¹)	pK_a
L ¹ Cu	2.44	7.16
L ² Cu	4.17	7.02
L ³ Cu	9.42	6.94

**Scheme 1.** Possible catalytic mechanism for the oxidation of 4-CP.

3.5. Comparison of the catalytic activity of three copper(II) complexes

From Table 3, it could be seen that the value of k'_2 of L³Cu was $9.42 \times 10^{-4} \text{ s}^{-1}$, which was far greater than those of L¹Cu and L²Cu. It was known that the pK_a of 4-CP in aqueous solution at 25 °C was about 9.4 [42], however, the pK_a of 4-CP associating with copper complex at 25 °C were evaluated as 7.16, 7.02 and 6.94 for L¹Cu, L²Cu and L³Cu, respectively. This indicated that LCu could remarkably decrease the pK_a of 4-CP, especially for L³Cu. The different catalytic activities of catalysts for 4-CP oxidation can be attributed to their distinct abilities to activate both H₂O₂ and 4-CP. According to the chemical structure of copper(II) complexes, we know that L³Cu has a closed-ring Ligand (L) structure, where a special conjugated π bonding can form. This structure may be favorable for the electron transfer between the copper ion and ligand L, hence favorable for the formation of reactive species.

To test the stability of catalyst in reaction solution, another portion of substrate was added into the reaction solution after 24 h. The initial oxidation rate of 4-CP was nearly unchanged, which indicated that LCu still kept active for 24 h. Therefore, we consider that three copper complexes remain the catalytic activity during the oxidation process.

4. Conclusions

Three synthetic copper(II) complexes all exhibited outstanding catalytic activities for the oxidation of 4-CP in neutral or weak alkaline solution at 25 °C. The order of catalytic activity was L³Cu > L²Cu > L¹Cu. LCu^I-•OOH was the possible predominant reactive species to oxidize 4-CP. The function of copper(II) complex could be concluded as two aspects: activating H₂O₂ to produce reactive species and decreasing the pK_a of 4-CP to give 4-chlorophenolate anion which could be oxidized easily.

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