

Oxidative Coupling of 2,6-Dimethylphenol Catalyzed by Copper(II) Complexes in Aqueous Solution

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ABSTRACT: The oxidative coupling reaction of 2,6-dimethylphenol (DMP) with H₂O₂ catalyzed by four copper(II) complexes was investigated in Tris-HNO₃ buffer solution at 25°C. The kinetics of formation of diphenoquinone (DPQ, 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone) from DMP was studied in detail. The kinetic parameters k_2 and K_m were obtained in the pH range of 6.0–9.0. The copper(II) complexes exhibited the optimal catalytic activity at around pH 7.0. The pH effect was reasonably explicated by the catalytic kinetic model suggested in this work. The catalytic mechanism was discussed. The deprotonized associ-

ated radical LCu^I(OH⁻)-•OOH was suggested as the possible predominant species to oxidize DMP. The C–C and C–O coupling products were analyzed and the ratio of poly (2,6-dimethyl-1,4-phenylene ether) (PPE) to DPQ was also evaluated. Both in weak acidic (pH < 6.5) and in alkaline aqueous solution (pH > 8) were suitable to the C–O coupling reaction in our catalytic systems. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2043–2049, 2010

Key words: oxidative coupling; organometallic catalyst; catalysis; kinetics; PPE

INTRODUCTION

The poly (2,6-dimethyl-1,4-phenylene ether) (PPE) is widely used as a high-performance engineering plastic because of its good mechanical character, high glass transition temperature and the properties of chemical stability and self-extinguish.^{1–6} Recently, PPE was also reported as a low dielectric constants material, which was applied in microelectronic devices required for faster signal propagation.^{7–10} As PPE has large potential applications as new functional material, it is of great significance to understand the reaction mechanism and to find new convenient and green preparation technologies.

PPE was generally prepared both industrially and in the laboratory by the oxidative polymerization of 2,6-dimethylphenol (DMP),^{11,12} which was first found

by Hay et al.¹³ In this reaction, PPE was formed by C–O coupling of phenolic moieties. The other product diphenoquinone (DPQ) generated from C–C coupling of two monomeric phenols, which was also recognized as an important material for electron transport.¹⁴ Therefore, it is still a goal of green synthesis to seek for the mild conditions and the appropriate reaction medium. However, up to now, many investigations have been confined on the way of using O₂ as oxidant^{15–18} and organic solvents such as toluene and benzene as medium.^{19–21} The reaction mechanism and kinetics of oxidative coupling reaction of DMP were not yet entirely elucidated.

In previous work,^{22–24} we reported the catalytic oxidation of phenols by H₂O₂ and found the associated radical may be the chief active species in copper complex/H₂O₂ systems.²⁴ In this work, four copper(II) complexes were synthesized as catalysts to catalyze the oxidation of DMP by hydrogen peroxide in aqueous solution under mild conditions. The goal of this study was to investigate the catalytic mechanism of this oxidative coupling reaction and try to find a new and green preparation process of PPE.

EXPERIMENTAL

Materials and synthesis

Cu(ClO₄)₂·6H₂O, CuCl₂·2H₂O, Cu(CH₃COO)₂·H₂O, basic copper carbonate, chloroform, absolute ethanol,

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methanol, 2-propanol, ceric sulfate, 30% hydrogen peroxide, dimethylformamide (DMF), 2,2'-Dihydroxydiethylamine, N-hydroxyethylethylenediamine, iminodiacetic acid, dipyriddyamine, 2,6-dimethylphenol (DMP) were all analytical grade and were purchased from commercial sources. The 2,6-dimethylphenol (DMP) was purified by recrystallization. All other chemicals and solvents used were also analytical grade.

The four copper(II) complexes, bis(2,2'-Dihydroxydiethylamine) copper(II) (L^1Cu), bis(N-hydroxyethylethylenediamine) copper(II) (L^2Cu), iminodiacetate copper(II) (L^3Cu) and dipyriddyamine copper(II) (L^4Cu) outlined in Figure 1, were prepared according to correlative literature procedures,^{25–28} respectively.

Preparation of Bis(2,2'-Dihydroxydiethylamine) copper(II) (L^1Cu)

By adding 2,2'-Dihydroxydiethylamine (21 g, 0.2 mol) to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (18.5 g, 0.05 mol) in 25 mL of methanol dropwise, a dark blue solution formed immediately. One drop of the solution was taken out, evaporated to dryness and yielded solid product which was put into mother liquor and then paste solid product formed after some minutes. The solid was separated, dissolved in a little methanol at 60°C and filtered immediately. The solution was left to cool and yielded blue crystals. These crystals were separated, washed with methanol and then recrystallized from methanol. Anal. Calcd. for $C_8H_{20}N_2O_4Cu$: C, 35.35; H, 7.42; N, 10.31%. Found: C, 35.30; H, 7.32; N, 10.28%. The Cu containing was determined to be 3.62 mmol/g by ICP-AES.

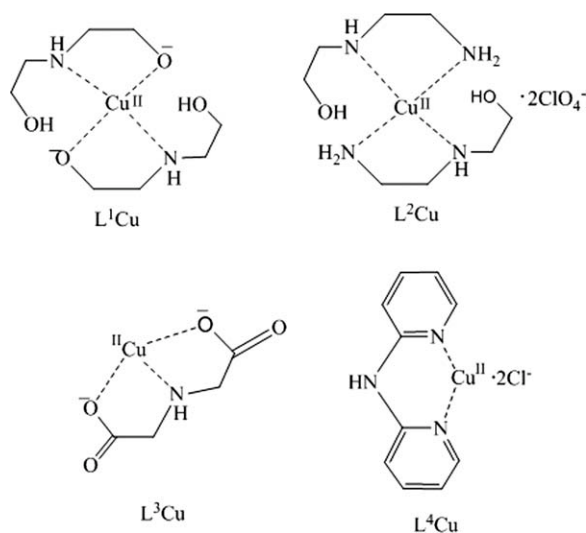


Figure 1 Structures of four Cu(II) complexes.

Preparation of Bis(N-hydroxyethylethylenediamine) copper(II) (L^2Cu)

N-hydroxyethylethylenediamine (8 ml, 79.1 mmol) was added dropwise to a stirred solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (10 g, 27 mmol) in 50 mL of ethanol and the reaction mixture was heated ($t < 60^\circ C$) for 15 min at room temperature. The resulting blue solution was filtered immediately and the filtrate was mixed with 2-propanol (50 mL). The solution was left to cool and yielded blue crystals. These were separated, washed with ethanol and then recrystallized from a mixture of 2-propanol and methanol. Anal. Calcd. for $C_8H_{24}N_4O_{10}CuCl_2$: C, 20.41; H, 5.14; N, 11.90; Cl, 15.06%. Found: C, 20.52; H, 5.02; N, 11.69; Cl, 14.92%. The Cu containing was determined to be 2.15 mmol/g by ICP-AES.

Preparation of Iminodiacetate copper(II) (L^3Cu)

A mixture of $Cu_2CO_3(OH)_2$ (9.04 mmol) and iminodiacetic acid (10 mmol) in water (20 mL) was stirred and heated (60°C) under controlled vacuum to remove the CO_2 , filtered and then the pH adjusted to 4.0 with dilute aqueous NaOH solution. The solution was evaporated slowly at room temperature to remove water and gave crude product which was recrystallized twice from water to give blue crystals. Anal. Calcd. for $C_4H_5NO_4Cu$: C, 24.68; H, 2.59; N, 7.20%. Found: C, 24.59; H, 2.50; N, 7.06%. The Cu loading was determined to be 5.08 mmol/g by ICP-AES.

Preparation of Dipyriddyamine copper(II) (L^4Cu)

A solution of dipyriddyamine (1.71 g, 9.8 mmol) in 60 mL of hot trichloromethane was added, under gentle stirring, to a hot solution of 1.7 g (10 mmol) of $CuCl_2 \cdot 2H_2O$ in 20 mL of DMF. The green powder formed, was filtered off after some minutes, washed with trichloromethane and dried in vacuo. Anal. Calcd. for $C_{10}H_9N_3CuCl_2$: C, 39.30; H, 2.97; N, 13.75; Cl, 23.20%. Found: C, 39.38; H, 2.90; N, 13.45; Cl, 23.50%. The Cu loading was determined to be 3.17 mmol/g by ICP-AES.

Instruments and methods

Mass spectrometry was performed with a Finnigan MAT 45,001 mass spectrometer. Ultraviolet-visible absorbance measurements were implemented with a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co.) equipped with a thermostatic cell holder. Elemental analysis was performed with a Carlo Erba 1106 instrument.

Tri (hydroxymethyl) aminomethane (Tris) (0.01M) buffer solution was prepared and its pH was adjusted by adding analytically pure nitric acid. The

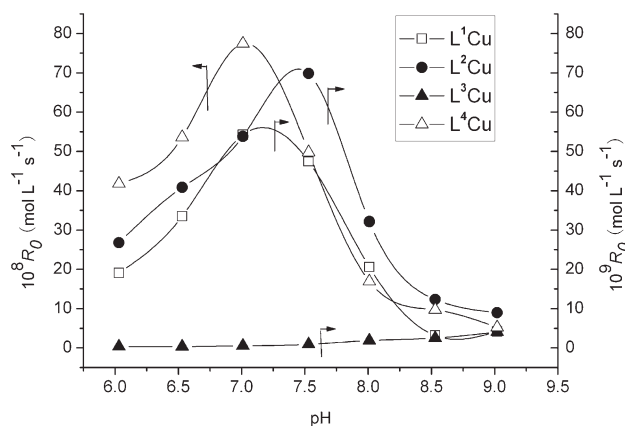


Figure 2 Effect of the pH on the initial DPQ formation rate (R_0) at 25°C, $C(\text{LCu}) = 5 \times 10^{-5} \text{M}$, $C_0(\text{H}_2\text{O}_2) = 0.02 \text{M}$, $C_0(\text{DMP}) = 1 \times 10^{-3} \text{M}$.

concentrations of H_2O_2 were determined by titrating a standardized ceric sulfate solution and the relative error in triplicate was less than 3%.

The typical initial reaction solution, containing: $5.0 \times 10^{-5} \text{M}$ catalysts, 0.02M hydrogen peroxide and desired concentration of substrate (DMP), was kept at 25°C. The initial DPQ formation rate R_0 was measured by monitoring the absorbance (A) at 421 nm vs. time: $R_0 = \Delta A / (\epsilon l \Delta t)$ and the relative error in triplicate was less than 3%.

RESULTS AND DISCUSSIONS

Effect of pH on the oxidative coupling reaction

The oxidative coupling of DMP by H_2O_2 catalyzed by four copper(II) complexes was conducted in aqueous buffer in the range of pH 6.0–9.0 at 25°C. The effect of pH on the initial formation rate of DPQ was investigated and illustrated in Figure 2. From Figure 2, it can be seen that for L^1Cu , L^2Cu and L^4Cu catalytic systems, the initial formation rate of DPQ (R_0) first increased and then fell down with increasing pH. It was clear that there was an optimal pH for the catalytic activity, which was similar to the natural enzyme.²⁹ The optimal pH values were evaluated as 7.18, 7.45 and 7.01 for L^1Cu , L^2Cu and L^4Cu , respectively. The effect of pH on the catalytic activity of L^3Cu was inconspicuous. From Figure 2, it could be also seen that the catalytic activity of L^3Cu was the lowest in the pH range of 6.0–9.0, but L^3Cu showed the good alkali resistance. Therefore, L^3Cu could be expected to be employed in highly alkaline environment. From Figure 2, it could be concluded that the four catalysts exhibited obviously different catalytic activities and the order of catalytic activity was $\text{L}^4\text{Cu} \gg \text{L}^2\text{Cu} > \text{L}^1\text{Cu} \gg \text{L}^3\text{Cu}$ in the pH range of 6.0–9.0.

Kinetic analysis

It was found that the oxidative coupling reaction of DMP with H_2O_2 did not occur in the absence of catalyst. The oxidative coupling reaction of DMP with H_2O_2 did not occur too, even when the copper(II) complex (L^4Cu) was replaced by L^4Zn and L^4Co , respectively, which showed that the copper(II) complex displayed special catalytic characteristic for the oxidative coupling of DMP by H_2O_2 in aqueous solution. As reported in previous studies,²⁴ the Cu(II) complex with H_2O_2 may form an active oxygen species (M^*). In this work, we also thought the active oxygen species (M^*) as oxidant react with substrate DMP to produce DPQ. According to the experimental data, it can be found that the plots of R_0 vs. $[\text{DMP}]_0$ were all saturated curves, which had the character of Michaelis-Menten mechanism model. Thus the kinetic model, which was similar to Michaelis–Menten form, was proposed as Scheme 1.

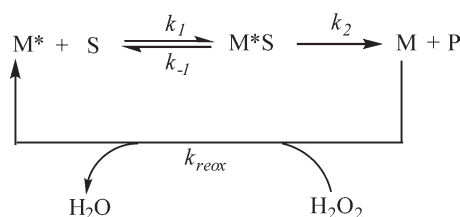
In the first step, the active oxidant (M^*) could combine with substrate DMP (S) reversibly to form the intermediates ($\text{M}^* \text{S}$) with rate constant k_1 and k_{-1} , respectively. Consequently the intermolecular reaction of $\text{M}^* \text{S}$ took place, which was the rate-determining step with a rate constant k_2 . The process that catalyst M was oxidized to M^* again by H_2O_2 is rapid, and the rate constant k_{reox} was far larger than k_2 . In this study, the concentration of H_2O_2 was far excessive over that of copper(II) complex. Thus, almost all of M was oxidized to active state M^* . Thus based on Scheme 1, eq. (1) could be obtained:

$$\frac{1}{R_0} = \frac{1}{k_2[\text{M}]_T} + \frac{K_m}{k_2[\text{M}]_T[\text{S}]_0} \quad (1)$$

where $[\text{M}]_T$ was the total concentration of catalyst. $[\text{S}]_0$ was the initial concentration of DMP. K_m was Michaelis constant

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (2)$$

Based on Eq. (1), the plot of $1/R_0$ vs. $1/[\text{S}]_0$ should be a straight line. The experimental results indicated that $1/R_0$ vs. $1/[\text{DMP}]_0$ for the four Cu(II) complexes catalyzed reactions in the range of pH 6.0–9.0



Scheme 1

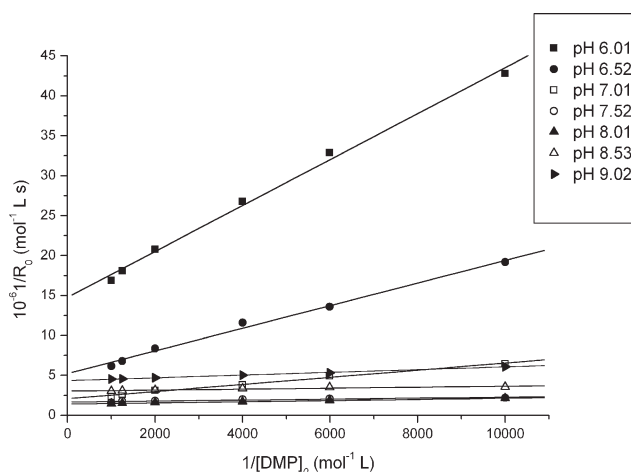


Figure 3 The plot of $1/R_0$ vs. $1/[DMP]_0$ catalyzed by L^3Cu at $25^\circ C$, $C_0(L^4Cu) = 5 \times 10^{-5} M$, $C_0(H_2O_2) = 0.02M$.

displayed really good linear relationship (all the correlation coefficient $R > 0.98$) as shown in Figure 3 (L^1Cu , L^2Cu , and L^3Cu were not shown here). Therefore, the proposed kinetics model was reasonable. The kinetic parameters k_2 and K_m could be evaluated from the slope and intercept of the plot of $1/R_0$ vs. $1/[DMP]_0$, which were listed in Table I.

From Table I, it was obvious that the K_m of L^3Cu was larger than that of L^1Cu , L^2Cu and L^4Cu , which implied that it was more difficult for DMP to associate with L^3Cu than with other complexes. Thus, L^3Cu displayed the lowest catalytic activity under this work conditions. From Table I, it was also found that the k_2 of oxidation reaction catalyzed by L^4Cu was the greatest.

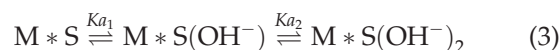
Catalytic decomposition of H_2O_2

To understand the interaction between catalyst and H_2O_2 , the decompositions of H_2O_2 catalyzed by L^1Cu , L^2Cu , L^3Cu and L^4Cu in buffer solution were investigated at pH 7.01 and $25^\circ C$. The change of concentration of H_2O_2 with reaction time in the reaction solution was analyzed by standard ceric sulfate solution. The results were illustrated in Figure 4. From Figure 4, it can be found that the initial rate of H_2O_2

decompositions were very fast. But with the progress of the reaction, the H_2O_2 destroyed the activities of catalysts and the decomposition rate of H_2O_2 became slow. Thus, it could be found that L^3Cu showed poor catalytic activity on the decomposition of H_2O_2 . However, L^1Cu , L^2Cu and L^4Cu displayed good catalytic activity on the decomposition of H_2O_2 . The results implied that for the $LCu-H_2O_2$ system the higher catalytic activity of the decomposition of H_2O_2 , the higher catalytic activity of the oxidative coupling of DMP. This clearly indicated that LCu complexes can activate H_2O_2 into active species in buffer solution and result in the efficient oxidation of DMP. When the pH of buffer solution varied from 6.0 to 9.0, the decomposition rate of H_2O_2 catalyzed by LCu increased with increasing pH (which was not shown here). The pH effect of catalytic activity of catalyst on the decomposition of H_2O_2 was not in accordance with that of catalyst on the reaction of formation of DPQ (Table I), which indicated that not only the activation of H_2O_2 but also the species of copper complex play important role in the oxidative coupling of DMP.

Catalytic reaction mechanism

From Figure 2 and Table I, it can be found that R_0 and k_2 first increased and then fell down with increasing pH. The pH effect implied that the intermediate ($M * S$) may have different existing form. Thus, we assumed that the intermediate $M * S$ existed in three kinds of forms with the following acidic dissociation balance in the reaction solution:



$$Ka_1 = \frac{[M * S(OH^-)][H^+]}{[M * S]} \quad (4)$$

$$Ka_2 = \frac{[M * S(OH^-)_2][H^+]}{[M * S(OH^-)]} \quad (5)$$

where $M * S(OH^-)$ and $M * S(OH^-)_2$ were the first and second deprotonized species, respectively. Ka_1 and Ka_2 were the first and second acidic dissociation

TABLE I
The Calculated Values of k_2 and K_m of the Formation of DPQ at $25^\circ C$

pH	L^1Cu		L^2Cu		L^3Cu		L^4Cu	
	$10^4 k_2$ (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)	$10^4 k_2$ (s^{-1})	$10^4 K_m$ (M)
6.03	4.68	2.03	6.25	1.72	0.14	14.2	96.6	1.92
6.53	7.70	1.45	10.4	2.09	0.16	15.5	131.0	1.82
7.01	12.8	1.36	14.2	2.21	0.43	20.9	178.2	1.83
7.53	9.81	0.66	15.3	1.61	0.63	31.4	115.3	1.78
8.01	4.25	0.73	6.90	1.26	1.91	38.5	35.1	1.04
8.53	1.90	0.59	2.59	0.98	3.01	61.5	20.4	0.92
9.02	0.88	0.33	1.86	0.61	16.9	183	10.5	0.91

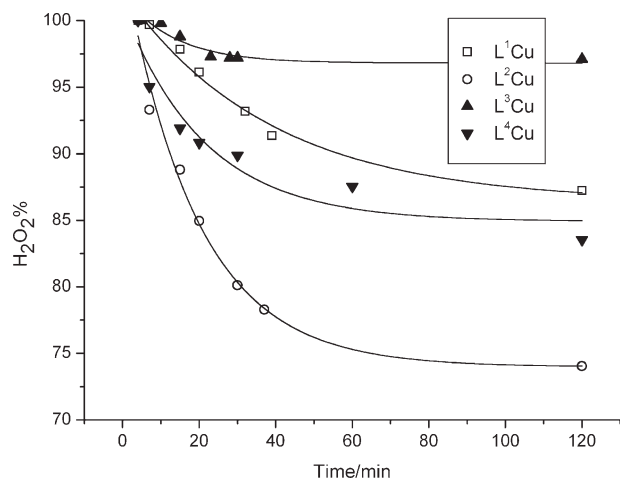


Figure 4 Decomposition of H_2O_2 catalyzed by four LCu complexes at pH 7.01 and 25°C , $C(\text{LCu}) = 5 \times 10^{-5}\text{M}$, $C_0(\text{H}_2\text{O}_2) = 0.02\text{M}$.

constants of intermediate $\text{M} \cdot \text{S}$, respectively. According to the material balance, we have

$$[\text{M} \cdot \text{S}]_T = [\text{M} \cdot \text{S}] + [\text{M} \cdot \text{S}(\text{OH}^-)] + [\text{M} \cdot \text{S}(\text{OH}^-)_2] \quad (6)$$

where $[\text{M} \cdot \text{S}]_T$ is the total concentration of $\text{M} \cdot \text{S}$. According to the pH effect, we suggested that the first deprotonized species $\text{M} \cdot \text{S}(\text{OH}^-)$ was the real reactive species, thus the rate equation can be rewritten as

$$R_0 = k_2[\text{M} \cdot \text{S}]_T = k'_2[\text{M} \cdot \text{S}(\text{OH}^-)] \quad (7)$$

The combination of eqs. (3)–(6) and rearrangement yield

$$[\text{M} \cdot \text{S}(\text{OH}^-)] = \frac{[\text{M} \cdot \text{S}]_T}{\frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]} + 1} \quad (8)$$

The combination of eqs. (7) and (8) and rearrangement yield

$$k_2 = k'_2 \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (9)$$

where k'_2 was considered as the real catalytic reaction rate constant, which was pH-independent.

Based on eq. (9) and the experimental data in Table I, the parameters K_{a1} , K_{a2} and k'_2 can be evaluated by nonlinear fitting method. Values of k'_2 were evaluated as 2.66×10^{-3} , 2.39×10^{-3} , and $2.91 \times 10^{-2}\text{M s}^{-1}$ for L^1Cu , L^2Cu and L^4Cu , respectively. $\text{p}K_{a1}$ and $\text{p}K_{a2}$ were evaluated as 6.83 and 7.35 for L^1Cu , 6.59 and 7.72 for L^2Cu and 6.43 and 7.34 for L^4Cu , respectively, all the correction coefficient $R^2 > 0.98$.

It was seen that the value of k'_2 of L^4Cu was over 10 times than that of L^1Cu and L^2Cu . Therefore, it was obvious that the catalytic activity of metal complex with pyridine group was better than that of complexes with the hydroxyl, carboxyl and amine groups. From Figure 1, it could be seen that the complex L^4Cu has two pyridine rings, where a special π - π conjugated 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.

The oxidation potential of DMP is less in alkaline solution than those of in neutral and acidic solution, thus the phenolate anion is easier to be oxidized than DMP.³⁰ In this study, $\text{M} \cdot \text{S}(\text{OH}^-)$ could transform DMP to phenolate anion easily by the intermolecular proton transfer, which could effectively decreased the oxidation potential of DMP, which promoted the oxidative coupling of DMP.

Based on the above-mentioned discussions, a possible catalytic reaction mechanism of DMP oxidation was proposed as illustrated in Figure 5: first, the Cu(II) coordinated with OOH^- , and then electron transferred between OOH^- and the copper(II) complex, the “association radical” $\text{LCu}^{\text{I}} \cdot \text{OOH}$ (M^*) formed,²⁴ which was considered as the active oxidant species. Then, one water molecule on M^* could be replaced by substrate DMP to yield $\text{M} \cdot \text{S}$. $\text{M} \cdot \text{S}$ lost a proton to generate $\text{M} \cdot \text{S}(\text{OH}^-)$. The OH^- in $\text{M} \cdot \text{S}(\text{OH}^-)$ complex could attack the hydrogen atom on hydroxyl of DMP (S) to form $\text{M} \cdot \text{S}^-$. Because of the lower oxidation potential of the phenolate anion (S^-) than that of DMP, the resulting phenolate anion (S^-) in $\text{M} \cdot \text{S}^-$ can be more easily oxidized to form associated phenoxy radical MS^\cdot , because of the inductive effect of the copper ion on phenoxy radical S $^\cdot$, the *p*-C atom could be easily attacked by nucleophilic molecule, so PPE formed. The phenoxy radical S $^\cdot$ could also separate from the associated complex MS^\cdot , therefore the free phenoxy radical reacted with each other to form C–C coupling products DPQ.

Products investigation

To check the ratio of PPE to DPQ in products, the catalytic reactions were performed in buffer solution at pH 7.01 and 25°C for 48 h. The salmon pink solid products were obtained by filtrating. Then, the products were dissolved in toluene. The amount of DPQ was obtained by monitoring the absorbance at 421 nm by UV–Vis analysis and the relative error in triplicate was less than 3%. Thus, the amount of PPE was evaluated by subtracting the weight of DPQ from total products and the weighing relative error was less than 5%. Furthermore, to detect the residual concentration of hydrogen peroxide, the reaction

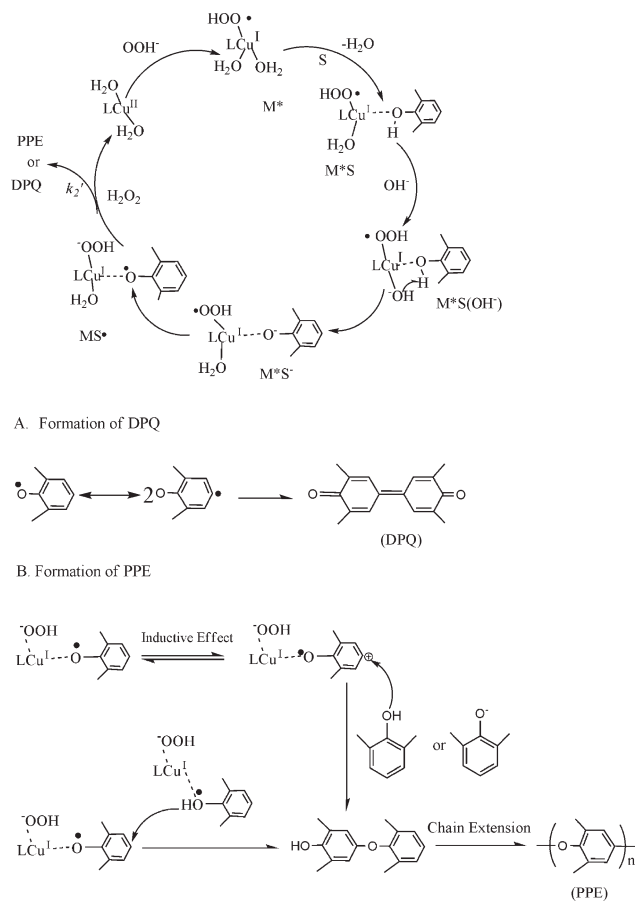


Figure 5 The possible catalytic mechanism of oxidative coupling of DMP.

solution after 20 h was titration analyzed by standard ceric sulfate solution. The results were summarized in Table II.

As shown in Table II, the chelating groups, such as $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$ and pyridine had great influence on the distribution of the products. It was obvious that the ratios of C–O coupling product (PPE) to C–C coupling product (DPQ) in the reactions catalyzed by L^4Cu and L^2Cu were larger than those of the reactions catalyzed by L^1Cu and L^3Cu . Thus, it was found that the catalyst with the alkaline chelating grounds, such as the pyridine and NH_2 , could promote the rate of DPQ formation (Table I), and even more strongly accelerate the formation of PPE, resulting in the high selectivity of PPE.

The pH of solution can affect not only the total yields but also the distribution of products. From Table III, it could be seen that for the L^4Cu catalyzed reaction the total yields of products first increased and then fell down with increasing pH, and the greatest was at pH 7.01. The percent of PPE ($W_{\text{PPE}}/W_{\text{DMP}}$) increased with increasing pH and nearly kept constant after pH 7.01. It was worthy of noting that pH of solution exhibited great effect on the ratio of PPE to DPQ. The ratio of DPQ to PPE was about

TABLE II
The Yields and Ratios of Products of Reaction^a
Catalyzed by Cu(II) Complexes

Systems	Yield (%) ^b	$W_{\text{PPE}}/W_{\text{DPQ}}$	H_2O_2 (%) ^c
L^1Cu	65.51	2.51	21.06
L^2Cu	75.66	3.06	27.52
L^3Cu	29.48	0.71	3.53
L^4Cu	80.58	3.16	18.57

^a $C_0(\text{LCu}) = 5 \times 10^{-5}\text{M}$, $C_0(\text{H}_2\text{O}_2) = 0.02\text{M}$, $C_0(\text{DMP}) = 1 \times 10^{-3}\text{M}$, pH = 7.01 and 25°C.

^b The precipitated products percent ($W_{\text{Products}}/W_{\text{DMP}}$) after 48 h.

^c The loss of H_2O_2 after 20 h.

30% in neutral aqueous solution; however it was less than 10% in weak acidic (pH 6.02) and weak alkaline (pH 8.53–9.01) solutions. Because of the high total yields of products and the low loss of H_2O_2 in neutral aqueous solution, it could be predicted that the optimal pH was around 7.0 in practice. The pH effect on product distribution was not entirely clear. Literatures³¹ reported that alkaline condition was in favor of the formation of PPE, while acidic solution led to the C–C coupling. However, in this work we found that both in weak acidic (pH < 6.5) and in alkaline aqueous solution (pH > 8) were suitable to the C–O coupling reaction in our catalytic systems. According to above-mentioned discussions on catalysis mechanism, we thought the phenoxy radical associated with metal complex, generated in the reaction process, was the main active species. It was possible that pH of solution affected the state of metal complex associated phenoxy radical, consequently influenced the ability of the copper complex associating with phenoxy radical and that of induction to *p*-C atom.

To analyze the C–O coupling product distribution, the reaction products after 48 h were dissolved in ethyl acetate and analyzed by low energy mass spectrometry which only appeared the molecular peaks. It was found that the C–O coupling of DMP

TABLE III
Effects of pH on the products^a and Loss of H_2O_2 at 25°C

pH	Yield ^b (%)	$W_{\text{PPE}}/W_{\text{DPQ}}$	W_{PPE} (%) ^c	H_2O_2 (%) ^d
6.02	38.98	12.89	36.17	11.27
6.52	67.47	6.93	58.96	11.64
7.01	80.58	3.16	61.21	18.57
7.52	78.61	3.69	61.85	42.96
8.01	76.97	9.94	69.93	75.02
8.53	65.84	11.61	60.62	76.99
9.01	64.85	14.31	60.61	80.61

^a $C_0(\text{L}^4\text{Cu}) = 5 \times 10^{-5}\text{M}$, $C_0(\text{H}_2\text{O}_2) = 0.02\text{M}$, $C_0(\text{DMP}) = 1 \times 10^{-3}\text{M}$.

^b Precipitate products percent ($W_{\text{Products}}/W_{\text{DMP}}$) after 48 h.

^c The percent of Product PPE ($W_{\text{PPE}}/W_{\text{DMP}}$) after 48 h.

^d The loss percent of hydrogen peroxide after 20 h.

was obvious, and phenolic oligomerizations including phenolic dimer, phenolic tetramer, phenolic heptamer and phenolic nonamer were detected. The amount of tetramer and heptamer were the most. It was also found that the methyl in phenyl of polymer can be partly oxidized to aldehyde and carboxylic acid in the relatively long reaction time.

CONCLUSIONS

This study indicated that the oxidative coupling of DMP by H_2O_2 could take place in aqueous solution by using copper(II) complexes as catalysts under mild conditions. The pH of solution strongly influenced the reaction rate and the distribution of products. The L^4Cu containing pyridine group showed the best catalytic activity. The associated radical $\text{LCu}^1(\text{OH}^-)\cdot\text{OOH} (\text{M}^*)$ was suggested as the possible predominant species to oxidize DMP, and $\text{M}^* \text{S}(\text{OH}^-)$ was the possible predominant reactive intermediate. The function of copper(II) complex was considered as activating H_2O_2 to produce reactive species and decreasing the pKa of DMP to give phenolate anion which could be oxidized easily. Furthermore, with reaction time increasing, the methyl in phenyl of polymer PPE could be further oxidized to form aldehyde and carboxylic acid. In practical industry, the complexes are easily prepared and cheap. Water, as an alternative for organic solvents, is friendly surroundings medium. And the macromolecule products can be easily separated from the aqueous solution because of its insolubility in water. This study may also provide useful information to better understand the mechanism of oxidative coupling of DMP and to find a new and green preparation process of PPE under mild conditions.

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