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Studies on the Electrochemical Behavior of Copper Paratolysulfate and its Complexes

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Abstract: Copper (II) paratolysulfate has been synthesized and characterized by thermogravimetric (TG) measurements and differential scanning calorimetric (DSC) analysis. This salt can easily lose all crystal water and the dehydrated salt does not deliquesce in the air. It is found for the first time that the complex of $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (1:1) can catalyze the oxidation of 1,1-bi-2-naphthol in DMSO and DMF, while the process is difficult to perform in H_2O and CH_3OH . The electrochemical behaviors of both $\text{Cu}(\text{p-OTs})_2$ and its complexes with ethanolamine have been studied on platinum electrode in DMF, DMSO, CH_3OH and H_2O respectively. The complexes of various copper salts with ethanolamine are also studied by cyclic voltammetry in different solvents. It is concluded that the two one-electron steps are essential condition for the oxidation of 1,1-bi-2-naphthol.

Key words: Copper paratolysulfate, Mimetic enzyme, Electrochemistry, 1,1-bi-2-naphthol

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1 Introduction

Copper complexes are involved in variety of important biochemical process, such as oxygen transport and oxygen activation by oxidase and monooxygenase enzymes^[1]. Synthesis and characterization of low molecular weight analogs for the active sites of metalloproteins is receiving increasing attention worldwide. Some copper complexes with different type of ligands have been synthesized and studied as mimetic enzyme^[2,3]. As a rule, their redox properties have been investigated by electro-

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chemical techniques, especially the cyclic voltammetry (CV) in appropriate solvents^[4,5]. It is recently reported that the complex of CuCl_2 /ethanolamine (11) can catalyze the oxidation of 1,1'-bi-2-naphthol in methanol with high yield^[6].

In the present paper we report that copper paratolylsulfate ($\text{Cu}(\text{p-OTs})_2$) can lose all the crystal water easily and the dehydrated salt does not deliquesce in the air. Preliminary study showed that the complex of $\text{Cu}(\text{p-OTs})_2$ /ethanolamine (11) could catalyze the oxidation of 1,1'-bi-2-naphthol by O_2 in DMF and DMF. The product was *peri*-xanthenoxanthene in accord with the result catalyzed by CuCl_2 /ethanolamine (11) in the same solvent^[6]. However, the catalytic reaction could hardly proceed in CH_3OH and H_2O .

The work on the electrochemical behavior of both $\text{Cu}(\text{p-OTs})_2$ and its complexes with ethanolamine is also reported here. This study is undertaken with the purpose of investigating the effect of solvents on the redox and catalytic properties of $\text{Cu}(\text{p-OTs})_2$ and analyze the reaction mechanism.

2 Experimental

2.1 Apparatus

Thermogravimetric (TG) analyses and differential scanning calorimetric (DSC) analyses were carried out with NETZSCH TG 209 Thermogravimetric analyzer and Perkin-Elmer Differential Scanning Calorimeter, respectively. ^1H NMR was recorded in a Varian Unity INOVA-500 spectrometer in CDCl_3 with TMS as the internal standard. Mass spectra (MALDI-TOF-MS) was taken on REFLEX 3 Bruker matrix assisted laser desorption/ionization time of flight mass spectrometry. The electrochemical measurements were carried out on a French VoltaLab 80 electrochemical workstation (Radiometer Analytical). The working electrode was a Pt (99.9%) wire (0.073 cm^2) and the counter electrode was a Pt (99.9%) sheet. The saturated calomel electrode (SCE) was used as reference electrode. All the potential values in this paper are versus SCE. Purified argon was bubbled through the electrolytic solution to remove oxygen. The electrochemical measurements were carried out in an argon atmosphere.

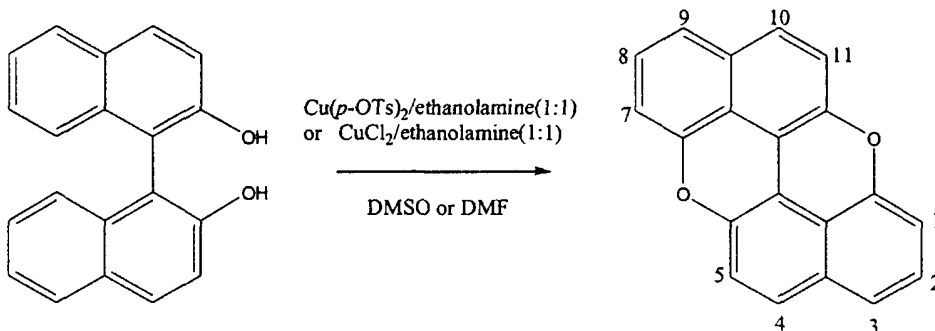
2.2 Reagents

Dimethyl sulfoxide (DMSO, AR) and *N,N*-Dimethylformamide (DMF, AR) and CH_3OH was distilled under vacuum after added 0.4 nm molecular sieves to remove water. The supporting electrolyte tetrabutyl ammonium perchlorate ($(n\text{-Bu})_4\text{NClO}_4$ or TBAP) was prepared following the literature^[7]. Copper paratolylsulfate was prepared by the reaction of CuO (99.95%) and $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (AR). The hydrated salt was dehydrated at 120 °C under 0.51 kPa and preserved in a desiccator containing anhydrous CaCl_2 for using in the electrochemical experiments. Unless stated otherwise, all the reagents were analytical pure. Aqueous solutions were prepared by double distilled water.

2.3 Catalytic Oxidation of 1,1'-bi-2-naphthol with $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$

(11) as Mimetic Enzyme

A 50 mg (0.17 mmol) sample of 1,1'-bi-2-naphthol was added to a flask containing 2 mL DMSO (or DMF) solution of 0.01 mol/L $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) complex dissolved in 20 mL of DMSO (or DMF). The solution was stirred at 60 °C and oxygen was bubbled through the solution. The reaction was allowed to take place until the oxygen consumption had ceased. A 2 mL ammonia solution and 50 mL water were added to the solution and extracted with chloroform (3 × 10 mL). The *peri-xanthenoxanthene* (10.5 mg, 21 % yield) oxidation product was then isolated by evaporation of CHCl_3 dried by anhydrous CaCl_2 followed by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1, V/V) as eluant. $^1\text{H NMR}$ (CDCl_3) (10^{-6} from TMS) 6.63 ~ 6.65 (m, 2H, 1-H, 7-H), 6.91 (d, 2H, J = 9.2 Hz, 3-H, 9-H), 7.07-7.09 (m, 4H, 2-H, 5-H, 8-H, 11-H), 7.29 (d, 2H, J = 8.9 Hz, 4-H, 10-H). MALDI-TOF-MS: 283 ($[\text{M} + \text{H}]^+$).



The complex of $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) precipitated from aqueous solution. The oxidation of 1,1'-bi-2-naphthol could not take place in CH_3OH and H_2O (monitored by thin layer chromatography, TLC) under the same condition as in DMSO (or DMF) since the 1,1'-bi-2-naphthol does not dissolve in H_2O .

3 Results and Discussion

3.1 Analysis of Copper Paratolysulfate

Two endothermic peaks (58.1186.6 °C) and two exothermic peaks (292.8 ~ 481.7 °C) were found from the DSC curve analysis of the salt in the temperature range of 30-630 °C as shown in Fig. 1. The TG curve showed four weight loss processes. The first two peaks are owing to water loss; according to the values of weight loss on the TG curve, the numbers of water molecules lost were calculated as 4 and 2 respectively. Therefore, the freshly prepared copper paratolysulfate should have the molecular formula of $\text{Cu}(\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$, this is also proved by X-ray crystal structure. The DSC and TG experiments showed that this salt can lose all crystal water easily and the dehydrated salt does not deliquesce in the air. Hence, the $\text{Cu}(\text{p-OTs})_2$ is suitable for the electrochemical studies in nonaqueous solvents.

3.2 The Electrochemical Behavior of $\text{Cu}(\text{p-OTs})_2$ in H_2O

The cyclic voltammograms of Pt electrode in $\text{Cu}(\text{p-OTs})_2/\text{KCl}$ aqueous solution at different scan rates were shown in Fig. 2. There were two pairs of redox peaks as shown in the figure. The surface of Pt electrode kept clean after 5 min electrolysis at the potential of 0.1 V (at the first cathodic peak); however, red color appeared on the Pt electrode after 5 min electrolysis at the potential of -0.2 V (at the second cathodic peak). It was proved that the electrochemical reduction of $\text{Cu}(\text{p-OTs})_2$ in aqueous solution was through two steps. The CV curves changed a little after added equivalent ethanolamine in $\text{Cu}(\text{p-OTs})_2/\text{KCl}$ aqueous solution.

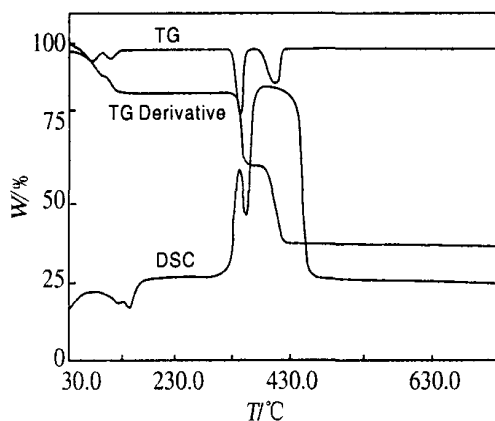


Fig1 The DSC and TG curves of $\text{Cu}(\text{p-OTs})_2 \cdot 6\text{H}_2\text{O}$

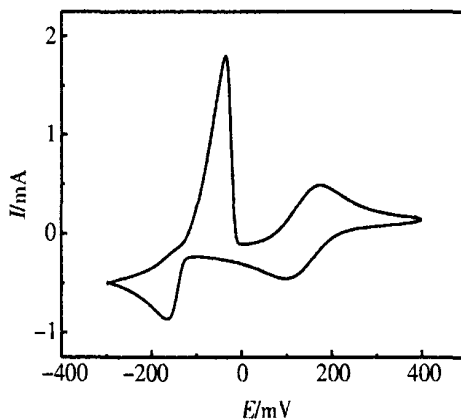


Fig.2 Cyclic voltammogram of $0.012 \text{ mol} \cdot \text{L}^{-1}$ $\text{Cu}(\text{p-OTs})_2/0.1 \text{ mol} \cdot \text{L}^{-1}$ KCl in H_2O solution t : 298 K, scan rate: 0.1 V s^{-1}

3.3 The Electrochemical Behavior of $\text{Cu}(\text{p-OTs})_2$ in CH_3OH

In Fig. 3 curve a shows the cyclic voltammogram of $\text{Cu}(\text{p-OTs})_2/\text{TBAP}/\text{CH}_3\text{OH}$ on Pt electrode. Only one pair of redox peak on the curve was found. Yellow compact deposit was appeared on the surface of Pt electrode after 5 min electrolysis at the cathodic peak potential. It is obvious that the peaks are corresponding to the cathodic reduction of Cu(II) to Cu and the anodic oxidation of Cu. Therefore, the result revealed that the electrochemical reduction of $\text{Cu}(\text{p-OTs})_2$ in CH_3OH was through one step.

The electrochemical reduction of $\text{Cu}(\text{p-OTs})_2$ was also a one step process after added equivalent ethanolamine (see Fig. 3b).

3.4 The Electrochemical Behavior of $\text{Cu}(\text{p-OTs})_2$ in DMSO

In Fig. 4, curve a shows the cyclic voltammogram of $\text{Cu}(\text{p-OTs})_2/\text{TBAP}/\text{DMSO}$ on Pt electrode at scan rate of 100 mV s^{-1} . There are two pairs of redox peaks on the curve, indicating that the first cathodic peak was due to the reduction of Cu(II) to Cu(I) and the second cathodic peak was the reduction of Cu(I) to Cu. Curve b is the cyclic voltammogram of $\text{Cu}(\text{p-OTs})_2/\text{TBAP}/\text{DMSO}$ after adding equivalent

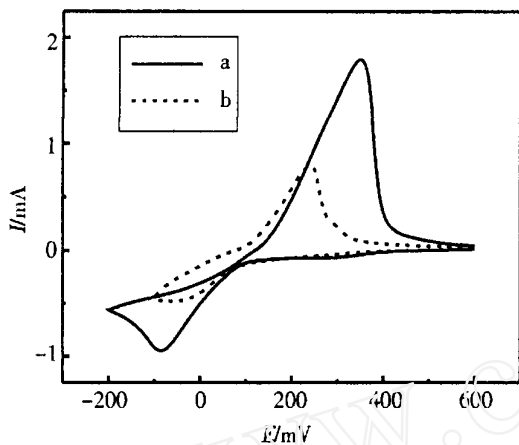


Fig. 3 The CV curves of $0.05 \text{ mol} \cdot \text{L}^{-1}$ TBAP + $0.011 \text{ mol} \cdot \text{L}^{-1}$ $\text{Cu}(p\text{-OTs})_2$ in CH_3OH (a) and after added $0.011 \text{ mol} \cdot \text{L}^{-1}$ ethanolamine (b) t : 298 K, scan rate: $0.1 \text{ V} \cdot \text{s}^{-1}$

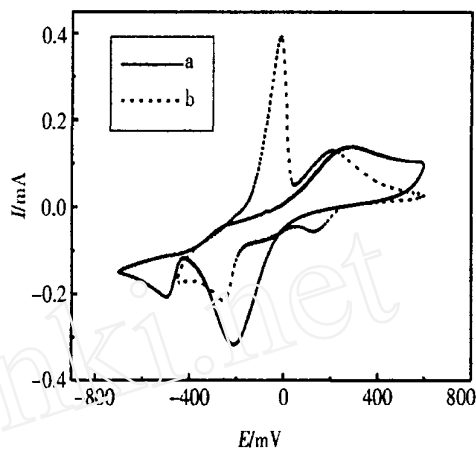


Fig. 4 Cyclic voltammograms of the $0.011 \text{ mol} \cdot \text{L}^{-1}$ $\text{Cu}(p\text{-OTs})_2$ + $0.05 \text{ mol} \cdot \text{L}^{-1}$ TBAP in DMSO (a) and after added $0.011 \text{ mol} \cdot \text{L}^{-1}$ ethanolamine (b) t : 298 K, scan rate: $0.1 \text{ V} \cdot \text{s}^{-1}$

lent ethanolamine. There are appeared two pairs of peaks. Both of two cathodic peaks shifted to more positive potentials. The first peak potential positively changed 351 mV and the second one changed 238 mV.

3.5 The Electrochemical Behavior of $\text{Cu}(p\text{-OTs})_2$ in DMF

One step mechanism was also found in $\text{Cu}(p\text{-OTs})_2/\text{TBAP}/\text{DMF}$ system. The cyclic voltammogram of $\text{Cu}(p\text{-OTs})_2/\text{TBAP}$ in DMF is shown in Fig. 5a. Only one pair of cathodic peak and anodic peak appeared. Black compact deposited on the electrode surface after 5 min galvanostatic electrolysis at the cathodic peak potential. However, the one step process changed to two steps processes for the system of $\text{Cu}(p\text{-OTs})_2/\text{TBAP}/\text{DMF}$ after added equivalent ethanolamine. Two cathodic peaks (at 202 mV and -105 mV) and one anodic peak (188 mV) appeared in Fig. 5b. Both of the cathodic peak potential moved positively compared with Fig. 5a (-216 mV) and the anodic peak potential moved negatively compared with Fig. 5a (233 mV).

$\text{Cu}(\text{II})$ can be solvated by DMF better than by CH_3OH , therefore, the oxidation of Cu is easier in DMF than that of in CH_3OH which resulting in the more negative anodic peak in DMF compared with that in CH_3OH . The reductive process became two steps processes by the addition of ethanolamine is probably due to the strong coordination power between solvated $\text{Cu}(\text{II})$ and the amino of ethanolamine.

3.6 Studies of $\text{Cu}(p\text{-OTs})_2/\text{ethanolamine}(11)$ as Mimetic Enzyme

The derivatives of xanthone are widely existed in natural products and have many physiological activities^[8]. This work aims to use the complex of $\text{Cu}(p\text{-OTs})_2/\text{ethanolamine}(11)$ as mimetic enzyme to synthesize physiologically active compounds and research the reactive mechanism.

In the present work, $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) was applied for the catalytic reactions. The preliminary results showed that the complex of $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) could catalyze the oxidation of 1,1-bi-2-naphthol in DMSO and DMF but could not work in CH_3OH and H_2O . In all the cases, the solution became brown in color and small quantity of brown precipitation produced after added $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) into 1,1-bi-2-naphthol as reported in the literature^[6]. The precipitation disappeared at the end of the reaction in DMSO and DMF, but kept the same in CH_3OH and H_2O . By comparing the CV curves of $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) in the four solutions, it was found that the electrochemical reduction of $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) is a two one-electron processes in DMSO and DMF. In that case, $\text{Cu}(\text{p-OTs})_2/\text{ethanolamine}$ (11) acts as a mimetic enzyme to catalytically oxidize 1,1-bi-2-naphthol. However, the process is a one two-electron reaction in CH_3OH , which can hardly work for the 1,1-bi-2-naphthol oxidation.

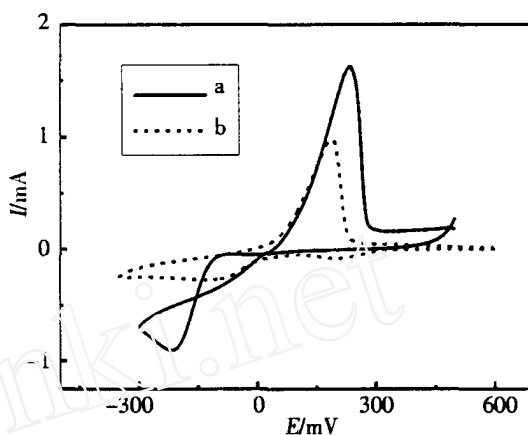


Fig. 5 The CV curves of the $0.05\text{mol L}^{-1}\text{TBAP} + 0.012\text{mol L}^{-1}\text{Cu}(\text{p-OTs})_2$ in DMF (a) and after added 0.012mol L^{-1} ethanolamine (b) $t: 298\text{K}$, scan rate: 0.1V s^{-1}

Tab. 1 Performance of cupric salt/ethanolamine (11) complexes in different solvents

Cupric salt	Solvents	Electrochemical reduction	1,1-bi-2-naphthol oxidation
CuCl_2	H_2O	Two steps	No
	DMSO	Two steps	Yes
	CH_3OH	Two steps	Yes
CuBr_2	H_2O	Two steps	No
	CH_3OH	Two steps	Yes
CuSO_4	H_2O	Two steps	No
	CH_3OH	One step	No
	DMF	Two steps	Yes
$\text{Cu}(\text{p-OTs})_2$	H_2O	Two steps	No
	DMSO	Two steps	Yes
	CH_3OH	One step	No
	DMF	Two steps	Yes
$\text{Cu}(\text{AcO})_2$	H_2O	Two steps	No
	CH_3OH	One step	No
$\text{Cu}(\text{NO}_3)_2$	H_2O	Two steps	No
	CH_3OH	One step	No
$\text{Cu}(\text{ClO}_4)_2$	H_2O	Two steps	No
	CH_3OH	One step	No

The complexes of various copper salts with ethanolamine have been tested and summarized in Table 1. The complexes that the reduction proceeds by two steps can be used as mimetic enzyme, the complexes that the reduction is through one step can not catalyze the oxidation of 1,1-bi-2-naphthol. So the oxida-

tion of 1,1'-bi-2-naphthol catalyzed by Cu(II)/ethanolamine is carried out by the transfer of Cu(I)/Cu(II).

Although the electrochemical reduction of copper-amine complexes in H₂O is a two one-electron processes, the catalytic oxidation of 1,1'-bi-2-naphthol can not carry out is mainly due to the poor solubility of copper-amine complexes and 1,1'-bi-2-naphthol in H₂O solution.

4 Conclusions

Copper paratolysulfate was synthesized and characterized by various techniques. The electrochemical behaviors of Cu(*p*-OTs)₂ on platinum electrode were studied in DMSO, DMF, CH₃OH and H₂O solutions for the first time. The results showed that the electrochemical reduction of Cu(II) to Cu is via a two one-electron steps in DMSO and H₂O solutions and proceeds by one two-electron step in CH₃OH and DMF solution. However, the reaction transforms to two one-electron steps by the addition of ethanolamine in DMF.

The complex of Cu(*p*-OTs)₂/ethanolamine (11) can catalyze the oxidation of 1,1'-bi-2-naphthol in DMSO and DMF. This reaction does not work in CH₃OH and H₂O. Summarizing the electrochemical behaviors of complexes of various copper salts with ethanolamine, it can conclude that two one-electron steps reduction of Cu(*p*-OTs)₂ is the essential condition for the oxidation of 1,1'-bi-2-naphthol.

The reaction is indistinguishable in aqueous solutions due to the limited solubility both Cu(*p*-OTs)₂/ethanolamine and 1,1'-bi-2-naphthol.

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对甲苯磺酸铜及其配合物电化学行为研究

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摘要: 本文合成了对甲苯磺酸铜,并应用热重(TG)和差示扫描量热法(DSC)进行分析.该铜盐容易脱除全部结晶水,且在空气中不潮解,如与乙醇胺形成等摩尔配合物,则在 DMSO 和 DMF 溶剂中能催化 1,1-联-2-萘酚的氧化,但在 H₂O 或 CH₃OH 溶剂中则不发生反应.此外,还分别研究了该铜盐及其它铜盐与乙醇胺(11)的配合物在 DMSO、DMF、CH₃OH 和 H₂O 中的电化学行为和催化活性.实验表明,铜胺配合物的两步单电子还原过程对催化氧化 1,1-联-2-萘酚是必要的条件.

关键词: 对甲苯磺酸铜;模拟酶;电化学;1,1-联-2-萘酚