Asian Journal of Chemistry Vol. 22, No. 9 (2010), 7389-7392

Macrocyclic Cu(II) and Co(II) Complexes as Catalysts for Hydroxylation of Phenol with H_2O_2

JIAN-HONG BI*, MENG LI† and YAN CHEN‡
Deparment of Chemistry and Chemical Engineering, Hefei Normal University,
327, Jinzhai Street, Hefei, Anhui-230061, P.R. China
E-mail: bi010101@126.com

The liquid phase catalytic hydroxylation of phenol to hydroquinone and catechol was carried out in the presence of the tetraaza macrocyclic copper(II) and cobalt(II) complexes using H_2O_2 as oxidant and water/ethanol as solvent. When the Cu(II) and Co(II) complexes were used as catalysts, 35.5 % phenol conversion was obtained with 42.5 % selectivity to dihydroxy benzene and 33.8 % phenol conversion was obtained with 36.8 % selectivity to diphenol under the optimum reaction conditions.

Key Words: Tetraazamacrocycle, Copper(II) complexe, Cobalt(II) complexe, Catalyst, Phenol, Diphenol.

INTRODUCTION

The dihydroxybenzenes, such as catechol (CAT) and hydroquinone(HQ), are high value chemical materials and intermediates, they are widely used in pharmaceutical, polymerization inhibitor, photographic developer and flavour industries[1]. catechol and hydroquinone are the mainly oxidation products of phenol. Hydroxylation of phenol with clean oxidants like H_2O_2 is a research topic of high industrial importance. Direct hydroxylation of phenol with H_2O_2 have a lot of catalysts such as zeolites, heteropoly compounds and metal oxides[2,3], however, few examples were reported that the Schiff base complexes as a catalyst for this reaction[4,5].

In this paper, the catalytic performance of the two tetraaza macrocyclic complexes $ML(ClO_4)_2$ ($M = Cu^{2+}$, Co^{2+}, L = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) in the hydroxylation of phenol with H_2O_2 and the reaction parameters were evaluated.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. The 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazamacrocyclic-4,11-diene (L) and $CuL(ClO_4)_2$ were synthesized according to the reported literature[6-8] and characterized by IR spectra and elemental analysis. $Co(ClO_4)_2·6H_2O$ was prepared by our Laboratory. IR spectra were record on a Nexus-870 spectrophotometer. Elemental analyses were

---

†School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P.R. China.
‡Anhui Institute of Geological Experiments, Hefei-230001, P.R. China.

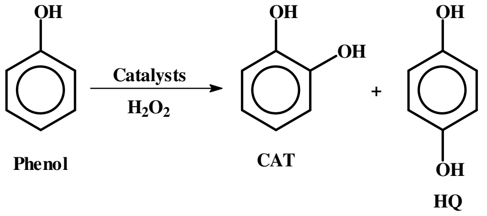
performed on a Elementar Vario EL-III elemental analyzer. The products of the catalytic phenol hydroxylation reaction were analyzed using an Agilent 1200 liquid chromatograph with a ZORBAX Eclipse XDB-C18 4.6 mm × 150.0 mm column, 1:1 H_2O/C_2H_5OH as the mobile phase and UV-vis detection ($\lambda = 277$ nm).

Synthesis of $CoL(ClO_4)_2$: Take 10 mmol of L in 20 mL methanol, 10 mmol of $Co(ClO_4)_2 \cdot 6H_2O$ in 20 mL water was added with stirring. After the brown turbid solution formed, the yellowish-brown powder precipitated upon standing, then collected and air dried at room temperature. Yield 40 %. IR (KBr, ν_{max}, cm^{-1}): 3481 ν(N-H), 1652 ν(-C=N), 1087, 623 $\nu(ClO_4^-)$, 767, 709 ν(Ar-H). Elemental anal. calcd. (%) for $C_{24}H_{32}Cl_2CoN_4O_8$: C, 45.44; H, 5.08; N, 8.83; found. (%): C, 45.37; H, 4.99; N, 8.86.

Catalytic activity studies: The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL flask fitted with a water-cooled condenser. In a typical reaction, an aqueous solution of 30 % H_2O_2 (5 g) and phenol (1 g) were mixed in 10 mL of H_2O and the reaction mixture was heated to 50 °C with stirring. An appropriate catalyst $\{[CuL](ClO_4)_2/[CoL](ClO_4)_2\}$(0.010 g) in 15 mL of ethanol was added to the reaction mixture. During the reaction, the products were analyzed using an Agilent 1200 liquid chromatograph after interval of time. Yields of the main reaction product (HQ and CAT) reported in following section were defined as $C_{phen.}$ (mol %) = ([HQ] + [CAT])/[ph] × 100, where $C_{phen.}$ is the conversion of phenol (%), [ph] is the mol number of phenol in the feed and [HQ], [CAT] are the mol numbers of hydroquinone and catechol produced.

RESULTS AND DISCUSSION

Study on the reaction conditions of hydroxylation of phenol: In order to achieve suitable reaction conditions for the maximum hydroxylation, the following experimental parameters such as solvent type, H_2O_2 concentration (moles of H_2O_2 per mole of phenol), reaction temperature, reaction time and pH value were studied in order to see their effect on the reaction product pattern.



Oxidation products of phenol using $ML(ClO_4)_2$ ($M = Co^{2+}$ or Cu^{2+}) as catalysts and H_2O_2 as oxidant

Effect of solvents: To study the influence of the reaction medium on hydroxylation of phenol, the reaction was performed in various solvents. Acetone, acetonitrile, methanol, DMF, ethanol, water and their mixture were used as solvents. Among them, experimental results showed that water and ethanol (1:1) mixture is best solvent for the reaction of phenol hydroxylation.

Effect of H_2O_2/phenol molar ratio: The effect of the H_2O_2/phenol molar ratios on the phenol conversion and H_2O_2 conversion was studied. A lower molar ratio of H_2O_2/phenol in the reaction leads to high efficiency of H_2O_2 and a higher H_2O_2/phenol molar ratio may lead result in formation of benzoquinone by-product. The experimental results showed that the best condition of H_2O_2/phenol molar ratio is about 4.

Effect of reaction temperature: The phenol conversion and product selectivity in reaction temperature range of 20-85 ºC were studied. At 20 ºC, reactants do not have enough energy, the reaction rate is relatively low, phenol conversion is also very low. However, the reaction temperature above 85 ºC, the higher reaction temperature may lead result in formation of much benzoquinone by-product. After many experiments, 50 ºC was choosen as a best reaction temperature condition.

Effect of pH value: The acidity of reaction medium also has a remarkable influence on the phenol conversion. The experimental results showed that the high phenol conversion was obtained at pH 6.

Effect of reaction time: The influence of reaction time on the catalytic activity of the tetraaza macrocyclic copper(II) and cobalt(II) complexes catalysts was studied at 50 ºC. At the beginning of the reaction, phenol conversion is at a high level. With the increase of reaction time, phenol conversion increases slowly. After 5 h, the reaction achieves steady-state, so the reaction time 5 h is suitable.

Catalysts for hydroxylation of phenol: The catalytic results are listed in Table-1. Although many kinds of catalysts, such as metal oxides, metal complexes, zeolites and zeolite-encapsulated metal complexes, have been developed for hydroxylation of phenols, in most cases, the ratio of HQ/CAT is less than 1[9,10], except in the case of a few catalysts[11]. It can be seen from Table-1 that tetraaza macrocyclic copper(II) and cobalt(II) complexes catalysts have certain catalyzed selectivity to the hydroxylation of phenol. This phenomenon indicates that the azamacrocyclic complexes would be potential catalysts for the hydroxylation of the phenol reaction.

TABLE-1
CATALYTIC ACTIVITY IN THE HYDROXYLATION OF PHENOL WITH H_2O_2

Catalysts complex	Phenol (%)	Selectivity (%)		HQ/CAT
		CAT	HQ	
Cu	35.3	16.5	26.0	1.58/1
Co	33.8	14.5	22.3	1.54/1

Reaction conditions: reaction temperature 50 ºC, reaction time 5 h, H_2O_2/phenol (molar ratio) = 4, solvent: water/ethanol = 1:1, pH = 6.

Conclusion

In conclusion, the results demonstrate that the tetraaza macrocyclic copper(II) and cobalt(II) complexes exhibited good catalytic activity in the hydroxylation of phenol with hydrogen peroxide as oxidant, under mild reaction conditions.

ACKNOWLEDGEMENTS

This work is financially supported by the National Natural Science Foundation of China (No. 20871039) and Anhui Provincial Science Research Projects (09020204030).

REFERENCES

1. C. Wu, Y. Kong, F. Gao, Y. Wu, Y.N. Lu, J. Wang and L. Dong, *Micro. Meso. Mater.*, **113**, 163 (2008).
2. J.H. Bi, L.T. Kong, Z.X. Huang and J.H. Liu, *Inorg. Chem.*, **47**, 4564 (2008).
3. K. Lemke, H. Ehrich, U. Lohse, H. Berndt and K. Jahnisch, *App. Catal. A-Gen.*, **243**, 41 (2003).
4. H.S. Abbo, S.J.J. Titinchi, R. Prasad and S. Chand, *J. Mol. Catal. A-Chem.*, **225**, 225 (2005).
5. V. K. Bansal, R. Kumar, R. Prasad, S. Prasad and Niraj, *J. Mol. Catal. A-Chem.*, **284**, 69 (2008).
6. J.H. Bi, *Acta Cryst.*, **E65**, m633 (2009).
7. J.H. Bi, W.T. Bi, Z.X. Huang and N.-L. Hu, *Asian J. Chem.*, **21**, 6619 (2009).
8. J.H. Bi, J.M. Song, Z.X. Huang, Y.H. Wang, L.T. Kong and N.L. Hu, *Asian J. Chem.*, **18**, 2365 (2006).
9. J.N. Park, K.Y. Chio, W.Y. Dong, S. Hong and C.W. Lee, *J. Mol. Catal. A-Chem.*, **247**, 73 (2006).
10. S. Seelan and A.K. Sinha, *Appl. Catal. A-Gen.*, **238**, 201 (2003).
11. Y.J. Jiang and Q.M. Gao, *Mater. Lett.*, **61**, 2212 (2007).

(*Received*: 8 March 2010; *Accepted*: 30 June 2010) AJC-8845