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Journal of Molecular Catalysis A: Chemical 218 (2004) 125–132

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Investigation of $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ catalyzed selective hydroxylation of phenol to catechol by H_2O_2 in the homogeneous medium

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Received 18 February 2004; received in revised form 11 April 2004; accepted 12 April 2004

Abstract

Chemical and electrochemical conversion of phenol to 1,2-dihydroxy benzene using H_2O_2 as oxidant was studied in presence of $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ as homogeneous catalyst. The reaction products were analyzed using gas chromatograph. The phenoxide salt of the complex, $[Ni\{Me_4Bzo_2[14]aneN_4\}](C_6H_5O)_2$ exhibits a new irreversible oxidation wave at $E_{p,c}$ 0.45 V versus Ag/AgCl, which is unlike that observed in its dichloride salt with $E_{p,c}$ 0.25 V, and arises due to catalyzed electro-oxidation of the phenoxide counter ions. The chemical oxidation by H_2O_2 was investigated in presence of different solvents and a predominant formation of catechol was observed over hydroquinone (with molar ratio 9:1). The reaction conditions were optimized, in terms of the effect of reaction temperature, amount of catalyst, H_2O_2 concentration, phenol concentration, nature and volume of solvent used, reaction time and pH, for the maximum transformation of phenol as well as for better selectivity towards the formation of catechol.

Keywords: Oxidation; N_4-macrocycle; Catalyst; Phenol; Catechol

1. Introduction

The study of homogeneous catalysis has gained prominence in the last two decades. In fact, they are being successfully used in a wide variety of chemical transformations. Design of new catalysts for the selective oxidation of organic substrates and enhancement of their selectivity and catalytic activity vis-à-vis the stability of the catalyst are the research areas of great interest. Mineral acids [1,2], metal ions [3] and metal complexes [4–6] have been successfully used as homogeneous catalysts in a variety of chemical reactions. Several transition metal macrocycle complexes, viz. cyclam and related N_4-macrocycle complexes with Fe(II) [7–9], Ni(II) [10–13], Ru(III), Cu(II), Pd(II) [10] as well as Mn(III) triazacyclononane complexes [14], have been used for the epoxidation of alkenes. The kinetic and mechanistic investigation of Ni(II) and Fe(II) cyclam catalyzed epoxidations, suggest involvement of an M(IV) oxo-intermediate, that transfers the oxygen atom to the substrate. In a comparative study of the epoxidation of *trans*-β-methylstyrene using various Ni(II) macrocycle complexes as homogeneous catalysts, it was shown that the Ni(II) cyclam is the most efficient homogeneous catalyst [12]. In fact the cyclam-type complexes lacking any pendent arm were found to be better catalysts than those with pendant arms or those with polycyclic ligands, as they exert steric hindrance in the axial approach of the oxidant [13]. Also it was found that in order to act as better catalyst, the Ni(II)/Ni(III) oxidation potential in the complex should be low.

There are a few reports that utilized metal–macrocyclic complexes as homogeneous catalysts for hydroxylation of phenols [15–18]. The cobalt(II) complexes with porphyrin, phthalocyanin, salen, amine, etc. have been found to catalyze oxidation/hydroxylation of phenols, anilines, thiols and alkenes. It has recently been authoritatively reviewed by Simandi [16]. Cobalt(II) tetraphenylprophyrins have been

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doi:10.1016/j.molcata.2004.04.012

used for the catalyzed oxidation of phenols to quinones using molecular oxygen as oxidant [17]. Various other metal phthalocyanines have also been used for the hydroxylation of phenol using H_2O_2 [18]. It was found that the metal ion in the catalyst influences both activity and selectivity of the reaction [19] as well as the distribution of catechol and hydroquinone in the product. Recently, efforts have been made to encapsulate metal macrocycle complexes in the zeolite cavities and clays in order to catalyze hydroxylation of phenols [20–22].

The hydroxylation of phenols and aromatic hydrocarbons is a field of great challenge. It is an industrially important reaction. The catalytic oxidation of phenol usually gives catechol and hydroquinone and in certain cases further oxidation occurs leading to formation of *para*-benzoquinone. Although, catechol and hydroquinone both are widely used in industry, the catechols are used as photographic developer, pesticides, antioxidants, flavoring agents and in electroplating industry. They are also used as polymerization inhibitor, and in pharmaceutical industry. Hence, the selective conversion of aromatic compounds to catechols has always been of great interest. The catalyzed hydroxylation of phenols could be carried out using hydrogen peroxide or alkyl hydroperoxides as oxidant. Hydrogen peroxide is a strong oxidizing agent although, not as reactive as organic peroxides, it shows good selectivity for *o*,*p*-phenol hydroxylation. The advantage with the use of H_2O_2 over organic oxidants is that it is environment-friendly and leaves only water as the end product. Contrary to this, the organic peroxides are of hazardous nature and produce undesirable residues.

We have recently synthesized nickel(II) complex of a new cyclam-type macrocycle, $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ [23]. Theoretical geometry optimization using MOPAC shows that the macrocycle, attains the saddle shape geometry. Owing to the presence of two fused C_6H_4 rings it also possess a relatively rigid framework in the complex. The vacant axial sites in the complex enable weak coordination interaction with anions like NO_2^-, NO_3^-, etc. [24]. Thus, we herein report the electrochemical behavior of $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ in presence of phenol and its homogeneous catalysis for the hydroxylation of phenol using H_2O_2 as final oxygen donor.

2. Experimental

2.1. Materials

Phenol (Aldrich), 30% H_2O_2 (E. Merck) and tetraethylammonium perchlorate (TEAP), (Fluka) were used. The complex, $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ was synthesized as reported elsewhere [23]. AR grade solvents and reagents were used in the electrochemical and chemical oxidation studies after appropriate purifications [25]. The acetonitrile used in the electrochemical studies was dried over P_2O_5.

2.2. Instrumentation

Electrochemical studies were carried out on a CHI 600A electrochemical analyzer. Three-electrode assembly with Ag/AgCl/KCl (saturated) reference electrode, Pt wire counter electrodes were used. Working electrode consisted of glassy carbon microelectrode (2 mm diameter). All investigations were made in acetonitrile solution in presence of tetraethylammonium perchlorate as supporting electrolyte. All catalyzed chemical oxidation products were analyzed using Nucon 5700 gas chromatograph fitted with FID detector, a 2 m × 2 mm (i.d.) OV-17 (SS) column and was operated through a ORACLE 2 computer software.

2.3. Preparations

2.3.1. Synthesis of $[Ni\{Me_4Bzo_2[14]aneN_4\}](C_6H_5O)_2$

$[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ (0.48 g, 1 mmol) was dissolved in 0.5 mL of water. To this added ca. 10 mL of concentrated solution of C_6H_5ONa. Red brown solid that separated out was collected by filtration. It was subsequently washed twice with cold water and was dried over $CaCl_2$. Yield (0.45 g, 75%), mp 130 °C. IR (KBr pellet, ν, cm^{-1}): 1632s, 1522w, 1391s, 1239w, 1161w, 1109w, 1035w, 762s. UV-Vis (in CH_2Cl_2, λ_{max}, nm): 454 (ε_{max}, 1400 mol^{-1} cm^{-1}) 269 (12,000), 261 (12,700).

2.4. Catalyzed electrochemical oxidation of phenol

Catalyzed electro-oxidation was investigated using cyclic voltammetry (CV) technique. The current voltage characteristics were recorded: (a) in blank runs for phenol and sodium phenoxide (0.01 M); and (b) the same in presence of ca. 0.001 M of the complex $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$, at different scan rates. The voltammograms were initially recorded in dry acetonitrile followed by introduction of increasing amount of water. Modification in the nature and position of the oxidation waves of the substrate in presence of the catalyst were carefully recorded.

2.5. Catalyzed chemical oxidation of phenol

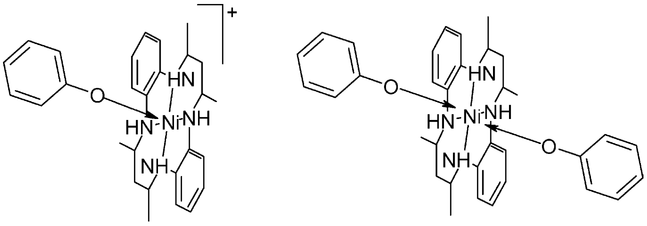
The catalytic hydroxylation of phenol using 30% H_2O_2 solution as an oxidant was carried out in a two-necked 50 mL glass round bottomed reaction flask fitted with a water condenser and immersed in thermostated oil bath that was maintained at different preset temperatures.

In a typical hydroxylation process, a mixture of phenol (4.7 g, 0.05 mol) and 30% H_2O_2 (5.67 g, 0.05 mol) in 2 mL acetonitrile were warmed to 80 °C. To this mixture, catalyst $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ (20 mg, 0.41 mmol) was added to start the reaction. The reaction mixture was continuously stirred using a magnetic stirrer; samples were periodically withdrawn from it and were analyzed by gas chromatograph. The reaction was studied as a function of time, temperature, amount of substrate and oxidant, amount of catalyst and volume of solvent.

3. Results and discussion

The complex [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 in acetonitrile exhibit only one irreversible oxidation wave in cyclic voltammetry scan at $E_{p,a}$ 0.25 V versus Ag/AgCl (Fig. 1a). As the presence of the low lying oxidation forms an important prerequisite for showing catalytic activity for phenol hydroxylation [13], the behavior of the complex seemed promising. Thus, corresponding phenoxide salt, [Ni{Me_4Bzo_2[14]aneN_4}]$(C_6H_5O)_2$ was prepared by the metathesis reaction and its electrochemical characteristics were investigated. It was observed that in dry acetonitrile phenoxide salt exhibits only the [Ni{Me_4Bzo_2[14]aneN_4}]$^{2+}$ oxidation wave. While upon addition of ca. 1% water (v/v) a new wave emerged at $E_{p,a}$ 0.37 V versus Ag/AgCl (Fig. 1b). With further addition of water (ca. 5%, v/v) this wave moved to slightly more positive potential and became very prominent. Since the aqueous cyclic voltammogram of $NaOC_6H_5$ shows irreversible oxidation wave at $E_{p,a}$ 0.60 V versus Ag/AgCl, it could be concluded that presence of the [Ni{Me_4Bzo_2[14]aneN_4}]$^{2+}$ has facilitated the oxidation process.

Furthermore, it was found that phenol do not exhibit any electrode process up to E_λ 2.0 V versus Ag/AgCl over the glassy carbon electrode in dry acetonitrile, nor even in presence of the complex [Ni{Me_4Bzo_2[14]aneN_4}]$Cl_{2.}$. Introduction of ca. 5% water also did not alter the voltammogram (scan 2, Fig. 1a). Hence it was concluded that presence of the phenoxide ion was essential for the catalysis process. It is likely that the oxidative electron transfer occurs through mono- or diphenoxide coordinated species.



3.1. *Hydroxylation of phenol using synthesized catalyst*

The liquid phase catalytic hydroxylation of phenol using synthesized catalyst, [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2. was studied as a function of time with 30% H_2O_2 as an oxidant. The main products of phenol hydroxylation using H_2O_2 were identified as catechol and hydroquinone and no other additional products were detected. The oxidation of phenol with H_2O_2 without catalyst was found to be very slow ($<1\%$ overall conversion). Different reaction parameters were studied in details using [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 catalyst, in order to determine optimum reaction conditions for the maximum transformation of phenol as well as for better selectivity towards the formation of catechol. These include the effect of reaction temperature, amount of catalyst, H_2O_2 concentration, phenol concentration, nature and volume of solvent used, reaction time and pH.

3.2. *Effect of reaction temperature*

The performance of the catalyst was investigated at three different temperatures, viz. 50, 65 and 80 °C, while keeping other parameters fixed. The results are shown in Fig. 2. It is apparent that the reaction temperature of 80 °C gives the maximum percentage conversion of phenol (40.2%) whereas the percentage of phenol conversion at 65 and 50 °C were significantly lower in comparison to that at 80 °C, i.e. 13.5 and 10.7%, respectively. Although the catechol and hydroquinone are the likely oxidation products, the [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 catalyzed oxidation of phenol shows a very high degree of selectivity for the formation of catechol over hydroquinone (molar ratio 97.3:2.7) at 50 °C. With increasing temperature, a slight drop in the selectivity for the catechol formation (at 80 °C, 89.6:10.4) was observed although it was still the predominant product (Table 1). At 80 °C, the catalyst complex shows the highest turn over frequency (TOF).

3.3. *Effect of amount of catalyst*

The amount of catalyst present in the system has significant effect on the over all catalytic efficiency and the selectivity pattern. Four different weights of catalyst, 5, 10, 20 and 30 mg of [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2, were used

Table 1
Effect of reaction temperature on percentage phenol conversion[a], product selectivity and TOF values

Reaction temperature (°C)	Phenol conversion (%)	Product selectivity (%)		Catechol/hydroquinone ratio	TOF (h^{-1})
		Catechol	Hydroquinone		
50	10.7	97.3	2.7	36.0	21.5
65	13.5	94.2	5.8	16.2	27.1
80	40.2	89.6	10.4	8.6	80.7

TOF: turn over frequency, moles of substrate converted per mole of the catalyst per hour.

[a] Reaction conditions: phenol = 0.05 mol; phenol/H_2O_2 molar ratio = 1; catalyst = 20 mg; solvent, CH_3CN = 2 mL; reaction time = 6 h.

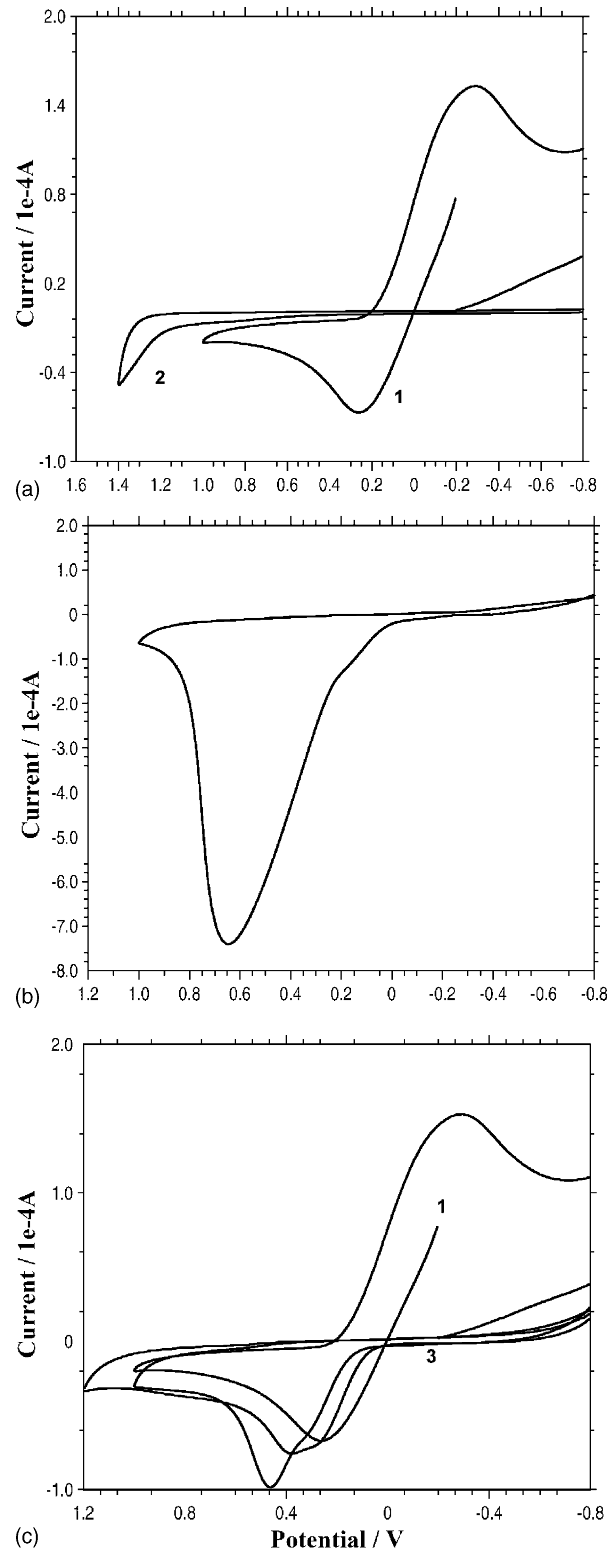


Fig. 1. Cyclic voltammograms of: (a) [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 (1) and phenol (2) in dry acetonitrile; (b) $NaOC_6H_5$ in water; (c) [Ni{Me_4Bzo_2[14]aneN_4}]$(OC_6H_5)_2$ in AN in presence of increasing amount of water (3). All potentials are with respect to Ag/AgCl reference electrode.

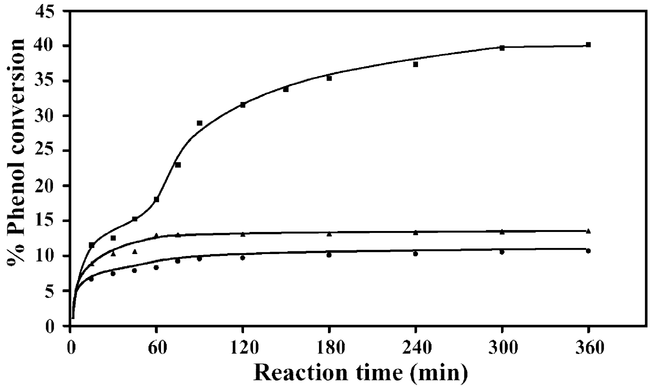


Fig. 2. Effect of reaction temperature on the percentage phenol conversion as a function of time in presence of [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 complex: (●) 50 °C; (▲) 65 °C; (■) 80 °C.

Table 2
Effect of catalyst weight on phenol hydroxylation

Catalyst weight (g)	Phenol/catalyst molar ratio	Phenol conversion after 6 h reaction time (%)	TOF (h^{-1})
0.005	4817	21.3	171.0
0.010	2409	25.9	104.0
0.020	1204	40.2	80.7
0.030	803	43.5	58.2

Reaction conditions: phenol = 0.05 mol; phenol/H_2O_2 molar ratio = 1; solvent, CH_3CN = 2 mL; reaction time 6 h; reaction temperature 80 °C. TOF: turn over frequency, moles of substrate converted per mole of metal (in solid catalyst) per hour.

to study the influence of the amount of catalyst on percentage phenol conversion (Table 2 and Fig. 3). Fig. 3 shows that increasing the amount of catalyst from 5 to 10 mg increased the overall percentage of phenol conversion from 21.3 to 25.9%. Further increasing the amount of the catalyst to 20 mg increased the percentage phenol conversion to ca. 40%. Upon further increasing the catalyst amount to 30 mg, only a little improvement in the percentage phenol conversion was observed. Table 2 also lists the effect of substrate

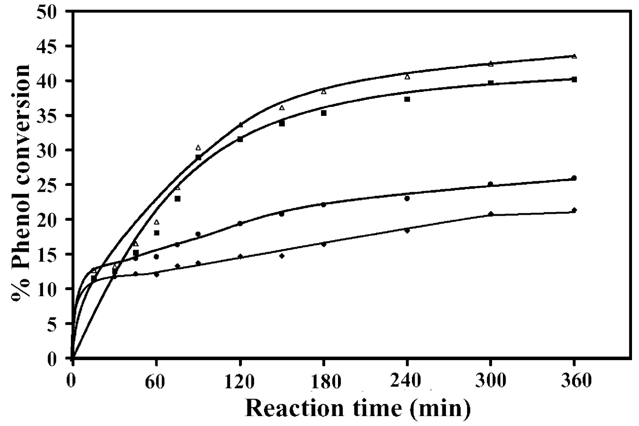


Fig. 3. Effect of amount of catalyst, [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2, on phenol hydroxylation: (△) 30 mg; (■) 20 mg; (●) 10 mg; (◆) 5 mg.

Table 3
Effect of H_2O_2:PhOH molar ratio on the percent phenol conversion[a], product selectivity and percent H_2O_2 efficiency

Molar ratio H_2O_2:PhOH	Phenol conversion (%)	H_2O_2 efficiency (%)[b]	Product selectivity (%)	
			Catechol	Hydroquinone
0.5:1	7.9	13.5	92.6	7.4
1:1	40.2	34.4	89.6	10.4
2:1	48.4	20.7	88.3	11.7

[a] Reaction conditions: phenol = 0.05 mol; catalyst = 20 mg; solvent, CH_3CN = 2 mL; reaction time = 6 h; reaction temperature 80 °C.

[b] H_2O_2 efficiency (%) = (moles of H_2O_2 utilized in products formation/moles of H_2O_2 added) × 100.

(i.e. phenol)/catalyst molar ratio on the over all conversion efficiency. It was found that a substrate/catalyst molar ration of 1204 is the best in terms of percent phenol conversion as well as in terms of the TOF value.

3.4. *Effect of H_2O_2 concentration*

In order to determine the influence of H_2O_2 to phenol molar ratio on the hydroxylation of the latter, three different H_2O_2:phenol molar ratios (0.5:1, 1:1 and 2:1) were taken and the results are presented in Table 3 and Fig. 4. With H_2O_2:phenol molar ratios of 2:1 and 1:1, maximum percent conversion of phenol observed were 48.4 and 40.2%, respectively. This shows that by increasing the oxidant/substrate ratio from 1:1 to 2:1 resulted into a ca. 8% increase in the over all conversion. These correspond with the percent H_2O_2 efficiency of 34.4% for molar ration of 1:1 and an efficiency of 20.7% for the molar ratio of 2:1. The percent conversion at a molar ratio of 0.5:1 (H_2O_2:phenol) was significantly lower (i.e. 7.4%) with even lower H_2O_2 efficiency (13.5%). Therefore, in order to obtain high percent conversion and high H_2O_2 efficiency, the molar ratio of 1:1 was considered to be the best. The product selectivity was found to be nearly unaffected by the H_2O_2:phenol molar ratio and ranged between 88.3 and 92.6% of catechol formation.

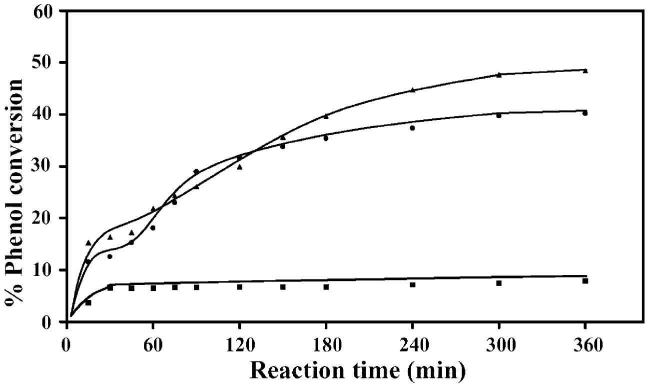


Fig. 4. Effect of H_2O_2:phenol molar ratio 2:1 (▲), 1:1 (●), 0.5:1 (■) on percentage phenol conversion as a function of time in presence of catalyst [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2.

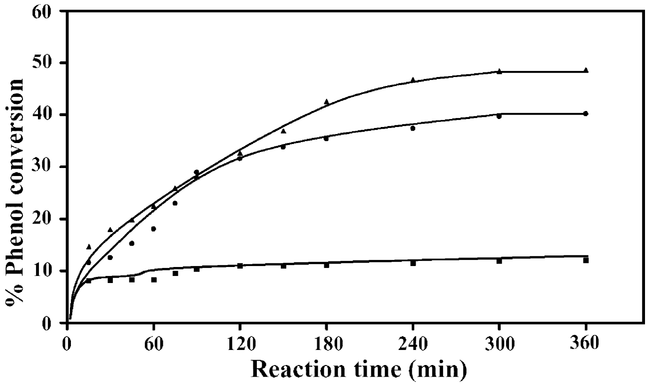


Fig. 5. Effect of phenol concentration on its hydroxylation as a function of time catalyzed by [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 complex in presence of 0.05 mol H_2O_2: (▲) 0.025 mol; (●) 0.05 mol; (■) 0.1 mol.

3.5. *Effect of phenol concentration*

Effect of phenol concentration on the rate of hydroxylation of phenol was studied by varying its initial concentration in the reaction mixture from 0.025 to 0.1 mol in presence of 0.05 mol H_2O_2, while keeping other parameters constant (Fig. 5). The higher percentage conversion of phenol was observed at lower phenol:H_2O_2 molar ratio, however the selectivity for catechol formation was moderately lower. With increasing the phenol:H_2O_2 molar ratio from 0.5:1 to 2:1, the overall percentage of phenol conversion decreased significantly from 40.2 to 12.0%. The variation in phenol concentration clearly indicate that in terms of percent phenol conversion, percent H_2O_2 efficiency and selectivity for catechol formation, phenol:H_2O_2 molar ratio of 1:1 is the optimum (Table 4).

3.6. *Effect of type of solvent*

The influence of solvent on the rate of the hydroxylation of phenol was studied using four different solvents, viz. acetonitrile, ethyl acetate, water and *n*-heptane. Results are shown in Fig. 6. Amongst the all solvents used, the highest percentage phenol conversion, percentage H_2O_2 efficiency and TOF were observed in acetonitrile (Table 5).

Table 4
Effect of PhOH:H_2O_2 molar ratio on the percent conversion to dihydroxy benzene[a], product selectivity and percent H_2O_2 efficiency

Molar amount of PhOH	Phenol conversion (%)	H_2O_2 efficiency (%)[b]	Product selectivity (%)	
			Catechol	Hydroquinone
0.025	48.6	20.8	85.2	14.8
0.05	40.2	34.4	89.6	10.4
0.10	12.0	20.5	95.1	4.9

[a] Reaction conditions: H_2O_2 = 0.05 mol; catalyst = 20 mg; solvent, CH_3CN = 2 mL; reaction time = 6 h; reaction temperature 80 °C.

[b] H_2O_2 efficiency (%) = (moles of H_2O_2 utilized in products formation/moles of H_2O_2 added) × 100.

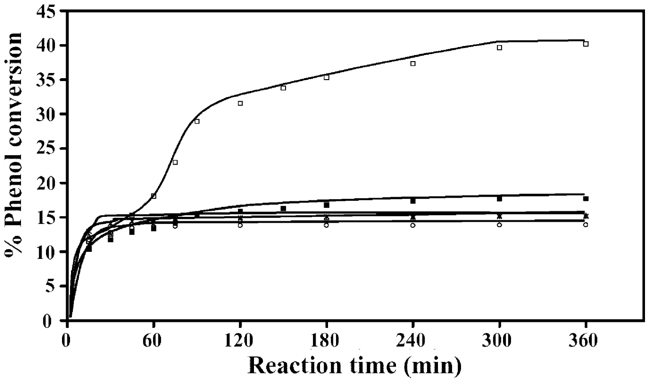


Fig. 6. Effect of type of solvent on the hydroxylation of phenol catalyzed by $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ complex: (□) 2 mL CH_3CN; (■) 2 mL ethyl acetate; (○) 2 mL H_2O; (●) 2 mL *n*-heptane; (△) without solvent.

Relatively low phenol conversion of 17.7 and 15.1% were observed in ethyl acetate and water respectively vis-à-vis that in acetonitrile of 40.2%. In the *n*-heptane, the lowest conversion (i.e. 13.9%) was observed possibly due to formation of a bilayer with phenol moving to organic *n*-heptane layer while the catalyst getting dissolved in the H_2O_2 causing the reaction to occur at the interface. The overall conversion efficiency in ethyl acetate and water are comparable but that in acetonitrile is markedly higher. It could be seen that acetonitrile is a better coordinating solvent than water or the ethyl acetate. Hence, it is likely that the catalyst $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ formed a five-coordinated complex with acetonitrile occupying one site while the phenoxide/oxo group the other site. Due to electron donor nature of the acetonitrile oxidation of phenol/phenoxide has been facilitated. From the Table 6, it is clear that nature of the solvent used affects the rate and the overall percent conversion but not the product selectivity. The phenol to dihydroxy benzene conversion decreases in the order $CH_3CN \gg EA \approx H_2O > n$-heptane.

Table 5
Effect of the nature of solvent on percent phenol conversion[a], product selectivity and H_2O_2 efficiency

Solvent	Phenol conversion (%)	H_2O_2 efficiency (%)[b]	TOF (h^{-1})	Product selectivity	
				Catechol	Hydroquinone
CH_3CN	40.2	34.4	80.7	89.6	10.4
CH_3COOEt	17.7	15.1	35.5	87.1	12.9
n-Heptane	13.9	11.9	27.9	84.1	15.9
H_2O	15.1	12.9	30.3	85.6	14.4
No solvent	15.3	13.1	30.4	92.9	7.1

[a] Reaction conditions: phenol = 0.05 mol; phenol/H_2O_2 molar ratio = 1; catalyst = 20 mg; solvent = 2 mL; reaction time = 6 h; reaction temperature 80 °C.

[b] H_2O_2 efficiency (%) = (moles of H_2O_2 utilized in products formation/moles of H_2O_2 added) × 100.

Table 6
Effect of reaction time on percentage phenol conversion[a] and product selectivity

Time (min)	Phenol conversion	Product selectivity (%)	
		Catechol	Hydroquinone
15	11.54	93.00	7.00
30	12.53	92.54	7.46
45	15.24	92.31	7.69
60	18.06	92.17	7.83
75	22.95	91.55	8.45
90	28.94	91.04	8.96
120	31.55	90.97	9.03
150	33.78	90.78	9.22
180	35.33	90.44	9.56
240	37.34	90.21	9.79
300	39.67	89.87	10.13
360	40.17	89.60	10.40
1440	42.08	86.11	13.89

[a] Reaction conditions: phenol = 0.05 mol; phenol/H_2O_2 molar ratio = 1; solvent, CH_3CN = 2 mL (0.04 mol); catalyst = 20 mg (0.04×10^{-3} mol); reaction temperature 80 °C.

3.7. *Effect of volume of solvent used*

In order to find out the optimum volume of the solvent, four different amounts of the best solvent, i.e. acetonitrile (1, 2, 5 and 10 mL) were taken while keeping other parameters constant and the results are shown in Fig. 7. It is clear that using 2 mL of acetonitrile gives maximum percentage phenol conversion. Upon increasing the solvent amount to 5 and 10 mL, the overall percent conversion dropped to less than 15%. Using less than 2 mL of acetonitrile, i.e. 1 mL the reaction mixture was inhomogeneous and also gave low performance. On the other hand, as reported earlier (Fig. 6) that carrying the reaction without using any solvent also show a low performance.

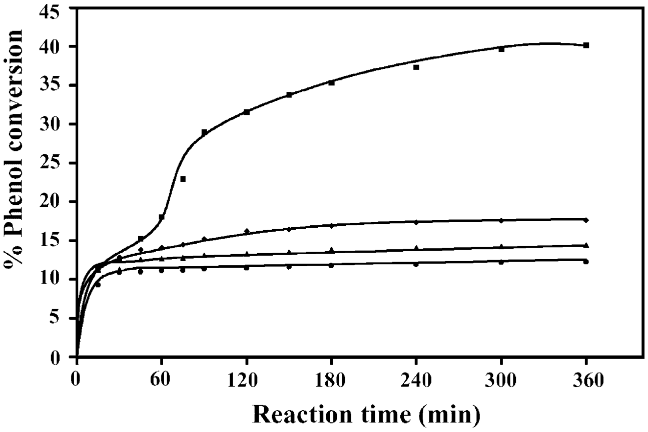


Fig. 7. Effect of solvent volume (CH_3CN) on the hydroxylation of phenol as a function of time in presence of $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ complex as catalyst: (◆) 1 mL; (■) 2 mL; (▲) 5 mL; (●) 10 mL.

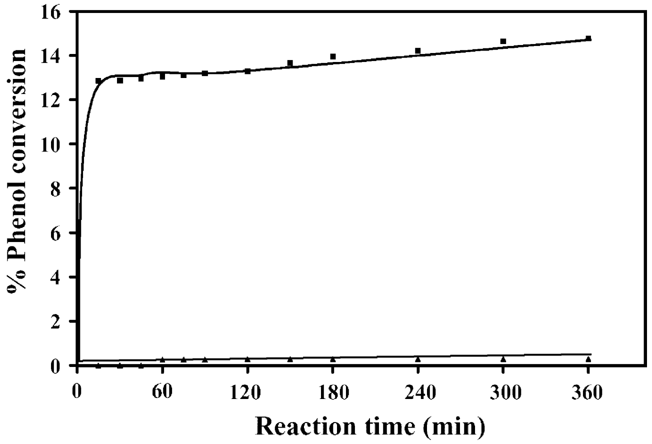


Fig. 8. Effect of reaction medium on the hydroxylation of phenol as a function of time in presence of [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 complex as catalyst: (■) 2 mL acetic acid; (▲) 2 mL of 25% aqueous ammonia.

3.8. Effect of the reaction medium

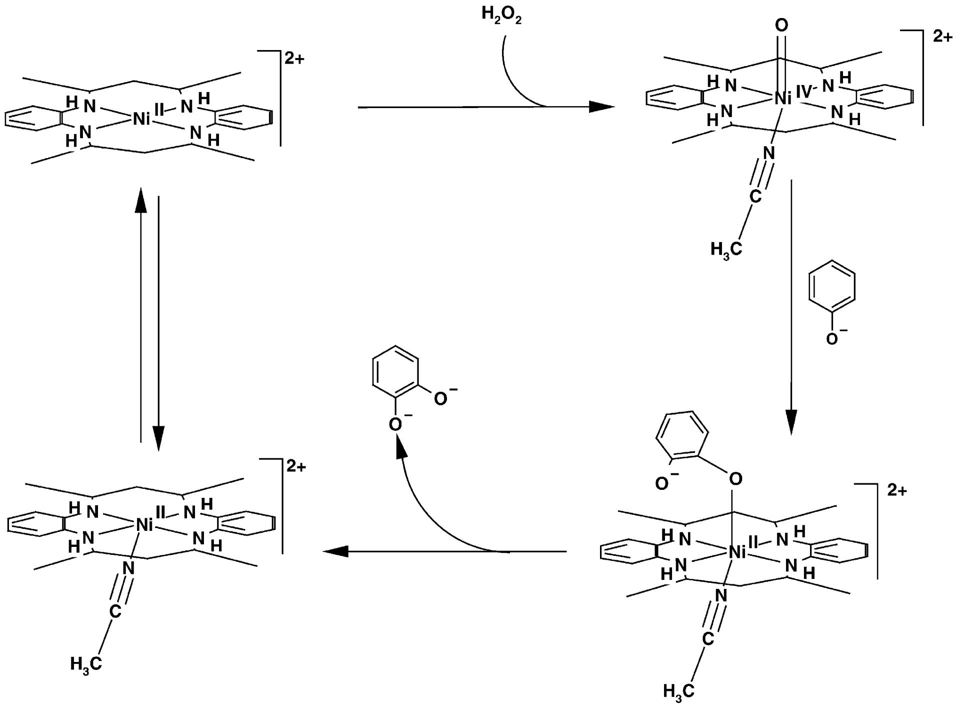
The hydroxylation of phenol was also studied in acidic and alkaline media in presence of 2 mL of either glacial acetic acid or 25% aqueous ammonia solution respectively (Fig. 8). It was found that the reaction was completely stopped in the alkaline medium. There could be two possible reasons for this. (i) catalyst getting poisoned due to blocking of the diaxial sites by the NH_3 coordination; and (ii) lowered oxidizing power of the H_2O_2 in the alkaline medium. In the acidic medium, hydroxylation reaction proceed unhindered like in presence of any other solvent except, acetonitrile where reaction rate was maximum. It was found that ca. 13% conversion was achieved within the first 15 min, with the maximum conversion reaching to 15% in 6 h in the acidic medium.

3.9. Effect of reaction time

The effect of time on the catalyzed hydroxylation of phenol by H_2O_2 in acetonitrile was studied in details and the results are given in Table 6. It was found that in general the overall percent phenol conversion increases with the increase in reaction time. There was a modest drop in the selectivity for the formation of catechol over hydroquinone when the reaction was allowed to proceed for longer time. In the beginning, the percentage of catechol formation was 93.0% but as conversion proceeded the formation of hydroquinone was also noticed. The oxidation proceeded rapidly during the first 3 h and reached to maximum of 40.6% conversion, in 6 h. Thereafter, only a very slow conversion was observed up to 24 h.

4. Conclusion

The results clearly suggest that [Ni{Me_4Bzo_2[14]ane-N_4}]Cl_2 efficiently catalyze conversion of phenol to catechol with ca. 90% selectivity over the formation of hydroquinone (Scheme 1). The overall conversion efficiency of 40% with high TOF value obtained in this study are significantly higher than that obtained using metallo-phthallocyanine encapsulated in zeolites [22,26,27].



Scheme 1. Proposed mechanism of [Ni{Me_4Bzo_2[14]aneN_4}]Cl_2 catalyzed hydroxylation of phenol by H_2O_2.

Also the $[Ni\{Me_4Bzo_2[14]aneN_4\}]Cl_2$ catalyzes selective formation of catechol (∼90%) over hydroquinone (<10%) with negligible formation of *p*-benzoquinone. As it was found that in presence of a small amount of acetonitrile, a moderately coordinating solvent, the highest catalytic conversion efficiency was obtained. Therefore, in conformity with the metallo-macrocycle catalyzed epoxidations [12,28,29] following mechanism could tentatively be assigned.

The acetonitrile possess higher coordinating power than water. Thus, its coordination with Ni^{2+} is likely to facilitate formation of axially coordinated oxo-acetonitrile complex. The role of oxo-intermediate has also been indicated in the nickel(II) cyclam catalyzed epoxidation of alkenes [12]. Mono acetonitrile coordination also serves another purpose of restricting the approach of the phenoxide anion towards the oxo-complex through oxo side only. Due to the orientation of the phenoxide dipole, the activated *ortho*-sites lie close to the complex and hence serve as the site of oxygen transfer. This could be the plausible reason that the *ortho*-hydroxylation is the predominant pathway in this catalysis. It is further supported from the fact that at higher acetonitrile concentrations, due to blockage of the both axial sites the catalysis is retarded. Similar is the case with ammonia, which is a very strong coordinating ligand. The catalysis proceeded well only in the moderately acidic medium. In strongly acidic medium, the protonation of phenoxide and in alkaline medium axial coordination by the two OH^- or ammonia molecules prevented the catalysis process.

The catalytic process reported here is interesting on two counts: (i) its simplicity; and (ii) the remarkable selectivity. The only by-product formed is the hydroquinone, i.e. in <10% yield. It may be of commercial interest as well.

References

[1] K. Takahashi, M. Uohama, T. Akiyama, European Patent Application EP 91-112421 19910724 (1992).
[2] S.W. Brown, British Patent Application 913323 (1991).
[3] M.A. Brook, L. Gastle, J.R.L. Smith, R. Higgins, K.P. Morris, J. Chem. Soc., Perkin Trans. 2 (1982) 687.
[4] L.Y. Litvintsv, Kinet. Catal. 34 (1993) 71.
[5] D.R.C. Hytbrechts, Catal. Lett. 8 (1991) 273.
[6] A.A. Danopoulos, S.M. Paraskevas, S. Savvogias, Erdoel Kohle Erdgas Petrochem. 47 (1994) 240 (Chemical Abstract no. 121:111886).
[7] W. Nam, R. Ho, J.S. Valentine, J. Am. Chem. Soc. 113 (1991) 7052.
[8] S. Taktak, A.M. Herrera, S.V. Kryatov,, E.V. Rybak-Akimova, in: Proceedings of the 226th ACS National Meeting, New York, NY, USA, 7–11 September 2003 (AN 2003:634404).
[9] L.T. Kist, M.J.F. Trujillo, B. Szpoganicz, M.A. Manez, M.G. Basallote, Polyhedron 16 (1997) 3827.
[10] Y.C. Park, S.S. Kim, H.G. Na, D.C. Lee, S.H. Shin, C.C. Byun, J. Korean Chem. Soc. 38 (1994) 295.
[11] C.J. Burrows, Inclusion Phenom. Mol. Recognit. (Proc. Int. Symp.) 5 (1990) 199.
[12] J.D. Koola, J.K. Kochi, Inorg. Chem. 26 (1987) 908.
[13] D. Lee, H. Bang, M.P. Suh, J. Mol. Catal. A: Chem. 151 (2000) 71.
[14] T.H. Bennur, S. Sabne, S.S. Deshpande, D. Srinivas, S. Sivasanker, J. Mol. Catal. A: Chem. 185 (2002) 71.
[15] J. Manriquez, J.L. Bravo, S.G. Granados, S.S. Succar, C.B. Charreton, A.A. Ordaz, F. Bedioui, Anal. Chim. Acta 378 (1999) 159.
[16] L.I. Simandi, Catal. Met. Complexes 26 (2003) 265.
[17] Y. Omura, M. Nakamura, M. Oka, Y. Fujiwara, Japanese Patent 74,127,937 (1999).
[18] Y. Misri, M. Hronee, Stud. Surf. Sci. Catal. 66 (1991) 455.
[19] R.A. Sheldon, J.K. Kochi, Metal Catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.
[20] M. Chibwe, L. Ukrainczyk, S.A. Boyd, T.J. Pinnavaia, J. Mol. Catal. A: Chem. 113 (1996) 249.
[21] S.S. Shevade, R. Raja, A.N. Kotasthane, Appl. Catal. A: Gen. 178 (1999) 243.
[22] S. Seelan, A.K. Sinha, Appl. Catal. A: Gen. 238 (2003) 201.
[23] R. Prasad, A. Kumar, Trans. Met. Chem. 26 (2001) 322.
[24] R. Prasad, A. Kumar, Electrochim. Acta, in press.
[25] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, fifth ed., Longman, UK, 1989, pp. 395–469.
[26] R. Raja, P. Ratnasamy, Appl. Catal. A: Gen. 143 (1996) 145.
[27] P.-S.E. Dai, R.H. Petty, C.W. Ingram, R. Szostak, Appl. Catal. A: Gen. 143 (1996) 101.
[28] V. Ramaswamy, M.S. Krishnan, A.V. Ramaswamy, J. Mol. Catal. A: Chem. 181 (2002) 81.
[29] L.I. Simándi, T.M. Simándi, Z. May, G. Besenyei, Coord. Chem. Rev. 245 (2003) 85.