Catalytic activity of the Schiff base complexes in some oxidation reactions

The oxidation of organic compounds is an important and widely used reaction in laboratory scale organic synthesis as well as in large scale. There are hundreds of different reagents and methods available for the oxidation of organic compounds. The selections of solvent, oxidant, reaction conditions such as temperature, pressure and number of reaction steps are crucial in affecting the speed of reaction and the type and qauntity of side-product produced. The Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability [1]. Important oxidation reactions include the transformation of alcohols to either the corresponding carbonyl compounds or carboxylic acids, the oxidation of sulfides to sulfoxides, alkenes to epoxides and diols, and the activation of hydrocarbons *etc*.

This chapter deals with the studies on the use of the Schiff base complexes as catalysts in the hydroxylation of phenol, oxidation of cyclohexane and oxidation

of benzyl alcohol and is divided into three sections. Section 7.1 deals with studies on the liquid phase hydroxylation of phenol. The section 7.2 presents the studies on the oxidation of cyclohexane and section 7.3 deals with the studies on catalytic activity of the copper(II) Schiff base complexes in the oxidation of benzyl alcohol.

7.1 SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE LIQUID PHASE CATALYTIC HYDROXYLATION OF PHENOL

7.1.1 Introduction

Liquid phase hydroxylation of phenol to catechol and hydroquinone using simple oxidants like O_2 and H_2O_2 is an important reaction. The oxidation of organic substrates with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle [2, 3]. Catechol and hydroquinone are two of the many phenolic derivatives of high value. They are widely used as photographic chemicals, antioxidants [4, 5], polymerization inhibitors, flavoring agents, and medicine [6, 7]. A number of novel estrane skeletons have been synthesized using catechol estrogens [8].
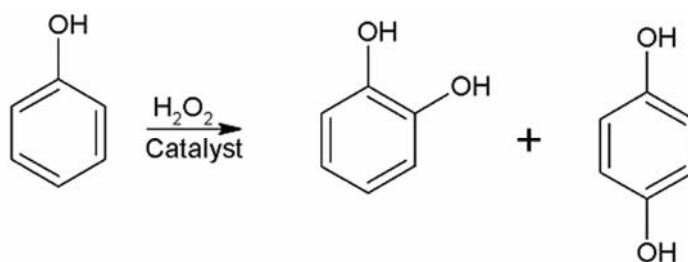
Scheme 7.1.1: *Catalytic hydroxylation of phenol to get Catechol and hydroquinone*

The catalytic hydroxylation of phenols in heterogenized systems has been reported in many cases [9-14]. Transition metal complexes containing nitrogen and phenolic oxygen donor atoms are of considerable interest in inorganic and biomimetic chemistry due to their potential application in catalysis, their biological relevance, and potentially interesting magnetic properties [15-20]. In the present study the phenol hydroxylation reaction was carried out using copper(II),

manganese(II), iron(III) and cobalt(II) complexes of ONN, ONO and ONS donor Schiff bases. Suitable reaction conditions have been optimized to give maximum hydroxylation.

7.1.2. Experimental

7.1.2.1. Materials and methods

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analyzed in a Chemito 8510 gas chromatograph with OV-17 column. Materials used in the catalytic activity studies are listed in chapter II.

7.1.2.2. Catalytic activity study

The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction, an aqueous solution of 30 % H_2O_2 (2.67 mL, 25 mmol) and phenol (2.2 mL, 25 mmol) were mixed in 10 mL of acetonitrile and the reaction mixture was heated at 343 K with continuous stirring in an oil bath. The complex (15 mmol) was added to the reaction mixture and the reaction was considered to be started at this time. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot. Quantification was done after considering the response factors of the reagents and products obtained using standard mixtures. The effects of various parameters such as concentration of the oxidant and catalyst, temperature and time of the reaction were studied to see their effect on the reaction product pattern.

7.1.3. Results and discussion

Liquid phase hydroxylation of phenol catalyzed by the Schiff base complexes using H_2O_2 as an oxidant was studied in CH_3CN. Although it is difficult to explain the effect of solvent and to identify the solvent parameters that are

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responsible for controlling the reaction rate, solvent plays a very significant role in controlling the overall % conversion. Abbob *et al.* [21] proposed that for phenol hydroxylation reaction, the solvent has a moderate influence on the ratio of Catechol to hydroquinone. In the current study acetonitrile was found to be the best solvent. As hydroxyl group present on phenol is ortho and para directing, the hydroxylation of phenol is expected to give two products *viz.* catechol and hydroquinone [22] as shown by scheme 7.1.1. Para benzoquinone is also likely to be formed due to the further oxidation of hydroquinone [23]. In the current study, formation of the benzoquinone is not observed or the percentage of benzoquinone formed may be below the detection limit.

7.1.3.1 Catalytic activity of the metal complexes towards phenol hydroxylation: Screening studies

The catalytic activities of the prepared Mn(II), Fe(III), Co(II) and Cu(II) complexes are screened for their activity towards phenol hydroxylation reaction. The results of these studies are given in Table 7.1.1. The reaction conditions employed are given in the experimental part. Almost all the complexes show good activity. The activities of these cobalt complexes are slightly lower than that of copper(II), iron(II) and manganese(II) analogues of the investigated Schiff bases. Similar observations were made by Wyk and co-workers [22, 24]. The major product of the reaction was found to be catechol in all cases [25]. The cobalt(II) complex of qamp is found to be inactive, which may be due to the coordinative saturation. In [Co(qamp)$_2$]H$_2$O two molecules of the Schiff bases are tightly bound the metal ion, so that it is unable to bind with the oxygen to form the intermediate. The complex, [Cu(qamp)Cl], was found to be the most active catalyst with ~16 % conversion.

Table 7.1.1: *Catalytic activity of the metal complexes towards phenol hydroxylation*

Catalyst	% C	% Products		% S (Cat)	Cat/HQ
		Cat	HQ		
[Cu(qamp)Cl]	16.10	14.48	1.62	89	8.9
[Cu(qlh)Cl]2H$_2$O	15.67	12.26	3.41	78	3.5
[Cu(hamp)(H$_2$O)]	7.90	7.45	0.45	94	16.5
[Cu(hatp)Cl]	5.52	4.65	0.87	84	5.3
[Mn(qamp)(OAc)]H$_2$O	11.70	10.30	1.40	88	7.3
[Mn(qlh)(OAc)]2H$_2$O	7.71	6.72	0.99	87	6.8
[Mn(hamp)(H$_2$O)]H$_2$O	10.48	9.41	1.07	89	8.8
[Mn(hatp)(OAc)(H$_2$O)$_2$]	4.28	3.90	0.38	91	10.2
[Fe(qamp)Cl$_2$]	9.29	7.95	1.34	86	5.9
[Fe(qlh)Cl$_2$ (H$_2$O)]H$_2$O	8.17	7.09	1.08	87	6.5
[Fe(hamp)Cl(H$_2$O)$_2$]	10.41	8.21	2.20	79	3.7
[Co(qlh)(OAc)]H$_2$O	4.76	4.31	0.45	91	9.6
[Co(hamp)(OAc)(H$_2$O)$_2$]H$_2$O	5.23	4.11	1.12	78	3.7
[Co(hatp)(H$_2$O)$_3$]H$_2$O	3.28	2.65	0.63	81	4.2
[Co(qamp)$_2$]H$_2$O	Negligible				

% C: percentage conversion, Cat: catechol, HQ: hydrquinone, % S: percentage selectivity

To acquire suitable reaction conditions for maximum transformation of phenol, [Cu(qamp)Cl] (the catalyst which showed highest activity during the screening studies) was studied in detail by varying the following reaction conditions: effect of the amount of catalyst, effect of temperature, effect of H$_2$O$_2$ concentration and effect of time.

7.1.3.2 Effect of reaction conditions on phenol hydroxylation of [Cu(qamp)Cl]

7.1.3.2.1. Effect of time

The appropriate reaction time is the main assurance for the perfect reaction. The catalytic hydroxylation of phenol, using H$_2$O$_2$ as oxidant was studied as a function of time. Too long a time appears to be unfavorable for phenol hydroxylation [26]. Table 7.1.2 shows that the fit reaction time is two hours. There

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was no significant change in the conversion and selective formation of catechol beyond three hours [20].

Table 7.1.2: *The influence of reaction time*

Time (hr)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
1	11.66	11.25	0.41
2	16.10	14.48	1.62
3	16.19	14.52	1.67
4	16.90	14.65	2.25
5	17.31	14.51	2.80

reaction temperature 343 K; catalyst 1.5 mmol; phenol:H_2O_2 (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.2. Effect of temperature

Table 7.1.3 presents the effect of reaction temperature on hydroxylation of phenol. Five different temperatures (303, 323, 333, 343 and 353 K) were considered, while keeping the other parameters same for the catalytic performance in 10 mL of CH_3CN. Below 343 K, conversion of phenol was very poor. At the same time above 343 K, decomposition of H_2O_2 gets accelerated which is not beneficial to phenol hydroxylation [24]. Thus, 343 K is the minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation.

Table 7.1.3: *The influence of temperature*

Temperature K	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
303	0	0	0
323	1.23	1.23	0
333	8.20	7.23	0.97
343	16.10	14.48	1.62
353	16.57	14.40	2.17

reaction time 2 h; catalyst 1.5 mmol; phenol:H_2O_2 (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.3. Effect of amount of catalyst

The reaction when carried out in the absence of catalyst did not yield any products. The effect of amount of catalyst on the rate of reaction is illustrated in table 7.1.4. Five different amounts (1, 3, 5, 7 and 9 mg) of the catalyst [Cu(qamp)Cl] were used for the fixed amount of phenol (2.2 mL, 25 mmol) and oxidant (2.67 ml, 25 mmol) in 10 mL CH_3CN. An amount of 10 to 20 mmol gave comparable results in both cases with *ca.* 14–16 % phenol conversion in 2 h of reaction time at 343 K. Lowering the amount of catalyst resulted in the poor conversion [11]. Thus, 1.5 mmol of catalyst was considered to be sufficient enough to give good performance. The conversion to products is not monotonic in its catalyst dependence. As expected for a homogeneous catalytic process, the conversion increases linearly with catalyst concentration over most of the available range of the variable, but eventually it decreases. Bush *et al.* [27] made similar observations. The decrease in conversion at high catalyst concentrations could arise from competitive formation of catalytically inactive dimeric μ-oxo- and/or μ-peroxo- bridged metal species. Such metal species are not active in catalyzing this reaction.

Table 7.1.4: *The influence of the amount of catalyst*

Catalyst weight, g (mmol)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
0.18 (0.5)	3.30	3.27	0.03
0.36 (1.0)	14.38	13.54	0.84
0.54 (1.5)	16.10	14.48	1.62
0.72 (2.0)	14.36	12.90	1.46
0.90 (2.5)	13.01	10.32	2.69

reaction time 2 h; reaction temperature 343 K; phenol:H_2O_2 (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.4. Effect of H₂O₂ concentration

Amount of H_2O_2 concentration has great influence on reaction rate. Table 7.1.5 presents the effect of H_2O_2 concentration on reaction rate. The influence of

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oxidant on reaction was monitored using five different amounts of aqueous 30 % H_2O_2 viz. 15, 20, 25, 30 and 35 mmol for a fixed amount of phenol (2.2 mL, 25 mmol) and catalyst (1.5 mmol) in 10 mL CH_3CN. The lowest H_2O_2 concentration results in only ca. 3 % phenol hydroxylation. Other two concentrations give comparable results. This information suggests that H_2O_2/phenol ratio of 1:1 is ideal for the maximum conversion as well as maximum efficiency. Thus, the larger concentration of oxidant is not an essential condition to maximize phenol conversion.

Table 7.1.5: *The influence of H_2O_2 concentration*

Hydrogen peroxide (mmol)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
15	3.27	3.27	0
20	7.57	7.44	0.13
25	16.10	14.48	1.62
30	13.37	11.81	1.56
35	15.00	13.17	1.83

reaction time 3 h; reaction temperature 343 K; catalyst 1.5 mmol; acetonitrile 10 mL

7.1.4 Conclusions

The catalytic activity of the prepared complexes was studied in the liquid-phase hydroxylation of phenol using H_2O_2 as an oxidant. Catechol and hydroquinone are the sole products of the reaction. The copper(II), manganese(II), iron(III) and cobalt(II) were screened for their activity towards the hydroxylation of phenol. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies was carried out by changing the different parameters like concentration of the oxidant and catalyst, reaction time, reaction temperature and the nature of solvent. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases or remains more or less the same.

7.2 SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE OXIDATION OF CYCLOHEXANE

7.2.1. Introduction

The natural oil and gas constituents contain a large amount of hydrocarbons. The functionalization of hydrocarbons has been identified as a key research strategy for the development of economical and sustainable global carbon management. Undoubtedly one of the most important functionalizations is selective oxidation. It is already known to oxidise aliphatic or cycloaliphatic compounds in the liquid phase using oxygen or hydrogen peroxide to corresponding alcohols and/or ketones. The chemical inertness of hydrocarbon makes the activation of C-H bonds really difficult, usually requiring drastic conditions, such as high temperature and pressure [28]. The selective oxidation of cyclohexane to cyclohexanone or cyclohexanol is of great industrial importance [29]. Over one billion tonnes of cyclohexanol and cyclohexanone are produced each year worldwide, which are mostly used in the manufacture of the polymers Nylon-6 and Nylon-6,6 [30, 31]. In the industrial process the cyclohexane is first oxidised to cyclohexanol and cyclohexanone using cobalt based homogeneous catalyst (4% conversion and 70-80 % selectivity towards cyclohexanol) and from the products, the adipic acid or ε-caprolactone is obtained [32]. High temperature and pressure (423–433 K and 0.9 MPa) are required to form cyclohexanol and cyclohexanone [33]. The subsequent oxidation to adipic acid uses nitric acid as oxidant which is a very unfriendly reagent [34]. As early as 1876, Fenton has found that iron(II) salts in an acidic aqueous solution using hydrogen peroxide as oxidant is capable of oxidising alkanes. Many mechanisms have been proposed for this reaction, mostly those involving OH˙ or OOH˙ and other involves reactive high valent metal ion species [35-37].

Cyclohexane oxidation is an interesting reaction in the past decades. In 1993, Schuchardt *et al.* published a review article entitled "Why is it interesting to study cyclohexane oxidation" [38]. In the review they presented new ideas on how

to improve the industrial cyclohexane oxidation reaction. In continuation of the previous review in 2001, they published another review article on "the cyclohexane oxidation continues to be a challenge" [30]. The review point towards the development of new catalysts to oxidise cyclohexane under mild conditions. The usage of metal complexes as catalyst for activation of hydrocarbons was initially developed with metalloporphyrins and later on applied on Schiff base complexes [39-42]. Groves *et al.* [43] did pioneering work towards utilisation of metalloporphyrins as the catalyst for cyclohexane oxidation. Cyclohexane oxidation using Schiff base complexes is an interesting area of research nowadays [44-47].

In the present study we have carried out the oxidation of cyclohexane using the oxidant hydrogen peroxide. The catalysts used are copper(II), iron(III) and manganese(II) complexes derived from the Schiff bases qamp, hatp, hamp and qlh.

7.2.2. Experimental

7.2.2.1 Materials and methods

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analyzed in a Chemito 8510 gas chromatograph with carbowax column. The adipic acid was determined by titration with sodium hydroxide. Materials used in the catalytic activity studies are listed in chapter II.
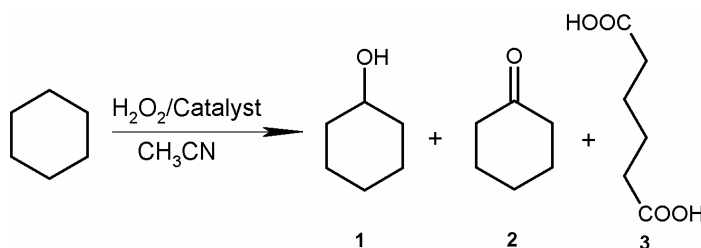
7.2.2.2 Catalytic activity study: oxidation of cyclohexane

The cyclohexane oxidation was carried out by the published procedure [48]. The reactions were carried out in acetonitrile as solvent, using hydrogen peroxide as the oxidant, and the copper(II), iron(III) or manganese(II) complexes as the catalysts. In a typical reaction, an aqueous solution of 30% H_2O_2 (1.06 mL, 10 mmol) and cyclohexane (1.08 mL, 10 mmol) were mixed in 5 mL of acetonitrile and the reaction mixture was heated at 343 K with continuous stirring in an oil

bath. The complex (0.010 mmol) was added to the reaction mixture and the reaction was considered to be started at this time. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot. Assignments of products were made by comparison with authentic samples. The effects of various parameters such as concentration of oxidant and catalyst, temperature and time of the reaction were studied in order to see their effect on the reaction product pattern.

7.2.3. Results and discussion

Oxidation of cyclohexane catalyzed by Schiff base complexes using H_2O_2 as the oxidant was studied in CH_3CN. To choose the best solvent, the oxidation reactions were carried out in common solvents under the same conditions. The results indicate that acetonitrile provided the best oxidation medium for higher substrate conversion and selectivity of cyclohexanol. It is interesting to note that acetonitrile was successfully used for many oxidation reactions [49-52]. Furthermore, the volatility of acetonitrile is lower than that of other solvents under open-wide system, so the utilization factor of acetonitrile is more here than that of other solvents. Therefore a lower environmental contamination is expected in such cases and acetonitrile is a suitable solvent for the oxidation of cyclohexane. The products obtained for the oxidation reaction are cyclohexanol, cyclohexanone and adipic acid as shown by scheme 7.2.1.

Scheme 7.2.1: *Oxidation of cyclohexane to cyclohexanol (1), cyclohexanone (2) and adipic acid (3).*

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7.2.3.1 Catalytic activity of the metal complexes towards cyclohexane oxidation: Screening studies

The catalytic activities of the prepared Mn(II), Fe(III) and Cu(II) complexes are screened for their activity towards cyclohexane oxidation reaction. The results of these studies are given in table 7.2.1. The reaction conditions employed are given in section 7.2.2.2. Almost all the complexes show good activity. The major product of the reaction was found to be cyclohexanol. Other products are cyclohexanone and adipic acid. Adipic acid formed was determined titrimetrically at the end of the reaction [48]. These products are of special interest in the nylon manufacture as well as the building blocks for a variety of commercially useful products. The copper(II) and iron(III) complexes are found to be more active compared to manganese(II) complexes. [Cu(qamp)Cl] and [Fe(qlh)Cl$_2$H$_2$O]H$_2$O are found to be the most active catalysts with ~30 % conversion. Both of the catalysts show good selectivity towards cyclohexanol (around 70 %). Control reactions were carried out in the absence of the catalysts and no oxidation products were observed.

Table 7.2.1: *Catalytic activity of the metal complexes towards cyclohexane oxidation*

Catalyst	% C	% Products			% S (C-nol)
		C-nol	C-one	AA	
[Cu(qamp)Cl]	30.94	22.17	6.56	2.21	72
[Cu(qlh)Cl]. 2H$_2$O	27.29	16.81	8.58	1.90	62
[Cu(hamp)(H$_2$O)]	15.00	12.05	1.72	1.23	80
[Cu(hatp)Cl]	11.36	6.92	3.43	1.11	61
[Mn(qamp)(OAc)].H$_2$O	7.12	3.02	2.11	1.89	42
[Mn(qlh)(OAc)]. 2H$_2$O	7.42	3.21	2.89	1.32	43
[Mn(hamp)(H$_2$O)].H$_2$O	3.28	1.80	1.03	0.45	55
[Mn(hatp)(OAc)(H$_2$O)$_2$]	4.88	2.10	2.50	0.28	43
[Fe(qamp)Cl$_2$]	18.37	10.70	6.46	1.21	58
[Fe(qlh)Cl$_2$(H$_2$O)]. H$_2$O	30.12	20.68	6.99	2.45	69
[Fe(hamp)Cl(H$_2$O)$_2$]	29.99	16.33	11.99	1.67	54

% C: percentage conversion, C-nol: cyclohexanol, C-one: cyclohexanone, AA: adipic acid, % S: percentage selectivity

In order to acquire suitable reaction conditions for maximum transformation of cyclohexane, [Cu(qamp)Cl] (the catalyst which showed highest activity during the screening studies) was studied in detail by varying the following reaction conditions: effect of the amount of catalyst, effect of temperature, effect of H_2O_2 concentration and effect of time.

7.2.3.2 Effect of reaction conditions on cyclohexane oxidation of [Cu(qamp)Cl]

The catalytic activity was investigated using various reaction conditions of temperature, amount of catalyst, time, oxidant to substrate ratio etc. in order to find out the optimum conditions for the oxidation reaction.

7.2.3.2.1. Effect of variation of time

The dependence of activity of [Cu(qamp)Cl] in phenol hydroxylation on the reaction time is displayed in Table 7.2.2. It is observed that cyclohexane oxidation was affected by reaction time and the conversion increases with time [43]. The cyclohexane conversion and the selectivity towards cyclohexanol were found to be enhanced with the increase of the contact time, and the reaction acquires steady state after 3 h.

Table 7.2.2: *The influence of reaction time*

Time (hrs)	% C	% C-one	% C-nol	% AA
1	16.14	2.70	12.23	1.21
2	27.53	5.90	20.18	1.45
3	30.94	6.56	22.17	2.21
4	32.31	6.55	23.54	2.22
5	32.55	6.97	23.05	2.53

catalyst: 0.01 mmol, H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K.

7.2.3.2.2. Effect of temperature

Table 7.2.3 presents the effect of reaction temperature on oxidation of cyclohexane. Four different temperatures (303, 323, 343 and 363 K) were considered, while keeping other parameters same as mentioned above. The catalyst employed is found to be active even at room temperature. But the conversion rate was very poor. As temperature increased, the conversion was found to increases [54]. The optimum temperature for carrying out the reaction is 343 K. There is a slight decrease in conversion above 343 K, which may be due to the accelerated decomposition of hydrogen peroxide [55]. So, 343 K is selected as the optimum temperature for carrying out cyclohexane oxidation reaction.

Table 7.2.3: *The influence of reaction temperature.*

Temperature (K)	% C	% C-one	% C-nol	% AA
303	7.82	1.87	4.33	1.62
323	20.15	2.93	15.18	2.04
343	30.94	6.56	22.17	2.21
363	28.97	4.00	22.73	2.24

catalyst: 0.01 mmol, H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, time: 3 h

7.2.3.2.3. Effect of amount of catalyst

The reaction when carried out in the absence of catalyst did not yield any products. The effect of amount of catalyst on the rate of reaction is illustrated in table 7.2.4. Five different amounts of the catalyst [Cu(qamp)Cl] were used without changing the other reaction parameters. On increasing the catalyst amount, the degree of conversion increased for all complexes as expected [56]. Thus, 0.01 mmol of catalyst was considered to be sufficient enough to give good performance. It is observed that at higher catalyst concentration there is a slight decrease in % conversion. Koda *et al.* [57] reported similar observations in the aerobic oxidation of cyclohexane catalyzed by {5,10,15,20-tetrabis (pentafluorophenyl) porphyrinato}

iron(III) chloride. The decrease in conversion and selectivity may be due to the formation of metal-oxo species [27, 58].

Table 7.2.4: *The influence of the amount of catalyst.*

Catalyst weight, mg (mmol)	% C	% C-one	% C-nol	% AA
0.45 (0.001)	4.57	1.8	2.45	0.32
1.8 (0.005)	13.77	2.9	9.43	1.44
3.6 (0.01)	30.94	4.56	20.17	2.21
5.4 (0.015)	32.11	6.57	21.65	3.89
7.2 (0.02)	31.56	7.95	19.89	3.72

H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K, time: 3 h

7.2.3.2.4. Effect of H_2O_2 concentration

The effect of hydrogen peroxide concentration on the rate of reaction was studied by keeping the other parameters constant. These studies indicate that the conversion increases with increase in the volume of hydrogen peroxide. But the higher concentration of hydrogen peroxide will lead to the higher yield of adipic acid, which is formed as an over oxidation product [59].

Table 7.2.5: *The influence of H_2O_2 concentration.*

H_2O_2 (mmol)	% C	% C-one	% C-nol	% AA
5	4.98	1.02	3.28	0.68
10	30.94	6.56	22.17	2.21
15	31.50	6.87	22.09	2.54
20	33.00	6.98	23.29	2.73
25	34.28	6.41	23.70	4.17

catalyst: 15 mmol, time: 3 h, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K

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7.2.4 Conclusions

The catalytic activity of the prepared complexes was studied in the cyclohexane oxidation using H_2O_2 as an oxidant. Cyclohexanol, cyclohexanone and adipic acxid are the products. The selectivity was found to be greater for cyclohexanol. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies was carried out by changing the different parameters like reaction time, reaction temperature, concentration of the oxidant and catalyst. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases. Increase in the amount of H_2O_2 has a positive effect on the reaction.

7.3 COPPER(II) SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE OXIDATION OF BENZYL ALCOHOL

7.3.1 Introduction

The oxidation of organic substrates is an important reaction in organic synthesis. Among them oxidation of benzyl alcohol to benzaldehyde is an industrially important reaction. Chlorine free benzaldehyde is a versatile chemical intermediate widely used in the manufacture of pharmaceuticals, perfume and flavouring chemicals [60]. Several research groups have developed different catalytic methods for oxidation of benzyl alcohol to benzaldehyde. Among the various methods, transition metal Schiff base complex catalysed oxidation is worth mentioning [61]. The oxidation of methoxy substituted benzyl alcohol especially veratryl alcohol which is a typical model compound for non lignin monomer and the enzyme lignin peroxidase has been studied [62-64]. Ruthenium(III) complexes of the monobasic tridentate ligand, formed by the condensation of o-phenylenediamine or ethylenediamine with salicylaldehyde or o-hydroxyacetophenone is found to catalyse the benzyl alcohol oxidation [65]. Solvent-free reactions are of general interest because of their potential in

combinational chemistry, simple processes, easy work-up, low cost and reduction in noxious waste materials [66]. However, only a limited number of such useful oxidation procedures have been reported [67-69].

Considering the important role of copper in enzymatic oxidations, it is hardly surprising that copper is frequently used in oxidation reactions in everyday laboratory practice. The Wacker Process, which uses a catalyst containing palladium and copper chlorides, is used for converting alkenes into alcohols and is a good example of an industrially important large scale oxidation reaction [70]. This chapter discusses the oxidation of benzyl alcohol to benzaldehyde, using small amount of copper(II) complexes in combination with hydrogen peroxide.

7.3.2. Experimental

7.3.2.1. Materials

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analysed in a Chemito 8510 gas chromatograph with OV-17 column. Materials used in the catalytic activity studies are listed in chapter II.

7.3.2.2. Catalytic activity study

The catalytic activity study towards the oxidation of benzyl alcohol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction, benzyl alcohol (3.11 mL, 30 mmol) and 30% H_2O_2 (4.8 mL, 45 mmol) were mixed and the reaction mixture was heated in an oil bath with continuous stirring at 343 K. An appropriate amount of catalyst (30 mmol) was added to the hot mixture and the reaction was continued. The progress of the reaction was determined by analyzing the reaction mixture using a gas chromatograph by withdrawing small aliquots of the reaction mixture at specific interval of time.

7.3.3. Results and discussion

Solvent free catalytic oxidation of benzyl alcohol was studied using hydrogen peroxide as the oxidant and copper(II) complexes as the catalysts. Generally benzyl alcohol oxidation gives benzaldehyde, benzoic acid and benzyl benzoate. We haven't detected any benzyl benzoate. The reaction was highly selective towards benzaldehyde. Slight amount of benzoic acid is also formed.

7.3.3.1 Catalytic activity of the metal complexes towards benzyl alcohol oxidation: Screening studies

The catalytic activities of the prepared Cu(II) complexes are screened for their activity towards benzyl alcohol oxidation reaction. The results of these studies are given in table 7.3.1. The reaction conditions employed are: time of 4 hours, temperature 343 K, substrate:catalyst:oxidant is 2:2:3. All the complexes show good activity. The major product of the reaction was found to be benzaldehyde. [Cu(qlh)Cl]2H$_2$O is found to be the most active catalysts with ~38 % conversion and very good selectivity towards benzaldehyde. In the absence of catalyst, no significant amount of benzaldehyde was produced indicating that hydrogen peroxide alone is unable to oxidise benzyl alcohol to benzaldehyde. In the endeavor to a greener benzyl alcohol oxidation the solvent-free reaction is more exciting [71]. In some cases, solvent-free reactions proceed efficiently [72, 73].

Table 7.3.1: *Catalytic activity of the metal complexes towards cyclohexane oxidation*

Catalyst	% C	% Products			% S (BAl)
		BAl	BAc	BB	
[Cu(qamp)Cl]	35.75	32.30	3.45	nd	90
[Cu(qlh)Cl]2H$_2$O	38.50	36.88	1.62	nd	96
[Cu(hamp)(H$_2$O)]	27.89	24.02	3.87	nd	86
[Cu(hatp)Cl]	13.66	12.45	1.21	nd	91

% C: percentage conversion, Bal: benzaldehyde, BAc: benzoic acid, BB: benzyl benzoate, % S: percentage selectivity

7.3.3.2 Effect of reaction conditions on benzyl alcohol oxidation of [Cu(qlh)Cl]2H₂O

The catalytic activity was investigated using various reaction conditions of temperature, amount of catalyst, time, oxidant to substrate ratio etc. in order to find out the optimum conditions for the oxidation reaction.

7.3.3.2.1. Effect of variation of time

The time dependence of catalytic solvent free oxidation of benzyl alcohol was studied by performing the reaction of benzyl alcohol (3.11 mL, 30 mmol) with 30% H_2O_2 (4.8 mL, 45 mmol) in the presence of 30 mmol of catalyst at 343 K with constant stirring. The percentage of conversion was monitored at different reaction times. The conversion was found to increase with time. It was seen that 38.50% conversion was observed at 4 h. When the reaction was allowed to continue for 12 h, 52 % conversion was observed.

Table 7.3.2: *The influence of reaction time*

Time (hrs)	% C	% BAl	% BAc
1	16.53	15.78	0.75
2	21.10	20.02	1.08
3	27.96	26.53	1.43
4	38.50	36.88	1.62
12	52.00	45.20	6.80

catalyst: 30 mmol, H_2O_2: 4.8 mL, benzyl alcohol: 3.11 mL, temperature: 343 K.

7.3.3.2.2. Effect of temperature

The effect of temperature on the oxidation of benzyl alcohol using [Cu(qlh)Cl].2H₂O as catalyst was investigated at four different temperatures viz. 303, 323, 343 and 363 K, keeping the other parameters fixed: namely benzyl alcohol (3.11 mL, 30 mmol), 30% H_2O_2 (4.80 mL, 45 mmol), catalyst (30 mmol)

and reaction time (4 h). The results are shown in table 7.3.3, which reveals that 5.76, 17.19, 38.50 and 41.86 % conversion were found corresponding to 303, 323, 343 and 363 K respectively. On increasing the temperature from 343 to 363 K, only very little improvement in conversion was observed, so that a temperature of 343 K was considered to be optimum [74].

Table 7.3.3: *The influence of reaction temperature.*

Temperature (K)	% C	% BAl	% BAc
303	5.76	5.76	0
323	17.19	16.81	0.38
343	38.50	36.88	1.62
363	38.86	37.05	1.81

catalyst: 30 mmol, H_2O_2: 4.8 mL, benzyl alcohol: 3.11 mL, time: 4 hrs.

7.3.3.2.3. Effect of amount of catalyst

The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. Four different amounts of catalyst viz., 10, 20, 30 and 40 mmol were used, keeping all the other reaction parameters fixed: namely benzyl alcohol (3.11 mL, 30 mmol), 30% H_2O_2 (4.80 mL, 45 mmol), temperature 343 K and reaction time (4 h). The results obtained are given in table 7.3.4, indicating 17.68, 31.97, 38.50 and 40.10 % conversion corresponding to 10, 20, 30 and 40 mmol catalyst respectively.

Table 7.3.4: *The influence of the amount of catalyst*

Catalyst weight (mmol)	% C	% BAl	% BAc
10	17.68	17.27	0.41
20	31.97	30.64	1.33
30	38.50	36.88	1.62
40	40.10	37.89	2.21

temperature: 343 K, H_2O_2: 4.8 mL, benzyl alcohol: 3.11 mL, time: 4 hrs.

7.3.3.2.4. Effect of H₂O₂ concentration

To determine the effect of H_2O_2 on the oxidation of benzyl alcohol to benzaldehyde, we have used four different benzyl alcohol: H_2O_2 molar ratios (2:1, 1:1, 1:1.5 and 1:2) keeping other parameter fixed: namely benzyl alcohol (3.11 mL, 30 mmol), catalyst (30 mmol), temperature 343 K and reaction time (4 h). The results are shown in table 7.3.5. A benzyl alcohol to H_2O_2 molar ratio of 2:1 and 1:1 resulted in 19.53 and 26.44 % conversion, and when benzyl alcohol to H_2O_2 molar ratio was changed to 1:1.5, conversion increased to be nearly 38.50%, keeping all other conditions similar. However, conversion was found to be almost the same at 39.19% when the benzyl alcohol to H_2O_2 molar ratio was further changed to 1:2.

Table 7.3.5: *The influence of H₂O₂ concentration.*

H₂O₂ (ml)	% C	% BAl	% BAc
1.60	19.53	19.01	0.52
3.20	26.44	25.51	0.93
4.80	38.50	36.88	1.62
6.40	39.19	37.42	1.77

catalyst: 30 mmol, benzyl alcohol: 3.11 mL, time: 4 hrs, temperature: 343 K.

7.3.4 Conclusions

The catalytic activity of the prepared complexes was studied in the benzyl alcohol oxidation using H_2O_2 as an oxidant. The products obtained are benzaldehyde and benzoic acid. The selectivity was found to be greater for benzaldehyde. The copper(II) complexes of hatp, hamp, qamp and qlh were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, [Cu(qlh)Cl]2H₂O, that gave maximum conversion in the screening studies, was carried out by changing the different parameters like catalyst amount, reaction time, reaction temperature and amount of oxidant. At optimum

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conditions [Cu(qlh)Cl]2H$_2$O gives very good selectivity (96 %) towards benzaldehyde.

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