

Hydroxylation of phenol with hydrogen peroxide catalysed by copper(II) complexes

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7.1 Introduction

Catalytic hydroxylation of phenol to catechol and hydroquinone using environmentally friendly oxidants such as dioxygen, hydrogen peroxide and alkyl hydroperoxide is an active area of research, especially in the fine chemicals industry [1,2]. Among these oxidants, hydrogen peroxide is easy to handle and ecofriendly as it produces only water as the by-product [3]. Over the past few decades, numerous reports have appeared on the hydroxylation of phenol with hydrogen peroxide as oxidant [4-13].

Schiff base transition metal complexes have been extensively studied because of their potential as catalysts in a wide range of reactions [7, 11, 14-15]. However, not all complexes are catalytically active. The formation of octahedral complexes with no vacant coordination sites or absence of labile ligands could be a possible reason. In this study, of the five copper(II) complexes synthesised from the bulky Schiff base ligands, four were found to have square planar geometry while one had an octahedral geometry with two coordinated water molecules. This favourable geometry could render the complexes catalytically active and hence we have made an attempt to study the efficiency of these mononuclear and binuclear copper(II) complexes towards the hydroxylation of phenol with H_2O_2 as an oxidant

7.2 Experimental

7.2.1 Materials

The materials used for the preparation Schiff base ligands, their copper complexes and their catalytic hydroxylation of phenol are presented in [Chapter 2](#).

7.2.2 Methods

The synthesis of Schiff base ligands and their copper(II) complexes are given in [Chapters 2 and 4](#).

7.2.3 Catalytic activity measurements

Hydroxylation of phenol was carried out in a two-necked glass reactor (50 ml) fitted with a condenser and a septum. Hydrogen peroxide (30% w/v) was added through the septum to the magnetically stirred solution of phenol containing catalyst and solvent (30 ml acetonitrile) kept at the desired reaction temperature. The reaction mixture was refluxed with continuous stirring in an oil bath provided with a digital temperature controller. The progress of the reaction was monitored by periodically withdrawing small samples (about 0.5 mL each) which were analyzed by using a gas chromatograph. Quantification was done after considering the response factors of the reagents and products obtained using standard mixtures.

7.3 Results and discussion

Details of the spectral characterisation of the Schiff base ligands and their copper(II) complexes are given in [Chapters 2 and 4](#) respectively.

7.3.2 Catalytic activity towards the hydroxylation of phenol

The liquid-phase catalytic hydroxylation of phenol generally gives two major products, catechol and hydroquinone. These are the expected products, as the –OH group on phenol is ortho and para directing. Sometimes *p*-benzoquinone is also observed as a minor product due to further oxidation of hydroquinone [16]. In the

case of the present complex, only catechol and hydroquinone are observed. The conversion and selectivity were calculated using the following relations [17].

$$X_{\text{phenol}} (\%) = 100 \times ([\text{phenol}]_i - [\text{phenol}]_f) / [\text{phenol}]_i,$$

where X_{phenol} is the conversion of phenol, $[\text{phenol}]_i$ is the molar concentration of phenol before reaction, and $[\text{phenol}]_f$ is the molar concentration of phenol after sampling.

$$S_{\text{phenol}} (\%) = 100 \times ([\text{CAT}]_f + [\text{HQ}]_f) / ([\text{phenol}]_i - [\text{phenol}]_f),$$

where S_{phenol} is the selectivity for phenol hydroxylation, and $[\text{CAT}]_f$ and $[\text{HQ}]_f$ are the molar concentration of catechol and hydroquinone, respectively, after the reaction.

$$\text{Product distribution (\%)} = 100 \times [\text{product}]_f / ([\text{phenol}]_i - [\text{phenol}]_f),$$

where $[\text{product}]_f$ is the molar concentration of product (catechol or hydroquinone) after reaction.

$$\text{H}_2\text{O}_{2\text{eff}} (\%) = 100 \times ([\text{CAT}]_f + [\text{HQ}]_f) / [\text{H}_2\text{O}_2]_{\text{add}},$$

where $\text{H}_2\text{O}_{2\text{eff}}$ is the effective conversion of H_2O_2 , and $[\text{H}_2\text{O}_2]_{\text{add}}$ is the molar concentration of the total added H_2O_2 in the reaction mixture.

A comparison of the activity of the different copper(II) complexes towards the hydroxylation of phenol showed $[\text{Cu}_2(\text{hqcdmn})\text{Cl}_2]$ to be the most active. So a detailed investigation aimed at studying the influence of various parameters was carried out. A turnover frequency (mol of phenol converted per mol of catalyst per hour) of 460 h^{-1} has been found for the reaction using this complex as catalyst at 80°C with 0.81×10^{-5} mol catalyst, 2.28×10^{-2} mol phenol and 18.70×10^{-3} mol H_2O_2 .

Table 1: Catalytic activity and selectivity of copper(II) complexes in the hydroxylation of phenol ^a

Complex (5 mg)	X _{phenol} (%)	S _{phenol} (%)	Product distribution (%) ^b		H ₂ O ₂ eff (%)	TOF
			CAT	HQ		
I	61.0	8.0	7.5	3.2	10.7	616
II	61.9	8.9	8.2	3.5	11.8	629
III	61.3	8.3	8.2	2.8	11.1	603
IV	61.4	8.3	7.3	3.9	11.2	627
V	61.6	8.5	7.4	4.0	11.4	483

^a Reaction conditions: acetonitrile (5 ml), temperature (80 °C), time (2 h), H₂O₂ (18.70 × 10⁻³ mol), phenol (2.28 × 10⁻² mol).

^b CAT = catechol, HQ = hydroquinone. The expected other products such as benzoquinone and tar is not formed. TOF = mol of phenol converted per mol of catalyst per hour. Here I, II, III, IV and V are [Cu₂(hqcdan)Cl₂].H₂O, [Cu₂(hqcdmn)Cl₂], [Cu₂(hqcdac)Cl₂].H₂O, [Cu₂(hqcap)₂] and [Cu(hqcaap)Cl(H₂O)₂] respectively.

7.3.2.1 Influence of the catalyst

The reaction when carried out in the absence of catalyst did not yield any products. The effect of varying the catalyst on the hydroxylation of phenol was studied at 80 °C by varying the amount of catalyst from 0.81 × 10⁻⁵ mol to 12.15 × 10⁻⁵ mol keeping the amount of solvent, oxidant and substrate constant and the results of which are given in Table 2. Percentage phenol conversion and H₂O₂ efficiency increased to a maximum with 1.62 × 10⁻⁵ mol of catalyst and then decreased with further increase in the amount of catalyst. This as explained earlier might be due to the decomposition of H₂O₂ with large amount of catalyst [9]. A similar trend was observed in the selectivity and product distribution.

Table 2: Effect of [Cu₂(hqcdmn)Cl₂] in the catalytic activity and selectivity of phenol hydroxylation ^a

Catalyst (10 ⁻⁵ mol)	X _{phenol} (%)	S _{phenol} (%)	Product distribution (%) ^b		H ₂ O ₂ eff (%)
			CAT	HQ	
0.81	58.4	7.4	6.9	0.4	5.2
1.62	60.7	10.3	7.9	2.3	7.6
2.43	59.4	8.7	6.8	2.0	6.3
3.25	59.2	8.4	6.5	1.9	6.1
12.15	58.7	7.7	6.0	1.8	5.5

^a Reaction conditions: acetonitrile (10 ml), temperature (80 °C), time (2 h), H₂O₂ (18.70 × 10⁻³ mol), phenol (2.28 × 10⁻² mol).

^b CAT = catechol, HQ = hydroquinone. The expected other products such as benzoquinone and tar is not formed.

7.3.2.2 Influence of the oxidant H₂O₂

The mode of addition of H₂O₂ to the reaction mixture is very important in the hydroxylation of phenol [5]. In the present case, H₂O₂ was added in one-lot at reaction temperature of 80 °C. With increase in the amount of the oxidant, H₂O₂, percentage phenol conversion, selectivity for phenol hydroxylation and percentage product distribution increases (Table 3). The H₂O₂ efficiency reaches a maximum at 14.03×10^{-3} mol of H₂O₂.

Table 3: Effect of 30 % H₂O₂ in the catalytic activity and selectivity of phenol hydroxylation ^a

H ₂ O ₂ (10 ⁻³ mol)	X _{phenol} (%)	S _{phenol} (%)	Product distribution (%)		H ₂ O ₂ eff (%)
			CAT	HQ	
9.35	57.3	5.9	5.4	0.5	8.2
14.03	60.9	10.5	7.8	2.7	10.4
18.70	61.9	11.8	8.2	3.5	8.9
23.36	63.4	13.5	9.1	4.4	8.3
28.05	65.4	15.7	10.3	5.4	8.3

^a Catalyst 0.81×10^{-5} mol, acetonitrile 5 ml and other reaction conditions are the same as those in Table 2.

7.3.2.3 Influence of solvent

It has been reported that solvents have a profound influence on the phenol conversion and on the ratio of catechol to hydroquinone [18]. To study the effect of solvent we carried out the hydroxylation in acetonitrile. An increase of the amount of acetonitrile from 0 to 30 ml decreases the percentage phenol conversion, selectivity for phenol hydroxylation, percentage product distribution and H₂O₂ efficiency (Table 4). It was further observed that the complex gives maximum conversion and selectivity without the solvent and hence the use of different solvents has no significance.

Table 4: Effect of the solvent in the catalytic activity and selectivity of phenol hydroxylation ^a

Acetonitrile (ml)	X _{phenol} (%)	S _{phenol} (%)	Product distribution (%)		H ₂ O ₂ eff (%)
			CAT	HQ	
0	68.7	19.0	11.9	7.2	15.9
5	61.9	11.8	8.2	3.5	8.9
10	58.4	7.4	7.0	0.4	5.2
15	57.1	5.6	5.3	0.3	3.9
20	55.9	3.8	3.6	0.2	2.6
25	55.3	2.9	2.8	0.1	2.0
30	54.0	1.0	1.0	0.0	0.7

^a Catalyst 0.81×10^{-5} mol, acetonitrile 5 ml and other reaction conditions are the same as those in Table 2.

7.3.2.4 Influence of reaction temperature

The effect of temperature on the conversion of phenol was studied in the temperature range 40 to 80 °C. Selection of this particular temperature range is to avoid the enhanced H₂O₂ decomposition [10] and further oxidation of dihydroxybenzene to quinones and then to tar formation [5]. Phenol conversion, selectivity for phenol hydroxylation and H₂O₂ efficiency increases with elevation of temperature (Table 5). The percentage distribution of the catechol reaches a maximum at 60 °C and then decreases whereas the percentage distribution of hydroquinone showed a gradual increase.

Table 5: Effect of temperature in the catalytic activity and selectivity of phenol hydroxylation ^a

Temperature (°C)	X _{phenol} (%)	S _{phenol} (%)	Product distribution (%)		H ₂ O ₂ eff (%)
			CAT	HQ	
40	56.0	3.9	3.9	0	2.7
50	59.2	8.4	8.1	0.3	6.1
60	60.2	9.7	8.9	0.8	7.1
70	61.3	11.1	8.4	2.6	8.3
80	61.9	11.8	8.2	3.5	8.9

^a Catalyst 0.81×10^{-5} mol, acetonitrile 5 ml and other reaction conditions are the same as those in Table 2

7.3.2.4 Influence of reaction time

The influence of reaction time on the hydroxylation of phenol was studied with 0.81×10^{-5} mol of catalyst in 5 ml of acetonitrile at 80 °C with 2.28×10^{-2} mol of phenol, 18.70×10^{-3} mol of H_2O_2 (Table 6). The conversion, selectivity, product distribution and H_2O_2 efficiency were found to increase with reaction time. The reaction time was varied from 0 to 5 hours. Since a longer reaction time is not beneficial for this reaction, we studied the effects of various parameters except the effect of reaction time for period of 2 h. This is because a longer reaction time would lead to oxidation of dihydroxybenzenes to quinones and further to tar formation [9].

Table 6: Effect of reaction time in the catalytic activity and selectivity of phenol hydroxylation ^a

Time (hrs)	X_{phenol} (%)	S_{phenol} (%)	Product distribution (%)		$\text{H}_2\text{O}_{2\text{eff}}$ (%)
			CAT	HQ	
1	59.5	8.8	6.8	2.0	6.4
2	61.9	11.8	8.2	3.5	8.9
3	63.1	13.1	8.7	4.4	10.1
4	63.7	13.8	8.9	4.9	10.7
5	64.5	14.8	9.5	5.3	11.6

^a Catalyst 0.81×10^{-5} mol, acetonitrile 5 ml and other reaction conditions are the same as those in Table 2.

Conclusions

The catalytic activity of the copper(II) complexes were 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. All the complexes were screened for their activity towards the hydroxylation of phenol. Detailed study of the catalytic activity of the complex, $[\text{Cu}_2(\text{hqcdmn})\text{Cl}_2]$, that gave maximum conversion in the screening studies was carried out by changing the different parameters like catalyst amount, reaction time, reaction

temperature, amount of oxidant, and the amount 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. Increase in the amount of H₂O₂ has a positive effect on the reaction while the quantity and nature of solvent have no significant effect.

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