Oxidation of cyclohexene with hydrogen peroxide catalysed by oxovanadium(IV) complexes

6.1 Introduction

Transition metal Schiff base complexes, in particular N_2O_2 Schiff base complexes, have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions [1,2]. One of the attractive features of the N_2O_2 Schiff base complexes is that it is possible to tune the electronic and steric properties of the complexes by making alterations in the Schiff base portion. The introduction of bulky substituent near the coordination sites may lead to low symmetry complexes and enhanced catalytic properties. Furthermore, by suitable incorporation of donating/accepting groups, it may be possible to tune the electronic environment around the metal centre and alter the catalytic properties. A variety of Schiff base complexes of oxovanadium(IV) ion have been shown to catalyze a wide range of oxidation reactions [3-9].

Oxovanadium(IV) ion can readily coordinate four, five and six donor atoms to form VOL_4, VOL_5 and VOL_6-type of complexes. Most of the oxovanadium(IV) complexes with N_2O_2 Schiff base ligands are reported to have mononuclear structures having square pyramidal geometries whereas very few have binuclear structure [10-12]. During our investigations we have been able to synthesize and characterize new binuclear oxovanadium(IV) Schiff base complexes derived from 3-hydroxyquinoxaline-2-carboxaldehyde and investigate the catalytic activities in the

oxidation of cyclohexene using an environmentally friendly oxidant, H_2O_2 [13]. The results of these studies are presented in this chapter.

6.2 Experimental

6.2.1 Materials

The details of the materials and instruments used for the synthesis and characterisation of oxovanadium Schiff base complexes and their catalytic studies towards the oxidation of cyclohexene are given in Chapter 2.

6.2.2 Methods

The details of the syntheses Schiff bases and their vanadyl complexes are given in Chapters 2 and 3.

6.2.3 Catalytic activity measurements

Catalytic oxidation 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 cyclohexene and the complex in 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 course of the reaction was monitored by periodically withdrawing small samples (about 0.5 mL each) which were analyzed by gas chromatography fitted with OV−17 packed column (4 m × 4 mm id). Quantification was done after considering the response factors of the reagents and products obtained using standard mixtures.

6.3 Results and discussion

The spectral characterisation of the Schiff base ligands and their vanadyl complexes are given in Chapters 2 and 3.

6.3.2 Catalytic activity towards the oxidation of cyclohexene

Oxidation of cyclohexene generally yields various products such as cyclohexene peroxide, cyclohexenol, cyclohexenone and cyclohexene oxide etc [14]. However, the selectivity towards these products depends on various parameters like reaction conditions, central metal ion, solvent, oxidant agent, nature of the catalyst etc. Hydrogen peroxide was chosen in this work as a clean oxidant agent, since it is inexpensive, environmentally friendly and generates water as by product [15]. We carried out a blank experiment without catalyst under identical conditions. Only very low amount of substrate was converted in the blank reaction (below 2%) suggesting that our complex is functioning as a catalyst for cyclohexene oxidation reaction [16]. Allylic oxidation products such as cyclohexenol and cyclohexenone were formed as the major products along with cyclohexene oxide as the minor product, indicating the involvement of Fenton-type oxidation reactions [17]. Major formation of the allylic oxidation products shows the preferential attack of the activated C−H bond over the C=C bond [18]. The conversion and selectivity were calculated using the following relations [19].

$X_{cyclohexene}$ (%) = 100 × ([cyclohexene]$_i$ − [cyclohexene]$_f$)/[cyclohexene]$_i$,

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

$S_{cyclohexene}$ (%) = 100 × ([OX]$_f$ + [OL]$_f$ + [ONE]$_f$)/([cyclohexene]$_i$ − [cyclohexene]$_f$),

where $S_{cyclohexene}$ is the selectivity for cyclohexene oxidation, and [OX]$_f$, [OL]$_f$, and [ONE]$_f$ are the molar concentration of cyclohexene oxide, cyclohexenol, and cyclohexenone, respectively, after reaction.

Product distribution (%) = 100 × [product]$_f$/([cyclohexene]$_i$ - [cyclohexene]$_f$),

where $[product]_f$ is the molar concentration of product (cyclohexene oxide, cyclohexenol, or cyclohexenone) after reaction.

$$H_2O_{2eff} (\%) = 100 \times ([OX]_f + [OL]_f + [ONE]_f)/[H_2O_2]_{add},$$

where H_2O_{2eff} is the effective conversion of H_2O_2, and $[H_2O_2]_{add}$ is the molar concentration of the total added H_2O_2 in the reaction mixture.

All the oxovanadium(IV) complexes were screened for their activity in the oxidation of cyclohexene. The results of the screening studies are given in Table 1. Among these the complexes, $[(VO)_2(hqcdmn)SO_4].H_2O$ was found to be the most active. So a detailed catalytic activity study of the $[(VO)_2(hqcdmn)SO_4].H_2O$ in the oxidation of cyclohexene using aqueous 30% H_2O_2 as the oxidant was done and effect of varying the parameters like amount of catalyst, temperature, amount of solvent and time was investigated.

Table 1: The influence of catalyst on conversion and selectivity of cyclohexene oxidation [a]

Complex (5 mg)	X cyclohexene (%)	S cyclohexene (%)	Product distribution (%) [b]			H₂O₂eff (%)	TOF
			OX	OL	ONE		
I	44.2	11.5	0.7	6.0	4.8	5.5	275
II	50.7	20.9	1.3	6.6	13.0	11.2	266
III	45.6	13.7	2.3	5.5	5.8	6.6	318
IV	43.2	9.8	1.4	4.9	7.2	4.5	217
V	45.4	13.5	0.7	5.6	3.6	6.4	454

[a] Reaction conditions: acetonitrile (30 ml), temperature (80 °C), reaction time (2 h), H_2O_2 (18.70×10^{-3} mol), cyclohexene (1.97×10^{-2} mol).
[b] Here OX = cyclohexene oxide, OL = cyclohexenol and ONE = cyclohexenone.
TOF = mol of cyclohexene converted per mol of catalyst per hour. Here I, II, III, IV and V are $[(VO)_2(hqcdan)SO_4].H_2O$, $[(VO)_2(hqcdmn)SO_4].H_2O$, $[(VO)_2(hqcdac)SO_4].H_2O$, $[(VO)_2(hqcap)_2].H_2O$ and $[(VO)_2(hqcaap)_2SO_4].2H_2O$ respectively.

6.3.2.1 Influence of the catalyst

The influence of catalyst on the oxidation of cyclohexene was studied at 80 °C by varying the amount of catalyst from 1.50×10^{-6} mol to 7.50×10^{-6} mol keeping the amount of solvent, oxidant and substrate constant and the results are

given in Table 2. With increase in the amount of catalyst, an increase was observed in the percentage conversion, selectivity for cyclohexene oxidation and H_2O_2 efficiency increases. It is also found that by increasing the amount of catalyst, the cyclohexene oxide formation decreases whereas the distribution of allylic oxidation products enhances.

Table 2: The influence of catalyst on conversion and selectivity of cyclohexene oxidation [a]

Catalyst (10^{-6} mol)	$X_{cyclohexene}$ (%)	$S_{cyclohexene}$ (%)	Product distribution (%) [b]			H_2O_{2eff} (%)
			OX	OL	ONE	
1.50	42.4	8.4	1.8	2.1	4.6	3.8
3.00	43.7	10.6	1.7	2.7	6.2	4.9
4.50	45.1	12.9	1.6	3.6	7.8	6.1
6.00	47.7	16.8	1.4	5.2	10.2	8.5
7.50	50.7	20.9	1.3	6.6	13.0	11.2

[a] Reaction conditions: acetonitrile (30 ml), temperature (80 °C), reaction time (2 h), H_2O_2 (18.70×10^{-3} mol), cyclohexene (1.97×10^{-2} mol).
[b] Here OX = cyclohexene oxide, OL = cyclohexenol and ONE = cyclohexenone.

6.3.2.2 Influence of the oxidant H_2O_2

Cyclohexene oxidation was carried out by adding the H_2O_2 to the reaction mixture in one-lot at the reaction temperature. To study the effect of varying the amount of H_2O_2, the reaction was carried out with 7.50×10^{-6} mol of catalyst and the amounts of H_2O_2 from 9.35×10^{-3} mol to 28.05×10^{-3} mol while keeping other conditions as in the case above. The results are tabulated in Table 3. Percentage conversion, selectivity for cyclohexene oxidation and H_2O_2 efficiency increases to a maximum value with 18.70×10^{-3} mol of H_2O_2 and then decreases. The distribution of allylic oxidation products shows the same trend but the cyclohexene oxide percentage shows a gradual increase. The lower values of H_2O_2 efficiency for this reaction might be due to the higher efficiency of the complex to catalyze the hydrogen peroxide decomposition.

Table 3: The influence of oxidant on conversion and selectivity of cyclohexene oxidation [a]

H_2O_2 (10^{-3} mol)	X cyclohexene (%)	S cyclohexene (%)	Product distribution (%) [b]			$H_2O_{2\text{eff}}$ (%)
			OX	OL	ONE	
9.35	42.7	9.0	1.1	4.3	3.6	8.1
14.03	46.7	15.4	1.2	5.3	8.9	10.1
18.70	50.7	20.9	1.3	6.5	13.0	11.2
23.36	46.9	15.8	1.6	4.2	10.0	6.2
28.05	45.2	13.4	1.7	3.0	8.4	4.2

[a] Catalyst (7.50×10^{-6} mol) and other conditions are the same as those in Table 2.

6.3.2.3 Influence of solvent

It is seen that variation of solvents has little influence on the conversion of cyclohexene and decreases in the order: dichloromethane (52.4 %) > chloroform (51.6 %) > methanol (51.0 %) > acetonitrile (50.7 %). However we chose acetonitrile as the solvent for common runs as the complex is more soluble in this solvent. Influence of the amount of acetonitrile on the oxidation of cyclohexene was studied by varying its volume from 10 to 40 ml while keeping the amount of catalyst, oxidant and substrate constant (Table 4). The amount of acetonitrile has a profound influence on the product distribution. With lower amounts of acetonitrile the three products are somewhat equally distributed whereas at higher amounts the percentage of epoxide decreases and that of the other two increases. An increase of the amount of solvent is also found to increase the percentage conversion, selectivity and H_2O_2 efficiency.

Table 4: The influence of solvent on conversion and selectivity of cyclohexene oxidation [a]

Acetonitrile (ml)	X cyclohexene (%)	S cyclohexene (%)	Product distribution (%) [b]			$H_2O_{2\text{eff}}$ (%)
			OX	OL	ONE	
10	41.8	7.3	2.8	1.5	3.0	3.2
15	43.9	11.0	2.7	2.6	5.9	5.1
20	45.7	13.9	2.3	3.7	7.9	6.7
25	48.5	17.9	1.9	5.4	10.8	9.2
30	50.7	20.9	1.3	6.5	13.0	11.2
35	51.4	21.8	1.0	7.0	13.8	11.8
40	53.2	23.9	0.8	7.9	15.0	13.4

[a] Catalyst (7.50×10^{-6} mol) and other conditions are the same as those in Table 2.

6.3.2.4 Influence of reaction temperature

The reaction was studied over a wide range of temperature in 30 ml acetonitrile from 40 to 80 °C keeping the amount of catalyst, oxidant and substrate as constant (Table 5). Selection of this particular temperature range is due to the reason that at higher temperatures the decomposition of H_2O_2 predominates [20]. As the temperature increases, percentage conversion, selectivity for cyclohexene oxidation, H_2O_2 efficiency and percentage product distribution increases.

Table 5: The influence of temperature on conversion and selectivity of cyclohexene oxidation [a]

Temperature (°C)	X cyclohexene (%)	S cyclohexene (%)	Product distribution (%) [b]			H_2O_{2eff} (%)
			OX	OL	ONE	
40	42.2	7.9	1.0	1.4	5.5	3.5
50	44.6	12.1	1.1	3.0	8.0	5.7
60	46.8	15.5	1.2	4.3	9.9	7.6
70	48.7	18.3	1.3	5.5	11.6	9.4
80	50.7	20.9	1.4	6.5	13.0	11.2

[a] Catalyst (7.50×10^{-6} mol) and other conditions are the same as those in Table 2.

6.3.2.5 Influence of reaction time

The influence of reaction time on the oxidation of cyclohexene was probed by carrying out the reaction with 7.50×10^{-6} mol of catalyst in 30 ml of acetonitrile, 1.97×10^{-2} mol of cyclohexene, 18.70×10^{-3} mol of H_2O_2 and a temperature of 80 °C (Table 6). The conversion, selectivity, product distribution and H_2O_2 efficiency are found to increase with time. We studied the effects of various parameters on the hydroxylation of phenol for period of 2 h because a longer reaction time would lead to oxidation of dihydroxybenzenes to quinones and further to tar formation [21].

Table 6: Effect of reaction time in the catalytic activity and selectivity of cyclohexene oxidation [a]

Time (hrs)	X cyclohexene (%)	S cyclohexene (%)	Product distribution (%) [b]			H_2O_{2eff} (%)
			OX	OL	ONE	
1	46.4	14.9	1.1	4..3	9.5	7.3
2	50.7	20.9	1.3	6.5	13.0	11.2
3	51.7	22.1	1.3	7.2	13.5	12.0
4	52.7	23.4	1.4	7.9	14.0	12.9
5	53.5	24.3	1.4	8.6	14.2	13.7
6	54.5	25.3	1.5	9.2	14.7	14.6

[a] Catalyst 5 mg, acetonitrile 5 ml and other reaction conditions are the same as those in Table 2.

Conclusions

In this study, the catalytic activity of the synthesized oxovanadium(IV) complexes in the oxidation of cyclohexene were tested. The oxovanadium(IV) complex of the Schiff base, N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)2,3-diaminomaleonitrile exhibit better catalytic activity. A detailed investigation was carried out by varying the amount of this complex, temperature, amount of solvent and time. With aqueous 30% H_2O_2 as the oxidant, the complex was found to catalyze the oxidation with more selectivity for allylic oxidation products than that for the epoxide. The lower H_2O_2 efficiency observed for this reaction might be due to the greater catalytic activity of the complex towards the decomposition of hydrogen peroxide.

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