SUMMARY

Study of selective oxidation or isomerization of hydrocarbons using transition-metal complex catalysts has become increasingly important in recent years. Among them the metal-oxo mediated oxygen transfer reactions and the metal-hydride catalyzed olefin isomerization reactions are of significance, as models for biological systems and also from synthesis point of view.

Synthetic models have been shown to be capable of mimicking the oxidations mediated by heme-enzymes of the cytochrome P-450 family in terms of reaction types, mechanism and reaction rates [1]. This has led to the pursuit of, both efficient and stable, metal complex systems capable of becoming competitive catalysts for large-scale oxidation processes, carried out by molecular oxygen or monooxygen donors. Such cytochrome P-450 mimic systems using single oxygen atom donors like iodosylbenzene follow the 'Oxygen Rebound' pathway [2].

$$M^{n+} + AO \longrightarrow M^{n+2}{=}O + A \qquad AO = \text{Oxidant}$$

$$M^{n+2}{=}O + S \longrightarrow M^{n+} + \dot{S}O \qquad S = \text{Substrate}$$

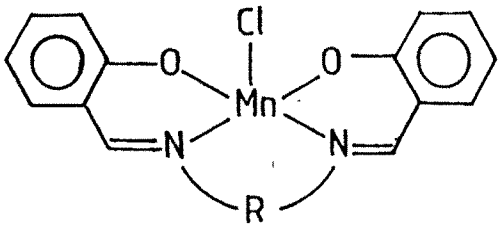
The catalytic cycle gets terminated either due to the formation of μ-oxo species or due to ligand based side reactions which destroy the active catalyst.

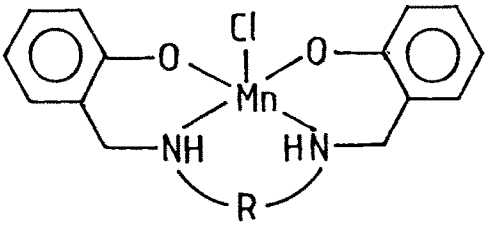
$$M^{n+2}{=}\acute{O} + M^{n+} \longrightarrow M^{n+1}\text{--}O\text{--}M^{n+1}$$

Ability of a metal complex to act as a catalyst largely depends on the type of metal centre and the ligand part. A systematic variation in the electronic nature of the ligand part can bring in gradual change in the efficiency of a catalyst by affecting redox potential of the metal centre. Keeping this in view, various catalyst systems for oxidation of olefins have been developed in the present work. Iodosylbenzene was used as oxidant for the epoxidation studies.

The first chapter presents a survey of the literature on epoxidation reaction using transition metal complexes. Various factors, affecting catalytic activity of the epoxidation catalysts, viz., metal centre, ligand nature, oxidant, axial ligand, solvent and substrate, have been discussed. Emphasis has been placed on the roles of metal centre and the ligand nature. More recent developments in the area, e.g., asymmetric epoxidation catalysis, have also been discussed.

The second chapter gives an account of the comparison of catalytic activity of manganese(III) schiff-base complexes of salen type of ligands, with their mannich-base complex analogues. Manganese(III)salen type of schiff-base complexes are known to epoxidize alkenes efficiently. It has been shown that electron donating/accepting substituents on the ligand part affect efficiency of these complexes as catalysts [3]. No studies had been done earlier to correlate the activity of the schiff-base and the corresponding mannich-base complexes as epoxidation catalysts. In this work the synthesis and characterization of the new complexes **3** and **4** are reported. These were studied along with the schiff-base complexes **1** and **2** to see the effect of substitution of a secondary amine in **1** and **2** by tertiary amine in **3** and **4** on epoxidation activity.





1. R = $(CH_2)_2$
2. R = $(CH_2)_3$

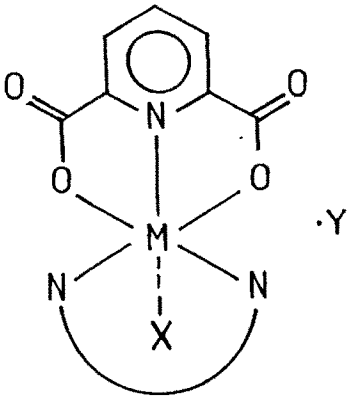
3. R = $(CH_2)_2$
4. R = $(CH_2)_3$

The preformed schiff-bases were reduced with sodium borohydride in methanol, yielding mannich-bases, which were used to synthesize **3** and **4** by reaction with $MnCl_2.4H_2O$ in ethanol. All the complexes were characterized by elemental analysis and IR spectroscopy, conductance and magnetic moment studies.

The observation that the complexes **3** and **4** are relatively poor epoxidation catalysts compared to **1** and **2**, was attributed to easy oxidation in the case of former complexes. It was shown by the IR study of the complex recovered after a catalytic run with **3** that the phenolic part of the ligand gets oxidized to quinone form. The IR spectrum of the recovered complex thus showed the characteristic bands due to the original complex **3** and a new band at 1665 cm^{-1}, which was assigned to the quinonic $\nu_{C=O}$.

It is known that mixed ligand complexes of Ru(III) bearing both poly-pyridyl and aminocarboxylate ligands act as efficient epoxidation catalysts [4]. The corresponding chromium(III) and iron(III) complexes were thought to be interesting for study as catalysts. The third chapter thus describes the mixed ligand complexes of iron(III) and chromium(III) with dipicolinic acid (dpa) as one ligand and ethylenediamine (en), 2,2'-dipyridyl (bpy) or 1,10-phenanthroline (phen) as the second ligand. These complexes were characterized by

elemental analysis, IR spectroscopy, magnetic and conductance studies and were used as epoxidation catalysts.



$M = Fe^{III}, Cr^{III}$

N N = en, bpy, phen

X, Y = Cl, H_2O

The chromium(III) complexes were active as epoxidation catalysts but the iron(III) complexes did not show catalytic activity. This was due to facile formation of the μ-oxo complex, which was isolated and characterized in the case of $Fe(dpa)(bpy)^{+}$. Formation of Cr(V)=O and the μ-oxo formation in the epoxidation reaction involving $Fe(dpa)(bpy)^{+}$ complex was confirmed by the CV studies.

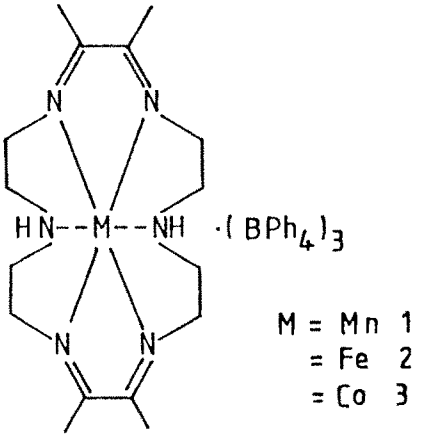
The fourth chapter presents a brief account of the effect of light on the epoxidation of *cis*-cyclooctene with PhIO, using the $Fe(dpa)(bpy)(H_2O)Cl$ and Cr(dpa)(bpy)Cl catalysts. The μ-oxo-bis(tetraphenylporphyrin)iron(III) on continuous or flash photolysis, is known to disproportionate to the ferrous complex and the ferryl Fe(TPP)(O).

$$(TPP)Fe^{III}\text{--}O\text{--}Fe^{III}(TPP) \xrightarrow{h\nu} Fe^{II}(TPP) + (TPP)Fe^{IV}(O)$$

The latter gives epoxide with alkene. This prompted us to study the effect of light on epoxidation reaction using iron(III) and chromium(III) complexes. It was seen that light effected epoxidation in absence or presence of metal complex catalyst. It was concluded that light acts independently as a catalyst and does not affect the catalytic reaction of the metal

complexes. The mechanism for the light catalyzed epoxidation has been suggested. Thus, greater yields of epoxide can be obtained by carrying the epoxidation of alkenes in the presence of both, metal complex and light as catalysts.

The fifth chapter presents an account of the poly-aza macrocyclic ligand complexes. The importance of such complexes is that their study correlates better with the biological systems, since the natural enzyme system of cytochrome P-450 involves iron porphyrins as the active site. Hexa-aza macrocyclic ligand complexes were used to study the effect of ring size and coordinative unsaturation on the epoxidation activity.

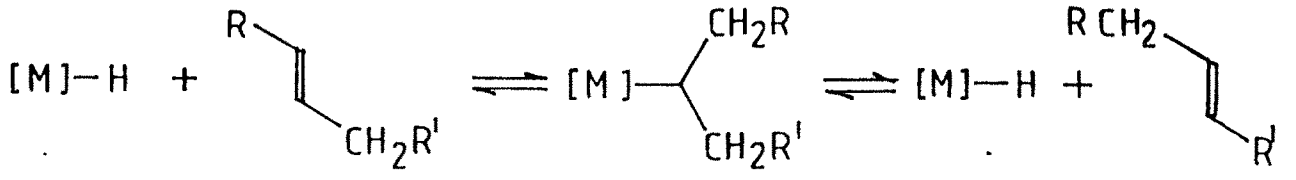


Diacetyl was condensed with diethylenetriamine in methanol and the complexes were prepared by reaction with appropriate metal salt in dilute solution to prevent polymerization. The complexes were precipitated as BPh_4^- salts They were characterized by elemental, IR and magnetic measurements.

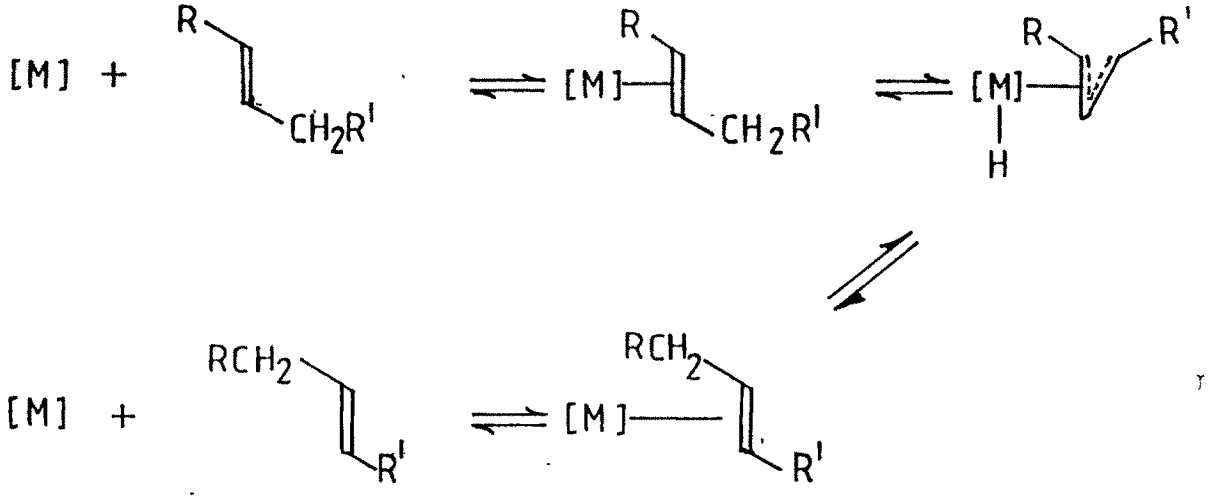
All the complexes show catalytic activity to epoxidation of olefins. However, the UV-vis and CV studies indicate absence of high-valent metal-oxo species on reaction with iodosylbenzene. Hence, catalysis by Lewis-acid mechanism was suggested to be operative for these systems.

The last chapter of the thesis presents an account of an isomerization reaction. Isomerization of olefins by transition metal complexes follow two general mechanisms [5].

1 The first mechanism involves the reversible addition of a metal-hydride (a stable species or generated in-situ) across a double bond to generate transition metal σ-alkyl species.

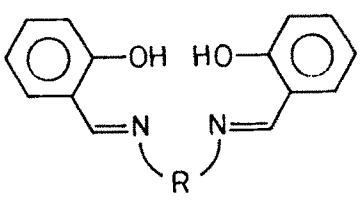


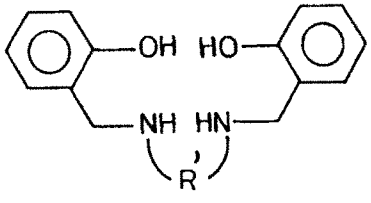
2 The second mechanism involves coordination of the olefin to the transition metal followed by insertion of the metal into an allylic C-H bond to generate π-allyl metal-hydride species.



5-Etylidene-2-norbornene (2), an industrially important diene co-monomer, is prepared by isomerization of 5-vinyl-2-norbornene (1) using heterogeneous catalysts.

The present chapter reports the system of the complexes CoL^1, CoL^2, CoL^3, CoL^4, CoL^1Im, CoL^1Py, CoL^1PPH_3 and their use as catalysts for isomerization of 1 to 2 homogeneously.

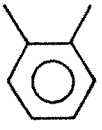




L^1 : R = $(CH_2)_2$

L^4 : R' = $(CH_2)_2$

L^2 : R =



L^3 : R = $(CH_2)_2$ NH $(CH_2)_2$

All the complexes, in conjunction with $AlEt_3$, catalyzed the isomerization of 1 to 2 in the temperature range of 25-100 °C. It was observed that variation of the ligand did not affect the yield of 2 to a great extent. However, use of axial ligands like Im, Py or PPh_3 influenced the reaction.

It is proposed that the isomerization reaction follows the expected general mechanism of the first type, involving Co(I)-H species formation in-situ by the action of $AlEt_3$ on the Co(II) complex. This was supported by UV-vis, EPR and CV measurements.

EPR study of the CoL^1-$AlEt_3$ system at -196 °C showed that the characteristic EPR signal of Co(II) disappeared and there was a new signal with g=2.07 supporting the generation of the ethyl radical. On warming to room temperature, the solution becomes EPR silent due to formation of Co(I)-H species, which is responsible for the isomerization reaction.

Further evidence for the formation of Co(I) species came from the CV measurements which show disappearance of redox peak due to Co(II)/Co(I) reduction on addition of $AlEt_3$ to the CoL^1 solution. No peak was observed for Co(III) ruling out the oxidation of Co(II) to Co(III) on reaction with $AlEt_3$.

References

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