Epoxidation of Alkenes Catalyzed by Iron(III) Schiff Base Chelates. A Monooxygenase Model

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Iron(III) Schiff base chelates $[Fe_2(PA_2ppd)_2Cl_4]Cl_2$ (**1**), $[Fe_2(PA_2mpd)_2Cl_4]Cl_2$ (**2**), and $[Fe(PA_2opd)Cl_2]Cl$ (**3**), were synthesized, where (PA_2ppd), (PA_2mpd), and (PA_2opd) are the Schiff bases derived from 2-pyridinecarbaldehyde (PA), and *p*-phenylenediamine (ppd), *m*-phenylenediamine (mpd), and *o*-phenylenediamine (opd) respectively. The complexes **1**, **2**, and **3** catalyzed the epoxidation of alkenes with iodosylbenzene as an oxidant providing a chemical model for cytochrome P-450. The binuclear complexes (**1**, **2**) were superior to the mononuclear complex (**3**) as the catalyst for epoxidation of norbornene. Addition of pyridine bases increased the rates, and yields of epoxidation.

The selective addition of oxygen to a hydrocarbon provides a direct means of increasing its commercial potential. But there are only a few preparatively or industrially useful liquid-phase catalytic oxidation processes which do not compromise on the selectivity. In contarst, nature has evolved monooxygenase enzymatic systems, such as cytochrome P-450 which catalyzes oxygenation reactions with utmost selectivity. Hemin forms part of the composition of cytochrome P-450 which are responsible for detoxification of living organisms by hydroxylation of saturated hydrocarbons and epoxidation of alkenes employing molecular oxygen, in their cells.[1)]

In the last few years, several chemical models of monooxygenases have been studied. In such systems a metalloporphyrin catalyzes the transfer of an oxygen atom to an alkene, either from a single oxygen donor (e.g. PhIO, $KHSO_5$, NaOCl) or from the combination of molecular oxygen and a reductant (e.g. ascorbic acid, $NaBH_4$).[2—11)] Recently, metal complexes other than metalloporphyrins have also been used for catalytic epoxidation of alkenes with iodosylbenzene or alkyl hydroperoxide as an oxygen source.[12—14)] However, the systems using iron complexes are limited to porphyrin ligands only.

In the present communication, we report studies on Fe(III) Schiff base chelates as catalysts for epoxidation of alkenes.

Experimental

The elemental analyses were carried out on a Coleman carbon, hydrogen analyzer. The IR spectra were recorded on Shimadzu IR-408 and UV-VIS spectra on Shimadzu UV-240 spectrophotometer. The thermal analyses were performed on Shimadzu DT-30 thermal analyzer. Magnetic moments were determined by Guoy method at room temperature. The conductivity measurements were carried out on Toshniwal conductivity bridge. Gas chromatography analysis were performed on Shimadzu GC 7AG.

Syntheses of Binuclear Complexes. To a solution of 2-pyridinecarbaldehyde (2 mmol), in dry ethanol (50 ml) was added a solution of *p*-phenylenediamine or *m*-phenylenediamine (1 mmol) in dry ethanol (70 ml) and the mixture stirred for 15 min. The Schiff base, thus formed, was added dropwise to a solution of anhydrous $FeCl_3$ (1 mmol) in dry ethanol (100 ml). The mixture was stirred at room temperature for 0.5 h and refluxed on a water bath for 5 h. After cooling to room temperature, the complex was filtered, washed thoroughly with ethanol and dried under vacuum at 100 °C.

Synthesis of Mononuclear Complex. To a solution of 2-pyridinecarbaldehyde (2 mmol) in dry ethanol (20 ml) was added a solution of *o*-phenylenediamine (1 mmol) in dry ethanol (35 ml) and the mixture stirred for 15 min. The mixture was warmed slowly to 45 °C and allowed to cool to room temperature. The Schiff base formed was then added dropwise to a solution of anhydrous $FeCl_3$ in dry ethanol (70 ml) and the mixture refluxed for 5 h. It was then cooled to room temperature, filtered and the filtrate was concentrated to one third. To the above solution was added excess of ether and the precipitated complex was filtered, washed first with ethanol and finally with ether, and dried under vacuum at 100 °C.

Epoxidation of Alkenes. All reactions were carried out in a Schlenk tube under nitrogen atmosphere. To a solution of catalyst (0.012 mmol) in acetonitrile (6 ml) and water (1 ml) were added alkene (2.5 mmol), an appropriate quantity of anisole as an internal standard, and iodosylbenzene (0.5 mmol). The mixture was stirred at ambient temperature for 5.5 h. Aliquots (1 µl) were withdrawn and analyzed by gas chromatography (GC column (3 M), Carbowax 20M, 15% on Chromosorb W, carrier gas nitrogen, flow 30 ml min^{-1}, detector FID, injector temp 240 °C).

Results

The metal complex $[Fe_2(PA_2ppd)_2Cl_4]Cl_2$, $[Fe_2(PA_2mpd)_2Cl_4]Cl_2$, and $[Fe(PA_2opd)Cl_2]Cl$, were characterized by elemental (C, H, N, and metal), spectral (IR and UV-VIS) and thermal analyses, and by conductivity and magnetic moment measurements. The elemental analyses and the magnetic moment data are presented in Table 1. Molecular conductivity was measured in water, methanol, and in a mixture of acetonitrile-water (6 : 1). However, molar conductance of **1** in methanol could not be measured because of its poor solubility. Molar conductance data have been

Table 1. Analytical and Magnetic Moment Data for the Metal Complexes

Complex	C%		H%		N%		M%		μ_{eff} (B.M.)
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$[Fe_2(PA_2ppd)_2Cl_4]Cl_2$	48.18	49.30	3.12	3.08	12.49	12.27	12.46	12.9	5.13
$[Fe_2(PA_2mpd)_2Cl_4]Cl_2$	48.18	49.01	3.12	3.42	12.49	12.49	12.46	12.19	4.2
$[Fe(PA_2opd)Cl_2]Cl$	48.18	48.7	3.12	3.56	12.49	12.86	12.46	12.36	4.6

Table 2. Molar Conductance of the Metal Complexes

Complex	Solvent	Molar conductance $\Omega^{-1}\,cm^2\,mol^{-1}$
1	H_2O	576
	CH_3OH	—[a]
	CH_3CN-H_2O(6 : 1)	341
2	H_2O	598
	CH_3OH	205
	CH_3CN-H_2O(6 : 1)	279
3	H_2O	344
	CH_3OH	144
	CH_3CN-H_2O(6 : 1)	133

a) Poor solubility.

Table 3. Epoxidation of Norbornene with Iodosylbenzene Catalyzed by Metal Complexes (**1**—**3**)

Metal complex	Yield[a] of norbornene oxide (%)
1	6
2	8
3	2

a) Yields based on iodosylbenzene charged.

presented in Table 2. All the three complexes are soluble in water, but sparingly soluble in acetonitrile, dichloromethane and benzene. However, they are soluble in the acetonitrile-water (6 : 1) solvent mixture, which was used as a reaction medium for the epoxidation reactions.

The effectiveness of the complexes (**1**—**3**) as catalysts for epoxidation were compared using norbornene as the substrate and iodosylbenzene as an oxidant. The addition of iodosylbenzene to a system containing catalytic amounts of the complex and norbornene in an acetonitrile-water solvent mixture leads to complete reaction within 4 h. The results are given in Table 3. Control experiments showed that norbornene gave extremely low quantity of epoxide in the absence of catalyst. The credibility of anisole as an internal standard was checked by carrying out an oxidation reaction using anisole as the substrate. Anisole did not react under these conditions.

From the catalytic epoxidation of norbornene using the three catalysts, **2** was selected as the catalyst of choice. Oxidation capability of this complex was then screened against various alkenes. The results are presented in Table 4. Effect of various base additives, such as pyridine, 4-picoline, and imidazole has been studied. These results are shown in Fig. 1.

Table 4. Epoxidation of Various Alkenes Catalyzed by $[Fe_2(PA_2mpd)_2Cl_4]Cl_2$

Alkene	Yield[a] of epoxide %
Norbornene	8
Styrene	3
Cyclohexene	4[b]
cis-Cyclooctene	7
trans-4-Octene	2

a) Based on iodosylbenzene charged. b) 2-Cyclohexen-1-ol (7%) and 2-cyclohexen-1-one (22%) were also formed.

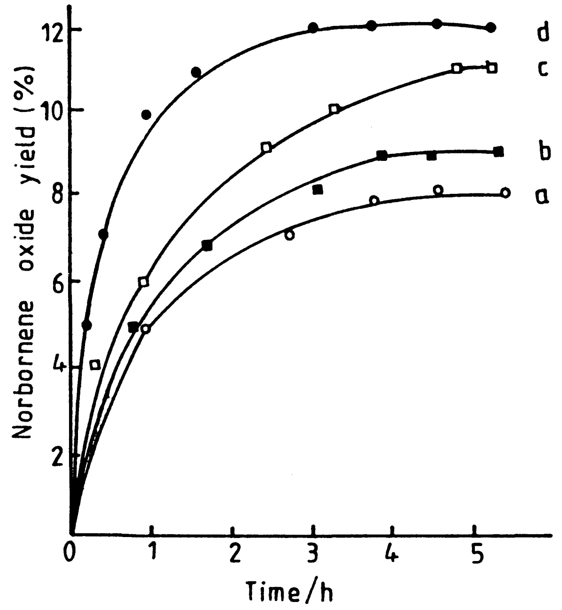
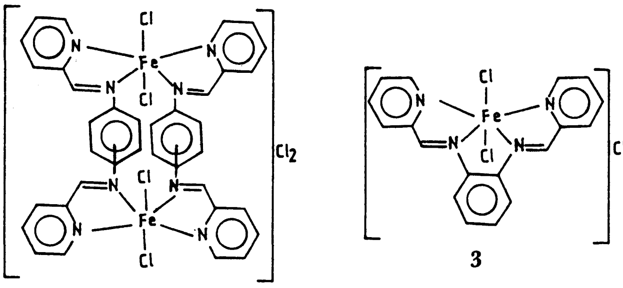


Fig. 1. Influence of base addition (3 mol equivalent) on epoxidation of norbornene catalyzed by $[Fe_2(PA_2mpd)_2Cl_4]Cl_2$. Conditions as given in experimental. a, without base; b, with imidazole; c, with pyridine and d, with 4-picoline.



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1, Bridge=*p*-phenylenediamine
2, Bridge=*m*-phenylenediamine

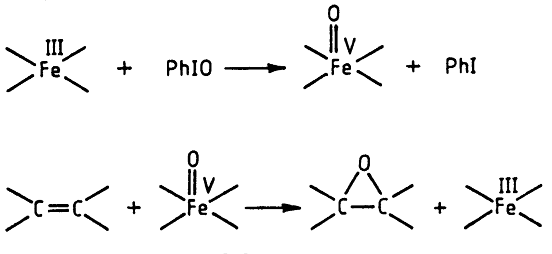
Fig. 2. Structures of the metal complexes.

Discussion

The analytical data presents the formula as $C_{36}H_{28}N_8Cl_6Fe_2$ for binuclear complexes and $C_{18}H_{14}N_4Cl_3Fe$ for the mononuclear complex. The structures of the complexes are shown in Fig. 2. Molecular conductivity measurements in water and in methanol show that four chloride ions in the binuclear complexes are inside, and two chlorides are outside the coordination sphere, whereas in the mononuclear complex one chloride is present outside and two inside the coordination sphere. Thermogravimetric analyses from ambient temperature to 800 °C rules out the possibility of any associated water molecules. The magnetic susceptibility measurements at room temperature show that the complexes (**1**—**3**) are high-spin paramagnetic compounds (4.2—5.13 BM). Infrared spectra of the complexes showed bands at 1615 cm^{-1} corresponding to the coordinated azomethine C=N-stretching, and at 1330 cm^{-1} corresponding to the coordinated C=N-stretching of the pyridyl ring.

Catalytic oxygenation of olefins is taken as evidence for the formation of the highly reactive oxoiron species. In iron porphyrin systems, this species have been identified as the Fe(IV) porphyrin π-radical complex $[FeO(P\cdot)]^+$. However, with one apparent exception no such oxoiron species has been isolated, but several have been spectroscopically detected in situ.[15]

In the present study, where iron Schiff base complexes are involved, the reaction probably proceeds through an oxoiron intermediate as in the porphyrin systems (Scheme 1). But electronic spectra of the complexes (**1**—**3**) in acetonitrile-water mixture (6 : 1) in the presence of iodosylbenzene did not show any new band for the transient oxoiron species. This may be due to the charge-transfer band masking the dd transition bands. However, it may be suggested that the catalytic reaction occurs via an oxoiron species as shown below (Scheme 1):



Scheme 1.

All the three catalysts were screened against norbornene to compare their oxidation capabilities. From the yields of norbornene oxide formed (Table 3), it is clear that both the binuclear complexes (**1**, **2**) are superior to the mononuclear complex (**3**). Out of the two binuclear complexes, the one with *m*-phenylenediamine Schiff base (**2**), is a better catalyst than the one with *p*-phenylenediamine Schiff base (**1**).

The formation of the oxo-bridged binuclear species Fe^{IV}-O-Fe^{IV} may be the reason for the termination of the catalytic activity. In case of binuclear complexes the formation of oxo-bridged species appear to be less probable than the mononuclear complex because of its bigger molecular size. However, the reasons for the superiority of the binuclear complex having *m*-phenylenediamine Schiff base over the one with *p*-pheneylenediamine Schiff base is not clear at present.

Addition of bases are known to increase the rates of the reaction dramatically without affecting much the overall yields.[16] However, in the present study of the epoxidation of norbornene, addition of various bases such as imidazole, pyridine, and 4-picoline, not only enhanced the rates but showed marked increase in the yields of epoxide. Addition of 4-picoline gave higher yield of epoxide, as compared to that with pyridine. In contrast to this, imidazole was comparatively less effective (Fig. 1).

Conclusion

The metal Schiff base complexes described here catalyze the epoxidation of olefins providing a good chemical model for monooxygenases. Their easy preparation from readily available materials as compared to that of metalloporphyrins makes them attractive catalyst for monooxygenase model studies.

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