Catalyzed Oxidation of Cyclohexene and Cyclooctene with First Row Transition Metallophthalocyanines

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ABSTRACT: *First row transition metal complexes of phthalocyanine are employed as catalysts for the oxidation of cyclohexene and cyclooctene using iodosylbenzene and pentafluoroiodosyl benzene. The catalysis was performed in dichloromethane:methanol:water (80:18:2) solvent mixture. The products of the catalysis for cyclohexene are epoxycyclohexane, 2-cyclohexene-1-ol and 2-cyclohexene-1-one whereas for cyclooctene it is specifically cyclooctene oxide. For cyclohexene oxidation epoxide yield and selectivity is in the order of $Mn^{II} > Fe^{III} > Fe^{II} > Co^{II} > Cr^{III} > Ni^{II} > Cu^{II}$, while for 2-cyclohexene-1-one production the ability of the catalysts are in the order of $Ni^{II} > Co^{II} > Cu^{II} > Cr^{III} > Fe^{III} > Fe^{II} > Mn^{II}$.*

KEY WORDS: *Oxidation, Cyclohexene, Cyclooctene, Phthalocyanine, Catalyzed Oxidation.*

INTRODUCTION

Cytochrome P-450 monooxygenases catalyze a variety of reactions such as hydroxylation of alkanes and epoxidation of alkenes [1-3]. Metalloporphyrins in oxidation of substrates with various single-oxygen atom donors were found to act as good catalysts and had a major role for understanding of biologically related reaction of cytochrome P-450 [4-8].

Metallophthalocyanines (MPc) have similar structure with metalloporphyrines (MP) and they are more readily available, inexpensive and are generally more stable than MP, however they are studied as a catalyst of oxidation in lesser extent. This fact is justified mainly by:

-Insolubility of MPc.

-Decolorination of MPc by addition of oxidant that

was believed to be due to degradation of catalyst [9-11].

-Catalytic decomposition of the peracids and hydroperoxide by MPc [12,13]. Previously, we have introduced a FePc / imidazole / iodosylbenzene in three components solvent system (CH_2Cl_2 : CH_3OH : H_2O, 80 : 18 : 2) to overcome the above difficulties [9]. So in this report we explore the effect of variation in the metal; Cr, Mn, Fe, Co, Ni and Cu on oxidation product and catalyst stability.

EXPERIMENTAL

Materials

The phthalocyanine complexes of Ni and Cu were prepared and purified according to literature method [14].

Table 1: Product yields for the oxidation of cyclohexene by IB in the presence of various catalysts.

	Product Yield (%)			Selectivity	
Catalyst	Epoxycyclohexaene	2-cyclohexene-1-ol	2-cyclohexene-1-one	Epoxy/other products	One/other products
CrPcF	Trace*	8±1	25±2	0.18	1.79
MnPc	33±4	_	7±3	4.71	0.21
FePc	25±3	Trace	8±2	2.27	0.29
FePcCl	30±4	7±2	15±3	1.36	0.40
CoPc	12±2	18±1	29±2	0.26	0.97
NiPc	Trace	11±5	37±1	0.08	2.50
CuPc	10±4	6±1	28±2	0.29	1.75

*Reaction is carried out in air at room temperature. Molar ratios for cyclohexene:oxidant:MPc:imidazole are $19.8:1:2\times10^{-2}:10^{-1}$ and IB is $6.98\times10^{-2}M$. The yield was calculated based on IB. * Trace= 0-5%*

Table 2: Cyclooctene oxide yields for the oxidation of cyclooctene by IB and PFIB in the presence of various catalysts.

Catalyst	IB	PFIB
CrPcF	30±4	24±2
MnPc	70±5	60±3
FePc	39±5	35±4
FePcCl	55±4	50±5
CoPc	31±2	28±2
NiPc	25±2	21±3
CuPc	22±2	19±2

Reaction is carried out in air at room temperature. Molar ratios for cyclooctene:oxidant:MPc:imidazole are $19.8:1:2\times10^{-2}:10^{-1}$ and IB or PFIB is $6.98\times10^{-2}M$. The yield was calculated based on oxidant.

Other metal complexes of phthalocyanine were purchased from Mid Century. Iodosylbenzene (IB) and pentafluoro-iodosyl- benzene (PFIB) were prepared in the laboratory according to literature methods [15,16]. Cyclohexene, cyclooctene, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were purchased from Fluka and used as received. Epoxy-cyclohexene, cycloocteneoxide, dichloromethane and methanol were obtained from Merck and used without further purification.

Oxidation reactions

The oxidation reactions were performed at room temperature. A solvent mixture containing dichloro-methane, methanol and water (80/18/2) was employed. Substrate (cyclohexene or cyclooctene) and metallo-phthalocyanine/ imidazole (molar ratio 1:5) solution were charged into a small test tube with a silicone stopper, the respective oxidant was then added and the reaction mixture was stirred and analyzed by GC after 24 hr. All reported yields are based on the mole percent of the products. All reactions were run in triplicates and always using the same batches of the catalysts, oxidants or substrates. The final concentration of substrate, catalyst and oxidant were 1.38 M , 1.5×10^{-3} M and 6.98×10^{-2} M, respectively. The oxidation products were indentified by using authentic samples with n-decane as internal standard and by measurements of retention times in GC.

RESULTS AND DISCUSSION

The products were analyzed by gas chromatography (Shimadzu 8A) equipped with Thermal Conductivity Detector and 30% SE-30 on chrosorb PAW column. The yield of each product was strongly dependent on the nature of the oxidant and the catalyst.

Catalytic oxidation of cyclohexene and cyclooctene by IB

IB were tested for cyclohexene and cyclooctene oxidation using metallophthalocyanines (MnPc, FePc, CoPc, NiPc, CuPc, CrPcF, FePcCl) catalyst. Product yields are reported in tables 1 and 2.

According to table 1, the selectivity of epoxide is 4.71 for MnPc and 2.27 for FePc, on the other side CrPcF and NiPc have higher selectivities toward formation of 2-cyclohexene-1-one.

Table 2 shows that cyclooctene is converted selectively to the epoxide and the order of activity is

Table 3: Product yields for the oxidation of cyclohexene by PFIB in the presence of various catalysts.

Catalyst	Product Yield (%)			Selectivity	
	Epoxycyclohexaene	2-cyclohexene-1-ol	2-cyclohexene-1-one	Epoxy/other products	One/other products
CrPcF	Trace[*]	6±4	45±1	0.08	4.50
MnPc	25±3	–	–	–	–
FePc	8±2	Trace	Trace	2.00	0.20
FePcCl	17±1	Trace	7±3	1.45	0.33
CoPc	5±1	7±1	30±2	0.13	2.50
NiPc	Trace	5±2	33±2	0.08	4.13
CuPc	Trace	Trace	18±1	0.05	6.00

Reaction is carried out in air at room temperature. Molar ratios for cyclohexene:oxidant:MPc:imidazole are $19.8:1:2\times10^{-2}:10^{-1}$ and IB is $6.98\times10^{-2}M$. The yield was calculated based on IB. [*] *Trace= 0-5%*

Table 4: Product yields for the oxidation of cyclohexene by IB in the presence of various metalloporphyrins.

Catalyst	Product Yield (%)			Selectivity	Ref.
	Epoxycyclohexane	2-cyclohexene-1-ol	2-cyclohexene-1-one	Epoxy/other products	
Fe(TPP)Cl	55	15	0	3.6	17
Mn(TPP)Cl	40	23	6	1.38	18
Cr(TPP)Cl	4	75	21	0.04	19
MnPc	33±4	–	7±3	4.71	This Work
FePc	25±3	3±2		2.27	This Work

$Mn^{II}PC > Fe^{III}PCCl > Fe^{II}PC > Co^{II}PC > Cr^{II}PC > Ni^{II}PC > Cu^{II}PC$. The best yield was obtained for MnPC followed by Iron phthalocyanine.

### *Catalytic oxidation of cyclohexene and cyclooctene by PFIB*

Tables 2 and 3 present the yields for the products of cyclohexene and cyclooctene oxidation by PFIB as oxygen donor in the presence of various metal complexes of phthalocyanine. Interestingly, stronger oxidant PFIB results in lower yield and confirms that stronger oxidant can accelerate degradation of the catalyst.

Table 4 demonstrates oxidation products obtained by three metalloporphyrine catalysts with iodosylbenzene. While a large yield of epoxycyclohexane and 2-cyclo-hexene-1-ol were observed for metalloporphyrine, further tendency were observed for formation of 2-cyclohexene-1-one product with metallophthalocyanines.

Large amounts of alcohols and ketones were rationalized by presence of cyclohexenyl radical by single electron transfer mechanism in which subsequent oxidation of alcohole produced ketone (Scheme 1). Although this matter is not compeletly settled, but our results are in agreement with radical intermediacy [9,20,21].

CONCLUSIONS

The oxidation of cyclohexene and cyclooctene in the presence of metallophthalocyanines as catalysts is remarkablely affected with metal change. For epoxide production the order of metallophthalocyanine ability is $Mn^{II}PC > Fe^{III}PCCl > Fe^{II}PC > Co^{II}PC > Cr^{II}PC > Ni^{II}PC > Cu^{II}PC$ whereas for alchole production the order is $CoPC > NiPC > CrPCF > FePCCl > CuPC > FePC > MnPC$. Highest selectivity with respect to 2-cyclohexene-1-one was obtained with CrPcF(1.79) and NiPc(2.5).
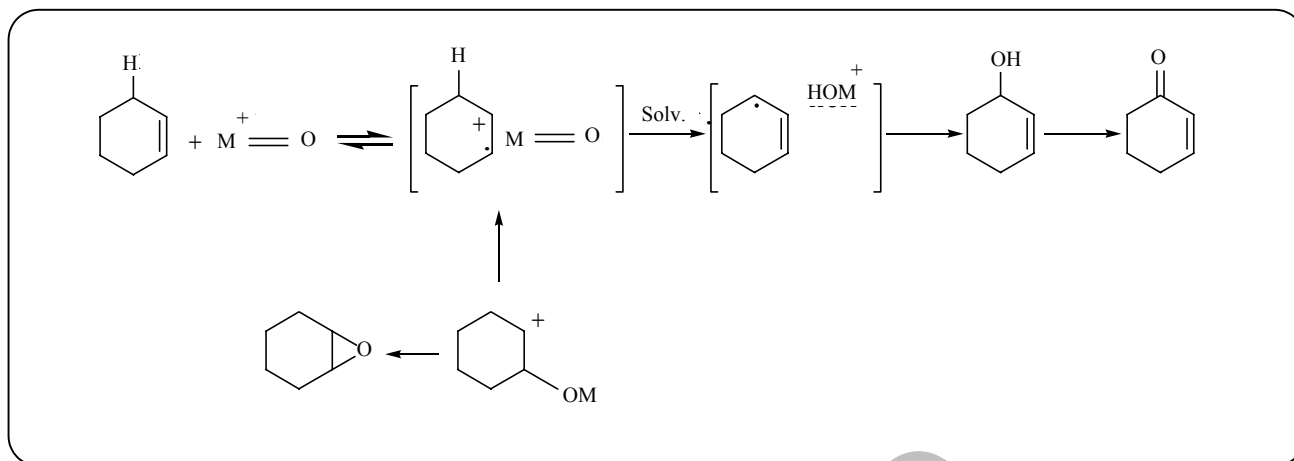
Scheme 1: Proposed mechanism for the formation of alcohole and ketone in cyclohexene oxidation by metallophthalocyanine.

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