

# Triphase Catalysis: Hydroxylation of Cyclo-octane by NaOCl Catalyzed by Coordinatively Bound Manganese(III) Porphyrin to Nitrogen-Based Polymer Supports

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**ABSTRACT:** The anionic manganese (III) porphyrin was immobilized onto crosslinked poly(benzylpicoline-co-styrene) resin through coordinate linkage. The immobilized metalloporphyrin was employed as a heterogeneous catalyst for the hydroxylation of cyclo-octane by NaOCl. The observed reaction rates depend on experimental parameters such as stirring speed, substrate amount, temperature, and catalyst amount. The influence of different polymer-based axial ligands, particle size, and percent crosslinking of the polymer support was also discussed. The imidazole-based polymer supports show higher rate constant values than the pyridine-based supports. The catalyst shows significant decrease in catalytic activity on recycling. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 104–111, 2000

**Key words:** triphase catalysis; polymer-supported catalyst; manganese porphyrin; hydroxylation of cyclo-octane

## INTRODUCTION

The active interest in hydrocarbon oxidation by cytochrome P-450-dependent mono-oxygenase has been a major driving force behind the extensive studies of the intuitively simpler metalloporphyrin systems.<sup>1,2</sup> The high efficiency of some of these systems make them potentially useful for preparative oxidations in organic chemistry by attaching large substituents to the porphyrin rings, which prevents large intermolecular self-oxidation and restricts access to the active oxidants.<sup>3</sup> Furthermore, the utility of these metalloporphyrin catalysts are increased significantly when they are immobilized on solid polymeric supports, which stabilize the catalyst and aid their recovery and reuse.<sup>4,5</sup>

The change in the polymeric backbone structure and additional crosslinking of the polymeric support may significantly influence the physical properties of the carrier, which may be reflected in different behavior of the catalyst.

The purpose of the present work was to prepare a series of polymer supports with N-based axial ligand and to evaluate them as supports for the attachment of metalloporphyrin complexes and further to study the influence of the polymer-supported nitrogen bases on the activity of the supported metalloporphyrin catalyst and to gain more information about its catalytic efficacy in hydroxylation of alkanes.

## EXPERIMENTAL

### General

All the reagents used were of AR grade, and used as such in polymer preparation. Copolymer of styrene and chloromethyl styrene crosslinked with

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divinylbenzene were prepared by the suspension copolymerization technique as described elsewhere.<sup>6</sup> The polymers with different percentage of crosslinking, viz., 2–10% by weight of divinylbenzene, were prepared and then sieved into different particle sizes viz., –40+60, –60+100, –100+140, –140+160, and above 200 mesh (US Standard). The porphyrin ligand, tetra(2,6-dichlorophenyl)porphyrin (TDCPPH<sub>2</sub>), was prepared by the reported procedure.<sup>7</sup>

UV-Vis spectras were recorded on a Specord UV-Vis spectrometer. IR spectra were recorded on a Perkin-Elmer 2831R spectrometer using KBr pellets. GLC analyses were performed on a Varian 3700 with a vista CDS-401 data system having a 3-m × 1/8-inch column of SE-30 on a 10% 80–100 chrom WHP.

#### Sodium 5,10,15,20-Tetrakis (2,6-dichloro-3-sulfonatophenyl) porphyrin

The porphyrin ligand, TDCPPH<sub>2</sub> (1.0 g) and conc. H<sub>2</sub>SO<sub>4</sub> (18–24% of SO<sub>3</sub>) 15 mL were ground together with mortar and pestle. The mixture was taken in a RB flask and heated carefully on a water bath for 4 h. The flask was stoppered and then set aside for 3 days. It was then transferred to a beaker, cooled in an ice bath and neutralized carefully with 5% NaOH solution. The neutral solution was concentrated by evaporation when sodium sulfate began to crystallize out. Methanol was added to cause further precipitation of salt. It was filtered off, and the filtrate was evaporated to dryness. The process was repeated by adding methanol until it was almost free from sodium sulfate.

The product obtained was freely soluble in water and further purified by column chromatography using silica gel as the adsorbent and a mixture of methanol (70%) and chloroform (30%) as the eluant. The structure of the eluted final product was confirmed by <sup>1</sup>H-NMR analysis (in CDCl<sub>3</sub>, ppm) and the corresponding data are: 9.02(m, 8 × H pyr), 8.6 (m, 4 × H p-Ph), 8.0 (m, 4 × H o-Ph).

#### Sodium 5,10,15,20-Tetrakis (2,6-dichloro-3-sulfonato phenyl) Manganese(III)porphyrin, [Mn(III)TDCPPS]

A solution of TDCPPS (1.0 g) and MnCl<sub>2</sub> · 4H<sub>2</sub>O (1.5 g) in 50 mL of water was adjusted to pH 9.0 with 0.5 N NaOH solution and heated to 90°C for 24 h. During the reaction, the pH was maintained

at 9.0 with 0.5 N NaOH. After cooling, a 0.5 N NaOH solution was added to attain pH 11.5. The brown mixture was evaporated to dryness. The residue was dissolved in methanol and passed through a column of Amberlite IR-120 (H<sup>+</sup> form). The eluate was treated with NaOH to neutralize the sulfonic acid groups of the manganese porphyrin. The filtrate was evaporated, and the residue was soxhlet extracted twice with methanol. The reddish-brown manganese porphyrin was obtained by drying in vacuum at 65°C.<sup>8</sup>

#### Preparation of Poly (benzyl picoline-co-styrene) [PBP] II

Porous (chloromethyl styrene-co-styrene) polymeric resin I (2 g) was swollen in THF (20 mL) for about 6 h and refluxed with a slight excess of 4-picolyllithium (400 mg) for about 24 h at 80°C. The resin was filtered, washed with THF, CH<sub>2</sub>Cl<sub>2</sub>, and dried in vacuum at 70°C.

IR spectra of the copolymer support shows the disappearance of characteristic —C—Cl present at 660–720 cm<sup>-1</sup> and the appearance of a new band corresponding to C=N at 1690–1640 cm<sup>-1</sup>.

#### Preparation of [Mn(III)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>] III

Resin (II) (1.0 g) was added to a solution of Mn(III)TDCPPS (5 μM; 7.93 mg) in 20 mL of methanol. The solution becomes colorless after overnight gentle mechanical stirring. The materials were subsequently washed with CH<sub>2</sub>Cl<sub>2</sub> and methanol, and the loading was determined by measuring (UV-Vis spectroscopy) the unloaded Mn(III) TDCPPS in the solvent and washings. The supported catalyst was dried under vacuum. The above sample was stirred for 30 min in an aqueous solution of *p*-toluene sulfonic acid (2 g of TsOH in 50 mL of water).

After filtration, the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum at 60°C. The same experimental procedure was used for the preparation of [Mn(III)TDCPPS-PVPH<sup>+</sup>][TsO<sup>-</sup>], [Mn(III)TDCPPS-PNVIH<sup>+</sup>][TsO<sup>-</sup>], and [Mn(III)-TDCPPS-PNBIH<sup>+</sup>][TsO<sup>-</sup>] using poly(vinylpyridine)(PVP), Poly(*N*-vinyl imidazole)(PNVI), and poly(*N*-benzylimidazole)(PNBI), respectively.

#### Procedure for Hydroxylation Kinetics

The typical oxidation experiment was carried in a flask equipped with a stirring bar, an adaptor fitted with a septum, and a glass stopcock. To the flask containing catalyst III (1 g:5 μM : Mn(III)-

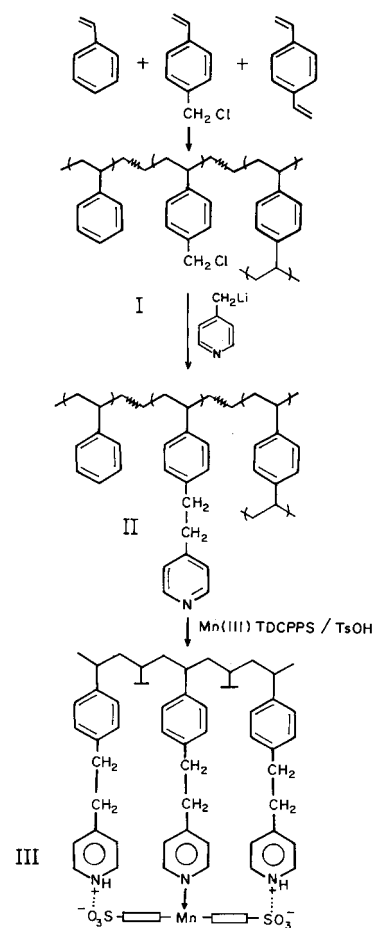
TDCPPS) and cyclo-octane (11.2 mmol) in dichloromethane (12 mL) and 10.0 mL of 0.35 M NaOCl was added to the organic phase and stirred at 27°C. Before adding to the flask, the pH of the NaOCl was first buffered to the desired value (pH = 10), by adding 0.2 g of  $\text{Na}_2\text{B}_4\text{O}_7$  (the slight pH corrections were made by the addition of few drops of 10% NaOH or 10% HCl solutions).

Aliquots (1  $\mu\text{L}$ ) of organic phase were withdrawn at regular intervals of time. The kinetics was followed using GLC by estimating the disappearance of cyclo-octane. The addition of NaOCl was taken as zero time. The pseudofirst-order rate constants were calculated from the plots of  $\log(a-x)$  vs. time, where  $(a-x)$  is the concentration of cyclo-octane at a given time " $t$ ." The duplicate experiments were also conducted under identical experimental conditions; the kinetic and other data are reproducible with in  $\pm 2\%$ .

## RESULTS AND DISCUSSION

The method used to prepare the insoluble polymer supports bearing benzyl picoline backbone is given in Scheme 1. The modified polymeric support with different crosslinking and with different particle sizes were also prepared to investigate the influence of the properties on the catalytic behavior. The Mn(III)TDCPPS was also bound to other polymeric supports like poly(*N*-benzyl imidazole-*co*-styrene) (PNBI),<sup>9</sup> poly(*N*-vinylimidazole-*co*-styrene) (PNVI), and poly(vinyl pyridine-*co*-styrene) (PVP). In all cases, the polymeric N-bases pyridine and imidazole are allowed to coordinate at one side of the metalloporphyrin, and other side remains free for the oxygen binding. The resultant modified polymer-bound metalloporphyrin was subsequently treated with *p*-toluene sulfonic acid (*p*-TsOH) to recover the physical adsorption properties of sulfonated groups of the tetra anionic porphyrin and cationic resin.<sup>10</sup>

The double interaction of sulfonated metalloporphyrin with poly(benzylpicoline) copolymer (pyridine proximal effect and sulfonato-pyridinium interactions) immobilized the catalyst more firmly on the support than that of simple electrostatic interaction of amberlite-type resins. In our case, there probably is an equilibrium between two possible modes of interactions, i.e., the "coating" mode, and "stacking" mode (Fig. 1). The stacking of metalloporphyrin in the support enhances the bleaching of the catalyst, when the



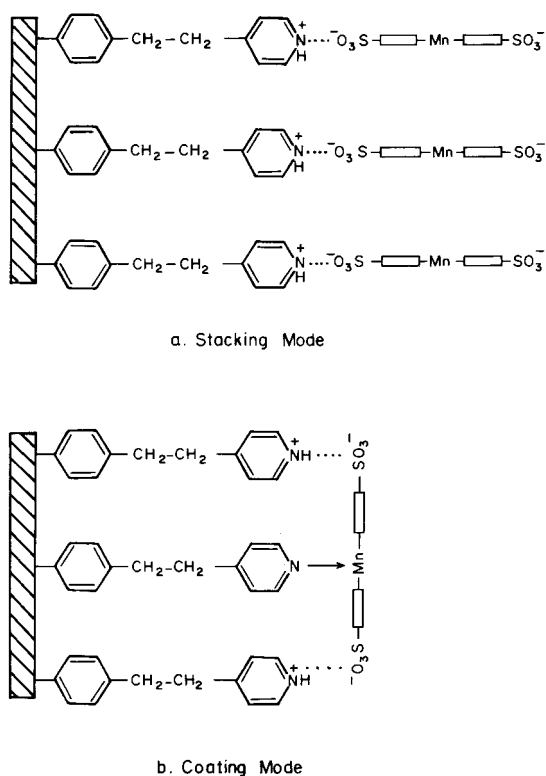
Scheme 1

high valent metal-oxo species ( $\text{Mn}^{\text{V}} = \text{O}$ ) are formed, which was also observed by Meunier et al.,<sup>11</sup> in the case of cationic manganese porphyrins in interactions with DNA.

Furthermore, the site isolation of the active centre by bonding to the solid support was thought to prevent the formation of less reactive  $\mu$ -oxo dimers.<sup>12</sup> Anchoring of the Mn(III)TDCPPS complex on the polymer matrix was confirmed by UV-Vis spectra recorded by depositing the mull of the crushed polymer-supported porphyrin and vaseline on the wall of the cuvette.<sup>13</sup>

The solution model was also carried out with benzyl picoline, which helps to characterize PBP support. A shift of about 9 nm to a shorter wave length from 464 to 455 nm was obtained, which indicates the possibility of N-ligation to the metal complex.<sup>14</sup>

Preliminary experiments using these  $[\text{Mn}(\text{III})\text{TDCPPS-PBPH}^+][\text{TsO}^-]$  catalysts for epoxidation of olefin by  $\text{KHSO}_5$  leads to excellent epoxide



**Figure 1** (a) Stacking mode; (b) coating mode.

yields. Owing to its better catalytic activity, this catalyst was selected for further experiments of alkane hydroxylation. The product distribution and yields from the oxidation of cyclo-octane, cyclohexane, ethyl benzene, cumene, and diphenylmethane were monitored (GLC analysis) with time. To compare the reactivity of the catalyst towards different substrates, the reaction time was fixed at 60 min for all the above substrates. The final yields typically after 60 min for the Mn(III)TDCPPS/NaOCl system are recorded in Table I.

The control reactions showed that in the absence of the catalyst, no detectable oxidation of the substrates occurred within 60 min. The kinetic experiments were carried out for the hydroxylation of cyclo-octane under pseudofirst-order experimental conditions and the rate constants were calculated from the plots of  $\log(a-x)$  vs. time, where  $(a-x)$  is the concentration of cyclo-octane at given time " $t$ ."

#### Effect of Stirring Speed on the Hydroxylation of Cyclo-octane

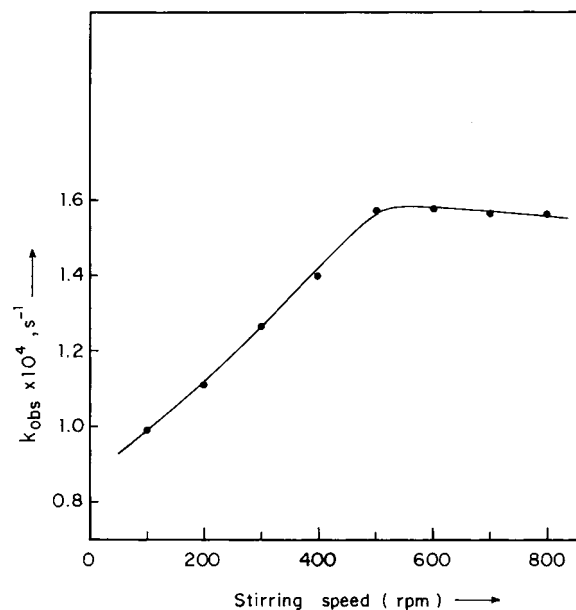
To ascertain the influence of stirring speed to mass transfer of reactants to the catalyst surface,

**Table I** Hydroxylation of Alkanes by NaOCl Catalyzed by  $[\text{Mn(III)TDCPPS-PBPH}^+][\text{TsO}^-]^a$

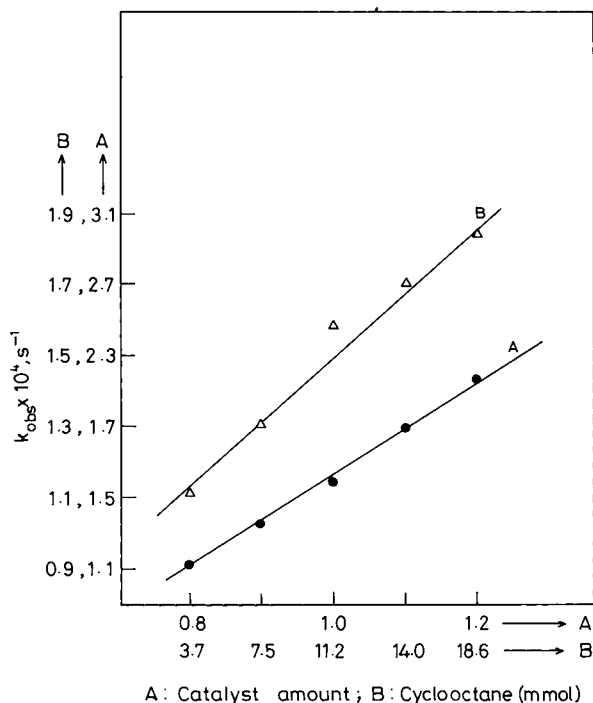
Substrate	Product	% Yield in 1 h
Cyclooctane	Cyclooctanol	59
	Cyclooctanone	7
Cyclohexane	Cyclohexanol	61
	Cyclohexanone	11
Ethylbenzene	1-phenyl ethanol	38
	Acetophenone	15
Cumene	2-Phenyl-2-propanol	22
Diphenyl methane	Benzhydrol	9
	Benzophenone	17

<sup>a</sup> All experiments were carried out by using alkane: 1.5 mL, 0.35M NaOCl: 10 mL pH: 10, Temperature: 27°C and 2% crosslinked, -160+200 mesh  $[\text{Mn(III)TDCPPS-PBPH}^+][\text{TsO}^-]$ : 1.0 g.

the speed of agitation was varied from 100 to 900 rpm for the hydroxylation of cyclo-octane. The experimental results shows that the observed reaction rate increases linearly with the increase of the stirring speed from 100 to 500 rpm, as shown in Figure 2. Further increasing the stirring speed does not increase the reaction rate. The reaction kinetics is controlled by the chemical reaction in the organic phase for the stirring speed greater



**Figure 2** Effect of stirring speed on the rate constant for the hydroxylation of cyclo-octane with 2% crosslinked, -160+200 mesh  $[\text{Mn(III)TDCPPS-PBPH}^+][\text{TsO}^-]$  catalyst.



**Figure 3** Recipe: line A:  $k_{obs} \times 10^4$  ( $s^{-1}$ ) vs. [catalyst amount, (g)]; line B:  $k_{obs} \times 10^4$  ( $s^{-1}$ ) vs. [cyclo-octane, mmol]. Lines A and B are catalyst amount and [cyclo-octane] on the rate constants of cyclo-octane hydroxylation with a 2% crosslinked, -160+200 mesh [Mn(II-I)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>] catalyst.

than 500 rpm. On the other hand, the interfacial mass transfer of the reactants from the bulk liquid to the surface of the catalyst is the key step in the reaction system<sup>15</sup> when the stirring speed is less than 500 rpm.

#### Effect of [Cyclo-octane] and Catalyst Amount

The initial rates of hydroxide formation was monitored in the case of cyclo-octane concentration using [Mn(III)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>]. The concentration of substrate was varied in the range of 3.7 to 18.6 mmol, keeping other reactants as such. The observed rate constant was found to increase on increasing the concentration of cyclo-octane. The observed rate constant values are recorded in Figure 3(A). The molar ratio of the substrate to catalyst increases considerably for the small increment of substrate concentration, and the probability of the substrate that reaches the catalytic surface also increases. Hence, the reaction rate increases.

The influence of catalyst amount was studied in the range 0.8 to 1.2 g of 2% crosslinked,

-160+200 mesh catalyst, [Mn(III)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>]. Figure 3(B) shows that there is linear relationship between the initial rate and the catalyst concentration. The observed rate constant values increases with the amount of catalyst added. The increase of catalyst amount increases the available catalytic site for a fixed amount of substrate. This increased rate of the added catalyst amount also indicates that the rate-limiting step of the reaction, i.e., the formation of metal-oxo species ( $Mn^V = O$ ), may take place within or on the surface of the catalyst.<sup>16</sup>

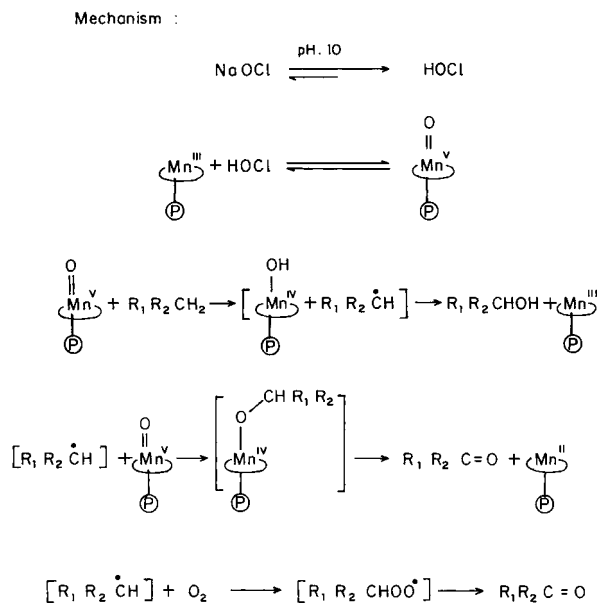
#### Mechanism

The proposed mechanism for hydroxylation of alkane into alcohols with NaOCl catalyzed by [Mn(III)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>] is given in Scheme 2. Montanari et al.,<sup>17</sup> reported that the significant amounts of HOCl in the aqueous phase are partitioned into the organic phase at a pH between 9.5–10.5. The high valent metal-oxo species<sup>18</sup> ( $Mn^V = O$ ) II are normally believed to be the intermediate responsible for the hydroxylation. This species is believed to abstract a hydrogen atom from alkane, leading to the corresponding radical  $R_1R_2CH\cdot$  and species III. The alcohols are formed by an oxidative OH ligand transfer from the species III. Our results confirm that alcohols are the main product along with lower but significant amount of ketones. Ketones may be formed by the oxidation of  $R_1R_2CH\cdot$  with species II and the reaction of atmospheric  $O_2$  with  $R_1R_2CH\cdot$  as shown in the Scheme 2.

#### Effect of Crosslinking and Particle Size of the Catalyst

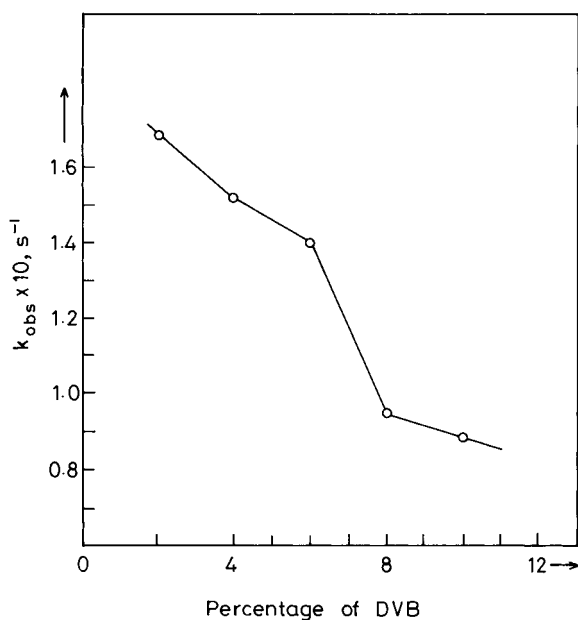
The hydroxylation reaction rate of cyclo-octane was measured by increasing the level of DVB crosslinking in the polymeric support PBP. The dependence of reaction rate on the degree of crosslinking of catalyst is shown in Figure 4. The rate constant values decreases as the crosslinking increases when using a -160+200 mesh catalyst. At the higher crosslinking, the activity of the catalyst is diminished because the cooperative effect of active sites is depressed due to the restriction of the flexibility<sup>19</sup> of the polymer chain.

It was well documented that the rate of triphase reactions that are limited by intraparticle diffusion depend on the catalyst particle size.<sup>20</sup> Table II shows the dependence of particle size in the hydroxylation reaction. The increase in



Scheme 2

$k_{\text{obs}}$  values with a decrease of the particle size indicates the importance of surface area of the catalyst. The observed rate constant also calculated for the finely powdered catalyst and found to very high. But some amount of catalytic deactivation was observed with ground catalyst particles.



**Figure 4** Dependence of percent crosslinking of the polymeric catalyst on rate constant at 500 rpm and 27°C, respectively.

**Table II** Dependence of  $k_{\text{obs}}$  on Catalyst Particle Size

Particle Size (mesh)	$k_{\text{obs}} \times 10^4, \text{s}^{-1}$
-40+60	1.01
-60+100	1.07
-100+160	1.30
-160+200	1.58
> 200	1.70
Powdered catalyst	2.05

### Dependence of Temperature

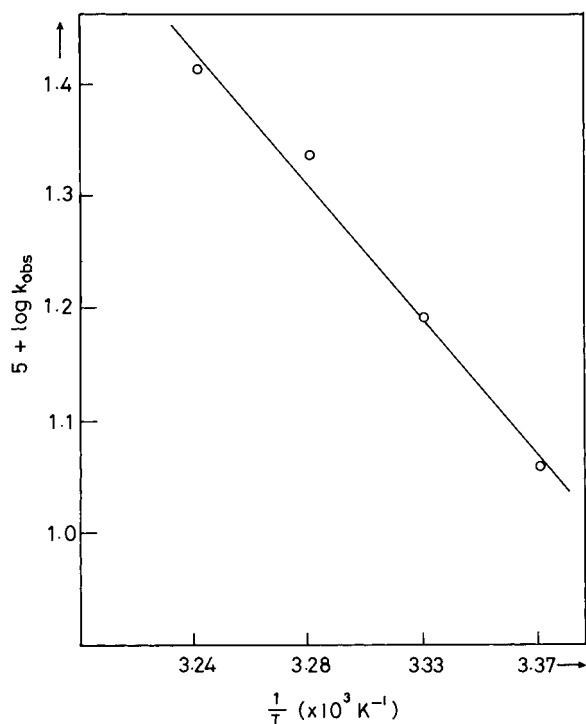
The effect of varying temperature on the rate of the hydroxylation of cyclo-octane was studied at four different temperatures, viz., 24, 27, 31, and 35°C, using a 2% DVB and -160+200 mesh in which 5  $\mu\text{M}$  of Mn(III)TDCPPS was loaded in the PBP support. The kinetic profile of the reaction is obtained by plotting  $\log(a-x)$  vs. time. The observed rate constants increases with increase of temperature (Table III). The energy of activation and other thermodynamic parameters are calculated from Arrhenius plot (Fig. 5).

### Influence of Polymer-Based Axial Ligands on the Catalyst

On comparing the activity of Mn(III)TDCPPS, which is coordinatively bound to four different N-based polymer supports, viz., poly(*N*-benzylimidazole-*co*-styrene) (PNBI), poly(benzylpicoline-*co*-styrene) (PBP), poly(*N*-vinylimidazole-*co*-styrene) (PNVI), and poly(vinylpyridine-*co*-styrene) (PVP), we observed that the PNBI and PNVI backbone catalysts show a slightly higher rate constant value than that of PVP and PBP

**Table III** Effect of Temperature on Rate Constants of Cyclooctane Hydroxylation with 2% Crosslinked, -160+200 Mesh [Mn(III)TDCPPS-PBPH<sup>+</sup>] [TsO<sup>-</sup>] Catalyst

Temperature (K)	$k_{\text{obs}} \times 10^4, \text{s}^{-1}$	
296	1.25	$E_a$ : 11.3 kcal mol <sup>-1</sup>
300	1.58	$\Delta H^\ddagger$ : 10.7 kcal mol <sup>-1</sup>
		$\Delta S^\ddagger$ : -40.2 cal k <sup>-1</sup>
304	2.17	mol <sup>-1</sup>
308	2.55	$\Delta G^\ddagger$ : 12.2 kcal mol <sup>-1</sup>



**Figure 5** Dependence of temperature on the hydroxylation reaction rate (Arrhenius plot).

(Table IV). The slower rates found in the case of the pyridine-based polymeric support may be due to their weaker ligand affinity to Mn(III) porphyrins.<sup>21</sup>

Based on the rate constant observed, it may be concluded that the homogeneous oxidation with Mn(III)TDCPPS was faster than that of the corresponding heterogeneous analogous. The reduced reaction rate with solid catalyst in these studies must arise due to more restricted access to the metalloporphyrin and slower diffusion of the reactant into the polymer catalyst.

#### Reuse of Catalyst

On subsequent reusing the catalyst, [Mn(III)TDCPPS-PBPH<sup>+</sup>][TsO<sup>-</sup>] (Table V), a decrease in the

**Table IV** Dependence of Polymer-Based Axial Ligands on the Rate Constants of Cyclooctane Hydroxylation

Catalyst	$k_{\text{obs}} \times 10^4, \text{s}^{-1}$
[Mn(III)TDCPPS-PBPH <sup>+</sup> ][TsO <sup>-</sup> ]	1.58
[Mn(III)TDCPPS-PVPH <sup>+</sup> ][TsO <sup>-</sup> ]	1.49
[Mn(III)TDCPPS-PNVIH <sup>+</sup> ][TsO <sup>-</sup> ]	1.72
[Mn(III)TDCPPS-PNBIH <sup>+</sup> ][TsO <sup>-</sup> ]	1.77

**Table V** Effect of Reuse of the 2% Crosslinked, -160 + 200 Mesh [Mn(III)TDCPPS-PBPH<sup>+</sup>][TsO<sup>-</sup>] Catalyst on the Rate Constant for the Reaction

No. of Run <sup>a</sup>	$k_{\text{obs}} \times 10^4, \text{s}^{-1}$	Yield in 1 h
1	1.58	59
2	1.58	57
3	1.57	50
4	1.32	44
5	0.99	31
6	0.97	24
7	0.75	22

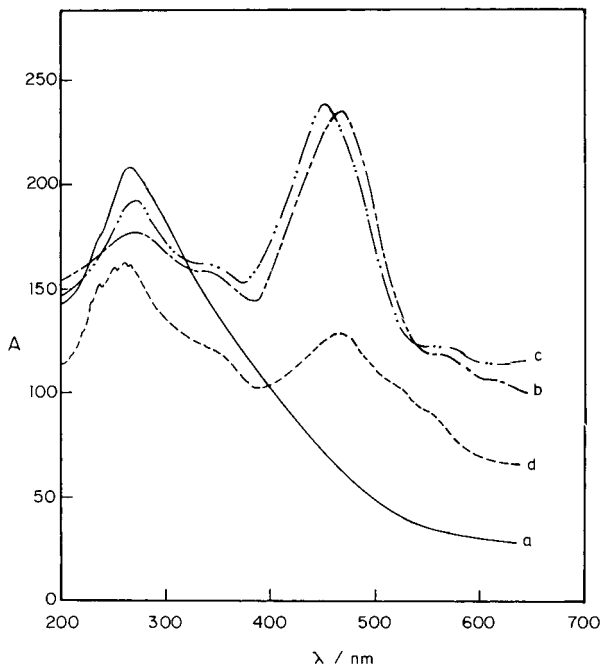
<sup>a</sup> Experimental conditions are same as given in Table I.

rate constant values and also significant reduction in the yield of hydroxylated products was observed. The loss of catalytic activity may be due to oxidative destruction of metalloporphyrin on the polymeric support, due to the rearrangement of oxo manganese active oxidant to a manganese porphyrin N-oxide as reported in the case of iron porphyrin complexes.<sup>22</sup> The intramolecular self oxidation is also one of the most important factors with the [Mn(III)TDCPPS-PBPH<sup>+</sup>][TsO<sup>-</sup>] catalyst because the solid support slows down the diffusion of substrate to the active oxidant in competing with excess NaOCl solution.<sup>23</sup>

Comparison of UV-Vis spectrum of the solid catalyst before and after use in repeated hydroxylation (Fig. 6) confirms that this sequence of reactions leads to a significant amount of catalyst loss to oxidative destruction.

#### CONCLUSION

From the studies of hydroxylation of alkanes with a polymer-supported manganese porphyrin catalyst, the following main features can be noted: (a) the polymer-supported manganese(III)porphyrin complex can be prepared with readily available materials and the complex is also characterized; (b) the catalyst is stable, and the reaction rate and the yield are very high for the hydroxylation of cyclo-octane; (c) this catalyst will be very useful in the hydroxylation of poor alkanes; and (d) the hydroxylation of cyclo-octane is accompanied by the formation of ketone, but the amount of ketone is less in this study compared to the homogeneous catalyst.



**Figure 6** UV-Vis spectrum of the polymer support PBP (a), soluble Mn(III)TDCPPS (b), with coordinated Mn(III)TDCPPS before use (c), with coordinated Mn(II)TDCPPS after usage of seven runs (d).

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