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Study of Synthesis of μ-Oxo-bismanganese(III)Porphyrin Compounds and Their Catalysis of Cyclohexane Oxidation by PhIO

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Ten substituted μ-oxo-bis[tetraphenylporphinatomanganese (III)] compounds ([TRPPMn^{III}]$_2$O) were synthesized by the reaction of chloro[tetraphenylporphinatomanganese(III)] (TRPPMn^{III}Cl) with NaOH. Their catalysis of cyclohexane monooxygenation by PhIO under moderate conditions was studied. In contrast with other metalloporphyrins reported so far, μ-oxo-bis[tetraphenylporphinatomanganese(III)] compounds are shown to have better catalytic power for cyclohexane hydroxylation by PhIO. The kinetic research showed that the rate constants k of the cyclohexane reactions had a Hammett relationship to the characteristic constants σ of substituents R on porphyrin rings. © 1999 Academic Press

Key Words: **[TPPMn^{III}]$_2$O; hydrocarbon oxidation; catalyze.**

INTRODUCTION

The catalytic effect of metalloporphyrins on the activity of inert hydrocarbon bonds has received considerable attention as a model for cytochrome P-450 monooxygenase (1–45). Recently, Ellis and Lyons have found that μ-oxo bisiron(III)porphyrin dimers, which are usually inactive, are active catalysts in the perhaloporphyrin series and that iron(III) μ-oxo dimers and ferryl (II) species coexist for the catalytic oxidation of hydrocarbon with dioxygen (46, 47). We reported in the preceding paper (48, 49) that nonhalide μ-oxo-bis[tetraphenylporphinatoiron(III)] derivatives can catalyze the oxidation of the inert hydrocarbon bond with PhIO as a model of cytochrome P-450 monooxygenase. In contrast with chloro[tetraphenylporphinatoiron(III)] TPPFe^{III}Cl, a μ-oxo-bis[tetraphenylporphinatoiron(III)] compound [TRPPFe^{III}]$_2$O has better catalytic power for cyclohexane oxidation by PhIO at room temperature and atmospheric pressure, and is also more stable to oxidants. It has not been reported up to now whether μ-oxo-bis[tetraphenylporphinatomanganese(III)] has the same catalytic effect on alkane monooxygenation by PhIO as μ-oxo-bis[tetraphenylporphinatoiron(III)]. In order to gain an insight into the catalytic effect of μ-oxo-bis[manganese(III)porphyrin] on the activity of the inert hydrocarbon bond, we synthesized 10 substituted μ-oxo-bis[tetraphenylporphinatomanganese(III)] derivatives [TRPPMn^{III}]$_2$O shown in Fig. 1 by the reaction of chloro[tetraphenylporphinatomanganese(III)] (TRPPMn^{III}Cl) with NaOH, and also studied their catalytic role in the oxidation of cyclohexane into cyclohexanol and cyclohexanone with PhIO.

The research results indicated that μ-oxo-bis[tetraphenylporphinatomanganese(III)] compounds could be used as models for cytochrome P-450 monooxygenase. The yields of cyclohexane oxidation by PhIO catalyzed by μ-oxo-bis[tetraphenylporphinatomanganese(III)] compounds were higher than those for oxidation catalyzed by iron(III) porphyrins TPPFe^{III}Cl, [TPPFe^{III}]$_2$O, and monomanganese(III)porphyrin TPPMn^{III}Cl. We found that both the yields and the rate constants k of the oxidation reaction have linear relationships to characteristic constants σ of substituents on the porphyrin ring. Simultaneously, electric and steric effects of the substituents R of [TRPPMn]$_2$O regularly influenced their catalytic properties.

EXPERIMENTAL

Instruments and Reagents

UV–vis spectra were obtained with a Perkin–Elmer L-17 UV–vis spectrophotometer; IR spectra were recorded on a Perkin–Elmer Model 783 IR spectrophotometer. GC analysis was performed on a Shimadzu GC-16A gas phase chromatography flame ionization instrument. A Perkin–Elmer 2400 elementary analyzer and a Model 5012 constant temperature water bath were used.

Before being used, benzene and dichloromethane were dehydrated; neutral Al_2O_3 was baked 5 h at 100°C; pyrrole and benzaldehyde were redistilled. All reagents were analytically pure or chemically pure as received.

TXPPH$_2$, TXPPMn^{III}Cl, and TPPFe^{III}Cl were synthesized according to the documented procedures (50–53). Their structures were confirmed by elementary analysis, IR spectra, and UV–vis spectroscopy. PhIO was synthesized by documented procedures (54); its purity measured by iodimetry was 99%.

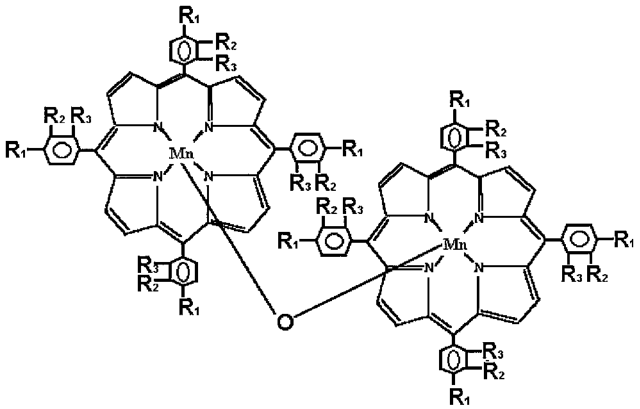

FIG. 1. Construction of $[TRPPMn^{III}]_2O$. 1, $R_1 = R_2 = R_3 =$ H;. 2, $R_1 = CH_3$, $R_2 = R_3 =$ H.; 3, $R_1 = i\text{-}C_3H_7$, $R_2 = R_3 =$ H; 4, $R_1 =$ F, $R_2 = R_3 =$ H; 5, $R_1 =$ Cl, $R_2 = R_3 =$ H; 6, $R_1 = OCH_3$, $R_2 = R_3 =$ H; 7, $R_1 = N(CH_3)_2$, $R_2 = R_3 =$ H; 8, $R_1 =$ H, $R_2 =$ Cl, $R_3 =$ H; 9, $R_1 = R_2 =$ H, $R_3 =$ Cl; 10, $R_1 = R_2 =$ H, $R_3 =$ Br.

Synthesis of $[TXPPMn^{III}]_2O$

Method 1. A typical procedure is described as follows: A solution of $TPPMn^{III}Cl$ (1.0 g), benzene (250 mL), and 5% aqueous NaOH (50 mL) was vigorously stirred; 3 h later, $[TPPMn^{III}]_2O$ was formed. When the absorption band of the solution at 320 cm^{-1} ($\nu_{Mn–Cl}$) in IR disappeared, 300 ml water was added into the reactor. Then benzene was evaporated under the vacuum until $[TPPMn^{III}]_2O$ was crystallized in water. The crude $[TPPMn^{III}]_2O$ was washed with water and dried in air and then recrystallized with absolute anhydrous benzene and cyclohexane. Ten $[TRPPMn^{III}]_2O$ compounds, shown in Fig. 1, were synthesized in the same procedure. Test data from elemental analysis IR and UV–vis maximum are listed in Table 1.

Method 2. A solution of $TPPMn^{III}OH$ (1.0 g) in 300 mL benzene was refluxed with metal sodium for 1 h and then 1.0 g $TPPMn^{III}Cl$ was added into the solution and the mixed solution was vigorously stirred for 3 h more. Benzene was evaporated under vacuum. The crude $[TPPMn^{III}]_2O$ was recrystallized with absolute anhydrous benzene and cyclohexane.

Cyclohexane Hydroxylation Catalyzed by $[TRPPMn^{III}]_2O$ with PhIO

Cyclohexane hydroxylation reported in this paper was carried out under nitrogen using the following procedures unless otherwise specified. A solution of PhIO (100 mg, 4.5×10^{-4} mol), $[TPPMn^{III}]_2O$ (10 mg, 7.5×10^{-6} mol), and cyclohexane (5 mL) in benzene (5 mL) was warmed to 303 K by circulation water and stirred 2 h with an electromagnetic stirrer. The products were analyzed by gas chromatography. Yields were calculated based on the input moles of PhIO. Samples for dynamic analyses were regularly collected from the reactant system by microinjector. Quantitative calculations used an internal standard method. The standard material was chlorobenzene.

RESULTS AND DISCUSSION

Synthesis of $[TRPPMn^{III}]_2O$

Smegal *et al.* (55) successfully synthesized a high valence μ-oxo-bis[tetraphenylporphinatomanganese(IV)] $[TPPMn^{IV}IOPh]_2O$ by the reaction of chloro[tetraphenylporphinatomanganese(III)] ($TPPMn^{III}Cl$) and PhIO at −50°C, and also studied its catalysis of alkane hydroxylation. It was reported that the high valence μ-oxo-bismanganese(IV)porphyrin was so unstable at room temperature that it was rapidly decomposed into three valence hydroxy[tetraphenylporphinatomanganese(III)] $TPPMn^{III}OH$. Fleischer *et al.* (56) synthesized μ-oxo-bis[tetraphenylporphinatoiron(III)] $[TPPFe^{III}]_2O$ by

TABLE 1

Data of Elemental Analysis, λ_{max}, $\nu_{Mn–O–Mn}$ of $[TRPPMn^{III}]_2O$

Compd. No.	Elemental analysis C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	λ_{max} benzene (nm)	$\nu_{Mn–O–Mn}$ (cm^{-1})
1	78.21	77.81	4.18	4.18	8.29	8.62	616, 578, 472, 418	876(m), 849(m)
2	78.78	78.25	4.96	4.80	7.66	7.87	618, 581, 471, 419	878(w), 848(w)
3	79.69	79.26	6.21	5.87	6.64	6.27	621, 582, 472, 420	853(s), 812(s)
4	70.69	69.80	3.24	3.27	7.50	7.58	615, 578, 470, 419	886(w), 852(s)
5	64.97	64.42	2.97	3.05	6.89	6.74	616, 578, 470, 420	883(s), 850(s)
6	72.45	71.85	4.56	4.47	7.04	6.99	627, 586, 472, 421	880(m), 849(s)
7	73.59	72.85	5.70	5.63	13.21	12.85	618, 572, 474, 438	878(s), 830(s)
8	64.97	64.63	2.97	3.14	6.89	6.53	615, 578, 470, 420	887(m), 850(m)
9	64.97	64.35	2.97	3.27	6.89	7.03	655, 586, 511, 471, 418	881(s), 835(w)
10	53.32	52.90	2.44	2.32	5.65	6.14	474, 419	883(m), 827(w)

means of the reaction of $TPPFe^{III}Cl$ with 40% aqueous NaOH. We synthesized 14 substituted μ-oxo-bisiron(III) porphyrins by means of forcing $TPPFe^{III}Cl$ through a neutral alumina chromatographic column (48). We tried to synthesize μ-oxo-bis[tetraphenylporphinatomanganese(III)] $[TPPMn^{III}]_2O$ by means of the same procedures used for μ-oxo-bisiron(III)porphyrins, but only hydroxyl[tetraphenylporphinatomanganese(III)] $TPPMn^{III}OH$ was gained. A new compound was discovered in the reaction process of $TPPMn^{III}Cl$ and NaOH by UV–vis spectrum monitoring the reaction system. This new compound can be obtained by the modified method reported in this paper, and it is stable in the solid state or in the nonproton solvent. The elemental analysis showed that this compound did not contain chlorine. Furthermore, this compound did not exist $\nu_{\mathrm{Mn-Cl}}$ absorption at 320 cm^{-1}. By comparing the electronic absorption and IR absorption of this compound with those of the compounds having Fe^{III}–O–Fe^{III}, Cr^{III}–O–Cr^{III}, and Mn^{IV}–O–Mn^{IV} constitution, we confirmed that this compound was μ-oxo-bis[tetraphenylporphinatomanganese(III)]. Because no oxidant was added into the reaction system, this compound should not be the high-valence μ-oxo-bis[manganese(IV)porphyrin] reported by the literature (55). In addition, the mixed d^2 and d^4 configurations were observed from ESR of $TPPMn^{III}Cl$, but were not observed in $[TPPMn^{III}]_2O$. Probably this is due to antiferromagnetic coupling between two Mn^{3+} of $[TPPMn^{III}]_2O$ through the oxygen bridge (56). This supplies further evidence for the μ-oxo structure of $[TPPMn^{III}]_2O$.

The preparation of 10 substituted μ-oxo-bis[tetraphenylporphinatomanganese(III)] $[TRPPMn^{III}]_2O$ shown in Fig. 1 can be easily accomplished by Method 1. The compounds have the same IR and electronic absorption spectra as $[TPPMn^{III}]_2O$ (Table 1).

In order further to confirm the structure of the new compound, we designed Method 2, by which $[TPPMn^{III}]_2O$ was obtained from the reaction of $TPPMn^{III}Cl$, $TPPMn^{III}OH$, and metallic sodium in anhydrous benzene. The experiment shows that the reaction product had the same IR and electronic absorption spectra as the product from the reaction of TPPMn(III)Cl and NaOH. This proves that products obtained from the above two different reaction routes are the same. In anhydrous benzene, the reactions among $TPPMn^{III}Cl$, $TPPMn^{III}OH$, and metallic sodium can be expected to take place as follows:

$$TPPMn^{III}OH + Na \rightarrow TPPMn^{III}ONa + 1/2H_2\uparrow$$

$$TPPMn^{III}ONa + TPPMn^{III}Cl \rightarrow [TPPMn^{III}]_2O + NaCl.$$

Because the above reactions were carried out in anhydrous solvent, and no oxidant was added into the reaction system, the reaction product should be a trivalent μ-oxo-bis[tetraphenylporphinatomanganese(III)] $[TPPMn^{III}]_2O$ and not a hydrous monomanganese(III)porphyrin or its other valence tautomers.

Spectral Characteristics of $[TRPPMn^{III}]_2O$

Electronic absorption spectra of 10 substituted μ-oxo-bis[tetraphenylporphinatomanganese(III)] compounds $[TRPPMn^{III}]_2O$ are listed in Table 1. There existed a characteristic absorption at about 420 nm and a wide shoulder peak at 510 nm for all $[TRPPMn^{III}]_2O$. This spectral character of $[TRPPMn^{III}]_2O$ is similar to that of Cr^{III}–O–Cr^{III} (57) and high-valence Mn^{IV}–O–Mn^{IV} (55) compounds. In addition, the Soret absorption by $[TRPPMn^{III}]_2O$ at about 470 nm decreased 5–10 nm compared with corresponding $TRPPMn^{III}Cl$, and the absorbency decreased greatly, too. This type of compound evidently had the μ-oxo dimer constitution. The decline of absorbency in μ-oxo-bismanganese(III)porphyrin was in accord with the expectation that the conjugated structure in μ-oxo-bismanganese(III)porphyrins may be twisted because of the crowd between two porphyrin ring planes.

Compared with $TRPPMn^{III}Cl$, $[TRPPMn^{III}]_2O$ existed as two characteristic IR absorption bands at the range of 800–1000 cm^{-1}, which are similar to the stretching contract vibration caused by Fe^{III}–O–Fe^{III} (56) and Cr^{III}–O–Cr^{III} (57) constitution. In addition, $[TPPMn^{III}]_2O$ presented two new absorption peaks at 760 and 745 cm^{-1}, but no absorption peak of $\nu_{\mathrm{Mn-Cl}}$ at 320 cm^{-1}. The absorption peak at 800 cm^{-1} for $TPPMn^{III}Cl$ shifted at 787 cm^{-1} for $[TPPMn^{III}]_2O$. $[TPPMn^{III}]_2O$ appeared as an obvious shoulder peak at 798 cm^{-1}. This shoulder peak is similar to the peak for Mn^{IV}–O–Mn^{IV} compound reported by the literature (55). IR analyses of the 10 substituted $[TRPPMn^{III}]_2O$ indicated that the change of the substituents on porphyrin benzene rings has little influence on the characteristic absorption of the Mn–O–Mn bonds.

Cyclohexane Hydroxylation Catalyzed by $[TRPPMn^{III}]_2O$

The products of cyclohexane oxidation catalyzed by $[TRPPMn^{III}]_2O$ are cyclohexanol and cyclohexanone. For all oxidation experiments, the products were detected after the reactions were run for 15 min. The yields of cyclohexane hydroxylation catalyzed by 10 different substituted μ-oxo-bismanganese(III)porphyrin compounds $[TRPPMn^{III}]_2O$ are listed in Table 2.

It can be seen from Table 2 that the reaction yields and the ratios of cyclohexanol to cyclohexanone did not have differences for the reactions catalyzed by the *para*-substituted porphyrins, except for compound 7. But the reaction yields and the ratios of cyclohexanol to cyclohexanone evidently increased for the *ortho*-substituted porphyrin catalysts. This showed that the catalytic power of μ-oxo-bismanganese(III)porphyrins was related to the steric effect of the substituents. The lower catalytic power of

TABLE 2

Results of Cyclohexane Monooxygenation

Catalyst	Cyclohexanol (10^{-4} mol)	Cyclohexanone (10^{-4} mol)	Ol: One
1	1.45	0.54	2.5
2	1.50	0.55	2.7
3	1.55	0.59	2.6
4	1.50	0.59	2.5
5	1.55	0.64	2.4
6	1.45	0.55	2.7
7	0.41	trace	
8	1.59	0.50	3.2
9	1.95	0.55	3.6
10	1.95	0.46	4.3

Note. Oxidation carried out by the reaction of 4.6×10^{-4} mol PhIO with cyclohexane (5 mL) in benzene (5 mL), containing 1.5×10^{-5} mol of catalysts at 303 K for 2 h.

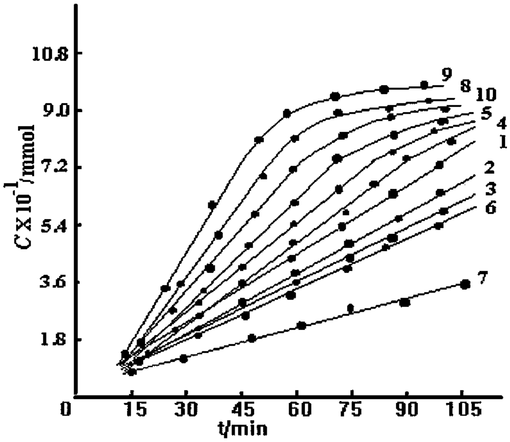

FIG. 2. Reaction yields change with the reaction time.

compound 7 was possibly related to the reaction between the PhIO and NMe_2 groups.

Relationship between Cyclohexanol Yields and Reaction Time

Cyclohexanol yields of cyclohexane hydroxylation catalyzed by compounds 1–10 with PhIO increased with the reaction time, and the reaction indicated a zero-order feature in the initial stages. Reaction rates decreased in the later stages of reaction (see Fig. 2).

Figure 2 shows the changes of cyclohexanol concentration c with reaction time t in benzene solvent in the case of $[TRPPMn^{III}]_2O$ being used as the catalyst. Substituents R obviously affect the rate of the reaction. The reaction gave a linear relationship between cyclohexanol concentration c and the reaction time t for all the reactions catalyzed by μ-oxo-bismanganese(III)porphyrin from 15 to 100 min after the start of the reactions. The time t in the linear relationship is related to the rate of oxidation reaction. The faster the rate of the reaction, the less the time. According to the reaction kinetic principle, the slopes of these lines stand for the estimated kinetic constants of the reaction (49). Table 3 lists the estimated kinetic constants k of the reaction catalyzed by μ-oxo-bismanganese(III)porphyrin compounds 1–10 and the characteristic constants σ of the corresponding substituents R.

For the cyclohexane hydroxylation catalyzed by μ-oxo-bismanganese(III)porphyrin, the rate of reaction is related to the position and electronic effect of the substituent. When Cl or Br replaced the *ortho*-H atom of the porphyrin benzene ring, the reaction yields and rates evidently increased. This was probably related to the fact that the *ortho*-substituents of the porphyrin benzene ring could decrease the rate of metalloporphyrin self-oxidation (59). Research has shown that cyclohexane hydroxylation catalyzed by metalloporphyrin and metalloporphyrin self-oxidation are a pair of competing reactions through the same intermediates. The *ortho*- substituents of the porphyrin benzene ring made the rate of self-oxidation of metalloporphyrin decline, but were favorable to the other competing reaction, and quickened the rate of cyclohexane hydroxylation catalyzed by metalloporphyrin.

Hammett Relationship of Cyclohexane Oxidation Catalyzed by $[TRPPMn^{III}]_2O$

For the cyclohexane hydroxylation catalyzed by *para*- and *meta*-substituted μ-oxo-bis[tetraphenylporphinatomanganese(III)] $[TRPPMn^{III}]_2O$, the characteristic constant σ of substituents R on the porphyrin ring had the Hammett relationship shown in Fig. 3 with the reaction rate

TABLE 3

Rate Constant k(mol/min) of Cyclohexane Monooxygenation Catalyzed by $[TRPPMn^{III}]_2O$

Catalyst	1	2	3	4	5	6	7	8	9	10
Substituent R	H	p-CH_3	p-(i-pr)	p-F	p-Cl	p-OMe	p-NMe_2	m-Cl	o-Cl	o-Br
σ	0	−0.17	−0.20	0.06	0.23	−0.27	−0.83	0.37	—	—
$k \times 10^6$	12.73	10.22	9.42	14.07	17.21	8.29	5.81	22.14	24.24	21.83
lg ($k \times 10^6$)	1.105	1.010	0.974	1.148	1.236	0.919	0.764	1.345	1.385	1.339

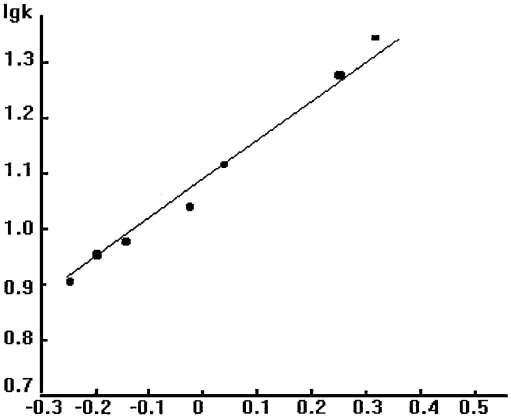

FIG. 3. Hammett relationship between the reaction rate constants k and the substituent constants σ.

constant k. The mathematical equation for the Hammett relationship is as follows: $\lg k = 0.530\sigma - 0.342$.

The reaction constant ρ is $+0.530$, and its value is positive and small. This shows that cyclohexane hydroxylation catalyzed by $[\mathrm{TRPPMn^{III}}]_2\mathrm{O}$ was accelerated by electrophilic substituents, but the reaction is insensitive to the electronic effect of the substituents. This fact means that no positive or negative ion intermediates are formed in the reaction process, and cyclohexane hydroxylation is a positive free radical reaction.

Figure 3 and Table 3 showed clearly that aromatic substituents in the mesoposition of the macrocycle that are more electron-withdrawing than the phenyl group are superior oxidation catalysts, whereas those that are more electron-donating are inferior catalysts compared to simple meso-phenyl-substituted μ-oxo-bismanganese porphyrins. In fact, the greater the degree of electron withdrawal, the more effective the catalyst. This phenomenon in oxidations that have a radical component when molecular oxygen is used as an oxidant in iron(III)-porphyrin-catalyzed high-conversion selective alkane oxidation corresponds to those reported by Lyons *et al.* (47). Why then does the induction of electron-withdrawing groups increase the rate of oxidation reactions? First, the catalytic turnovers for alkane oxidations were related to the reduction potential of the metal ion of the substituted metalloporphyrins. As the degree of electron withdrawal increases, the reduction potential of metalloporphyrins also increases and the catalytic activity improves (47). Second, as electron-withdrawing groups are inducted into the macrocycle, the oxidative and thermal stability of metalloporphyrins is greater (60), and the macrocycle also becomes more stable to reduction by the central metal atom (5). Third, in the catalytic oxidation of hydrocarbon, the intermediate exists as the high-oxidation-state porphinatometal oxo radical cation, and electrons are transferred from the macrocycle to the metal center. With increased electron withdrawal from the macrocycle, there may be a greater tendency for the active catalyst to behave as an oxo-centered radical, $\mathrm{(P)Fe{-}O^{\bullet}}$, than a ferryl species, $\mathrm{(P^{+\bullet}){=}O}$ (5).

Comparing of the Catalytic Power of $[\mathrm{TPPMn^{III}}]_2\mathrm{O}$ with the power of the Other Metalloporphyrins

As chloro[tetraphenylporphinatoiron(III)] $\mathrm{TPPFe^{III}Cl}$, chloro[tetraphenylporphinatomanganese(III)] $\mathrm{TPPMn^{III}}$ Cl, and μ-oxo-bis[tetraphenylporphinatoiron(III)] $[\mathrm{TPP\,Fe^{III}}]_2\mathrm{O}$ catalyzed the reaction transferring an oxygen atom from PhIO to cyclohexane under moderate conditions, so did μ-oxo-bis[tetraphenylporphinatomanganese(III)] $[\mathrm{TPPMn^{III}}]_2\mathrm{O}$. The reaction products were cyclohexanol and cyclohexanone. The results in Table 4 show that the yields and rate constant k of the reaction catalyzed by μ-oxo-bis[tetraphenylporphinatomanganese(III)] were greater than those for $\mathrm{TPPFe^{III}Cl}$, $\mathrm{TPPMn^{III}Cl}$, and μ-oxo-bis[tetraphenylporphinatoiron(III)] $[\mathrm{TPPFe^{III}}]_2\mathrm{O}$. The ratios of cyclohexanol to cyclohexanone for cyclohexane hydroxylation catalyzed by $[\mathrm{TPPMn^{III}}]_2\mathrm{O}$ were smaller than those for hydroxylation catalyzed by iron(III)porphyrin $\mathrm{TPPFe^{III}Cl}$ and $[\mathrm{TPPFe^{III}}]_2\mathrm{O}$, but greater than those for hydroxylation catalyzed by monomanganese(III)porphyrin $\mathrm{TPPMn^{III}Cl}$.

Combining the results in Tables 2 and 4, it can be seen that the yields of the oxidation reaction catalyzed by

TABLE 4

Cyclohexane Hydroxylation Catalyzed by Different Metalloporphyrins

Catalyst	Catalyst m mol	Rate constant $k \times 10^6$ (mol/min)	Total yields m mol	Catalyst turnovers	Product selectivity (%)	
					Cylohexanol	Cyclohexanone
$\mathrm{TPPFe^{III}Cl}$	0.030	11.47	0.10	3.3	90.5	9.5
$\mathrm{TPPMn^{III}Cl}$	0.030	10.73	0.15	5.0	69.7	30.3
$[\mathrm{TPPFe^{III}}]_2\mathrm{O}$	0.015	10.27	0.12	8.0	84.6	15.4
$[\mathrm{TPPMn^{III}}]_2\mathrm{O}$	0.015	12.73	0.21	14.0	71.7	28.3

Note. Oxidation carried out by the reaction of 4.6×10^{-4} mol PhIO with cyclohexane (5 mL) in benzene (5 mL) at 303 K for 2 h.

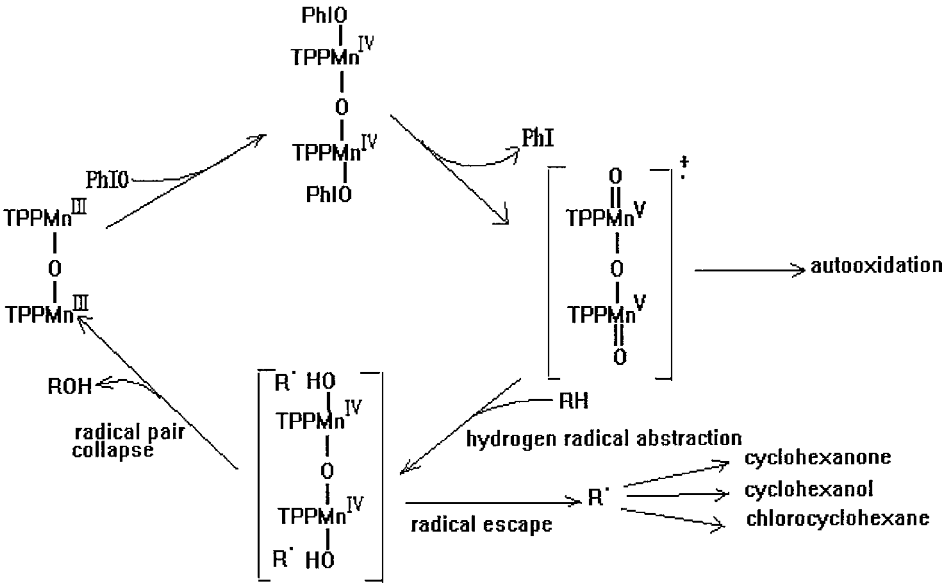

FIG. 4. Mechanism of hydrocarbon hydroxylation catalyzed metalloporphyrins.

$[TRPPMn^{III}]_2O$ are more significantly improved than the yields of the reactions catalyzed by other known metalloporphyrins. Perhaps this is related to the greater oxidative stability of $[TRPPMn^{III}]_2O$ than of other metalloporphyrins. Further studies will be carried out.

Preliminary Study of the Reaction Mechanism

So far, all evidence (61) has shown that the active intermediate in alkane hydroxylation catalyzed by trivalent iron or manganese porphyrin is a high-valence metal–oxygen positive radical $M(IV)O^{+}(M = \text{Fe, Mn, Cr})$. Do μ-oxo-bismanganese(III)porphyrins, $[TRPPMn^{III}]_2O$, as a new class of porphyrin complex, catalyze alkane oxidation through a radical pathway like other known metalloporphyrins? If the reaction proceeds through a radical pathway, a free radical inhibitor should quench the reaction. We have found that 2,6-di-tert-butyl-*p*-cresol can substantially quench the oxidation reaction. In addition, from Table 2 we can see that when the substituent *R* of the macrocycle of $[TRPPMn^{III}]_2O$ is a dimethylamino group, the cyclohexanol yield is very small. Perhaps this is related to the inhibition action of amine compounds. It is interesting to find that the influence of solvents used on the products of cyclohexane oxidation catalyzed by $[TRPPMn^{III}]_2O$ is the same as for other known metalloporphyrins. There were only cyclohexanol and cyclohexanone, but no radical coupling products in benzene. In methylene chloride, cyclohexyl chloride was detected, though no radical coupling products were found. This solvent action corresponds to a radical pathway (62). By monitoring the reactions of PhIO with $TPPMn^{III}Cl$ and $TPPFe^{III}Cl$ with a UV–vis spectrometer, we found the differences in electronic absorption between the reactions of metalloporphyrins and PhIO (63). When PhIO was added, the electronic absorption spectra of $[TPPMn^{III}]_2O$ included a new absorption peak at 448 nm, and the Soret absorption at 420 nm gradually disappeared. The same phenomenon was observed for $TPPMn^{III}Cl$, and in addition, a new absorption peak appeared at 435 nm. However, no new absorption peak appeared for $TPPFe^{III}Cl$ and $[TPPFe^{III}]_2O$, but the Soret absorption peak disappeared.

The reaction of $[TPPMn^{III}]_2O$ and PhIO had an electronic absorption change similar to that for the reaction of $TPPMn^{III}Cl$ with PhIO. This fact means that $[TPPMn^{III}]_2O$ and TPPMnCl possibly catalyze the process transforming an oxygen atom from PhIO to cyclohexane in the same way. According to the above results and the fact that the reaction between TPPMnCl and PhIO can form a high-valence μ-oxo dimer $[ClTPPMn^{IV}(OIPh)]_2O$ (55), a possible reaction mechanism for the μ-oxo-bismanganese(III) porphyrin-PhIO-RH system is that shown in Fig. 4.

Cyclohexanol is the product formed by the cage collapse of radical pairs, and cyclohexanone is the product formed by the reaction of the escaped radical $R\cdot$ and oxidants. The research results on the Hammett relationship of this reaction were in accord with the assumed positive radical intermediate. The experiments showed that cyclohexanone yield increased when the above reaction was carried out in air. This can be considered as evidence of the cyclohexanone source.

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