JOURNAL OF CATALYSIS **178,** 182–187 (1998)
ARTICLE NO. CA982138

Synthesis of μ-Oxo-bisiron(III)Porphyrin Compounds and Their Catalysis for Cyclohexane Hydroxylation

Can-Cheng Guo[1]

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

Received December 4, 1997; revised April 16, 1998; accepted April 28, 1998

Fourteen substituted μ-oxo-bis[tetraphenylporphinatoiron(III)] derivants ([TXPPFe^{III}]$_2$O) were synthesized by passing chlorotetraphenylporphinatoiron(III) (TPPFe^{III}Cl) through a neutral alumina chromatographic column, and nine of which were used in cyclohexane hydroxylation with PhIO as a new type of catalyst under moderate conditions. The experiments have shown that the yields, rate constants k of the cyclohexane hydroxylation have a linear relationship to characteristic constants σ of substituents on porphyrin rings, a physical constant characterizing the electronic effects and steric effects of a substituent group, and that the product distributions and kinetic properties of the reactions are dependent on the reaction temperature, solvent as well as air. In contrast with monoironporphyrin TPPFe^{III}Cl, μ-oxo-bisironporphyrin [TPPFe^{III}]$_2$O is shown to have the better catalytic power for cyclohexane hydroxylation with PhIO under moderate conditions and stability to PhIO. The research results show that μ-oxo-bisironporphyrin can be used as the model compound of cytochrome P-450 monooxygenase.

Key Words: **porphyrin; catalyze; oxidation.**

INTRODUCTION

In 1978, Groves first reported that chlorotetraphenylporphinatoiron(III) (TPPFe^{III}Cl) could catalyze the activity of the inert hydrocarbon bond as a model of cytochrome P-450 monooxygenase (1). The behavior of metalloporphyrins catalyzing the activity of the inert hydrocarbon bond is just the same as that of cytochrome P-450 monooxygenase in biological phenomena, of which many scientists are strongly interested (2). In order to obtain insight into the possibility of μ-oxo-bisiron(III)porphyrin compounds to catalyze the inert hydrocarbon bond, we prepared 14 μ-oxo-bis[tetraphenylporphinatoiron(III)] derivants [TXPPFe^{III}]$_2$O, shown in Fig. 1, with chlorotetraphenylporphinatoiron(III) (TPPFe^{III}Cl) through a neutral alumina chromatographic column, and nine of which were used to catalyze the oxidation of cyclohexane into cyclohexanol and cyclohexanone with PhIO under moderate conditions. We found that the yields and rate constants of the cyclohexane hydroxylation have a linear relationship with the constants of substituents on porphyrin rings and that the product distributions and kinetic properties of the reactions connected with the reaction temperature, solvent as well as air. The study showed that μ-oxo-bisironporphyrin [TPPFe^{III}]$_2$O has better catalytic power for cyclohexane hydroxylation with PhIO under moderate conditions and is more stable than monoironporphyrin TPPFe^{III}Cl. The research results show that μ-oxo-bisironporphyrin can be used as the model compound of cytochrome P-450 monooxygenase.

EXPERIMENTAL

Instruments and Reagents

UV-Vis spectra were obtained with a Perkin Elmer L-17 UV-Vis spectrophotometer; Perkin-IR spectra were recorded on a 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 analyser and a Shanghai mini-motor plant model 5012 constant temperature water-bath were used.

Before being used, benzene and dichloromethane were dehydrated; neuteral 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$_2$ and TXPPFe^{III}Cl were synthetized according to the documented procedures (3, 4). Their structures were confirmed by elementary analysis, IR spectra, and UV-Vis spectroscopy. PhIO was synthetized by documented procedures (5), and the purity measured by iodimetry was 99%.

Synthesis of [TXPPFe^{III}]$_2$O

A typical procedure is described as follows: 2 g of TPPFe^{III}Cl was passed through a chromatographic column filled with 500 g Al_2O_3 using the wet method. Benzene containing 5% of C_2H_5OH was used as a drip washing liquid. [TPPFe^{III}]$_2$O was formed in the above procedure. Effluent

---

[1] E-mail: ccguo@mail.hunu.edu.cn.

0021-9517/98 $25.00

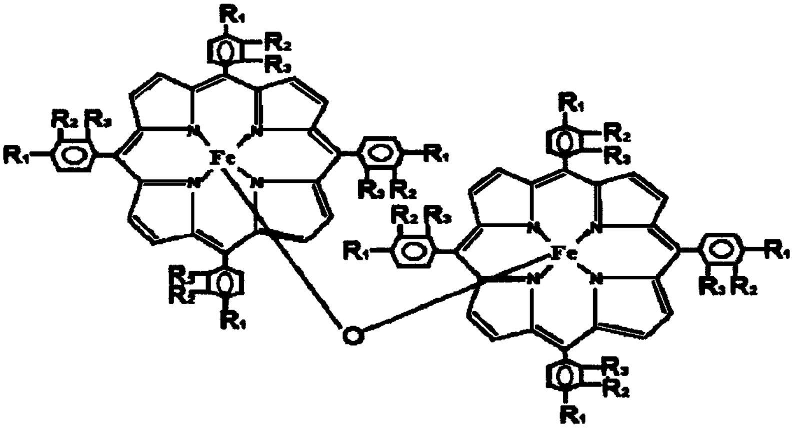


FIG. 1. Structure of 14 $[TXPPFe^{III}]_2O$. 1. $R_1 = R_2 = R_3 = H$; 2. $R_1 = CH_3$, $R_2 = R_3 = H$; 3. $R_1 = Cl$, $R_2 = R_3 = H$; 4. $R_1 = i\text{-}C_3H_7$, $R_2 = R_3 = H$; 5. $R_1 = F$, $R_2 = R_3 = H$; 6. $R_1 = Br$, $R_2 = R_3 = H$; 7. $R_1 = I$, $R_2 = R_3 = H$; 8. $R_1 = H$, $R_2 = F$, $R_3 = H$; 9. $R_1 = H$, $R_2 = Cl$, $R_3 = H$; 10. $R_1 = H$, $R_2 = Br$, $R_3 = H$; 11. $R_1 = H$, $R_2 = CH_3$, $R_3 = H$; 12. $R_1 = R_2 = H$, $R_3 = F$; 13. $R_1 = R_2 = H$, $R_3 = Cl$; 14. $R_1 = R_2 = H$, $R_3 = Br$.

was evaporated to dryness under reduced pressure. The purity of $[TPPFe^{III}]_2O$ was checked with HPLC or IR. If the components with the retention time 2.87 min of $TXPPFe^{III}Cl$ in HPLC, or the absorption band at 380 cm^{-1} (ν_{Fe-Cl}) in IR disappeared, the reactants were thought to be transformed completely. Otherwise, the above-mentioned procedure was repeated until $TPPFe^{III}Cl$ was transformed completely into $[TPPFe^{III}]_2O$. Fourteen $[TXPPFe^{III}]_2O$ compounds, shown in Fig. 1, were synthesized in the same procedure. Their elementary analysis, IR, and UV-Vis maximum are listed in Table 1.

Cyclohexane Hydroxylation with PhIO

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

Oxidation of $[TXPPFe^{III}]_2O$ with PhIO

PhIO was dissolved in benzene. Its concentration was determined by iodimetry. Accurately weighed metalloporphyrin in a volumetric flask was diluted to about

TABLE 1

Data of Element Analyses, λ_{max}, and $\nu_{Fe-O-Fe}$ of $[TXPPFe^{III}]_2O$

Compd. no.	Element analyses C Found	C Calcd.	H Found	H Calcd.	N Found	N Calcd.	λ_{max} benzene/nm	$\nu_{Fe-O-Fe}/cm^{-1}$
1	78.09	78.11	4.23	4.17	8.05	8.28	407.6, 570.0, 611.2	870, 895
2	78.23	78.68	4.86	4.95	7.66	7.68	409.2, 572.8, 612.8	870, 895
3	64.73	64.90	2.88	2.97	7.11	6.88	408.0, 570.8, 611.2	870, 895
4	79.27	79.61	6.25	6.20	6.64	6.63	409.6, 572.4, 613.6	870, 895
5	69.81	70.58	2.95	3.21	7.74	7.49	408.0, 570.0, 610.8	875, 895
6	52.83	53.26	2.08	2.44	5.35	5.65		872, 893
7	45.13	44.76	2.26	2.03	4.95	4.77		878, 890
8	70.01	70.58	2.95	3.21	7.61	7.49	405.6, 568.4, 607.2	880, 905
9	64.52	64.90	2.78	2.97	7.03	6.88	407.6, 568.8, 608.8	880, 910
10	52.95	53.26	2.13	2.44	6.02	5.65	408.0, 569.4, 611.4	880, 910
11	78.33	78.68	4.85	4.95	7.68	7.68	406.4, 570.4, 610.4	885, 920
12	71.02	70.58	3.15	3.21	7.63	7.49	410.5, 571.3, 610.8	870, 895
13	64.35	64.90	3.13	2.97	7.05	6.88	409.7, 569.9	870, 894
14	52.45	53.26	2.05	2.44	5.35	5.65	420.9, 572.3	868, 893

10^{-5} mol · dm^{-3} with benzene. After the PhIO and metalloporphyrins were mixed at 298 K, the time-variation of the Soret absorption intensity of $[TXPPFe^{III}]_2O$ in the reaction system was measured immediately by UV-Vis spectrophotometery.

RESULTS AND DISCUSSION

Syntheses and Spectral Characteristics of $[TXPPFe^{III}]_2O$

Fleischer *et al.* (6) synthesized $[TPPFe^{III}]_2O$ by the reaction of $TPPFe^{III}Cl$ with 40% NaOH, but this method gave only a poor yield and a not so pure product. It was discovered by moniting the reactant system with HPLC that metal ions fell off in the course of this reaction, so the method was modified in this paper. Thus, $TPPFe^{III}Cl$ can change to $[TPPFe^{III}]_2O$ (7) with a good yield (98%) and purity by passing it through a neutral Al_2O_3 chromatographic column. The procedure is easy to operate. The preparation of all 14 μ-oxo-bis[tetraphenylporphinatoiron(III)] compounds shown in Fig. 1 can be easily accomplished by this modified method.

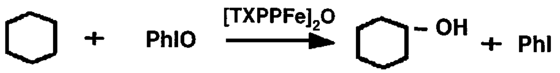
It can be seen from Table 1 that, compared with $TXPPFe^{III}Cl$, there exist the characteristic absorptions at 870 and 895 cm^{-1} in the IR spectrum of $[TXPPFe^{III}]_2O$, which are consistent with the Fe–O–Fe stretching contract vibration reported in (6). IR analyses of compounds 1–14 indicate that the change of the substituting group on porphyrin benzene rings has little influence on the characteristic absorption of the Fe–O–Fe bonds.

Fe atoms of $[TXPPFe^{III}]_2O$ and $TXPPFe^{III}Cl$ are in the d^5 configuration. The high-spin d^5 feature is observed from ESR of $TXPPFe^{III}Cl$ at room temperature, but is unobserved in $[TXPPFe^{III}]_2O$. Probably this is because of antiferromagnetic coupling between two Fe^{3+} atoms of $[TXPPFe^{III}]_2O$ though the oxygen bridge (8). This supplies further evidence for a μ-oxo construction of $[TXPPFe^{III}]_2O$.

There exists a strong Soret absorbance at 410–420 nm in UV-Vis spectra of both $[TXPPFe^{III}]_2O$ and $TXPPFe^{III}Cl$, but $[TXPPFe^{III}]_2O$ shifts to violet at about 5 nm, compared with the corresponding $TXPPFe^{III}Cl$. There is no characteristic absorption at 380 nm for $[TXPPFe^{III}]_2O$, but there is for the corresponding $TXPPFe^{III}Cl$.

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

Cyclohexane hydroxylation catalyzed by $[TXPPFe^{III}]_2O$ with PhIO is



The reaction products are cyclohexanol and cyclohexanone. In the absence of $[TXPPFe^{III}]_2O$ no cyclohexanol nor cyclohexanone was formed, indicating that $[TXPPFe^{III}]_2O$ acts as a catalyst in the reaction. There is a linear relationship between the quantity of cyclohexanol and reaction time, and the reaction indicates a zero-order feature in initial stages. Reaction rates decrease in the latter stages of reaction (Fig. 2).

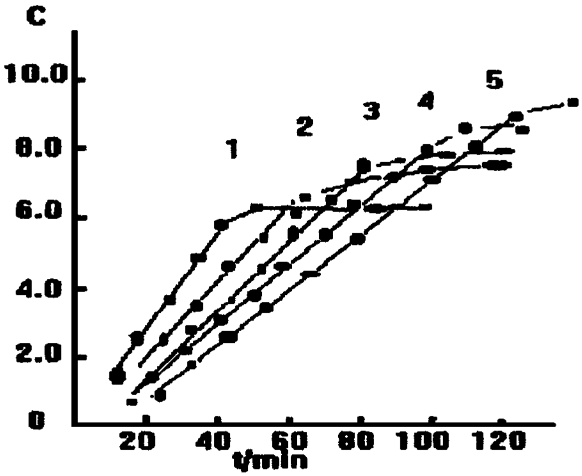


FIG. 2. Change of cyclohexanol concentration *c* with reaction time *t* at different temperatures. Catalyst: $[TPPFe^{III}]_2O$; solvent: benzene; temperature: 1, 321 K; 2, 316 K; 3, 311 K; 4, 306 K; 5, 301 K.

The above-mentioned dynamics relationship does not exist when reactions are carried out in air, and the proportion of cyclohexanone in the reaction products increases clearly. Reaction temperature, reaction solvent, and substituent groups X of $[TXPPFe^{III}]_2O$ have a regular effect on product rates and the kinetics of the reaction.

Influence of Reaction Temperature

Figure 2 shows the changes of cyclohexanol concentration *c* (mol · dm^{-3}) with reaction time *t* at different temperatures in benzene solvent in the case of $[TPPFe^{III}]_2O$ being used as the catalyst. In the range of the test temperatures, the zero-order kinetic relationship between the reaction product cyclohexanol and reaction time is present. With temperature variation, the rate, yield, and time needed to complete the reaction all change. Reaction yield and the time needed to complete the reaction decrease with increasing the temperature, but the mole ratio of cyclohexanol and cyclohexanone are hardly affected. The observed rate constant k_a obtained from Fig. 2 increases with the increasing temperature (Table 2). Figure 3 shows that k_a and temperature T have an Arrhenius relationship for which the linear correlation coefficient is 0.9910.

The mathematics expression is

$$\mathrm{Ln}\, k_a = -2704/T + 1.9734. \qquad [1]$$

Influence of Solvent on the Reaction

The influence of solvent on cyclohexane monooxygenation catalysized by $[TXPPFe^{III}]_2O$ is remarkable. Table 3

TABLE 2

Cyclohexane Hydroxylation Results at Different Reaction Temperatures

Reaction temperature T (K)	301	306	311	316	321
Time t complete reaction (min)	116	85	69	57	45
Cyclohexanol yield (%)	22.0	19.8	17.2	15.4	13.4
Alcohol : ketone (mol ratio)	5.70	5.75	5.82	5.67	5.42
$k_a \times 10^4$ (mol · dm^{-1} · min^{-1})	9.04	10.53	12.17	13.14	16.30
$-\ln(k_a/\text{mol} \cdot \text{dm}^{-1} \cdot \text{min}^{-1})$	7.01	6.86	6.71	6.64	6.42

Note. Yield is based on inputed PhIO.

lists the results of cyclohexane hydroxylation catalysized by $[\text{TPPFe}^{\text{III}}]_2\text{O}$ with PhIO in five kinds of solvents. In cyclohexane solvent, the products were detected after the reaction was run for 3 h. The rate of this reaction was the lowest, but the reaction yield was the highest. Reaction induction periods disappeared, when 0.5 mL benzene was added to the cyclohexane reaction system, and reaction speed increased, but the yield decreased. The induction period of the reaction was not present when other solvents were used. Table 3 indicates that with the increase of solvent polarity, the reaction yield decreased, but selectivity of the reaction converting cyclohexane into alcohol increased. The influence of solvent polarity on the rate of the reaction is especially outstanding. Solvent polarity speeds up the reaction rates. It is found that the reaction yield decreases when methanol is used as the solvent, probably because a part of oxidant PhIO is depleted due to the reaction between PhIO and methanol. The linear relationship between the product cyclohexanol and reaction time does not exist, and the proportion of cyclohexanone in the reaction products is so little that it cannot be checked by gas chromatography. In addition, μ-oxo-bisiron(III)porphyrin can be partly transformed into monoiron(III)porphyrin in CH_2Cl_2 (9), therefore, no linear relationship between cyclohexanol and the reaction time was observed when CH_2Cl_2 was used as solvent.

Influence of the Presence of Air on the Reaction

In the presence of air, the sum of cyclohexanol and cyclohexanone yields and the ratios of alcohol to ketone changed for cyclohexane hydroxylation catalyzed by μ-oxo-bis[tetraphenylporphinatoiron(III)]. Table 4 lists the results of cyclohexane oxidation catalysized by $[\text{TPPFe}^{\text{III}}]_2\text{O}$ with PhIO in the presence of air or nitrogen. In the presence of air, the total yields of the reaction increased, but selectivity of the reaction to the product cyclohexanol decreased. In addition, in the presence of the air, there is not a linear relationship between the quantity of cyclohexanol and the reaction time.

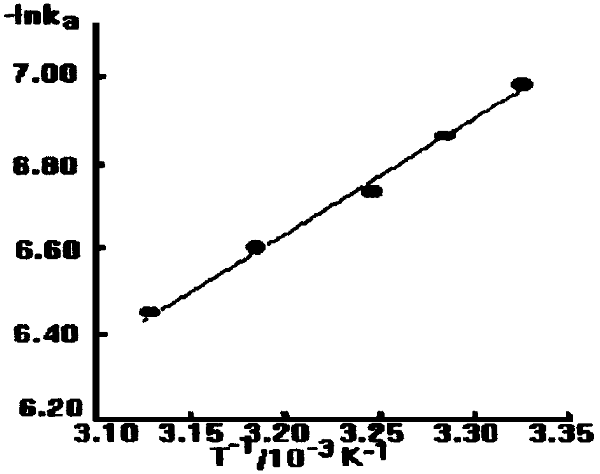


FIG. 3. Relationship between reaction rate constant k_a and temperature T.

Influence of Substituting Group X in $[\text{TXPPFe}^{\text{III}}]_2\text{O}$ on the Reaction

Cyclohexane hydroxylation catalyzed by μ-oxo-bis [tetraphenylporphinatoiron(III)] compounds 1–9 with different substitute groups X on the porphyrin ring gives a linear relationship between cyclohexanol yield and reaction time t in 2 h after the start of the reaction. But substitute groups X obviously affect the rate of reaction. Reaction yield, product distribution, and reaction rate constant k_b of cyclohexane hydroxylation, catalyzed by different substitute groups X $[\text{TXPPFe}^{\text{III}}]_2\text{O}$, are listed in Table 5.

Experimental results indicated that changing the substitute X on porphyrin rings scarcely affects the proportion

TABLE 3

Result of Cyclohexane Hydroxylation in Different Solvents

Solvent	CH_2Cl_2	CH_3OH	CH_3COCH_3	C_6H_6	C_6H_{12}	$C_6H_6 + C_6H_{12}$
Total yield (%)[a]	14.97	6.54	12.53	29.13	62.60	37.52
Alcohol : ketone (mol ratio)	12.80	[b]	7.27	5.70	3.64	4.52
$k_a \times 10^4$ (mol · dm^{-1} · min^{-1})	—	—	16.80	9.45	4.42	7.45
Time t complete reaction (min)	2	1	1	2	16	4

[a] Total yield is the sum of cyclohexanol and cyclohexanone yields.

[b] Mol number of cyclohexanone is lower than the limit of detection.

TABLE 4

Cyclohexane Hydroxylation Results in the Presence of Air[a]

	Total yields (%)	Alcohol : ketone
Air	20.53	7.5
Nitrogen	14.97	12.8

[a] The reaction time is 2 h. The reaction solvent is CH_2Cl_2.

of cyclohexanone and cyclohexanol, but the yield and the rate of reaction changes regularly. A linear relationship exists between the characteristic constant σ of the substitute group on the porphyrin ring and the cyclohexanol yield, as well as the observed rate constant k_b (shown in Fig. 4).

The above relationship can be expressed mathematically as

$$\text{Cyclohexanol yield (\%)} = 16.66\sigma + 25.40 \quad [2]$$

$$\lg k_b = 0.318\sigma - 0.6545. \quad [3]$$

The slope of the line is larger than zero, indicating that electron-attracting groups make rates and yields of the reaction increase. This result is consistent with a report by Tsuchira and Seno (10). In addition, the yield and rate of reaction are greater than the expected values when the isopropyl group or heavy atom Br is introduced to the porphyrin benzene ring, which relates well to the facts that a large group on a porphyrin ring will increase stability of the porphyrin and raise the reaction yield (11).

Oxidation of [TXPPFe^{III}]$_2$O by PhIO

[TXPPFe^{III}]$_2$O can catalyze cyclohexane monooxygenation with PhIO, but alternately, [TXPPFe^{III}]$_2$O also can be oxidized by PhIO and lose catalytic power. The spectrum absorption of [TXPPFe^{III}]$_2$O in the visible region disappeared when PhIO is present, which indicates that the π-electron conjugation system of porphyrin has been destroyed. Kinetics of oxidation of [TXPPFe^{III}]$_2$O by PhIO in dichloromethane is complicated because [TXPPFe^{III}]$_2$O is transformed into monoiron(III) porphyrin and undergoes oxidation of the porphyrin ring, but the reaction shows first-order dynamic reaction features in benzene. The rate constants k_c of the oxidation of [TXPPFe^{III}]$_2$O by PhIO are listed in Table 6.

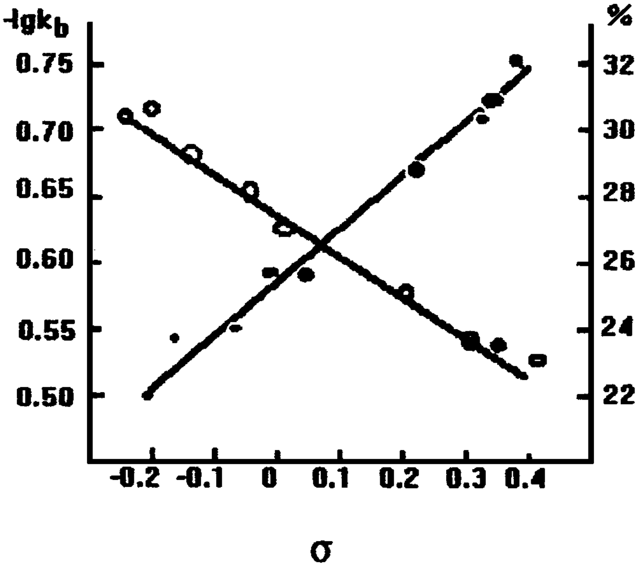


FIG. 4. Relationship between substituting group constant σ and cyclohexanol yield and rate constant k_b.

The linear relationship between the substitute group constant σ and reaction rate constant k_c is

$$\lg k_c = 0.3973\sigma - 1.5882. \quad [4]$$

It shows that electron-attracting groups make the rate of the reaction increase.

Comparison of the Catalytic Power between [TPPFe^{III}]$_2$O and TPPFe^{III}Cl

Both [TPPFe^{III}]$_2$O and TPPFe^{III}Cl can catalyse cyclohexane hydroxylation, and the products are also the same, but their catalytic powers have obvious differences. The results of cyclohexane hydroxylation catalyzed separately by [TPPFe^{III}]$_2$O and TPPFe^{III}Cl are listed in Table 7.

Compared with TPPFe^{III}Cl, the yields of the reaction catalyzed by [TPPFe^{III}]$_2$O are higher, but the rates of reaction are clearly lower. The reaction catalyzed by TPPFe^{III}Cl has no induction period in cyclohexane, but the reaction by

TABLE 5

Result of Cyclohexane Hydroxylation Catalyzed by Different [TXPPFe^{III}]$_2$O Catalysts

Catalyst X	1 H	2 *p*-F	3 *p*-Cl	4 *p*-CH_3	5 *p*-(*i*-Pr)	6 *m*-F	7 *p*-Cl	8 *m*-Br	9 *m*-CH_3
σ	0	0.06	0.23	−0.17	−0.15	0.34	0.37	0.39	−0.07
Cyclohexanol yield (%)	24.80	25.95	28.50	22.10	24.53	30.50	31.83	33.00	24.00
Alcohol : ketone (mol ratio)	5.70	5.89	5.95	5.98	5.71	5.90	5.91	5.87	5.76
k_b (min^{-1})	0.225	0.233	0.265	0.199	0.189	0.287	0.295	0.283	0.213
$-\lg$ (k_b/min^{-1})	0.647	0.633	0.577	0.702	0.723	0.542	0.530	0.548	0.671

TABLE 6

Rate Constant k_C of the Oxidation of $[TXPPFe^{III}]_2O$ with PhIO

$[TXPPFe^{III}]_2O$ X	1 H	2 p-F	3 p-Cl	4 p-CH_3	5 p-(i-Pr)	6 m-F	7 p-Cl	8 m-Br	9 m-CH_3
σ	0	0.06	0.23	−0.17	−0.15	0.34	0.37	0.39	−0.07
Detected wavelength (nm)	408.1	407.6	409.8	409.2	410.4	405.8	407.8	409.0	406.0
$k_c \times 10^2$ (nm)	2.745	2.841	3.159	2.378	1.816	3.426	3.551	3.713	2.642

Note. $[PhIO] = 5.26 \times 10^{-3}$ mol · dm^{-3}. $[[TPPFe^{III}]_2O] = 1.5 \times 10^{-5}$ mol · dm^{-3}.

$[TPPFe^{III}]_2O$ has an induction period of 3 h. In addition, the ability of $[TPPFe^{III}]_2O$ to anti-PhIO is better than that of $TPPFe^{III}Cl$ (12). The difference in catalytic power and the stability, as well as the induction period of $[TPPFe^{III}]_2O$ and $TPPFe^{III}Cl$ is possibly related to the antiferromagnetism property of $[TPPFe^{III}]_2O$ (8). Further studies will be carried out.

Preliminary Exploration on the Competing Mechanisms between Cyclohexane Oxidation and the Ring Splitting Reaction of the Porphyrin Ring in Hydrocarbon Hydroxylation in the $[TXPPFe^{III}]_2O$-PhIO System

It can be seen from Eqs. [3] and [4] that the signs of the reaction constants are positive for cyclohexane oxidation catalyzed by $[TXPPFe^{III}]_2O$ with PhIO and the ring splitting reaction of the porphyrin ring with PhIO, which shows that the two reactions are promoted by electron-attracting substitute groups on porphyrin rings. The fact that the two reaction constants are 0.3186 and 0.3973 indicates that there is little difference between the sensitivities of the reactions to the electronic effect of substitute groups. The above facts mean the two reactions possibly are competing reactions via the same intermediate:

$$PhIO + [TXPPFe^{III}]_2O$$

$$\rightarrow \text{[intermediate]} \begin{array}{l} \nearrow \text{porphyrin oxidation} \\ \searrow \text{hydrocarbon hydroxylation.} \end{array}$$

The competing mechanism between cyclohexane oxidation and the ring-splitting reaction of the porphyrin ring in hydrocarbon hydroxylation in the $[TXPPFe^{III}]_2O$-PhIO system and the intermediate formed from PhIO and $[TXPPFe^{III}]_2O$ will be studied further.

TABLE 7

Comparison of Cyclohexane Hydroxylation by $[TPPFe^{III}]_2O$ and $TPPFe^{III}Cl$

Catalyst	$[TPPFe^{III}]_2O$		$TPPFe^{III}Cl$	
Solvent	Cyclohexane	Benzene	Cyclohexane	Benzene
Total yield (%)	62.60	35.80	43.87	24.55
Alcohol : ketone (mol ratio)	3.64	5.70	4.50	7.10
Time (h)	16	10	8	4
$k \times 10^{10}$ (mol/min)	0.442	0.964	1.65	0.953
Induction period (h)	3	0	0	0

ACKNOWLEDGMENT

This project was financially supported by The Chinese National Natural Science Fund.

REFERENCES

1. Groves, J. T., Nemo, T. E., and Myers, R. S., *J. Am. Chem. Soc.* **104**, 1032 (1978).
2. Meunier, B., *Chem. Rev.* **92**, 1411 (1992), and references therein.
3. Adler, A. D., Longo, F. R., Finarelli, J. D., Goldmacher, J., Assour, J., and Korsakoff, L. J., *Org. Chem.* **32**, 476 (1967). [Guo, C.-C., He, X.-T., Zhou, G.-Y., and Youji Huaxue, **11**, 416 (1991), CA 115:255864]
4. Adler, A. D., Longo, F. R., Kampas, F., and Kim, J., *J. Inorg. Nucl. Chem.* **32**, 2443 (1970).
5. Lucas, H. J., Kennedy, E. R., and Frormo, M. W., "Organic Syntheses," Coll. Vol. 3 (E. C. Horning, Ed.), p. 482. Wiley, New York, 1955.
6. Fleischer, E. B., and Srivastava, T. S., *J. Am. Chem. Soc.* **91**(9), 240 (1969).
7. Guo, C.-C., Gui, M.-D., Zhu, S.-J., and Huaxue Shiji, **12**, 270 (1990), CA 114:134975.
8. Guo, C.-C., Zhu, S.-J., and Gui, M.-D., *Acta Chim. Sin.* **50**, 129 (1992), CA 116:206669.
9. Zhu, S.-J., Gui, M.-D., Guo, C.-C., *Chem. J. Chinese Univ.* **10**, 1100 (1989), CA 112:186647.
10. Tsuchira, S., Seno, N., *Chem. Lett.* **206**, 263 (1989).
11. Mansuy, D., Leclaire, J., and Fontecave, M., *Biochem. Biophys. Res. Commun.* **119**, 319 (1984).
12. Guo, C.-C., Zhang, S., and Lei, Y.-W., *Acta Chim. Sin.* **51**, 928 (1993), CA 120:63397.