Studies of simple μ-oxo-bisiron(III)porphyrin as catalyst of cyclohexane oxidation with air in absence of cocatalysts or coreductants

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Abstract

We report the use of simple μ-oxo-bis[tetraphenylporphinatoiron(III)] ([TPPFe^{III}]$_2$O) as a catalyst for the selective oxidation of cyclohexane into cyclohexanone and cylcohexanol with air. This is the first time that [TPPFe^{III}]$_2$O has been used as a catalyst for the aerobic liquid phase oxidation of cyclohexane in absence of any cocatalyst or coreductants. The oxidation of cyclohexane catalyzed by a very small amount of [TPPFe^{III}]$_2$O gave 90% selectivity to cyclohexanol and cyclohexanone at 12.55% yield and catalyst turnover numbers of 90,000 (based on the metal) under the conditions of 398 K and 0.6 MPa. We showed that the reaction yields and the turnover numbers of the catalyst changed with reaction temperature, pressure and the amount of catalyst. In contrast with the corresponding monoironporphyrin, chloro[tetraphenylporphinatoiron(III)] (TPPFe^{III}Cl), the oxidation of cyclohexane catalyzed by (TPPFe^{III})$_2$O with air had higher yields and greater turnovers.
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1. Introduction

During the last two decades, there have been exciting achievements in the field of hydrocarbon oxidations catalyzed by metalloporphyrins as a model of cytochrome P-450 under mild conditions [1,2]. Many scientists have utilized all kinds of metalloporphyrins for the catalysis of hydrocarbon oxidations [3–25] and even further developed these systems for industrial use. However, most of these catalytic systems are based on monometalloporphyrins and monooxy-genases, which have an inevitable disadvantage of low yields of products due to the weak resistance of porphyrin catalysts to the stoichiometric oxidants. The use of dioxygen offers a partial solution to the oxidation reaction. A few research groups reported a catalytic system consisting of monometallopor-phyrin and molecular oxygen [26,27]. Unfortunately, this system needs to use the reducers. To improve this system, Lyons et al. [28] synthesize the per-halogenated metalloporphyrin complexes and use the complexes as catalysts for alkane hydroxylation with molecular oxygen, in which coreductants are not required. But this work did not reported whether the simple μ-oxo-bis[tetraphenylporphinatoiron(III)] (TPPFe^{III})$_2$O was active catalyst in the hydrocarbon

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oxidation with molecular oxygen or not. Inspired by the success of the work of Lyons et al., we tried to use the simple μ-oxo-bismetalloporphyrin $(TPPFe^{III})_2O$ to catalyzed hydroxylation of hydrocarbons using air as the terminal oxidant to gain a better understanding of the possibility of using simple μ-oxo dimeric metalloporphyrin to catalyze the hydrocarbon oxidation directly by air. This has really been an extension of the systematic study of μ-oxo dimeric metalloporphyrins as catalysts in the hydrocarbon oxidation in this laboratory [15–18]. Lately, we reported a novel catalytic system for aerobic oxidation of the active benzyl carbon–hydrogen bond of ethylbenzene using the simple μ-oxo dimeric metalloporphyrins as catalysts and air as oxygen donor in absence of any cocatalyst or coreductant, simply under a certain of reaction temperature and atmosphere pressure [19]. In this paper, we hope further report the development of this new catalyst system for the aerobic oxidation of the inactive carbon–hydrogen bond of cyclohexane catalyzed by a very small amount of simple μ-oxo dimeric ironporphyrin $(TPPFe^{III})_2O$. Catalyzed by $(TPPFe^{III})_2O$, cyclohexane was oxidized into cyclohexanol and cyclohexanone with air in absence of solvent and cocatalyst under the conditions of 398 K and 0.6 MPa. The cyclohexane conversion and the turnover numbers of the catalyst are all high. The effects of a series of experiment parameters such as reaction temperature, pressure and the amount of catalyst on the yield and turnover numbers have been studied and the optimum conditions obtained.

2. Experimental

2.1. 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. Mass spectra were measured using a Agilent 1100C LC/MSD instrument. ^{1}H NMR spectra were determined using a Bruker-80, usually in CDCl$_3$ solution with tetramethylsilane as internal standard, at 80 MHz. GC analyses of our catalytic oxidations products were accomplished using a Shimadzu GC-16A gas phase chromatography equipped with a 0.5 mm i.d. × 25 m PEG20000 capillary column

and flame ionization detector. A Model 3KCF-10 500 ml autoclave fitted with a magnetic stirrer and a Model CYS-1 digital oxygen meter were used.

All reagents and solvents used were analytical grade and obtained commercially. Pyrrole was redistilled before used. There was no impurity found in cyclohexane by GC analysis before use.

$TPPFe^{III}Cl$ was synthesized by a method similar to that used in the literatures [29,30]. The $(TPPFe^{III})_2O$ was prepared according to our published procedures [15]. Their structures were confirmed by IR, UV-Vis, MS and ^{1}H NMR analysis.

2.2. Cyclohexane oxidation with molecular oxygen

Except where special explanation is given, all cyclohexane oxidations were carried out according to the following procedures: a certain amount of catalysts and 350 ml cyclohexane were put into a 500 ml autoclave reactor, which then was heated to the reaction temperature after having been sealed up. Once the temperature had equilibrated, air was pumped into the system continuously. A needle valve was used to regulate the flow of the tail gases in order to maintain constant pressure in the reactor. The flow of the tail gases was measured by a rotary flow meter. In order to monitor the process of the reaction, a digital oxygen meter was used to record the oxygen content of the tail gases in real-time. Product samples were identified and quantified immediately by GC with internal standard method using chlorobenzene as the standard substance. The reaction was terminated when the oxygen content in the tail gases ceased reducing.

3. Results and discussion

3.1. Catalysis of $(TPPFe^{III})_2O$ for cyclohexane oxidation with air

Scientists have made common consent of the catalytic mechanism of the metalloporphyrins [31–36], including electrocatalysis [37,38] and photocatalysis [39,40]. Ozawa et al. [41] and Momenteau and Reed [42] all reported that monometalloporphyrins could be rapidly converted to the μ-oxo dimer in presence of O$_2$, which is usually considered inactive [43,44]. Therefore, the use of μ-oxo dimeric metalloporphyrin

as catalyst is relatively uncommon. However, our former researches have proved the catalytic property of $(TPPFe^{III})_2O$ [15–18]. Moreover, the research of Weber et al. [40] clearly showed that $(TPPFe^{III})_2O$ could generate $[TPPFe^{IV}=O]^{\bullet+}$ at the condition of illumination and accomplish the photocatalytic reaction. Therefore, we consider that $(TPPFe^{III})_2O$ play a catalytic role of hydrocarbon oxidation with air under a certain temperature and pressure. Recently, we used the simple μ-oxo dimeric iron and manganese porphyrins as catalysts of aerobic oxidation of ethylbenzene in absence of any cocatalyst or coreductant, simply at 70 °C and atmosphere pressure, and the oxidation of ethylbenzene gave exclusively oxidation products of the active benzyl carbon–hydrogen bond [19]. We try to oxidize carbon–hydrogen bond of cyclohexane under same conditions, which is more inactive than ethylbenzene. Unfortunately, we were unsuccessful. However, we found that the cyclohexane oxidation gave cyclohexanol and cyclohexanone as the products at 12.5% yields and 90% selectivity only by increasing the reaction temperature and pressure to an appropriate extent. This is the first time that μ-oxo dimeric iron metalloporphyrins were used as the catalyst for the aerobic selective oxidation of the inert carbon–hydrogen bond of hydrocarbons in absence of solvent or coreductants.

Aerobic oxidation of cyclohexane catalyzed by $(TPPFe^{III})_2O$ in absence of solvent gave cyclohexanone and cyclohexanol at greater than 90% selectivity when this reaction proceeds at 398 K and 0.6 MPa (Scheme 1), as is a relatively mild system for industry. It is unnecessary to add solvent and any reductant to the system. The by-products of the reaction were dicyclohexyl, hexanedioic acid and esters. It was interest that there existed an optimum catalyst concentration and reaction temperature at which the oxidation gave the greatest selectivity and yields.

Contrary experiment results showed that there were no cyclohexanone or cyclohexanol formed after reaction of 24 h neither in absence of $(TPPFe^{III})_2O$ nor in the systems of some inorganic iron salts instead, such
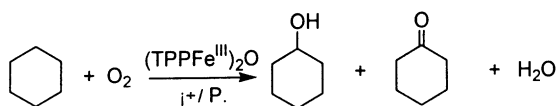
as $FeCl_3$ and $Fe(OAc)_3$, under the same experiment conditions. This confirms that $(TPPFe^{III})_2O$ act as a catalyst in the reaction.

3.2. Effect of reaction time on cyclohexane oxidation

The reaction time determines the product yield and the selectivity to cyclohexanol and cyclohexanone in the reaction catalyzed by $(TPPFe^{III})_2O$. Fig. 1 shows the change of the product yields and the oxygen uptakes with reaction time in the cyclohexane oxidation catalyzed by $(TPPFe^{III})_2O$. The yields of cyclohexanone and cyclohexanol increased with the reaction time and reached the maximum at about 3 h. The amount of cyclohexanol and cyclohexanone was increased earlier and then decreased as reaction time increases. The experiment results showed that the oxidation could give the greater than 90% selectivity and 12% total yield of cyclohexanol and cyclohexanone when the reaction lasted 3 h. However, the selectivity and yield of cyclohexanol and cyclohexanone deceased with the further increase of the reaction time. The possible reason is the deep-oxidation of cyclohexanol and cyclohexanone. We can also see from Fig. 1 that the increase of products and the consumption of O_2 are both slow in the initial 90 min. Then, they change significantly from 90 to 165 min. There are smaller changes of the yield of products and the consumption of O_2 after 3 h, indicating that the rate of the catalytic reaction diminishes. This is due to the destroying of $(TPPFe^{III})_2O$ by the oxidizer during the reaction.

3.3. Effect of reaction temperature on cyclohexane oxidation

Temperature affects the yields of the catalytic cyclohexane oxidation (see Table 1). Only when the temperature is above 353 K, can the reaction take place. The products are increased obviously until the temperature of 393 K. When the temperature is 398 K, the yield of the reaction is 12.55% and the turnover numbers of $(TPPFe^{III})_2O$ reaches 91,580. As the temperature increases further, the yield of the reaction decreases due to the excessive oxidation. In the contrary, the catalytic circulation is hard to be induced so that the yield is decreased. It is of interest that the yield increase five-fold from 2.46 to 12.55% when the
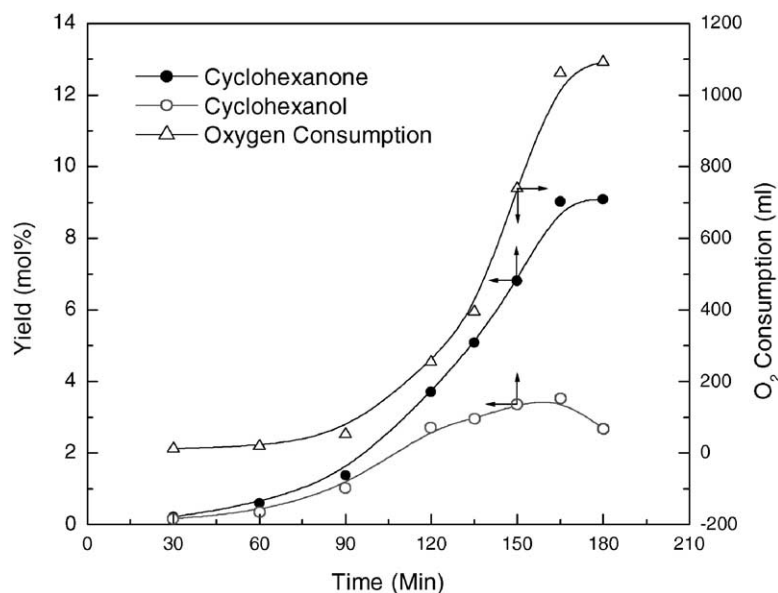
Scheme 1.

Fig. 1. Plot of cyclohexane oxidation catalyzed by μ-oxo-bisironporphyrin. Catalyst: 3 mg; cyclohexane: 350 ml; temperature: 398 K; pressure: 0.6 MPa.

temperature increases just by 5 K from 393 to 398 K. This is very different from the general catalytic reaction. The possible reason is studying in our group.

3.4. Effect of reaction pressure on cyclohexane oxidation

Gas–liquid phase reactions usually occur under extreme conditions. The activity of air, which is employed as oxygen donor in our work, is determined by air pressure in the system. If the pressure is too low, the concentration of O_2 in liquid substrate is so small that it cannot activate the reaction and the capability of the oxidizer is discounted. On the other side, if the

pressure is too high, the catalyst autooxidation is easy to happen. Consequently, the catalyst is quickly out of activity and the times of the catalytic circulation are dropped. Based on the data presented in Table 2, 0.6 MPa is the optimum pressure of the reaction when all other factors are fixed.

3.5. Effect of the amount of catalyst on cyclohexane oxidation

The amount of catalyst influences the yields of the reaction. Table 3 lists the yields of cyclohexane oxidation in presence of various amount of $(TPPFe^{III})_2O$. The catalytic effect of the system with

Table 1
Effect of temperature on the oxidation reaction[a]

Temperature (K)	Yield (mol%)	Cyclohexanone (%)	Turnover numbers
393	2.46	66.11	17,951
398	12.55	70.36	91,580
403	7.01	70.38	51,153

Yield is total yield of cyclohexanol and cyclohexanone. Turnover is based on the mmol of products per mmol of catalyst used.

[a] Experimental conditions: catalyst, 3 mg; cyclohexane, 350 ml; pressure, 0.6 MPa.

Table 2
Effect of pressure on the oxidation reaction[a]

Pressure (MPa)	Yield (mol%)	Cyclohexanone (%)	Turnover numbers
0.5	1.95	59.67	14,230
0.6	12.55	70.36	91,580
0.7	5.63	63.93	41,083

Yield is total yield of cyclohexanol and cyclohexanone. Turnover is based on the mmol of products per mmol of catalyst used.

[a] Experimental conditions: catalyst, 3 mg; cyclohexane, 350 ml; temperature, 398 K.

Table 3
Effect of the amount of catalyst on the oxidation reaction[a]

Catalyst (mg)	Yield (mol%)	Cyclohexanone (%)	Turnover numbers
15	8.35	67.84	12,186
5	7.78	67.88	34,063
4	9.08	70.64	49,694
3	12.55	70.36	91,580
2	8.55	69.45	93,587

Yield is total yield of cyclohexanol and cyclohexanone. Turnover is based on the mmol of products per mmol of catalyst used.

[a] Experimental conditions: cyclohexane, 350 ml; temperature, 398 K; pressure, 0.6 MPa.

3 mg $(TPPFe^{III})_2O$ in 350 ml cyclohexane is the best, of which the calculation result is $1:1.5 \times 10^6$ (mol/mol). The use of more catalyst results in lower yields, because the more intermediates are tended to cause the interaction so that the effect of catalyst is reduced. When a 2 mg catalyst is used, the reaction gains a lower yield though the turnovers increase a little. Table 3 also shows that the amount of catalyst has little influence on the selectivity of the products. The proportion of ketone and alcohol is about 2:1 in our reactions.

3.6. Comparison of the catalytic power between $(TPPFe^{III})_2O$ and $TPPFe^{III}Cl$

Both $(TPPFe^{III})_2O$ and $TPPFe^{III}Cl$ can catalyze cyclohexane oxidation with molecular oxygen, and the products are the same. However, their catalytic capabilities are obviously different. The results of cyclohexane hydroxylation catalyzed separately by $(TPPFe^{III})_2O$ and $TPPFe^{III}Cl$ under the same conditions are listed in Table 4. It is clear that $(TPPFe^{III})_2O$

Table 4
Comparison of molecular oxygen oxidizing cyclohexane catalyzed by different metalloporphyrins[a]

Catalyst	$TPPFe^{III}Cl$	$(TPPFe^{III})_2O$
Total mole yield	1.36	9.08
Ketone:alcohol	1.25	2.41
Turnover	7745	49,694
Reaction time (h)	3	3

Turnover is based on the mmol of products per mmol of catalyst used.

[a] Experimental conditions: catalyst, 4 mg; cyclohexane, 350 ml; temperature, 398 K; pressure, 0.6 MPa.

gains about 6.5 times of yield and turnover numbers as that of $TPPFe^{III}Cl$. In addition, the use of $(TPPFe^{III})_2O$ results in higher proportion of ketone. Preliminary investigation shows that the two types of catalysts have different catalytic mechanisms, which leads to the difference of the reaction results. Another possible reason is that $(TPPFe^{III})_2O$ has superior stability for oxidant to that of $TPPFe^{III}Cl$. Further studies of the mechanisms is underway.

4. Conclusions

Under the condition of a certain temperature and pressure, $(TPPFe^{III})_2O$ can catalyze cyclohexane oxidation with air. This reaction gains a higher yield and a ideal selectivity of the products. The optimum condition is as followed: 398 K, 0.6 MPa, catalyst:substrate $= 1:1.5 \times 10^6$ (mol/mol), and reaction time of 3 h. Compared with other catalytic systems referred, this process is more suitable for industrial use.

Acknowledgements

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