



Remarkable enhancement of aerobic epoxidation reactivity for olefins catalyzed by μ -oxo-bisiron(III) porphyrins under ambient conditions

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ABSTRACT

With μ -oxo dimeric iron(III) porphyrins [(Fe^{III}TPP)₂O] as catalyst, isobutylaldehyde as co-reductant, and dioxygen as oxidant, an efficient model system for epoxidation of olefins has been developed. Compared with mono-metalloporphyrins as catalyst, a remarkable enhancement of reactivity was obtained for the present olefin epoxidation system, in which the turnover number (TON) of the catalyst has doubled from about 700 million to 1400 million. Moreover, a plausible mechanism involving both binuclear and mono-nuclear intermediate has been proposed.

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1. Introduction

Catalytic epoxidation of olefins has attracted much attention both in industry and in organic synthesis, for epoxides are among the most useful synthetic intermediates.¹ Epoxidation of olefins could be carried out with various catalytic systems, in which complexes of ruthenium,² manganese,³ polyoxometalates,⁴ and oxovanadium Schiff base⁵ could all be used as catalysts.

As model catalysts of cytochrome P-450, metalloporphyrins have been used in the highly efficient epoxidations of olefins in combination with various oxidants for example, iodosylbenzene,⁶ hydrogen peroxide,⁷ and sodium periodate.⁸ To pursue the economical and environmentally friendly processes for the production of epoxides, selective epoxidation of olefins by molecular oxygen is particularly desirable.⁹ Mukaiyama et al. reported an efficient approach for epoxidation of olefins using dioxygen as oxidant under ambient conditions. The process involved the use of β -diketonate complexes of Ni²⁺, Co²⁺, and Fe³⁺ as catalysts and an aldehyde as oxygen acceptor.¹⁰ Subsequently, many metal catalysts for example, manganese complex,¹¹ cobalt-containing molecular sieves,¹² and metalloporphyrins¹³ demonstrated highly catalytic performance for the aerobic oxidation in the presence of aldehyde. We have also developed a series of catalytic systems for the aerobic oxidation of sulfide, alcohol, and ketone with metalloporphyrins as catalysts.¹⁴

Bismetalloporphyrin dimers are composed of two covalently bound mono-metalloporphyrin molecules. Investigations over the past decades indicated that μ -oxo-bisiron porphyrins are inactive or have low activity for hydroxylation of alkanes. Recently, high catalytic activities of μ -oxo dimeric metalloporphyrins for the oxidation of cyclohexane, ethylbenzene, and toluene have been reported.¹⁵ However, the catalysis of simple μ -oxo dimeric metalloporphyrins for epoxidation of olefins by dioxygen has not been reported up to now.

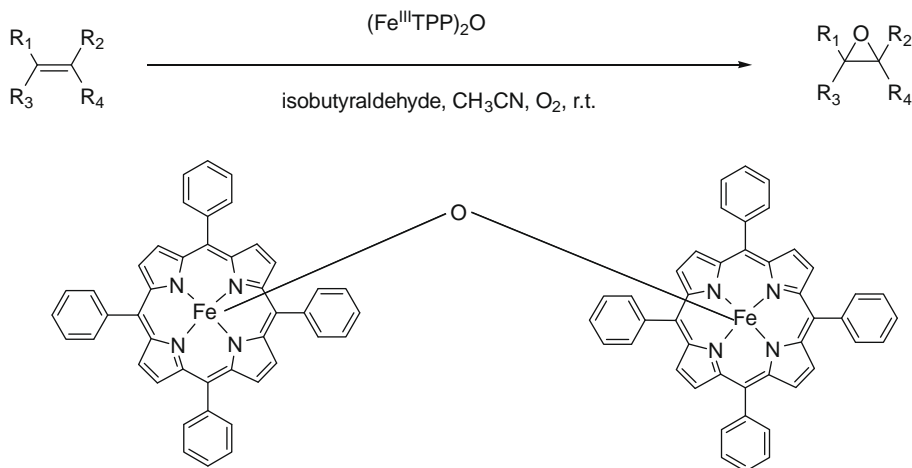
In our previous works, simple structural mono-manganese porphyrin conferred high activity and selectivity for the epoxidation of olefins, its turnover number could reach up to 700 million, which is comparable to enzyme catalysis.¹⁶ Based on the high efficiency of the metalloporphyrin-catalyzed epoxidation system, we have employed the simple μ -oxo dimeric iron porphyrins for catalyzing the epoxidation of olefins by dioxygen in the presence of isobutylaldehyde in the present Letter, as shown in Scheme 1.¹⁷ The catalytic system has been proved to be efficient for the aerobic epoxidation of olefins under ambient conditions. Compared with mono-metalloporphyrins, a remarkable enhancement of reactivity has been observed. It is the first time that dimeric iron(III) porphyrins are used for aerobic epoxidation, and the TON obtained is higher than other catalysts reported.

2. (Fe^{III}TPP)₂O Catalytic epoxidation of cyclohexene

With cyclohexene as model compound, the effects of reaction conditions on the epoxidation in the presence of (Fe^{III}TPP)₂O with molecular oxygen as oxidant have been investigated.¹⁸ Table 1

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Scheme 1. Aerobic epoxidation of olefins catalyzed by $[\text{Fe}^{\text{III}}\text{TPP}]_2\text{O}$ in the presence of molecular oxygen and isobutyraldehyde.

Table 1

Aerobic epoxidation of cyclohexene catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ in the presence of isobutyraldehyde^a

Entry	Amount of catalyst (ppm)	Conv. (%)	Yield (%)
1	0	21	21
2	0.01	96	93
3	0.05	>99	96
4	0.1	90	88
5	1.0	81	80
6	10.0	84	81
7 ^b	0.05	0	0
8 ^c	0.05	92	90
9 ^d	0.05	>99	96
10 ^e	0.1	85	82

^a Substrate (2 mmol), isobutyraldehyde (0.011 mol), acetonitrile (6 mL), O_2 bubbling, 4 h, rt.

^b No isobutyraldehyde.

^c Substrate/isobutyraldehyde = 1:5.

^d Substrate/isobutyraldehyde = 1:6.

^e $\text{Fe}^{\text{III}}\text{TPP}\text{Cl}$ as catalyst.

summarizes the main results obtained under different reaction conditions. It could be found from entry 1 of Table 1 that only 21% cyclohexene could be converted in the absence of catalyst, indicating that the $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ catalyst is crucial for the epoxidation. As depicted in Table 1, it was observed that the yield was considerably enhanced when the catalyst was used. The conversion of cyclohexene could reach up to 96% even when the amount of catalyst was only 0.01 ppm (entry 2). The optimal amount of catalyst for the epoxidation was 0.05 ppm (entry 3). On the contrary, attempts for enhancing the yield by increasing the amount of catalyst were unsuccessful. The yield decreased with the increase of catalyst amount (entries 4–6). This is the typical characteristics of metalloporphyrins-catalyzed oxidation, which was caused by the shielding effect due to the increasing catalyst intermediates.¹⁹

The effects of isobutyraldehyde on the reaction were also investigated. As shown in Table 1, the reaction could not take place in the absence of isobutyraldehyde (entry 7), strongly implying that $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ could not activate molecular oxygen without aldehyde as an oxygen acceptor under ambient conditions. The epoxidation with various molar ratio of substrate to isobutyraldehyde were examined. When the substrate/isobutyraldehyde molar ratio reached 1:5, 92% cyclohexene could be converted (entry 8). Increasing molar ratio gave higher conversion (entry 9). However, no significant difference was observed when the substrate/isobutyraldehyde molar ratio exceeds 1:5.5.

Compared with the aerobic epoxidation catalyzed by mono-metalloporphyrin, $(\text{Fe}^{\text{III}}\text{TPP}\text{Cl})$ (entry 10), it is clear that μ -oxo dimeric iron(III) porphyrin exhibited higher catalytic performance for the aerobic epoxidation of cyclohexene, probably because $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ has superior stability for epoxidation than $\text{Fe}^{\text{III}}\text{TPP}\text{Cl}$.

3. Effects of solvent on the epoxidation of cyclohexene

Using μ -oxo-bisiron(III) porphyrin as the catalyst, the aerobic epoxidation of cyclohexene with various solvents has been investigated, and the results were summarized in Table 2.

It has been observed that the solvent played an important role for the oxidation reaction. Polar solvents for example, acetonitrile and benzonitrile seemed to be more favorable for the epoxidation of cyclohexene. Dichloromethane was not suitable for this catalytic epoxidation, although it was commonly used in metalloporphyrins-catalyzed epoxidation systems.²⁰ It may be due to the instability of $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ in dichloromethane, which could be partly converted to mono-metalloporphyrins.²¹

4. Epoxidation of various substrates catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$

To evaluate the scope of the catalytic system, various alkenes were subjected to the reaction system using only 0.05 ppm of catalyst (Table 3). As shown in Table 3, most substrates could be smoothly converted to corresponding epoxides with high conversion rate and excellent selectivity.

It seems that the efficiency of the epoxidation in this catalytic system is not closely related with the steric conformation of substrates. For instance, slightly longer reaction time was required for 1-methylcyclohexene than cyclohexene (entries 1 and 2). However, slow oxidation occurred and an unsatisfactory conversion





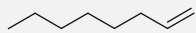
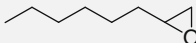
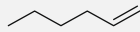
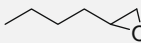
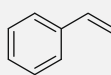
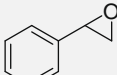
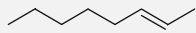
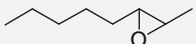
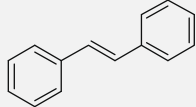
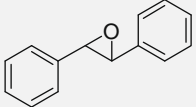

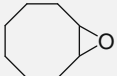
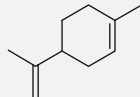
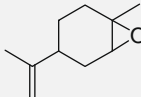
Table 2

Effect of the solvent on the aerobic epoxidation of cyclohexene catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ ^a

Entry	Solvent	Conv. (%)	Yield (%)	Selectivity (%)
1	Acetonitrile	>99	96	96
2	Benzotrifluoride	73	71	97
3	Methanol	66	64	97
4	Dichloromethane	60	57	95
5	Toluene	61	59	96

^a Substrate (2 mmol), substrate/isobutyraldehyde = 1:5.5 (molar ratio), $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ (0.05 ppm), acetonitrile (6 mL), O_2 bubbling, 4 h, rt.

Table 3
Aerobic epoxidation of various alkenes catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}^{\text{a}}$

Entry	Substrate	Product	Reaction time (h)	Conv. (%)	Yield (%)
1			4	>99	96
2			5	>99	98
3			7	42	41
4 ^b			7	73	72
5			7	36	34
6 ^b			7	76	73
7			7	23	13
8 ^b			7	70	64
9			4	>99	98
10			8	96	94
11			4	93	92
12			6	96	72

^a Substrate (2 mmol), isobutylaldehyde (0.011 mol), acetonitrile (6 mL), O_2 bubbling, rt.

^b $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ (1.0 ppm).

could be obtained for the simple α -olefins or terminal alkenes such as 1-octene, 1-hexene, and styrene (entries 3, 5, and 7). When the amount of catalyst increased to 1.0 ppm, a remarkable enhancement for conversion and yield was observed (entries 4, 6, and 8). While for the non-terminal linear olefin for example, *trans*-2-octene, the catalytic system showed excellent catalytic performance, in which *trans*-2-octene was converted to the corresponding epoxide in 4 hours (entry 9). The catalytic system also seems favorable for the conversion of other cycloolefin for example, cyclooctene, in which the reaction system exhibited highly catalytic performance with 92% yield of cyclooctene epoxide (entry 11).

Another salient feature of the present epoxidation is its high regioselectivity. When (+)-limonene was subjected to the epoxidation, the monoepoxide with the epoxide group on the ring was the main product and its selectivity was 72% (entry 12).

5. Large scale epoxidation of cyclohexene

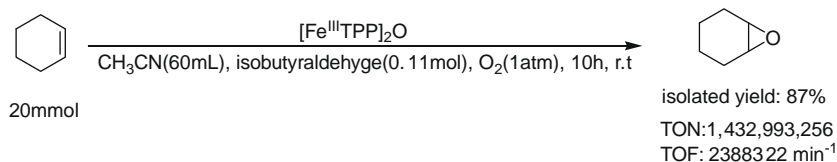
To further investigate the efficiency of the catalytic system, a large scale experiment for the aerobic epoxidation of cyclohexene was carried out as shown in Scheme 2.²²

When the amount of $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ catalyst used was 6.0×10^{-9} mmol, cyclohexene oxide could be obtained with the isolated yield of 87%. It should be mentioned that the turnover number of the μ -oxo dimeric porphyrin could reach 1,432,993,256, and its TOF was $2.4 \times 10^6 \text{ min}^{-1}$.²³ A remarkable enhancement of reactivity for μ -oxo dimeric iron(III) porphyrins was observed compared with mono-metalloporphyrins, in which its TON was about 700 million.

6. A plausible mechanism for the aerobic epoxidation catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$

As reported previously, the oxygenation of organic substrates catalyzed by metalloporphyrin complexes plus aldehyde is usually considered to involve a radical and high-valent metal intermediate mechanism.²⁴ 2,6-Di-*tert*-butyl-4-methylphenol as a radical trap has been used in the epoxidation of cyclohexene, and it was found that the reaction was completely inhibited. Therefore, the aerobic epoxidation should involve radical species.

In order to obtain further information about the role of the high-valent iron porphyrin on the epoxidation, in situ UV-vis spec-



Scheme 2. Large scale epoxidation of cyclohexene catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$.

tra was used. The catalytic epoxidation in CH_3CN was carried out in a quartz colorimetric cell with dioxygen bubbling. UV-vis spectra were recorded with 5 min intervals. Figure 1 exemplifies the UV-vis results observed for μ -oxo dimeric iron(III) porphyrins during the epoxidation process. The initial spectrum of $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ catalyst with a characteristic of Soret band at 408 nm was shown in Figure 1a. When isobutyraldehyde was added into the mixture, a shift from 408 to 417 nm with a loss in intensity was observed, as shown in Figure 1b. Besides, the disappearance of the two Q-band peaks at 570 and 610 nm was found with the addition of isobutyraldehyde. As the reaction continued, a decrease in the Soret band at 417 nm was recorded. The changes of UV-vis spectra are indicative of the existence of an active species expected as the high-valent iron porphyrin.²⁵

It is usually considered that μ -oxo dimeric metalloporphyrins could easily form mono-metalloporphyrins during the catalytic process. In fact, whether the dinuclear intermediate or the mononuclear intermediate is the active species remains controversial for the oxygenation of hydrocarbons catalyzed by μ -oxo dimeric metalloporphyrins. The possible mononuclear metalloporphyrins existing in the catalytic system are FeTPPCL or FeTPPOH . Attempts to obtain some useful information from UV-vis spectrum have been made.

From the UV-vis spectra, FeTPPOH as the mononuclear intermediate in the process is impossible. The active intermediate of FeTPPOH would form a new peak at 461 nm, while no such peak was found from the in situ UV-vis spectra as shown in Figure 1. Figure 2a shows the UV-vis spectra of $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ with isobutyraldehyde and cyclohexene after reacting for 20 min. Similar UV-vis spectra curves could be obtained for FeTPPCL catalyst as shown in Figure 2b. If the high-valent intermediate was mononuclear iron porphyrin (FeTPPCL), the Soret peak at 416 nm would disappear as the reported previously.²⁶ However, a certain degree loss of intensity for the Soret peak at 416 nm could be observed for the present system. As shown in Figure 1, the intensity of Soret peak at 416 remains unchanged after 20 min. The above results indicate that both the dinuclear and the mononuclear high-valent intermediates exist in the catalytic system. Probably two kinds of oxo-iron inter-

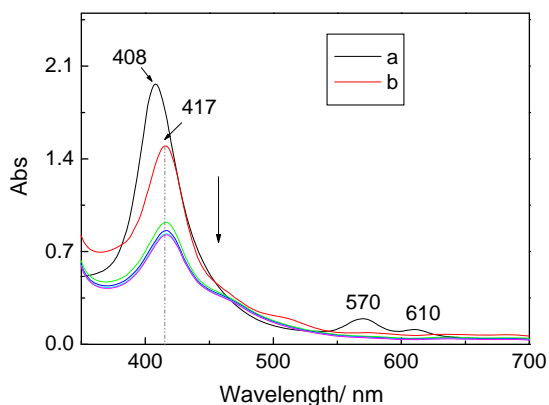


Figure 1. In situ UV-vis spectra of cyclohexene epoxidation catalyzed by $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ in the presence of molecular oxygen and isobutyraldehyde.

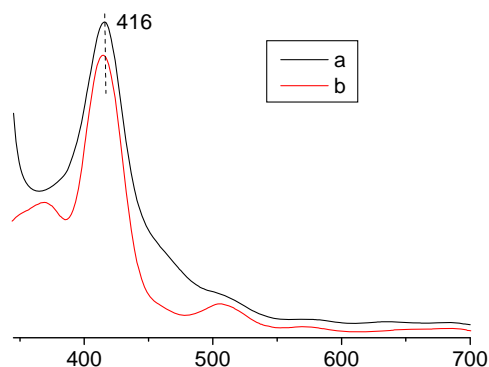


Figure 2. The UV-vis spectra of $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ with isobutyraldehyde and cyclohexene after 20 min of reaction time (a), FeTPPCL (b).

mediates, that is, $\text{O}=\text{VFe}-\text{O}-\text{Fe}^{\text{V}}=\text{O}$ and $\text{Fe}^{\text{V}}=\text{O}$ were formed by series of free radical processes. Formation of epoxide is assumed by the reaction of oxo-iron intermediates with olefins.

In conclusion, highly efficient epoxidation of olefins by the molecular oxygen in the presence of 50 ppb $(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$ was reported. The catalyst conferred high activity and selectivity for the olefins epoxidation under ambient conditions. The turnover number of the catalyst could reach up to 1400 million, which is the highest reported so far. The epoxidation was via a radical process with the formation of high-valent iron intermediates, which were confirmed by in situ UV-vis spectroscopy. The results also indicate that both binuclear and mononuclear exist simultaneously in the reaction system.

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17. Fe^{III}TPPCl and (Fe^{III}TPP)₂O were prepared according to the procedure reported previously, see: Ref. 13. The spectral and analysis data of (Fe^{III}TPP)₂O. FAB: *m/z* 1353. Anal. Calcd for C₈₈H₅₆Fe₂N₈O: C, 78.11; H, 4.17; N, 8.28. Found: C, 77.97; H, 4.29; N, 8.09. UV-vis(CH₂Cl₂) λ_{max}: 409 nm (Soret band), 548 nm and 592 nm (Q-band); IR: 889 cm⁻¹ (ν_{Fe-O-Fe}). The spectral and analysis data of FeTPPCl are FAB: *m/z* 705. Anal. Calcd for C₄₄H₂₈N₄FeCl: C, 74.98; H, 3.98; N, 7.95. Found: C, 75.12; H, 4.01; N, 7.89. UV-vis(CH₂Cl₂) λ_{max}: 417 nm (Soret band), 527 nm (Q-band). IR: 1006 cm⁻¹ and 325 cm⁻¹.
18. General procedure for the catalytic epoxidation of olefins to epoxides. Dioxygen was bubbled to a solution of acetonitrile (6 mL), cyclohexene (2 mmol), isobutylaldehyde (11 mmol), μ-oxo-bisiron(III) porphyrin catalyst (0.05 ppm, 6.0 × 10⁻⁹ mmol) and naphthalene (0.8 mmol, inert internal standard) at room temperature. The consumption of the starting olefins and formation of oxidized products were monitored by GC (Shimadzu GC-14C) and GC-MS (Shimadzu GCMS-QP2010 plus).
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22. General procedure for the large scale catalytic epoxidation of cyclohexene. Cyclohexene (20 mmol), isobutylaldehyde (0.11 mol), and (Fe^{III}TPP)₂O (6.0 × 10⁻⁹ mmol) were added to 60 mL dichloromethane in the presence of molecular oxygen at room temperature while stirring. The crude products were purified via column chromatography (silica gel and cyclohexane as eluting agents). After removing the solvent under reduced pressure, the pure cyclohexene oxide was obtained with the yield of 87%.
23. TOF is commonly used to express the catalytic efficiency of the catalyst with the definition as converted substrate (mol) per catalyst (mol) per minute.
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