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Biomimetic kinetics and mechanism of cyclohexene epoxidation catalyzed by metalloporphyrins

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ABSTRACT

The cyclohexene epoxidation by molecular oxygen in the presence of tetraphenylporphyrin chloride of Mn, Fe, Co and Ru and isobutyraldehyde have been investigated. The results showed that high yield of epoxide was obtained by the liquid phase epoxidation of cyclohexene in the presence of isobutyraldehyde using Mn(TPP)Cl as catalyst. The reaction mechanism has been proposed, and the results indicated (according to the mechanism) that cyclohexene epoxide was mainly formed from the reaction of high-valent metal oxo intermediate with olefin directly, which was verified by in situ EPR and in situ UV–vis spectroscopy respectively. The factors influencing epoxide generation rate, e.g. the concentration of cyclohexene, manganese porphyrin catalyst and isobutyraldehyde, have been well investigated. The kinetics of cyclohexene aerobic epoxidation developed from the proposed mechanism was consistent with the experimental kinetics accurately.

1. Introduction

Metalloporphyrins are effective catalysts for selective oxidation of hydrocarbons and other organic compounds under mild conditions [1,2]. During the past two decades, metalloporphyrins have been applied for epoxidation of olefins to give epoxides since the leading works of Groves and co-workers [3,4]. Thereafter various oxidants with active oxygen, e.g. hydrogen peroxide, iodosobenzene, *t*-butyl peroxide, *m*-chloroperbenzoic acid, have been employed as oxygen atom donors in combination with different metalloporphyrin catalysts [5–11].

The selective aerobic oxidation of hydrocarbons catalyzed by metalloporphyrins is attracting more interests for its low cost and environmental-friendly nature of oxidant [12,13]. However, in most cases, the metalloporphyrins catalyzed oxidation by dioxygen requires high temperature and pressure. It also forms undesirable by-products since the oxidation is occurred *via* an uncontrollable free radical mechanism [14]. Generally, high yield epoxide could be obtained for metal complexes catalyzed homogeneous epoxidation system in the presence of an aldehyde which acts as a reducing agent for the reductive activation of oxygen [15]. Mukaiyama and co-workers have reported that olefins were monooxygenated to epoxides with high yield and selectivity in the co-existence of aldehyde in the presence of metal catalysts such as Ni(dmp)$_2$, Mn salen complexes and Co(acac)$_2$ [16–18]. Other metal complexes, e.g. tetrabutylammonium salts of metal-substituted heteropolyanions, manganese (II) Shiff base, manganese (III) acetate dehydrate combined with various aldehydes, were efficient in the epoxidation of olefins either [19–21]. Moreover, investigations have been made on the mechanism of catalytic epoxidation with aldehyde and metal complexes catalyst, in which the role of metal complexes has attracted more attention [22–24].

Although aerobic epoxidation of olefins with aldehyde catalyzed by transition metal complexes, especially metal-β-diketonate complexes, have been well investigated [25–27], few reports were found for such aerobic epoxidation with metallporphyrins as catalyst [28–29]. In the previous studies, the simple structural metalloporphyins exhibited high catalytic performance for oxidation of alkanes, sulfides and alcohols by molecular oxygen [30–33]. Highly efficient aerobic epoxidation of olefins catalyzed by manganese porphyrin/isobutyraldehyde under mild conditions has ever reported [34]. High turnover number (TON) of the catalyst was obtained for the system, which is comparable to enzyme catalysis, making this process suitable for large-scale production of epoxides.

Based on the high efficiency and enzyme-likeness of the metalloporphyrin-catalyzed epoxidation system, the mechanism of the epoxidation of cyclohexene with metalloporphyrins (Fig. 1) and isobutyraldehyde has been investigated in the present paper. To verify whether the high-valent oxo intermediate is the epoxidizing species, the solution of cyclohexene epoxidation was measured by EPR (Electron Paramagnetic Resonance) and UV–vis in situ. Further studies on the kinetics and factors which affect the rate of epoxidation were also carried.

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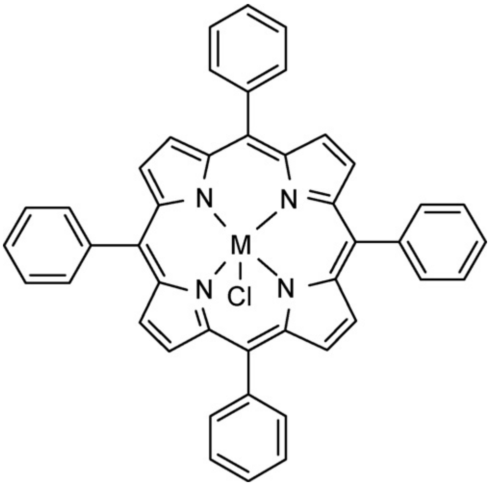


Fig. 1. Schematic structures of metalloporphyrins, M = Mn, Fe, Co and Ru.

2. Experimental

2.1. Materials and instruments

Olefins of analytical grade were obtained from Aldrich or Fluka Chemical Co. without further purification unless indicated. Pyrrole and isobutyraldehyde were purified before use. Other solvents were all of analytical grade.

UV–vis spectra were recorded on a HITACHI U-3010 spectrophotometer. EPR spectra were recorded on a Bruker EPR/ESR 320 spectrometer at 293 K. Elemental analysis data were obtained on Vario EL III. FT-IR spectra were recorded on a Bruker EQUINOX55 spectroscopy.

2.2. Studies of reaction

2.2.1. General procedure for catalytic epoxidation of olefins to epoxides

Dichloromethane (5 mL), cyclohexene (2 mmol), isobutylaldehyde (10 mmol), manganese (III) *meso*-tetraphenylporphyrin chloride (2×10^{-6} mmol) and 0.8 mmol naphthalene (as internal standard) were mixed with stirring at room temperature. Then, dioxygen was bubbled through the solution. The consumption of the olefins and formation of oxidized products were monitored by GC (Shimadzu GC14C) and GC–MS (Shimadzu GCMS-QP2010).

2.2.2. Catalytic aerobic epoxidation of cyclohexene monitored by EPR spectroscopy in situ

The aerobic catalytic epoxidation in CH_3CN were carried out in a Wilmad WG-810-A quartz-flat cell with 0.5 mL CH_3CN solution of manganese (III) *meso*-tetraphenylporphyrin chloride (4×10^{-4} mol L^{-1}), cyclohexene (0.4 mol L^{-1}) and isobutyraldehyde (4 mol L^{-1}). The cell was sealed after filling dioxygen. The EPR analyses were carried out at X-band (ca. 9.8 GHz) at 293 K.

2.2.3. Catalytic aerobic epoxidation of cyclohexene monitored by UV–vis spectroscopy in situ

Catalytic oxidation in dichloromethane was carried out in a quartz-cell containing 3 mL dichloromethane solution of manganese (III) *meso*-tetraphenylporphyrin chloride (4×10^{-5} mol L^{-1}), cyclohexene (0.4 mol L^{-1}) and isobutyraldehyde (4 mol L^{-1}). Dioxygen was bubbled through the mixture and the spectrophotometer was programmed with intervals of 10 min. After the UV–vis monitoring, the products were analyzed by GC–MS (Shimadzu GCMS-QP2010).

Table 1
Epoxidation of cyclohexene by molecular oxygen in the presence of various metalloporphyrins and isobutyraldehyde[a].

Entry	Catalyst	Conv. (%)	Yield (%)
1	Mn(TPP)Cl	>99	>99
2	Fe(TPP)Cl	93	92
3	Co(TPP)Cl	90	90
4	Ru(TPP)Cl	86	85
5	–	15	13
6[b]	Mn(TPP)Cl	78	76
7[c]	Mn(TPP)Cl	>99	>99
8[d]	Mn(TPP)Cl	0	0

[a] Cyclohexene (2 mmol), isobutyraldehyde (0.01 mol), catalyst (2×10^{-6} mmol), CH_2Cl_2 (5 mL), O_2 bubbling, room temperature, 4 h.

[b] Cyclohexene/isobutyraldehyde = 1/4 (molar ratio).

[c] Cyclohexene/isobutyraldehyde = 1/6 (molar ratio).

[d] No isobutyraldehyde.

2.2.4. Kinetic measurements

Epoxidations were carried out as described in the general procedure. The sample (0.1 mL) was withdrawn periodically from the solution and mixed with 1.0 mL dichloromethane and analyzed by GC–MS (Shimadzu GCMS-QP2010).

3. Results and discussion

3.1. Oxidative catalysis

The catalytic activity and selectivity of different metalloporphyrins for cyclohexene epoxidation by molecular oxygen were investigated and the results were listed in Table 1.

As shown in Table 1, only 15% cyclohexene could be converted in the control experiment, which indicates that metalloporphyrin catalyst is crucial for the epoxidation system (entry 5). However, in the presence of metalloporphyrins catalyst, all the reactions proceeded with high conversions and selectivity for the desired cyclohexene epoxide (entries 1–4). Comparing the catalytic activities of different porphyrin catalysts, it was found that manganese porphyrin was the most effective since cyclohexene could be completely converted within 4.0 h. Ruthenium porphyrin presented the lowest catalytic performance although it favored for the oxidation of thioanisole [31]. The catalytic activity of different metalloporphyrins is probably influenced by their electric potential and the stability of different valences of metal atoms.

The addition of isobutyraldehyde was necessary for the smooth conversion of cyclohexene in the aerobic epoxidation system. Neither cyclohexene epoxide nor 2-cyclohexen-1-ol and 2-cyclohexen-1-one could be obtained by conducting the reaction for 4 h without isobutyraldehyde (entry 8), demonstrating that metalloporphyrin catalyst hardly activates dioxygen under ambient pressure in the absence of aldehyde as an oxygen acceptor. When the molar ratio of cyclohexene to isobutyraldehyde was 1/4, 78% cyclohexene could be converted (entry 6). Higher molar ratio of substrate to isobutyraldehyde gave higher conversion (entry 7). However, no significant difference was observed when the substrate/isobutyraldehyde molar ratio reached 1:5 for the present system.

3.2. Plausible mechanism for aerobic epoxidation of cyclohexene

The mechanisms of alkene epoxidation by molecular oxygen in the presence of metal complexes and aldehyde have been already investigated [35–36]. For such oxidation system, all evidence indicates that the reaction proceeded *via* free radical process. Oxygenation of substrates is assumed to occur *via* reactive high-valent metal oxo intermediates that are produced by the reaction of peroxyacid with the metal catalysts from this mechanism.

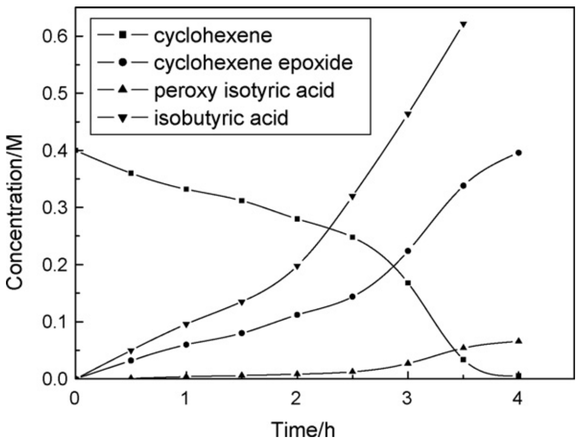


Fig. 2. Oxidation of cyclohexene by molecular oxygen in the presence of Mn(TPP)Cl and isobutyraldehyde: concentration of cyclohexene, 0.4 M; concentration of isobutyraldehyde, 2.0 M; concentration of catalyst, 4×10^{-5} M; O_2 bubbling; room temperature.

In the system of olefin epoxidation by dioxygen, the process of epoxidation can follow different pathways depending on catalyst and reaction conditions. Nam and coauthors concluded that acylperoxy radicals from the autoxidation reaction or complexes of metal with the acylperoxy radicals were the active epoxidants [29], and the metal complexes could accelerate the free radical autoxidation of aldehyde during the initiation step. Ravikumar reported that the epoxidation of olefin in perfluoro-2-butyltetrahydrofuran occurred either by the direct reaction of metal-peroxy species with olefins or through metal oxo species [21]. However, Kaneda et al. proposed that the key epoxidizing agent was not the metal oxo species [37], the peroxyacid was generated during the autoxidation of aldehyde, and the role of transition metal catalyst could be omitted.

For the manganese porphyrin catalyzed epoxidaiton system, the typical product compositions of aerobic oxidation of cyclohexene are shown in Fig. 2. Except the epoxide, isobutyric acid and perisobutyric acid generated from isobutyraldehyde could be detected in the reaction mixture. The formation of perisobutyric acid could be hardly detected within the first 2-h period. After reacting for 2 h, the concentration of perisobutyric acid increased slightly while that of epoxidized cyclohexene increased sharply. It seems that the epoxidation occurred first with induction period, and then followed by sharp acceleration till completion, which agree with the feature of radical-involved reaction. In order to verify the free radical mechanism for the aerobic epoxidation of cyclohexene catalyzed by manganese porphyrins, a free radical inhibitor, 2,6-di-tert-butylphenol (2 mmol) was added to the oxidation system. It has been found that the running oxidation of cyclohexene could be subsequently quenched. In addition, epoxide, isobutyric acid or perisobutyric acid could not be found when the reaction was carried out under nitrogen atmosphere.

In contrary to Kaneda's results, the metalloporphyrins catalyst is absolutely necessary for the epoxidation of cyclohexene from the fact that only 13% yield of epoxide can be obtained in the blank experiment (entry 5 in Table 1). Therefore, the mechanism of epoxides production *via* metallporphyrins-peroxy (as mentioned by Nam et al. [29]) from the reaction of acylperoxy radical with metallporphyrins is impossible. The epoxide (yields up to 13%) in the absence of catalyst should be attributed to the reaction of acylperoxy radical with olefins directly. In the none-catalysis process, the acylperoxy radical was generated from acyl radical and dioxygen, and acyl radical was initiated from the auto-oxidation of aldehyde [29]. A mechanism for the epoxidation of olefins by dioxygen in the presence of metalloporphyrins and isobutyraldehyde has been proposed from the experimental results, as shown in Fig. 3.

Based on the proposed mechanism, the manganese porphyrin reacts with the aldehyde to generate an acyl radical (a) at first. The acyl radical then reacts with dioxygen to give an acylperoxy radical (b). The acylperoxy radical is assumed to play two roles. Firstly, it reacts with olefins to yield epoxides directly accompanying the generation of carboxyl radical (c), which reacts with aldehyde to generate another acyl radical and carboxylic acid (pathway A). Secondly, in pathway B, the acylperoxy radical acts as a carrier by reacting with another aldehyde molecule to give peroxyacid (d), thereby generating another acyl radical. Formation of epoxide is assumed by active high-valent Mn porphyrin intermediates (e), which are formed by the reaction of the peroxyacid with the manganese porphyrin. The evidence described above suggests that pathway B is usually superior over pathway A.

3.3. In situ EPR spectra study of cyclohexene epoxidation

In order to obtain further information on the role of the high-valent Mn porphyrin species for the present oxidation, in stiu EPR measurement was used for the aerobic oxidation of cyclohexene. The catalytic epoxidation in CH_3CN was carried out in a sealed Wilmad WG-810-A quartz-flat cell filled with dioxygen. EPR spectra were recorded with 20 min intervals. Fig. 4 exemplifies the EPR results observed for Mn(III) porphyrin. Fig. 4a shows the initial EPR spectrum of the Mn(TPP)Cl and the silent spectrum is characteris-

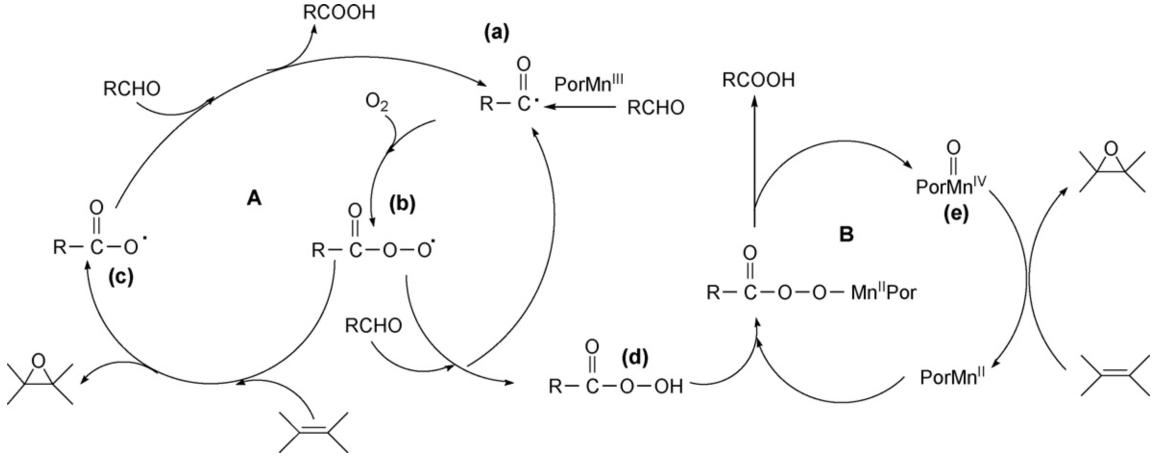


Fig. 3. Plausible mechanism of olefin epoxidation catalyzed by Mn(III) porphyrins in the presence of molecular oxygen and isobutyraldehyde.

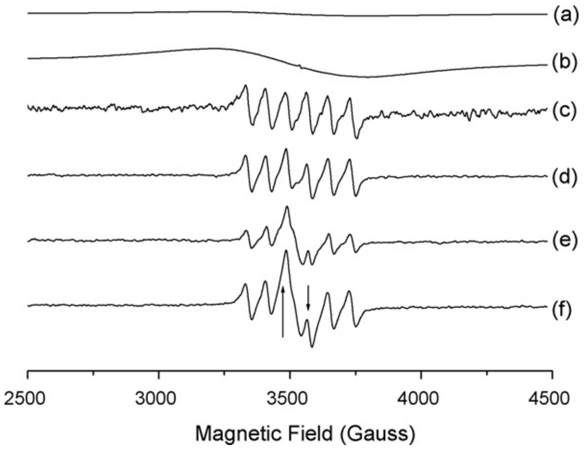


Fig. 4. In situ EPR spectra of cyclohexene epoxidation catalyzed by Mn(TPP)Cl in the presence of dioxygen and isobutyraldehyde. (a) Spectrum of Mn(TPP)Cl; (b) spectrum of Mn(TPP)Cl plus isobutyraldehyde; (c) initial spectrum of cyclohexene epoxidation; (d) epoxidation spectrum after 20 min; (e) epoxidation spectrum after 40 min; (f) epoxidation spectrum after 60 min.

tic of Mn(III) species from integer-spin (non-Kramers) Mn(III) $S=2$ porphyrin compound [38–40]. When isobutyraldehyde was added into Mn(TPP)Cl solution, a broad EPR signal of Mn(II) was observed (Fig. 4b) [41]. The change of EPR signal was attributed to the reaction of Mn (III) porphyrin with aldehyde, from which an acyl radical was generated and the Mn (III) porphyrin was converted to Mn(II) species. This is in agreement with the first step of the proposed mechanism. The six lines shown in Fig. 4c are a typical signal of Mn(IV) species, which indicates the catalytic process should involve high-valent oxo intermediate [42–43].

As the reaction went on, it was interesting to find that the intensity of signal ($g=2.02$) increased, the peak became stronger and sharper, coupling with the decreasing intensity of adjacent signal ($g=1.98$). The EPR spectra are shown in Fig. 4d–f. The fact demonstrated that Mn(II) porphyrins species might be there in the mixture, which are formed by the reduction of Mn(IV) intermediate.

3.4. In situ UV–vis absorption study of cyclohexene epoxidation

The curves of UV–vis spectra for metalloporphyrins during the reaction process are shown in Fig. 5. The spectrophotometer was programmed to acquire UV–vis spectrum every 10 min. As shown in Fig. 5, a decrease in the Soret band at 445 nm was observed, with a concomitant slight increase in the typical Soret band at ~417 nm. The disappearance of the peak (445 nm) suggested that oxidant active species ($Mn^{IV}{=}O$) were consumed by substrate [44–47]. In addition, during the reaction, the color changes in the reaction mixture also indicate the presence of such high-valence species. GC analysis revealed the formation of the epoxide, which is indicative of the presence of an active oxidation species.

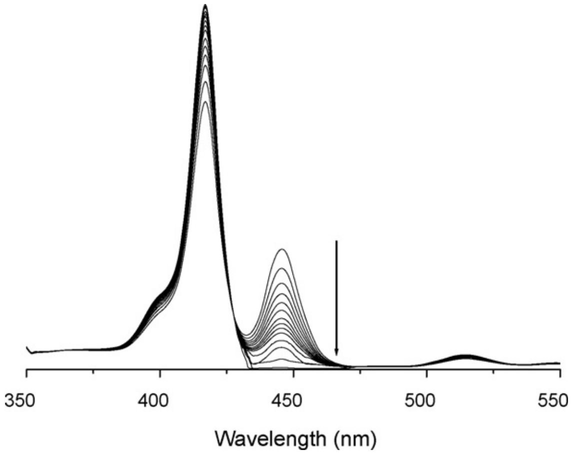


Fig. 5. In situ UV–vis spectra of the aerobic epoxidation of cyclohexene catalyzed by Mn(TPP)Cl (0.04 mM) in dichloromethane solution (time scan: 120 min, interval 10 min). Reaction conditions: cyclohexene (0.4 mol L^{-1}), catalyst (0.04 mM) and isobutyraldehyde (4 mol L^{-1}).

3.5. Kinetic study on the epoxidation of cyclohexene by dioxygen in the presence of Mn(TPP)Cl and isobutyraldehyde

The epoxidation of cyclohexene in the presence of isobutyraldehyde and dioxygen to produce epoxidized cyclohexene with Mn(TPP)Cl as catalyst is a combination of oxidation of aldehyde and epoxidation of cyclohexene. Following the reaction mechanism given in Fig. 3, the reaction equations can be listed as below:

Initiation: Eq. (1) is the initiation step.

$$\mathrm{PorMn^{III}} + \mathrm{RCHO} \xrightarrow{k_0} \mathrm{PorMn^{II}} + \mathrm{RC^{\bullet}O} + \mathrm{H^{+}} \tag{1}$$

Propagation:

$$\mathrm{RC^{\bullet}O} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{RCO_3{}^{\bullet}} \tag{2}$$

$$\mathrm{RCO_3{}^{\bullet}} + \mathrm{RCHO} \xrightarrow{k_2} \mathrm{RCO_3H} + \mathrm{RC^{\bullet}O} \tag{3}$$

Termination: The main termination step is

$$2\mathrm{RCO_3{}^{\bullet}} \xrightarrow{k_3} \text{inactive} \tag{4}$$

The other termination steps are

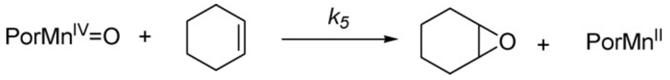
$$2\mathrm{RC^{\bullet}O} \rightarrow \text{inactive} \tag{5}$$

$$\mathrm{RCO_3{}^{\bullet}} + \mathrm{RC^{\bullet}O} \rightarrow \text{inactive} \tag{6}$$

Epoxidation: The epoxidation steps include pathway A and B.

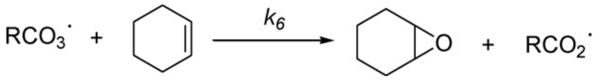
Pathway B:

$$\mathrm{PorMn^{II}} + \mathrm{RCO_3H} \xrightarrow{k_4} \mathrm{PorMn^{IV}} = \mathrm{O} + \mathrm{RCOOH} \tag{7}$$



(8)

Pathway A:



(9)

$$\mathrm{RCO_2{}^{\bullet}} + \mathrm{RCHO} \xrightarrow{k_7} \mathrm{RCOOH} + \mathrm{RC^{\bullet}O} \tag{10}$$

The molar balance equations for each component of the reactions are presented as follows:

First, the changes of the free radicals concentrations are:

$$\begin{aligned}\frac{d[\mathrm{RC^{\bullet}O}]}{dt} &= k_0[\mathrm{RCHO}][\mathrm{PorMn^{III}}] - k_1[\mathrm{RC^{\bullet}O}][\mathrm{O_2}] \\ &\quad + k_2[\mathrm{RCO_3{}^{\bullet}}][\mathrm{RCHO}] + k_7[\mathrm{RCO_2{}^{\bullet}}][\mathrm{RCHO}]\end{aligned} \tag{11}$$

$$\frac{d[\mathrm{RCO_2{}^{\bullet}}]}{dt} = k_6[\mathrm{RCO_3{}^{\bullet}}][\text{cyclohexene}] - k_7[\mathrm{RCO_2{}^{\bullet}}][\mathrm{RCHO}] \tag{12}$$

$$\begin{aligned}\frac{d[\mathrm{RCO_3{}^{\bullet}}]}{dt} &= k_1[\mathrm{RC^{\bullet}O}][\mathrm{O_2}] - k_2[\mathrm{RCO_3{}^{\bullet}}][\mathrm{RCHO}] - 2k_3[\mathrm{RCO_3{}^{\bullet}}]^2 \\ &\quad - k_6[\mathrm{RCO_3{}^{\bullet}}][\text{cyclohexene}]\end{aligned} \tag{13}$$

Table 2
Effect of cyclohexene concentration on the aerobic epoxidation rate in the presence of isobutyraldehyde[a].

Entry	Concentration of cyclohexene (M)	$R \times 10^3$ (mol L^{-1} min^{-1})
1	0.1	2.30
2	0.2	2.42
3	0.3	2.60
4	0.4	2.76
5	0.5	2.83

[a] Temperature: 308 K; Concentration of isobutyraldehyde: 2.0 M; Concentration of Mn(TPP)Cl, 0.4×10^{-6} M; O_2 bubbling.

Assuming that the system is in pseudo steady state, Eqs. (11)–(13) become

$$\frac{d[RC^{\bullet}O]}{dt} = \frac{d[RCO_2{}^{\bullet}]}{dt} = \frac{d[RCO_3{}^{\bullet}]}{dt} = 0 \tag{14}$$

Summing Eqs. (11)–(13):

$$k_0[RCHO][PorMn^{III}] = 2k_3[RCO_3{}^{\bullet}]^2 \tag{15}$$

In addition, Eqs. (16) and (17) can be deduced from Eqs. (7) and (8):

$$\frac{d[Mn^{IV} = O]}{dt} = k_4[PorMn^{II}][RCO_3H] - k_5[Mn^{IV} = O][cyclohexene] \tag{16}$$

$$\frac{d[RCO_3H]}{dt} = k_2[RCO_3{}^{\bullet}][RCHO] - k_4[PorMn^{II}][RCO_3H] \tag{17}$$

Based on pathways A and B, the total rate equation of epoxide (Re) can be expressed as

$$Re = \frac{d[epoxide]}{dt} = k_5[Mn^{IV} = O][cyclohexene] + k_6[RCO_3{}^{\bullet}][cyclohexene] \tag{18}$$

Through the pseudo steady state hypothesis for the Mn(IV) high-valent intermediate and RCO_3H, Eqs. (16)–(18) can be summarized to get the generating rate of epoxide as

$$Re = k_2\left(\frac{k_6}{2k_3}\right)^{0.5}[RCHO]^{1.5}[PorMn^{III}]^{0.5} + k_6\left(\frac{k_6}{2k_3}\right)^{0.5}[RCHO]^{0.5}[PorMn^{III}]^{0.5}[cyclohexene] \tag{19}$$

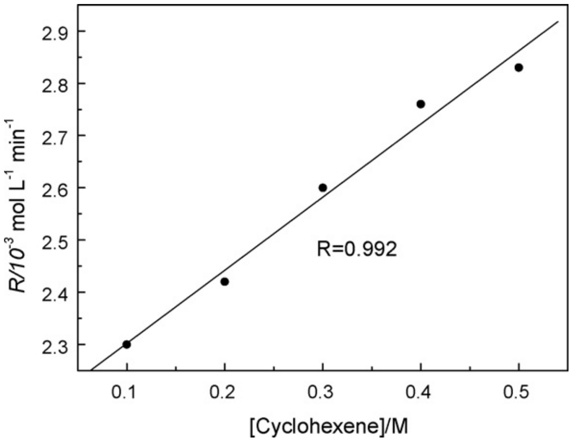


Fig. 6. Effect of cyclohexene concentration on the epoxidation rate in the presence of isobutyraldehyde and molecular oxygen: concentration of isobutyraldehyde, 2.0 M; concentration of Mn(TPP)Cl, 0.4×10^{-6} M; O_2 bubbling; room temperature.

Table 3
Effect of concentration of Mn(TPP)Cl catalyst on the aerobic epoxidation rate in the presence of isobutyraldehyde[a].

Entry	[Mn(TPP)Cl] (M)	$[Mn(TPP)Cl]^{0.5} \times 10^2$ ($M^{0.5}$)	$R \times 10^3$ (mol L^{-1} min^{-1})
1	0.8×10^{-4}	0.89	1.98
2	1.6×10^{-4}	1.26	2.94
3	2.4×10^{-4}	1.55	3.61
4	3.2×10^{-4}	1.79	4.01
5	4.0×10^{-4}	2.00	4.47

[a] Temperature: 308 K; Concentration of isobutyraldehyde: 2.0 M; Concentration of cyclohexene: 0.4 M; O_2 bubbling.

Then, Eq. (19) can be simplified as

$$Re = k_1[RCHO]^{1.5}[PorMn^{III}]^{0.5} + k_2[RCHO]^{0.5}[PorMn^{III}]^{0.5}[cyclohexene] \tag{20}$$

From Eq. (20), it can be seen that the rate of epoxidation is related with the concentration of cyclohexene, manganese porphyrins catalyst and isobutyraldehyde with 1, 0.5 and 1.5 power, respectively. In order to verify the equation of the epoxidation rate further, the factors that influence epoxidation rate were investigated using cyclohexene as model substrate. The rate of epoxidation was obtained based on the following assumption: (1) There is very large excess of cyclohexene compared to catalyst (the [catalyst]/[cyclohexene] ratio is $1/10^6$) in the catalytic system; (2) The conversion rate of cyclohexene should be controlled within 5%.

3.5.1. *Effect of cyclohexene concentration on the epoxidation rate*

The catalytic epoxidation of cyclohexene in the presence of isobutyraldehyde and molecular oxygen was carried out with the range of cyclohexene concentration from 0.1 to 0.5 M. The results of epoxidation rate with different concentrations of cyclohexene are listed in Table 2. It indicated that increasing concentration of cyclohexene accelerated the epoxidation rate from 2.30×10^{-3} to 2.83×10^{-3} mol L^{-1} min^{-1}.

A plot of epoxidation rate against the concentration of cyclohexene yields a straight line, as shown in Fig. 6.

As seen in Fig. 6, linear correlation between epoxidation rate and [cyclohexene] was evident using Mn(TPP)Cl as catalyst, in which correlation coefficient was 0.992. Consequently, the catalytic

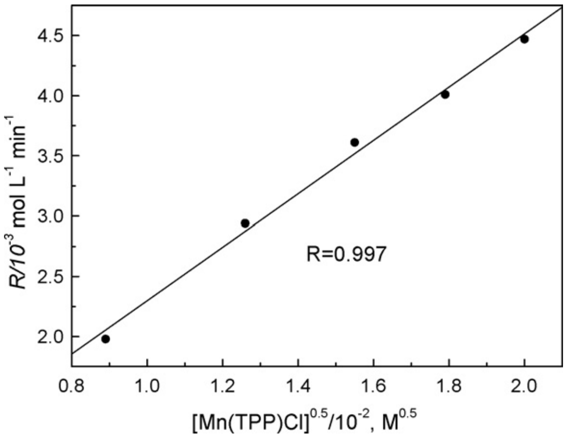


Fig. 7. Effect of the concentration of Mn(TPP)Cl catalyst on the epoxidation rate in the presence of isobutyraldehyde and molecular oxygen: concentration of isobutyraldehyde, 2.0 M; concentration of cyclohexene, 0.4 M; O_2 bubbling; room temperature.

Table 4
Effect of isobutyraldehyde concentration on the aerobic epoxidation rate in the presence of molecular oxygen[a].

Entry	[Aldehyde] (M)	$[\text{Aldehyde}]^{1.5}$ ($M^{1.5}$)	$[\text{Aldehyde}]^{0.5}$ ($M^{0.5}$)	$R \times 10^3$ ($\text{mol L}^{-1}\text{ min}^{-1}$)
1	0.80	0.72	0.89	1.11
2	1.20	1.31	1.10	1.64
3	1.60	2.02	1.26	2.16
4	2.00	2.83	1.41	2.75
5	2.40	3.72	1.55	3.41

[a] Temperature: 308 K; Concentration of cyclohexene: 0.4 M; Concentration of Mn(TPP)Cl, 0.4×10^{-6} M; O_2 bubbling.

reaction also exhibited first-order dependence in relation to the concentration of cyclohexene. Thus, the experimental results are in good agreement with the theoretical analysis as shown in Eq. (20).

3.5.2. *Effect of the catalyst concentration on epoxidation rate*

The results indicated that increasing the concentration of catalyst results in an increase of the initial reaction rate. Increasing the concentration of catalyst from 0.8×10^{-4} to 4.0×10^{-4} M increases the epoxidation rate from 1.98×10^{-3} to 4.47×10^{-3} $\text{mol L}^{-1}\text{ min}^{-1}$ as shown in Table 3.

Plot of the initial rate of epoxidized cyclohexene versus the concentration of $[\text{Mn(TPP)Cl}]^{0.5}$ yields a straight line as shown in Fig. 7.

As can be observed in Fig. 7, linear correlation between epoxidation rate and $[\text{Mn(TPP)Cl}]^{0.5}$ was evident, in which correlation coefficient was 0.997. The line can be expressed by

$$Re = 0.081 \times 10^{-3} + 2.217 \times [\text{Mn(TPP)Cl}]^{0.5}$$

3.5.3. *Effect of the isobutyraldehyde concentration on epoxidation rate*

As shown in Table 4, the results indicated that increasing of isobutyraldehyde concentration from 0.8 to 2.4 M resulted in an increase of the initial rate of epoxidized cyclohexene from 1.11×10^{-3} to 3.41×10^{-3} $\text{mol L}^{-1}\text{ min}^{-1}$.

The plot of the epoxidation reaction rate versus $[\text{isobutyraldehyde}]^{0.5}$ is shown in Fig. 8.

The graph shown in Fig. 8 illustrated clearly that the reaction rate versus $[\text{isobutyraldehyde}]^{0.5}$ yielded a cube curve, which was consistent with the analysis as shown in Eq. (20).

As shown above, the experimental results correlate the theoretical analysis well. The good agreement for kinetics could further explain that the metalloporphyrin-catalyzed epoxidaiton of cyclohexene is *via* a high-valent metal intermediate.

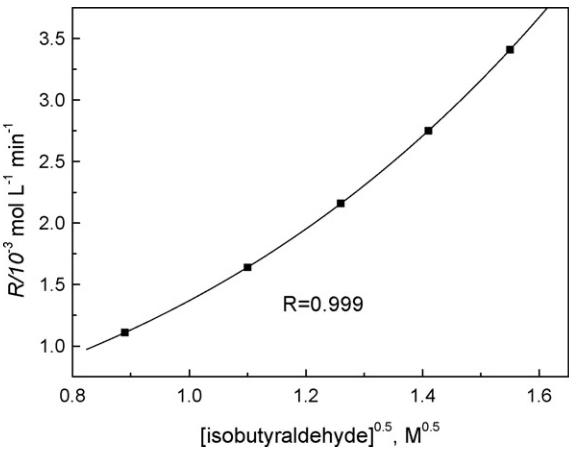


Fig. 8. Effect of isobutyraldehyde concentration on the epoxidation rate in the presence of molecular oxygen: concentration of cyclohexene, 0.4 M; concentration of Mn(TPP)Cl, 0.4×10^{-6} M; O_2 bubbling; room temperature.

4. Conclusion

The mechanism and kinetics of cyclohexene epoxidation by molecular oxygen in the presence of Mn(III) tetraphenylporphyrin chloride [Mn(TPP)Cl] and isobutyraldehyde have been investigated in the present work. First, metalloporphyrin catalysts were synthesized and characterized. However, the use of [Mn(TPP)Cl] as catalyst, provided high yield of cysclohexene under ambient conditions. Then, the reaction mechanism of cyclohexene epoxidation with isobutyraldehyde and dioxygen was found to be a series of free radical reactions. The experimental results indicated that the cyclohexene epoxide was mainly formed through a metal high-valent oxo intermediate which reacted with cyclohexene. It was verified by EPR and UV–vis spectroscopy in situ. The factors that influence epoxide generating rate were investigated in detail. The kinetics of theoretical analysis correlated well with the experimental results.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.10.066.

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