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### ARTICLE

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## Direct aerobic liquid phase epoxidation of propylene catalyzed by Mn (III) porphyrin under mild conditions: Evidence for the existence of both peroxide and Mn(IV)-oxo species from *in situ* characterizations

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Generally, gaseous propylene is hard to be oxidized directly in liquid phase by dioxygen under mild conditions. Here, the liquid phase epoxidation of propylene to propylene oxide (PO) using molecular oxygen catalyzed by manganese porphyrins (MnTPPCI) in presence of benzaldehyde was developed. Manganese (III) porphyrin exhibited excellent activity for the selective oxidation of propylene under mild conditions. The conversion of propylene and selectivity towards PO can reach 38% and 80%, respectively. The turnover frequency (TOF) of MnTPPC1 catalyst reached 1840  $h^{-1}$ . Experimental evidences that the generation of peroxide and Mn (IV) oxo species during propylene epoxidation were provided, which was well confirmed by *in situ* IR, *in situ* UV and Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). On the basis of the experimental results, the mechanism for the epoxidation of propylene in the presence of metalloporphyrins and benzaldehyde with dioxygen was proposed. The mechanism is also supported by density functional theory (DFT) calculations.

#### Introduction

Propylene oxide (PO), an important derivative of propylene, is used for the production of polyurethane, unsaturated resins, surfactants, and several other products. Market demand for PO has been significantly increasing over the years <sup>1, 2</sup>. However, the current technology for the production of PO suffers from environmental problems or low atom economy <sup>3</sup>. Moreover, it leads to equipment corrosion and needs heavy capital investment. Thus, it is more desirable to develop a protocol catalytic route for the production of PO using molecular oxygen that is economic and environmentally friendly.

Compared to ethylene, there are three-hydrogen atoms in propylene molecule, which are extremely reactive and could be competitive to C=C bond. Several processes involving heterogeneous catalyst for direct epoxidation of propylene using molecular oxygen as oxidant have been developed. However, high reaction temperature was necessary to activate molecular oxygen which inevitably resulted in poor selectivity

toward PO<sup>4-8</sup>. Therefore, epoxidation of propylene involving homogeneous catalytic systems is an alternative way to produce PO under mild conditions. Although homogeneous aerobic catalytic systems exhibited excellent activity for various liquid alkenes epoxidation like cyclohexene and styrene<sup>9-10</sup>, but the gaseous propylene is hard to be oxidized directly in general. Therefore, peroxide is used as the oxidant in most epoxidation of propylene process. And peroxide generated from O<sub>2</sub> *in situ* is a good way which was also considered to be a method of direct epoxidation of propylene <sup>11-13</sup>.

Beckman reported the epoxidation of propylene in ScCO<sub>2</sub> (13.1 MPa, 318 K) catalyzed by Pd/TS-1 using molecular oxygen as oxidant<sup>14-15</sup>. In presence of H<sub>2</sub>, hydrogen peroxide was the real oxidant from the *in situ* generation. In this process, 6.5% propylene conversion and 91% PO selectivity were obtained, and the turnover frequency (TOF) was 26 h<sup>-1</sup>.

Metalloporphyrins, as one of the representative biomimetic catalysts, are known to exhibit excellent ability for activating dioxygen <sup>16-19</sup>. They were used as homogeneous catalysts in the selective aerobic epoxidation of liquid alkenes <sup>20-26</sup>. For the epoxidation of liquid alkenes catalyzed by metalloporphyrins,

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high metal valence complexes were mainly considered to be the active intermediates (Jacobson mechanism)  $^{27-33}$ . Though the oxidations of metal complex with *m*-CPBA, HClO<sub>4</sub> or PhIO, various metal high-valent complexes with other ligands were obtained and well confirmed  $^{34-42}$ . However, the evidence on the existence of high-valent metalloporphyrins has not been obtained directly, especially for the first generation simple structural metalloporphyrins.

Herein we report the direct aerobic gas–liquid epoxidation of propylene catalyzed by manganese porphyrins in the presence of benzaldehyde (BA). The conversion of propylene and selectivity toward PO was 38% and 80%, respectively. The TOF of manganese porphyrins (MnTPPC1) reached 1840 h<sup>-1</sup>. Experimental evidences that the generation of peroxide and Mn (IV) oxo species during propylene epoxidation were provided, which was well confirmed by *in situ* IR, *in situ* UV and MS. On the basis of the experimental results, the mechanism for the epoxidation of propylene in the presence of metalloporphyrins and benzaldehyde with dioxygen was proposed. The mechanism is also supported by density functional theory calculations.

#### 2. Experimental

#### 2.1. General methods

Propylene and molecular oxygen were purchased from Zhuozheng Gas Co., Ltd. All other solvents were of analytical grade. Metalloporphyrins were prepared according to our previously described methods<sup>21, 43-45</sup> and characterized as follows. All the regents were used as received without further purification unless indicated. Benzaldehyde was redistilled prior to its use.

The spectral and analysis data of of MnTPPCI. FAB: m/z 703 (calcd. for  $[M]^+$  703). Anal. calcd for  $C_{44}H_{28}N_4MnCl$ : C, 75.09; H, 3.98; N. 7.96. Found: C, 74.89; H, 4.02; N. 7.92. UV-Vis(CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 474 (2.45), 534 (1.08). IR (KBr)v, cm<sup>-1</sup> 1007, 321.

Mass spectra were obtained on liquid chromatography-mass spectrometry (LC-MS) system (Thermo) by the electrospray ionization method. MALDI-TOF-MS spectra were performed on MALDI-TOF-TOF ultrafleXtreme (Bruker Daltonics). Electron paramagnetic resonance (EPR) spectroscopy was performed on a JESFA-200 (JEOL, Japan) EPR spectrometer using *N*-tert-butyl-alpha-phenylnitrone (PBN) as free radical spin trapping agent. UV–Vis spectra were recorded on a Shimadzu UV-2450 UV–Vis spectrophotometer. *In situ* UV spectra were recorded on AvaSpec-2048 spectrometer (Avantes, Netherlands). *In situ* IR spectra were recorded on Mettler-Toledo iC IR 10. High pressure reaction was performed in a 25 mL Parr stainless steel vessel.

#### 2.2. General procedures for epoxidation of propylene

In a typical experiment, the stainless steel reactor was sealed after liquid reagents and metalloporphyrins solution were added in, subsequently, propylene and dioxygen were introduced successively inside the reactor and kept for 20 min to achieve the gas–liquid balance. The mixture was heated at 80 °C for 12 h. After the completion of the reaction, the reactor was quenched in ice for sampling. Further, the product of each reaction was determined by gas chromatography (GC, Shimadzu GC-2010 plus) and GC–MS (Shimadzu GCMS-QP2010 plus) systems. Each catalytic reaction was repeated three times to secure reproducibility.

# 2.3. Propylene epoxidation monitored by in situ IR and UV spectroscopy

In a typical experiment, the stainless steel reactor was sealed after liquid reagents and metalloporphyrins solution were added in, subsequently, propylene and dioxygen were led in successively and kept for 20 min to achieve the gas–liquid balance. The mixture was heated at 80 °C. The in situ infrared spectra were recorded on Mettler-Toledo iC IR 10 equipped with a mercury cadmium telluride (MCT) detector. The in situ UV–Vis spectra of metalloporphyrins were recorded on a spectrophotometer connected to an AvaSpec-2048 spectrometer.

#### 2.4. Computational details

Calculations were performed using Gaussian 09 program <sup>46</sup>. Epoxidation of propylene was studied using DFT with QST3 methods. The stationary points on the reaction potential energy surfaces were optimized on the computational level of B3LYP/6-31g(d,p). Analytical harmonic vibration frequencies were computed at the same level to the characterization of stationary point. The relation between the transition states and the corresponding minima was verified by performing intrinsic reaction coordinate calculations.

#### 3. Results and discussion

# **3.1. Liquid phase epoxidation of propylene catalyzed by MnTPPCl**

Table	1	Liquid	epoxidation	of	propylene	catalyzed	by
MnTPI	PCl	a					

Entry	Benzaldehyde (mmol)	MnTPPCl (mmol L <sup>-1</sup> )	Conv.% (C <sub>3</sub> H <sub>6</sub> )	S% (PO)	TOF(h <sup>-1</sup> )
1	0	0	0	0	0
2	0	0.1	1.8	76	80
3	1	0	9.2	59	0
4	1	0.1	11	54	460

 $^a$  Propylene (150 mmol), pressure (1.5 MPa), ethyl acetate (25 mL), 80 °C, 12 h.

Effects of MnTPPCl catalyst and benzaldehyde as co-reductant on the epoxidation of propylene were investigated and the results are listed in Table 1. In the absence of both MnTPPCl catalyst and benzaldehyde, no reaction was observed (entry 1). In the absence of benzaldehyde, the conversion of propylene

catalyzed by MnTPPCl (0.1 mmol  $L^{-1}$ ) was only 1.8% (entry 2). In the catalyst control experiment, the conversion could reach 9.2% in the presence of benzaldehyde (entry 3). Oddly, no obvious increment was obtained toward the conversion of propylene when MnTPPCl was added in the system (entry 4).

# **3.2.** Effect of the amount of MnTPPCl on the aerobic epoxidation of propylene

Fig. 1 shows that the conversion of propylene almost remains constant (about 10%); however, the selectivity toward PO apparently decreases with the continuous increase in the amount of MnTPPCl catalyst. This is the characteristic of metalloporphyrins-catalyzed oxidation, which indicates that the excess catalyst promotes the side oxidation of propylene under the reaction conditions  $4^{7,48}$ .



Fig. 1 Effect of the amount of MnTPPCl on the aerobic epoxidation of propylene. Propylene (0.15 mol), pressure (1.5 MPa), benzaldehyde (1 mmol), ethyl acetate (25 mL), 80  $^{\circ}$ C, 12 h.

# **3.3.** Effect of the amount of benzaldehyde on aerobic epoxidation of propylene

Effect of the amount of benzaldehyde on the aerobic epoxidation of propylene was investigated and the results are presented in Fig. 2.



Fig. 2 Effect of the amount of benzaldehyde on the aerobic epoxidation of propylene. Propylene (0.15 mol), pressure (1.5 MPa), MnTPPCl (0.1 mmol  $L^{-1}$ ), ethyl acetate (25 mL), 80 °C, 12 h.

Fig. 2 exhibits that benzaldehyde plays an important role in the propylene oxidation when molecular oxygen is employed as the sole oxidant. The reaction rate is closely related to the amount of benzaldehyde. Conversion of propylene increases from 10 to 38% with the increase in amount of benzaldehyde from 1 to 10 mol% (based on propylene). The TOF of catalyst also increases sharply with increasing amount of benzaldehyde. The increased consumption of benzaldehyde indicated that the initial concentration of radical was enhanced during the reaction, which promoted the oxidation of propylene.

#### 3.4. Influence of temperature on epoxidation of propylene

Fig. 3 displays the results of the influence of reaction temperature on the aerobic epoxidation of propylene. Conversion of propylene increases significantly from 4.2 to 29% with the increase in temperature. However, the selectivity toward PO decreases with the increasing reaction temperature, which indicated high temperature is favorable for the side oxidation of propylene.



Fig. 3 Effect of temperature on the aerobic epoxidation of propylene. Propylene (0.15 mol), pressure (1.5 MPa), MnTPPCl (0.1 mmol  $L^{-1}$ ), benzaldehyde (1 mmol), ethyl acetate (25 mL), 12 h.

#### **3.5. Mechanism of epoxidation of propylene**

Further experiments were performed to explore the mechanism of epoxidation of propylene. In the presence of benzaldehyde, only 1.4% propylene was converted in the blank experiment (without MnTPPCI) after 30 min (Entry 2, Table 2). However, 15.4% conversion of propylene was observed by adding 0.2 mM MnTPPCI catalyst in the system (Entry 1, Table 2). It indicated that Mn (III) porphyrins were efficient toward the aerobic epoxidation of propylene, which could remarkably accelerate the oxidation rate. However, no obvious increment was observed when the reaction time was increased to 2.0 hours (entry 3, Table 2). It indicated that the epoxidation almost completed within 0.5 h. Fig. 4 demonstrates the profiles

obtained by monitoring the *in situ* IR spectroscopy. The peaks at 913 cm<sup>-1</sup> are attributed to =C–H wagging out of plane as shown in Fig. 4 (b).

Table 2 Reaction conditions for the epoxidation of propylene in the presence of benzaldehyde  $^a$ 

Entry	MnTPPCl (mM)	Time (h)	Conversion (%)		Select. of PO	TOF
			$C_3H_6$	BA	(%)	$(h^{-1})$
1	0.2	0.5	15.4	27.4	64.6	1004
2	0	0.5	1.4	0.2	46.8	-
3	0.2	2.0	15.6	28.8	66.8	256
4	0	2.0	3.7	8.9	44.2	-
5 <sup>b</sup>	0.2	2.0	-	73.4	-	-

<sup>*a*</sup> propylene (1.0 mol), pressure (1.5 MPa), solvent (ethyl acetate, 1.0 L), 80 °C; BA (1.0 mol).

<sup>b</sup> Without propylene.

Fig. 4 (a) demonstrates that the reaction rate is extremely low in the absence of catalyst which is confirmed from the exothermic curve (red line) displaying that negligible amount of heat is released when the oxygen is charged in. Almost no conversion of benzaldehyde is observed in the absence of catalyst (Entry 2, Table 2), indicating that the free radical autoxidation hardly occurred without metal complex catalyst. However, the reaction rate is significantly enhanced in the presence of Mn (III) porphyrin catalyst (b), and obvious exothermic peaks are observed. Moreover, the conversion of benzaldehyde is sharply increased to 27% within 30 min. The EPR spectra (Fig. S1) exhibit that benzoyl radical is the main radical before oxygen is charged in, and the concentration of benzoyl radical is one order of magnitude higher, compared the presence and absence of Mn (III) porphyrins, indicating that Mn (III) porphyrins catalyst promotes the generation of benzoyl radical 49-53



Fig. 4 Trends of the feature peak of the epoxidation of propylene oxidized by O2. Conditions: propylene (1.0 mol), pressure (1.5 MPa), solvent (ethyl acetate, 1.0 L), 80 °C. (a) without MnTPPCl, (b) MnTPPCl (0.2 mM).

To confirm the generation of high-valent Mn porphyrin intermediate, *in situ* UV–Vis spectra under reaction conditions were recorded on a spectrophotometer connected to an AvaSpec-2048 spectrometer. As the reaction proceeds, the Soret band of MnTPPCI (474 nm) decreases gradually. However, the peak at 422 nm increases gradually and then decreases, which consider to be Mn (IV) oxo <sup>54, 55</sup>, as shown in Fig. 5. Subsequently, reaction sample was detected by MAIDI-TOF-MS, as shown in Fig.S2. The signal at *m/z* 682.6 referred to Mn<sup>IV</sup>=O. It indicates that Mn high-valent species was existed during the reaction.



Fig. 5 Spectrum of reaction solution by *in situ* UV spectroscopy, scan speed: 2 ms<sup>-1</sup>; Reaction condition: MnTPPCl,  $1 \times 10^{-5}$  mol L<sup>-1</sup>; Solvent, ethyl acetate, 40 mL; BA, 10 mM, which was added in at 200 s. Peak at 474 nm is the absorption of Soret band of MnTPPCl.

Extremely active benzoyl radical might react with molecular dioxygen or propylene directly. Calculations based on DFT show that the binding energy of benzoyl radical with propylene, or oxygen are 85.03, 47.21, and -64.62 kJ mol<sup>-1</sup>, respectively (Fig. S3). This indicated that the combination of benzoyl radical with dioxygen to generate benzoyl peroxide radicals is a rapid incompetent barrier process. Acylation products of propylene were not detected during the reaction which was in good agreement with the results of the calculations. The benzoyl peroxide radicals probably then reacted with benzaldehyde to generate benzoic acid, or played roles in the process for epoxidation of propylene.

Besides, the weak wide peak, observed in IR spectrum during in situ monitoring, at about 876 cm<sup>-1</sup> is attributed to the O–O bond <sup>56, 57</sup>. It revealed that O–O bond was generated in the reaction with low concentration (Fig. S4), which indicated that the peroxyacid was generated *in situ* and reaction could follow the mechanism of Prilezhaev epoxidation <sup>58-62</sup>.

However, the conversion of benzaldehyde reaches 73.4% in 2 h under the MnTPPCl catalysis without propylene (Entry 5 in Table 2). It indicated that propylene offered a strong competition to benzaldehyde and interacted strongly with

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benzoyl peroxide radical. This might be attributed to the high steric hindrance effect of benzaldehyde which made the hydrogen transfer mainly as Equation 1 and not Equation 2 (Fig. S5)<sup>63</sup>. Besides, Esposti et al. <sup>64</sup> mentioned that it was difficult to obtain acyl radicals directly from corresponding aldehydes; however, metalloporphyrins could act as promising candidates for catalytic reactions in order to obtain acyl radicals easily and conveniently.

Further experiments confirmed the above mentioned results, as shown in Fig. S6. The feature of peak 2,2-diphenyl-1-picrylhydrazyl (DPPH) at 511 nm decreases gradually and shifts to 450 nm after the addition of the reaction solution. The blue shift indicates weak intermolecular conjugation of DPPH, which contributed to the combination of the nucleophilic radicals and DPPH. There would be a red shift because of the combination of benzoyl radical with DPPH, attributed to its strong conjugation effect. Thus, blue shift occurred because of the combination of several alkyl radicals with DPPH in the solution.

However, it was still unclear that which type of alkyl radicals were formed in the reaction. Both allylic hydrogen and double bond hydrogen were reactive to benzoyl peroxide radical. The calculation showed that the energy barriers of these two types of hydrogen generating transition state with benzoyl peroxide radical were 72.73 and 32.04 kJ mol<sup>-1</sup>, respectively, as shown in Equations 3 and 4, TS1 and TS2 (Fig. S4), which indicated that TS2 would be the main transition state. Our previous study oxidation of cyclohexene involving catalyzed hv metalloporphyrins showed that the products of oxidation at the allylic site were more than 90% <sup>21</sup>, which indicated that allylic hydrogen was more reactive than double bond hydrogen. Tysoe and his group <sup>65</sup> observed that the alkyl hydrogen of propylene was more likely to react with Ag catalyst by monitored the absorption of deuterium-labelled propylene including CD<sub>2</sub>=CH-CH<sub>3</sub> and CH<sub>2</sub>=CH-CD<sub>3</sub>. Misako Imachi and his group<sup>66</sup> found that the selectivity of epoxide was increased, but did not change the equilibrium kinetics when propylene-1,2-d<sub>2</sub> changed to propylene- $1,2,3,3,3-d_5$ . It revealed that the oxidation of alkyl hydrogen decreased the selectivity of PO.

Studies on the  $\beta$ -secondary isotope effects indicated that the hydrogen at allylic position could influence the activation of carbon double bond for the hyperconjugation effects <sup>59, 67, 68</sup>; however, strong affects related to the activity of carbon double bond could be observed when the allylic hydrogen is substituted by the functional groups. Therefore, the effect of substitution of allylic hydrogen by the functional groups with different electronic effects on the carbon–carbon double bond was investigated and the related values are listed in Table 3.

The values listed in Table 3 revealed that the electron-donating group shortened the double bond, which increased the electron density of the carbon double bond; thus, making it to be nucleophilic and more receptive to attack by oxygen. As shown in Table 3 (entry 2), the conversion of alkene could reach 99% in 8 h when the allylic hydrogen was substituted by propyl

group, and the selectivity of epoxide enhanced to 80.8%, indicating that high electron density might stabilized the three-membered ring. In contrast, the electron withdrawing group reduced the election density, lengthened the distance, and weakened carbon double bond; thus, the bond was easy to break when it was attacked by the peroxides and formed aldehyde. However, an exceptional behaviour was observed when amine group substituted the allylic hydrogen. Although amine was an electron-donating group, it was prone to aldimine condensation rather than epoxidation reaction because of the presence of active lone pair of electrons on nitrogen atom which led to high conversion of allylamine by aldimine condensation rather than epoxidation.

Table 3 Epoxidation of different alkenes using dioxygen by MnTPPCl <sup>a</sup>							
Entry	gubstrata	C=C	Conv /0/	S/%	S/%		
Enuy	substrate	length/Å	/Å CONV.//0	(Ep)	(Ad)		
1	CI	1.33296	24.3	5.38	81.2		
2b	C3H7	1.33000	>99	80.8	11.6		
3b	H <sub>2</sub> N	1.33155	95.6	0	44.2 <sup>c</sup>		
4	N ( )3	1.33187	10.68	0	97.3 <sup>d</sup>		
5	$\sim$	1.33282	12.6	15.8	2.3		

<sup>*a*</sup> Alkene (10 mmol), MnTPPCl ( $1 \times 10^{-4}$  mol L<sup>-1</sup>), 90 °C, 12 h, ethyl acetate (25 mL), pressure (1.8 MPa), benzaldehyde (1 mmol), Ep referred to epoxies, and Ad referred to aldehyde.

<sup>b</sup> 8 h, 80 °C

<sup>c</sup> the main product was *N*-allylacetamide

the main product was 1-(diallylamino)propan-2-one

Based on the above mentioned discussions, a plausible mechanism was proposed for the epoxidation of propylene in the presence of metalloporphyrins and benzaldehyde in an oxygen atmosphere, as shown in *Scheme 1*.

Scheme 1 demonstrates the generation of PO is preceded in two pathways. At the first step in path A, the Mn(III)PorCl functions as oxidizing agents to produce acyl radical from an aldehyde, and Mn(III) was reduced to Mn(II). The acyl radical then reacts with dioxygen to give an acylperoxy radical. Subsequently, the benzoic peroxide radical is surrounded by propylene to generate two types of transition states, TS1 and TS2, most of which is TS2. Later, TS2 is attacked by another perbenzoic acid to form TS2', which is decomposed rapidly in two different ways <sup>57, 69, 70</sup>. In the first route, PO and benzoic acid are generated directly, and the second route involves the interaction of benzoic peroxide radical with allylic hydrogen of PO which further decomposes to aldehyde and formaldehyde. The two different routes are competitive to each other leading to low selectivity toward PO in the reaction. However, in path B, Mn<sup>IV</sup>=O can oxidize propylene to produce PO directly with less by-products. The research on the dominant way to produce PO is in progress.



Scheme 1 Mechanism of the aerobic epoxidation of propylene in the presence of metalloporphyrins and benzaldehyde

#### Conclusions

In this study, we developed a method for the direct gas–liquid homogenous epoxidation of propylene catalyzed by MnTPPC1 in the presence of benzaldehyde as co-reductant. The conversion of propylene and selectivity towards PO can reach 38% and 80%, respectively. The TOF of MnTPPC1 catalyst reached 1840 h<sup>-1</sup>. The existence of peroxide and Mn (IV) oxo species during propylene epoxidation was well confirmed by *in situ* IR, *in situ* UV and MS. On the basis of the experimental results, the mechanism for the epoxidation of propylene in the presence of metalloporphyrins and benzaldehyde with dioxygen was proposed. The mechanism is also supported by density functional theory calculations.

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#### Notes and references

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