



# Efficient and ecofriendly options for the chemoselective oxidation of alkenes using manganese porphyrin and dioxygen



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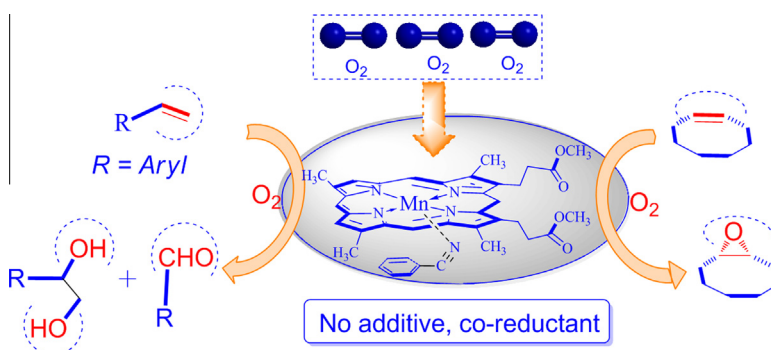
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## HIGHLIGHTS

- Mn-porphyrins show high activity and selectivity in oxidation of alkenes.
- The effect of *meso* substituents on porphyrin activity and stability was studied.
- An alternative mechanism for the aerobic oxidation of styrene has been discussed.
- The catalytic method was proved to be more adequate for oxidation of bulk alkenes.

## GRAPHICAL ABSTRACT

Selective oxidation of alkenes was carried out for the first time in homogeneous system by using a green and easily prepared manganese porphyrin as an efficient catalyst under elevated oxygen pressure in the absence of additive and co-reductant.



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## ABSTRACT

Selective oxidation of styrene to benzaldehyde was carried out for the first time in homogeneous system by using a green and easily prepared manganese porphyrin as an efficient catalyst under elevated oxygen pressure in the absence of additive and co-reductant. Effect of temperature (80–130 °C), pressure (0.6–1.0 MPa), the amount of catalyst (2–15 mg) and reaction media was studied to obtain the optimum conditions for the reaction. The best results were obtained at 110 °C and 0.8 MPa pressure using manganese deuteroporphyrin dimethyl ester (Mn-DPDME) with 98% styrene conversion and 82% selectivity of benzaldehyde in benzonitrile solvent. In order to elaborate the effect of *meso* substituents on porphyrin catalytic activity and stability, four different Mn-porphyrins were selected and compared under the identical condition. It was found that the natural Mn-DPDME which has no substituents in the *meso*-sites but does have the methyl and propionate groups in the  $\beta$ -sites exhibited the higher activity than the synthetic manganese tetraphenylporphyrin, however, the later showed the superior stability and high selectivity of benzaldehyde. Furthermore, the catalytic method was widely used in the oxidation of various cycloalkenes, which exhibited excellent selectivity of epoxide. An alternative mechanism for the aerobic oxidation of styrene has been proposed and discussed.

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## 1. Introduction

Catalytic oxidation of alkenes is a key reaction in organic synthesis [1–4], because the oxidation of alkenes gives a variety of products such as carbonyl compounds, epoxides, diols, and products

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of oxidative cleavage of C–C bond (aldehydes). Most of them are among the most useful synthetic intermediates in view of the commercial value as well the synthetic utility of the ensuing oxidation products [5,6]. Over the past several decades, various transition metal catalysts, such as ruthenium, vanadium, gallium, cobalt and molybdenum have been successfully utilized to convert alkenes into epoxides or carbonyl compounds in combination with peroxides, peracids, and other oxidizing reagents [7–13]. While acknowledging the contributions made by the early pioneers, some drawbacks are still issues to be addressed. For example, these oxidizing agents are frequently used in over stoichiometric amounts and too expensive for industrial use. Particularly, the nature of the oxidant concerns the product selectivity and separation. However, using molecular oxygen will be more adequate for synthesis of bulk, fine chemicals and commodity products, because oxygen is the ideal oxidizing agent from the environmental point of view. It forms water as the only by-product and contains the maximum oxidizing weight percentage [14,15]. Given its advantages, Sahle-Demessie reported that under atmospheric and pressurized conditions ( $O_2$  3.5 bar and  $N_2$  10.3 bar), iron nitrate could effectively catalyze the aerobic oxidation of styrene, giving 80% conversion and 61% selectivity of benzaldehyde [6]. Subsequently, Jasra and co-workers revealed that cobalt(II)-exchanged zeolite X catalyzed selective oxidation of cycloalkenes to corresponding epoxides under the conditions of dioxygen pressure 60 psi and temperature 373 K in modest yields (47% cyclooctene conversion) [16]. Recently, Kleist et al. have found that Co-based metal-organic framework is an effective catalyst for the epoxidation of olefins in DMF with molecular oxygen as the oxidant, resulting in the low selectivity of styrene oxide (21%) [17]. In these cases, it could be found that the search for an efficient, selective, and environmentally benign catalytic method for the selective oxidation of alkene with dioxygen under high pressure is currently an important synthetic goal, and both improving the conversion of alkene and the selectivity of product remain one of the greatest challenges [18].

Metalloporphyrins have been synthesized and used as models of cytochrome P450 enzymes for various oxo transfer reactions, such as hydroxylation of alkanes, epoxidation of alkenes, oxidation of heteroatoms, dealkylation reactions, and oxidation of aromatics [19,20]. The industrial application of these synthetic metalloporphyrin complexes is restricted by the fact that they catalyze the oxidative hydroxylation of hydrocarbon in a biomimetic manner generally requiring either (a) stoichiometric oxygen atom donors other than oxygen, (b) sacrificial co-reductants, (c) electrochemical reduction, or (d) photolytic assistance [21–27]. Thus, the search for an efficient biomimetic catalytic method for the selective oxidation of alkenes with molecular oxygen or air in the absence of additives remains an objective. Herein, we report the results of the study on the oxidation of alkenes with dioxygen catalyzed by metalloporphyrins without any additive or co-reductant, including the optimization of the reaction conditions and clearing the effect of structure of metalloporphyrins on the catalytic activity. In addition, comparison of catalytic activity of different methods for the oxidation of alkenes under dioxygen pressure are summarized in Table 1. We wished to explore our catalytic method to industrial application.

## 2. Experimental

### 2.1. Materials and methods

All reagents and solvent used were of analytical grade. Porphyrins including tetraphenyl porphyrin (TPP), deuteroporphyrin dimethyl ester (DPDME), deuteroporphyrin dimethyl esters diphenylmethyl ester (DPDPH) were synthesized (Fig. 1); and purified as reported previously [28–30]. The *meso*-tribromo-deuteroporphyrin dimethyl ester (DPDBR) was prepared by bromination of DPDME with NBS using the stand chloroform method and the metallation of porphyrin was based on the procedure of Alder et al. [31,32].

GC/MS analyses were performed on a Thermo Trace DSQ mass spectrometer, under the following conditions. Helium was used as carrier gas at a flow rate of 1.2 mL/min. Gas chromatography was conducted using a RTX-5MS column (15 m x 0.25 mm ID x 0.25  $\mu$ m df, RESTEK CORP., US). The column temperature was programmed from 40 °C (1.5 min hold) to 260 °C at 15 °C/min. The injector temperature was set at 220 °C with a split ratio of 20:1. Both interface temperature and ion source temperature were set at 250 °C. The column outlet was inserted directly into the electron ionization source block, operating at 70 eV. Mass spectra (ESI) were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. The UV–Vis spectra were measured by a Shimadzu UV-1800 spectrophotometer. Thermal stability (TG–DTA) studies were carried out on a Mettler Toledo TG–DTA 851e instrument with a heating rate of 20 °C/min in nitrogen atmosphere.

### 2.2. Oxidation reaction

Alkene oxidation was carried out in the liquid phase in a stainless steel reactor of 100 mL under pressurized conditions equipped with a magnetic stirrer–heater. Dioxygen was continuously fed to the reactor through the oxygen bottle and the pressure can be changed from 0.1 to 1.4 MPa. In a typical reaction procedure, alkene (45 mmol) along with benzonitrile solvent (20 mL) and 5 mg catalyst were added. The mixture was heated to 80–150 °C and pressurized to desired pressure with  $O_2$  gas. After 6–8 h, the reaction was stopped followed by cooling the reactor to room temperature. The mixture was separated by distillation under reduced pressure and the catalyst was recovered from the residue and could be reused after silica gel chromatography. Furthermore, the reaction mixture was sampled by an “on-line means” every 30 min until the yield reached the maximum value. The samples and the final products were analyzed by GC–MS. The product selectivity is defined as follows (aldehyde as an example):

$$\text{Aldehyde selectivity} = \frac{\text{GC/MS peak area of aldehyde}}{\sum \text{GC/MS peak area of all products}} \times 100\%$$

## 3. Results and discussion

### 3.1. Optimization of reaction conditions

In order to obtain the best reaction conditions, a series of experiments was carried out by choosing Mn-DPDME as a catalyst to

**Table 1**  
Comparison of catalytic activity for the oxidation of alkenes under dioxygen pressure.

No	Catalyst	Substrate	Reaction condition	Conversion (%)	Selectivity (%)
1 [6]	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Styrene (100 mmol)	O <sub>2</sub> (3.4 bar) and N <sub>2</sub> (10.3 bar), 6 h, 80 °C	80	61 (aldehyde)
2 [16]	NaCoX96	Cis-cyclooctene (18 mmol)	O <sub>2</sub> (60 psi), 6 h, 373 K, DMF solvent	47	100 (epoxide)
3 [17]	STA-12(Co)	Styrene (2 mmol)	O <sub>2</sub> (50 mL/min), 100 °C, 5 h	>90	21 (epoxide), 12 (aldehyde)
		Styrene (45 mmol)	O <sub>2</sub> (0.8 MPa), 110 °C, 7 h benzonitrile	98	83 (aldehyde)
4	Our work	Cyclooctene (45 mmol)	O <sub>2</sub> (0.8 MPa), 110 °C, 8 h benzonitrile	92	100 (epoxide)

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