



## Short communication

## A novel system comprising metalloporphyrins and cyclohexene for the biomimetic aerobic oxidation of toluene

Hong-Yu Chen<sup>a</sup>, Meng Lv<sup>a</sup>, Xian-Tai Zhou<sup>b,\*</sup>, Jie-Xiang Wang<sup>a</sup>, Qi Han<sup>b</sup>, Hong-Bing Ji<sup>a,\*</sup><sup>a</sup> Fine Chemical Industry Research Institute, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, PR China<sup>b</sup> Fine Chemical Industry Research Institute, School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, PR China

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## ABSTRACT

In this study, a novel system comprising metalloporphyrins and cyclohexene for the biomimetic aerobic oxidation of toluene and its derivatives was developed, which exhibited relatively benign reaction conditions, good catalytic activity, and broad substrate scope. Based on a series of *in situ* EPR (Electron Paramagnetic Resonance) and UV–vis experiments, the effect of cyclohexene on the reaction and the catalytic mechanism were preliminarily investigated.

## 1. Introduction

Typically, molecular oxygen, which is usually activated by metal catalysts or stoichiometric co-oxidants such as aldehyde, is thought to be an ideal green oxidant for several purposes [1,2]. However, a majority of the involved industrial processes are far less benign, which usually proceed at high temperatures and pressures. For example, benzoic acid is produced from toluene in a manner analogous to the Amoco process using acetic acid as the solvent at approximately 190 °C and 1.5 MPa [3]. Accordingly, the development of green, industrially feasible methodologies for the activation of dioxygen under mild, bromide-free conditions is still a considerable challenge [4].

To address this challenge, the dioxygen activation mechanisms based on heme and nonheme biomimetic catalysts have been extensively examined [5–7]. Guo and coworkers have developed the selective aerobic oxidation of toluene using metalloporphyrin as catalysts [8,9]. Nature, however, has utilized porphyrin-dependent monooxygenases that can activate triplet oxygen using organic co-catalysts, e.g., FAD or FMN, and mildly oxidize diverse substrates under mild conditions. Notably, to facilitate the vital electron transport chains within these bio-enzymatic catalytic systems, reductive NAD(P)H, as a hydrogen donor (HD) to regenerate the catalytic sites, should be highly valued.

Inspired by nature's tendency to promote oxidative process by HDs under mild conditions, our group has recently reported a simple metalloporphyrin that can catalyze the aerobic epoxidation of cyclooctene with isopropylbenzene as the HD, with excellent conversion and selectivity up to 94% [10]. Meanwhile, on the basis of extensive *in situ*

monitoring techniques such as electron spin resonance spectroscopy, the HD-assisting activation mechanism of dioxygen has been completely elucidated.

Aiming to further explore the efficiency of the HD-assisting oxidation system, herein we report the biomimetic aerobic oxidation of toluene catalyzed by metalloporphyrins using cyclohexene as the auxiliary. The effects of various reaction parameters, such as catalyst components, reaction temperature, and dioxygen pressure, were thoroughly investigated. Furthermore, a plausible HD-assisted catalytic mechanism for the oxidation of toluene was proposed on the basis of extensive *in situ* monitoring techniques.

## 2. Experimental

## 2.1. Materials and methods

All of the reagents and solvents were purchased from commercial sources and used without any purification unless anhydrous conditions were noted. EPR spectra were recorded at a microwave frequency of 9.05 GHz at 333 K on a JEOL electron spin spectrometer equipped with an X-band microwave unit. *In situ* UV–vis spectra were recorded on an Ocean optics UV–vis spectrometer.

## 2.2. General procedure for the aerobic oxidation of toluene

First, the substrate (5.0 mmol), cyclohexene (3.0 mmol), catalyst (if used), and acetonitrile (10 mL) were charged into an autoclave at RT. Second, the autoclave was sealed and flushed with dioxygen several

\* Corresponding authors.

E-mail addresses: [zhoutai@mail.sysu.edu.cn](mailto:zhoutai@mail.sysu.edu.cn) (X.-T. Zhou), [jihb@mail.sysu.edu.cn](mailto:jihb@mail.sysu.edu.cn) (H.-B. Ji).

**Table 1**  
Oxidation of toluene catalyzed by metalloporphyrins.<sup>a</sup>

| Entry           | Catalyst | Amount (10 <sup>-3</sup> mmol) | Conv. (%) | Select. (%) |      |      |
|-----------------|----------|--------------------------------|-----------|-------------|------|------|
|                 |          |                                |           | BA          | BAL  | BAC  |
| 1 <sup>b</sup>  | None     | 0                              | –         | –           | –    | –    |
| 2 <sup>b</sup>  | MnTPPCL  | 1.0                            | 6.3       | 33.8        | 19.2 | 47.0 |
| 3               | None     | 0                              | 6.1       | 39.7        | 14.9 | 45.4 |
| 4               | FeTPPCL  | 1.0                            | 6.0       | 34.3        | 18.9 | 46.8 |
| 5               | CoTPP    | 1.0                            | 6.5       | 35.4        | 15.4 | 49.2 |
| 6               | MnTPPCL  | 1.0                            | 12.5      | 39.4        | 17.2 | 43.4 |
| 7               | MnTPPCL  | 0.5                            | 8.8       | 37.4        | 23.3 | 39.3 |
| 8               | MnTPPCL  | 1.5                            | 11.3      | 36.9        | 16.9 | 46.2 |
| 9 <sup>c</sup>  | MnTPPCL  | 1.0                            | 10.6      | 41.9        | 22.0 | 36.1 |
| 10 <sup>c</sup> | MnTPPCL  | 1.0                            | 13.2      | 30.8        | 15.6 | 53.6 |
| 11 <sup>d</sup> | MnTPPCL  | 1.0                            | 12.0      | 38.9        | 12.8 | 48.3 |

<sup>a</sup> Toluene (5 mmol), cyclohexene (3 mmol), acetonitrile (10 mL), O<sub>2</sub> (1.2 MPa), 160 °C, 4 h.

<sup>b</sup> In the absence of cyclohexene.

<sup>c</sup> Reaction temperature was 150 °C and 170 °C, respectively.

<sup>d</sup> Reaction pressure was 1.5 MPa.

times to maintain the reactor pressure at 1.0 MPa. Subsequently, the autoclave was heated at 160 °C for 4 h. The conversion and selectivities were determined using biphenyl as the internal standard and measured on a GC2010 Gas Chromatograph (GC, Shimadzu) equipped with a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 m) and a flame ionization detector.

### 3. Results and discussion

#### 3.1. The optimization of reaction conditions towards toluene oxidation

Using toluene as model substrate, the reaction conditions were optimized with metalloporphyrins as catalyst. The main products in the oxidation of toluene are benzyl alcohol (BAL), benzaldehyde (BA) and benzoic acid (BAC) (Table 1). In control experiments without the catalyst and cyclohexene, no obvious conversion was observed (entry 1 in Table 1). On the other hand, when the reaction was conducted with either MnTPPCL or cyclohexene as the hydrogen donor, almost the same efficiency was obtained (entries 2 and 3 in Table 1). This result also indicated that cyclohexene plays a significant role in the activation of C–H bond of toluene.

The catalytic activity of metalloporphyrins for the aerobic oxidation of toluene has been reported to be significantly affected by their chelated metal ions [11]. Accordingly, the effect of different metalloporphyrins on the aerobic oxidation of toluene with HDs was first investigated. Metalloporphyrins with different metal ions, FeTPPCL, CoTPP and MnTPPCL, combined with cyclohexene, were examined. The

**Table 2**  
Biomimetic aerobic oxidation of derivatives of toluene.<sup>a</sup>

| Entry | Substrate                | Main product | Conv. (%) | Select. (%) |
|-------|--------------------------|--------------|-----------|-------------|
| 1     | R = MeO (1a)             | 3a           | 14.0      | 44.3        |
| 2     | R = H (1b)               | 3b           | 12.5      | 43.4        |
| 3     | R = F (1c)               | 2c           | 9.4       | 47.9        |
| 4     | R = Cl (1d)              | 2d           | 8.8       | 61.4        |
| 5     | R = Br (1e)              | 2e           | 7.2       | 66.7        |
| 6     | R = NO <sub>2</sub> (1f) | 2f           | 6.2       | 60.0        |

<sup>a</sup> Substrate (5 mmol), MnTPPCL (1.0 × 10<sup>-3</sup> mmol), cyclohexene (3 mmol), acetonitrile (10 mL), O<sub>2</sub> (1.2 MPa), 160 °C, 4 h.

toluene conversion over the catalysts was 6.0%, 6.5% and 12.5%, respectively. The highest toluene conversion was observed in the catalytic system comprising MnTPPCL and cyclohexene (entries 4–6).

Subsequently, the catalyst loading amount was examined. No significant difference was observed when the amount of catalyst was increased (entry 8). High reaction temperatures have been reported to dramatically decrease the induction period and accelerate the reaction rate [12]. In this study, the effect of the reaction temperature on the aerobic oxidation of toluene was investigated at 150–170 °C. The conversion of toluene increases with the enhancing reaction temperature. Considering the conversion and selectivity of toluene, a reaction temperature of 160 °C was considered to be suitable conditions. As to reaction pressure, no obvious enhancement could be obtained when the amount of molecular oxygen was increased (entry 11).

#### 3.2. Screening of the substrate on the oxidation of toluene derivatives

With the optimized conditions in hand, the scope of different toluene derivatives for the cyclohexene-facilitated aerobic oxidation with MnTPPCL was investigated as shown in Table 2.

A series of toluene derivatives with electron-donating and -withdrawing groups on the phenyl ring were subjected to the reaction, affording desired products (Table 2). This result is indicative of good tolerance. *para*-Methoxytoluene (entry 1) exhibited better conversion compared to the other derivatives bearing electro-withdrawing groups (entry 1 vs entries 3–6). Moreover, in the biomimetic catalytic system, it is interesting to find that aldehyde is the main product for the substrates bearing electro-withdrawing groups (entries 3–6).

#### 3.3. Plausible mechanism of aerobic toluene oxidation in the presence of cyclohexene

As the classic biomimetic model of C–H activation using cytochrome P450 monooxygenase, the catalytic mechanisms of aerobic oxidation using metalloporphyrins have been extensively investigated [13,14]. By the comparison of our previously reported study on the isopropylbenzene-facilitated aerobic epoxidation of cyclooctene [10], the synergistic effect of cyclohexene was also considered as a key factor, which possibly induces the reaction to follow a similar two-step oxidation process, namely, the oxidation of cyclohexene and substrate, respectively.

However, considering that cyclohexene is far easier to undergo autooxidation in air compared to toluene [15], it was first examined by *in situ* EPR experiments (Fig. 1). In the absence of catalyst, two stable PBN radical adducts (*a* and *b*) were observed (Left in Fig. 1). When MnTPPCL catalyst was added in the solution, the same two adducts (*a* and *b*) were obtained (Right in Fig. 1).

However, the intensity of adduct *a* significantly decreased, coupled

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