



## Highly efficient aerobic oxidation of oximes to carbonyl compounds catalyzed by metalloporphyrins in the presence of benzaldehyde

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### ARTICLE INFO

#### Article history:

Received 4 October 2009

Revised 9 November 2009

Accepted 17 November 2009

Available online 20 November 2009

#### Keywords:

Oxime

Carbonyl compound

Oxidation

Metalloporphyrins

### ABSTRACT

Highly efficient oxidation of oximes to carbonyl compounds by molecular oxygen with benzaldehyde as an oxygen acceptor in the presence of metalloporphyrins has been reported. The simple structural manganese porphyrin showed an excellent activity for the oxidative deoxygenation reactions of various oximes. Moreover, different factors influencing oximes oxidation, that is, catalyst, solvent, and temperature, have been investigated. A possible mechanism for the deoxygenation reaction has been proposed.

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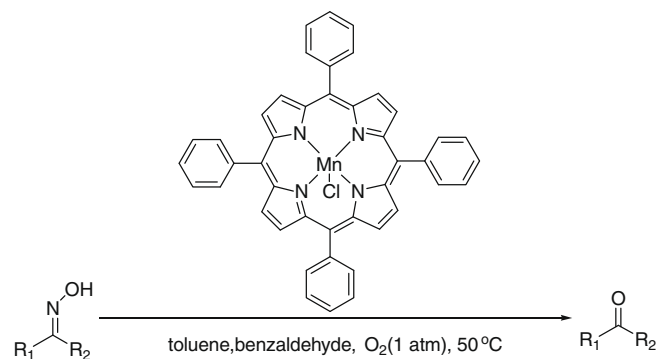
### 1. Introduction

Oximes are extensively used for purification and characterization of carbonyl compounds and preparation of amides via Beckmann rearrangement.<sup>1</sup> At the same time, the synthesis of oximes from noncarbonyl compounds also provides an alternative for preparing aldehydes and ketones.<sup>2</sup> So far, a variety of methods for deoxygenation based on acid-catalytic hydrolysis,<sup>3</sup> reductive cleavage,<sup>4</sup> oxidative cleavage,<sup>5</sup> and photosensitized oxidative deprotection<sup>6</sup> have been developed. The oxidation methods employed several oxidizing agents, that is, chromium reagents,<sup>7</sup>  $\text{KMnO}_4$ ,<sup>8</sup> manganese triacetate,<sup>5c</sup> *N*-bromosuccinimide,<sup>9</sup>  $\text{N}_2\text{O}_4$ ,<sup>10</sup>  $\text{NaIO}_4$ ,<sup>11</sup> and *tert*-butylhydroperoxide.<sup>5d</sup> Most of the reagents used in the methods are hazardous or very toxic, usually causing severe environmental pollution. Therefore, using clean and inexpensive oxidants such as dioxygen for deoxygenation reactions are extremely significant and particularly attractive from an environmental and cost effective viewpoint.

As model catalysts of cytochrome P-450, metalloporphyrins have been widely used for the oxygenation of various organic compounds, that is, alkanes, alkenes, and alcohols.<sup>12</sup> However, few studies on deoxygenation have ever been reported. Chauhan and co-workers reported the oxidation of  $\text{C}=\text{NOH}$  bonds in ionic liquid catalyzed by water soluble iron(III) porphyrins ( $\text{Cl}_8\text{TTPS}_4\text{Fe}^{\text{III}}$ ) with hydrogen peroxide, in which various carbonyl compounds could be obtained with yields of 45–80%.<sup>13</sup> The only example on the aerobic

oxidation of fluorenone oxime catalyzed by iron porphyrin under high pressure conditions was reported by Groves group, in which the reaction rate increased with the increasing pressure of dioxygen.<sup>14</sup> When the pressure of molecular oxygen was about 3.5 MPa, fluorenone could be obtained with the yield of 86%.

In previous studies, a series of efficient catalytic systems for the metalloporphyrins-catalyzed aerobic oxidation of olefin, sulfide, alcohol, ketone, etc. have been developed in the presence of aldehyde as an oxygen acceptor.<sup>15</sup> In continuation of our ongoing research on the metalloporphyrins-catalyzed oxidations, herein the efficient deoxygenation reaction catalyzed by manganese porphyrins by dioxygen in the presence of benzaldehyde under ambient conditions is reported (Scheme 1). Various oximes were readily re-



**Scheme 1.** Oxidation of oximes catalyzed by MnTPPCL in the presence of dioxygen and benzaldehyde.

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acted to afford the corresponding carbonyl compounds under mild conditions. Furthermore, high-valent oxo intermediate was verified by UV–vis spectroscopy in the deoxygenation reaction, and a plausible mechanism was proposed.

## 2. Oxidation of cyclohexanone oxime catalyzed by various metalloporphyrins

The catalytic activity and selectivity of different metalloporphyrins for the oxidation of oxime to carbonyl compounds by molecular oxygen were investigated by using cyclohexanone oxime as a model substrate.<sup>16</sup> The engaged catalysts for the oxidation reactions were simple structural metalloporphyrins that have the same ligand *meso*-tetraphenylporphyrin (TPP) but different metals, including MnTPPCL, RuTPPCL, FeTPPCL, and CoTPPCL. The results are summarized in Table 1.

The oxidation of cyclohexanone oxime catalyzed by these catalysts produced cyclohexanone as the main product. As listed in Table 1, almost no reaction was observed in blank experiment even though the reaction time was prolonged to 8 h (entry 5). The catalytic activity of metalloporphyrins for oxidation appeared to be dependent on the nature of central ions. Manganese porphyrin showed the best activity among the four simple structural metalloporphyrin catalysts, and presented excellent catalytic performance for the oxidation of cyclohexanone oxime under mild condition (entries 1–4). The catalytic activation of the four metalloporphyrins was in the sequence of MnTPPCL > FeTPPCL > CoTPPCL > RuTPPCL. The differences of the catalytic activities for various metalloporphyrins were probably influenced by the stability of different valences of metal atoms and their electric potential.<sup>17</sup> Manganese porphyrin, the most reactive among the studied catalysts, was chosen for further investigations. Attempts to obtain higher activities of the electron-withdrawing metalloporphyrins (tetra-(*o*-nitrophenyl) and tetra-(*o*-chlorophenyl) manganese porphyrin, abbreviated as T(*o*-NO<sub>2</sub>)MnPPCL and T(*o*-Cl)MnPPCL) for oxime oxidation were unsuccessful, in which the conversions of cyclohexanone oxime were 91% and 87%, respectively (entries 6 and 7).

## 3. Effect of temperature on the oxidation of cyclohexanone oxime

The effect of reaction temperature on the aerobic oxidation of cyclohexanone oxime to cyclohexanone catalyzed by MnTPPCL has been investigated, and the results are summarized in Table 2.

As shown in Table 2, it seemed that the conversion of cyclohexanone oxime was closely related to reaction temperature, and the reaction rate increased with the raising temperature from 40 °C to 60 °C. When the temperature was 40 °C, almost no cyclohexanone oxime could be converted to the corresponding product, although the mixture was stirred for the prolonged reaction time (entry 1). However, the conversion of cyclohexanone oxime increased rap-

**Table 2**

Effect of temperature on the aerobic oxidation of cyclohexanone oxime<sup>a</sup>

| Entry | T (°C) | Time (h) | Conv. (%) | Yield (%) |
|-------|--------|----------|-----------|-----------|
| 1     | 40     | 10       | 2         | 2         |
| 2     | 45     | 6        | 48        | 43        |
| 3     | 50     | 5        | 93        | 90        |
| 4     | 55     | 3        | 94        | 82        |
| 5     | 60     | 1.5      | 97        | 80        |

<sup>a</sup> MnTPPCL (1 × 10<sup>-3</sup> mmol), cyclohexanone oxime (1 mmol), toluene (5 mL), benzaldehyde (15 mmol), O<sub>2</sub> bubbling.

idly to 93%, while the temperature rose to 50 °C (entry 3). With the elevated temperature from 50 °C to 60 °C, no obvious increment was observed for the conversion of cyclohexanone oxime, but its selectivity for cyclohexanone lowered. The substrate was further converted to lactone at higher temperature (entries 5–6). Such results indicated that 50 °C was the optimal reaction temperature for the aerobic oxidation of cyclohexanone oxime.

## 4. Effect of solvent on the oxidation of cyclohexanone oxime

With MnTPPCL as a catalyst, the aerobic oxidation of cyclohexanone oxime in various solvents has been investigated and the results are summarized in Table 3. The engaged solvents for the oxidation reactions are toluene, acetonitrile, isopropanol, and cyclohexane.

It could be observed from Table 3 that solvent played an important role in the oxidation system. It seemed that acetonitrile and toluene were favorable to the aerobic oxidation of cyclohexanone oxime to cyclohexanone, which gave the yield of 90% and 88%, respectively (entries 1 and 2). When isopropanol and cyclohexane were used instead, very low yield of product could be obtained (entries 3 and 4). The distinct results should be attributed to the inherent characteristic of each solvent. Toluene as a solvent is often the choice for radical reactions because of its reluctance to undergo radical addition,<sup>18</sup> and acetonitrile is an ideal replacement in the oxidations catalyzed by metalloporphyrins.<sup>19</sup>

## 5. Effect of the amount of benzaldehyde on the oxidation of cyclohexanone oxime

The effect of the amount of benzaldehyde on the aerobic oxidation of cyclohexanone oxime under ambient conditions was investigated and the results are listed in Table 4.

As shown in Table 4, it can be found that benzaldehyde played an important role in the cyclohexanone oxime oxidation system when dioxygen was employed as the sole oxidant. The oxidation reaction stopped completely in the absence of benzaldehyde (entry 1), indicating that the metalloporphyrins have excellent performance for activating dioxygen in the presence of benzaldehyde. It also seemed that the reaction rate was related closely with the amount of benzaldehyde. The higher molar ratio of benzaldehyde could accelerate the oxidation. The conversion increased with the

**Table 1**

Aerobic oxidation of cyclohexanone oxime catalyzed by various metalloporphyrins<sup>a</sup>

| Entry          | Catalyst                             | Conv. (%) | Yield (%) |
|----------------|--------------------------------------|-----------|-----------|
| 1              | MnTPPCL                              | 93        | 90        |
| 2              | FeTPPCL                              | 32        | 30        |
| 3              | CoTPPCL                              | 14        | 14        |
| 4              | RuTPPCL                              | 15        | 11        |
| 5 <sup>b</sup> | —                                    | 5         | 4         |
| 6              | Mn( <i>o</i> -NO <sub>2</sub> )TPPCL | 91        | 86        |
| 7              | Mn( <i>o</i> -Cl)TPPCL               | 87        | 80        |

<sup>a</sup> Catalyst (1 × 10<sup>-3</sup> mmol), substrate (1 mmol), toluene (5 mL), benzaldehyde (15 mmol), 50 °C, 5 h, O<sub>2</sub> bubbling.

<sup>b</sup> Reaction time was 8 h.

**Table 3**

Effect of solvent on the aerobic oxidation of cyclohexanone oxime<sup>a</sup>

| Entry | Solvent      | Time (h) | Conv. (%) | Yield (%) |
|-------|--------------|----------|-----------|-----------|
| 1     | Toluene      | 5        | 93        | 90        |
| 2     | Acetonitrile | 6        | 93        | 88        |
| 3     | Isopropanol  | 6        | 21        | 21        |
| 4     | Cyclohexane  | 6        | 2         | 2         |

<sup>a</sup> MnTPPCL (1 × 10<sup>-3</sup> mmol), cyclohexanone oxime (1 mmol), solvent (5 mL), benzaldehyde (15 mmol), O<sub>2</sub> bubbling, 50 °C.

**Table 4**Effect of the amount of benzaldehyde on the aerobic oxidation of cyclohexanone oxime<sup>a</sup>

| Entry          | Amount of benzaldehyde (mmol) | Time (h) | Conv. (%) | Yield (%) |
|----------------|-------------------------------|----------|-----------|-----------|
| 1              | 0                             | 7        | 0         | 0         |
| 2              | 5                             | 7        | 40        | 39        |
| 3              | 10                            | 7        | 70        | 66        |
| 4              | 15                            | 5        | 93        | 90        |
| 5              | 20                            | 5        | 92        | 88        |
| 6 <sup>b</sup> | 15                            | 5        | 50        | 45        |

<sup>a</sup> MnTPPCI ( $1 \times 10^{-3}$  mmol), cyclohexanone oxime (1 mmol), toluene (5 mL), O<sub>2</sub> bubbling, 50 °C.<sup>b</sup> Isobutyraldehyde (15 mmol).

amount of benzaldehyde raised from 0 to 15 mmol (entries 1–4), which could be attributed to the continual consumption of benzal-

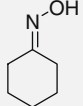
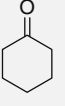
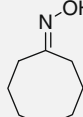
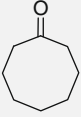


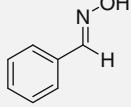
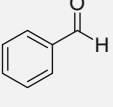
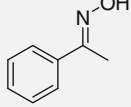
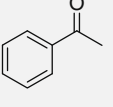
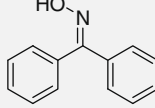
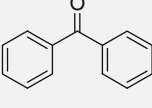
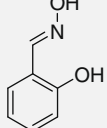
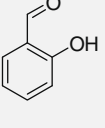
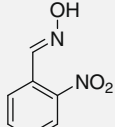
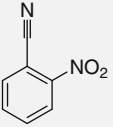
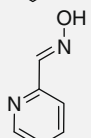
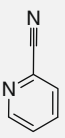
dehyde during the reaction. However, no significant difference was observed when the amount of benzaldehyde was higher than 15 mmol (entry 5). Some papers reported that isobutyraldehyde was effective for epoxidation,<sup>20</sup> but it has been found that the yield of cyclohexanone was only 45% when isobutyraldehyde was used as the only oxygen transfer agent in the oxidative system (entry 6).

## 6. Aerobic oxidation of various oximes catalyzed by MnTPPCI

Different substrates were examined for the aerobic oxidation catalyzed by the MnTPPCI and the typical results are summarized in Table 5.

As shown in Table 5, the oxidations of most oximes occurred smoothly to afford selectively the corresponding carbonyl compounds by dioxygen in the presence of MnTPPCI under mild conditions. Among the cyclic oximes, it seems that six-membered cyclic

**Table 5**Aerobic oxidation of various oximes catalyzed by manganese porphyrin<sup>a</sup>

| Entry          | Oxime   | Product   | Time (h) | Conv. (%) | Yield (%) |
|----------------|---|---|----------|-----------|-----------|
| 1              |    |    | 5        | 93        | 90        |
| 2 <sup>b</sup> |   |   | 8        | 56        | 56        |
| 3              |  |  | 8        | 85        | 85        |
| 4              |  |  | 6        | >99       | >99       |
| 5              |  |  | 2        | >99       | >99       |
| 6 <sup>c</sup> |  |  | 2        | 98        | 84        |
| 7              |  |  | 6        | >99       | 95        |
| 8              |  |  | 8        | 15        | 15        |
| 9 <sup>c</sup> |  |  | 6        | 30        | 30        |

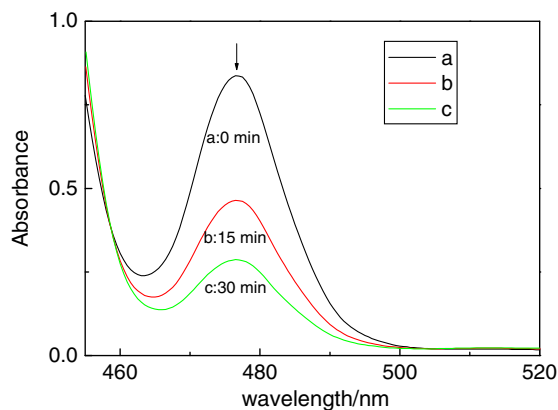
<sup>a</sup> MnTPPCI ( $1 \times 10^{-3}$  mmol), substrate (1 mmol), toluene (5 mL), benzaldehyde (15 mmol), O<sub>2</sub>, 50 °C.<sup>b</sup> Isobutyraldehyde (15 mmol).<sup>c</sup> Acetonitrile (5 mL).

oxime was more efficiently oxidized than other cyclic oximes, that is, cyclooctanone and cyclopentanone oximes (entries 1–3). The catalytic system seems favorable for the conversion of aromatic oximes in short reaction times (entries 4–9). For example, acetophenone oxime could be converted to the corresponding acetophenone completely within 2 h (entry 5). Steric structure almost has no effect on the conversion of oximes, but has a slight effect on the selectivity of carbonyl compound such as benzophenone oxime (entry 6).

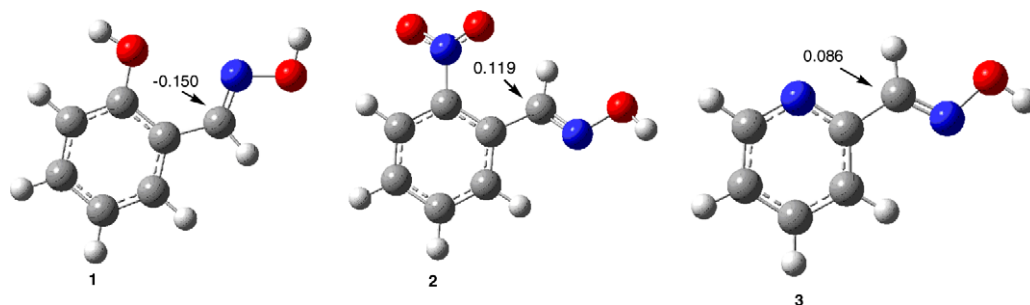
The oxidation efficiency for this catalytic system seems very dependent on the electronic property of substrates. It is interesting to find that the obtained product was nitrile rather than carbonyl compound for the substrates with electron-withdrawing groups at *ortho*-position (entries 8 and 9). Meanwhile, the yield of nitrile was very low even with long reaction time, indicating that electron-withdrawing effect retarded the deprivation of oxime group. However, the oxidation efficiency was not affected by electron-donating group of substrate (entry 7).

### 7. Plausible mechanism for the aerobic oxidation of oxime catalyzed by MnTPPCL

When the oxidation of cyclohexanone oxime was conducted with dioxygen and benzaldehyde in the absence of MnTPPCL, the yield of cyclohexanone could only reach 4% (Table 1, entry 5). However, the yield was remarkably increased by adding  $1 \times 10^{-3}$  mmol of manganese porphyrin in the mixture (Table 1, 90%, entry 1). The results clearly suggest that manganese porphyrin is crucial for the deoxygenation reaction. Meanwhile, it was found that the reaction was completely inhibited when the radical trap (2,6-di-*tert*-butyl-4-methylphenol) was used. Therefore, the deprivation of oxime



**Figure 1.** UV-vis spectra of cyclohexanone oxime oxidation by molecular oxygen in the presence of benzaldehyde and MnTPPCL.



**Figure 2.** Optimized structures and of oximes (1: *o*-hydroxy benzaldehyde oxime, 2: *o*-nitro benzaldehyde oxime, and 3: picolinaldehyde oxime) calculated at the B3LYP/6-31+G(d,p) level of theory.

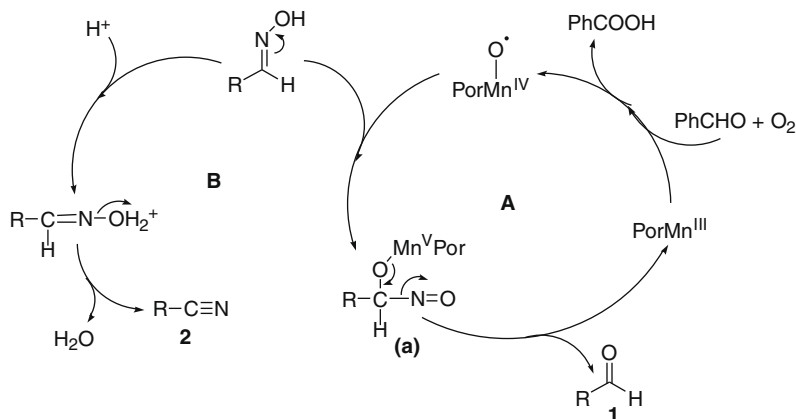
catalyzed by manganese porphyrin should involve radical species. As described in our previous works,<sup>15a,21</sup> high-valent metal intermediate is generated from a series of radical species in the presence of dioxygen and aldehyde.

High-valent porphyrin intermediate is generally accepted as the active species for the oxidations catalyzed by metalloporphyrins.<sup>22</sup> The presence of manganese-oxo porphyrin was confirmed by UV-vis spectra for the oxidation of cyclohexanone oxime, as demonstrated in Figure 1. Curves a, b, and c show the spectra of solution at the beginning, reacted for 15 min and 30 min, respectively. The strength of Soret band of MnTPPCL at 476 nm decreased gradually, suggesting the consumption of the oxidant active species ( $\text{Mn}^{\text{IV}}=\text{O}$ ) by substrate.<sup>19a,22a,23</sup> In addition, color changes of the reaction mixture from dark green to tinge also indicated valence change of manganese. The GC results for these reactions revealed the formation of cyclohexanone, which is indicative of the presence of an active oxidation species.

While investigating the catalytic efficiency for various substrates, it is interesting to find that nitrile was the only product for the substrates with electron-withdrawing groups at *ortho*-position (Table 5, entries 8 and 9), while carbonyl compound was the main product for the substrates with electron-donating group (Table 5, entry 7). Such extremely different results could be attributed to different electronic atmosphere of C=N bond.

To get a better understanding, calculations were performed with the GAUSSIAN03W package using the density functional theory (DFT).<sup>24</sup> Full geometry optimizations of different substrates were performed employing Becke's three parameter Lee–Yang–Parr correlation functions (B3LYP) combined with 6-31+G(d,p) basis set. The optimized structures for the substrates listed in Table 5 (entries 7–9, *o*-hydroxy benzaldehyde oxime, *o*-nitro benzaldehyde oxime and picolinaldehyde oxime as the substrates) are presented in Figure 2. According to the calculated results, the Mulliken charges for the carbon atom in C=N bond are  $-0.150$  eV,  $0.119$  eV, and  $0.086$  eV, respectively. The oximes with electron-withdrawing groups have a positive charge for the carbon atom, which retards the nucleophilic attack of high-valent metal intermediate to carbon atom. The oxidation of such oximes may proceed with another mechanism, in which the oximes tend to be protonated firstly.

According to the above discussions, a plausible reaction mechanism for the deoxygenation reaction using MnTPPCL as a catalyst has been proposed as shown in Figure 3. Based on the proposed mechanism, the high-valent Mn porphyrins intermediate is generated as described in previous literatures. A adduct (a) could be generated from the nucleophilic attack of the high-valent oxo species to C=N bond, which produces the corresponding carbonyl compounds **1** by decomposition (pathway A). Substrates with electron-withdrawing groups tend to be protonated to give intermediate (b), which yields nitrile **2** via dehydration (pathway B).



**Figure 3.** Plausible reaction mechanism of the oxidative deoxygenation catalyzed by MnTPPCL in the presence of molecular oxygen and benzaldehyde.

In conclusion, an efficient method for an aerobic oxidation of oximes to the corresponding carbonyl compounds with manganese porphyrin as a catalyst in the presence of benzaldehyde has been developed. All the factors that effected cyclohexanone oxime oxidation were well investigated. Various oximes could be successfully oxidized. The oxidative deoxygenation was through radical process with the formation of high-valent manganese intermediate, which was confirmed by UV–vis spectroscopy. A possible mechanism for the oxidative deoxygenation has been proposed.

### Acknowledgments

The authors thank the National Natural Science Foundation of China (20976203), the Key Fundamental Research Foundation (2008CB617511), China Postdoctoral Science Foundation (20080440792), and the Program for New Century Excellent Talents in University (NCET-06-740) for providing financial support for this project.

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