

Selective catalysis of manganeseporphyrins on aerobic oxidation of different carbon–hydrogen bonds of methyl cyclohexane

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Abstract

The selective catalysis of manganeseporphyrins for the aerobic oxidation of the different C–H bonds of methyl cyclohexane was reported. The effects of the peripheral substituents of metalloporphyrins and the reaction conditions on the catalytic selectivity were also investigated. It was found that manganeseporphyrins are effective catalysts for the aerobic oxidation of C–H bonds of methyl cyclohexane. The results showed that the increase of reaction temperature and pressure is benefited to selective oxidation of secondary C–H bonds, and the concentration of catalysts does not significantly influence the oxidation selectivity of every grade C–H bond. The electron-contributing substituents on porphyrin rings assist the selective oxidation of the secondary C–H bonds, while the electron-withdrawing substituents are favorable to selective oxidation of the tertiary C–H bonds. © 2005 Elsevier B.V. All rights reserved.

Keywords: Manganeseporphyrin; Methyl cyclohexane; Oxidation; Selectivity

1. Introduction

The selective oxidation of alkanes has been extensively applied in the synthesis of chemical industry, medicine, spices and fine chemicals [1–4]. Therefore, considerable efforts have been made to investigate the methods of high-efficient selective oxidation of alkanes under mild conditions [5–7]. Metalloporphyrins have recently been reported to be efficient catalysts in the hydroxylation of alkanes; however, this catalysis system is mostly employed to oxidize substrate with sole active centers [8,9]. Few reports can be found on the direct selective oxidation of the different kinds of C–H bonds of the same substrate [10–13], especially the aerobic oxidation of the low grade C–H bonds.

It has already been reported by our group that the simple metalloporphyrins have the excellent catalytic performances for the oxidation of hydrocarbons with air in the absence of any assistant reductants or co-catalysts [13–16]. In this paper, the selective catalysis of metalloporphyrins for the aerobic oxidation of different C–H bonds of hydrocarbons in the system of manganeseporphyrin–methyl cyclohexane–air was investigated in detail.

2. Experimental

The reagents were all obtained commercially without further purification except that pyrrole was redistilled before use. Manganeseporphyrins shown in Fig. 1 were synthesized and purified according to documented procedures [17], their structures were confirmed by IR, UV–vis, ¹H NMR and elementary analysis.

The methyl cyclohexane oxidation reactions were carried out in a 500 mL semi-autoclave in which air was continuously flowed. In a typical experiment, 350 mL of methyl cyclohexane and 5.0 mg of catalyst were added to the autoclave pressured to 0.8 MPa by air. The reactants were stirred continuously at 140 °C for 2 h. After reaction completed, the autoclave was cooled to room temperature. Then, oxidation products were detected by GC-FID equipped with a 0.5 mm i.d. × 25 m PEG20000 and HPLC with an UV (216 nm) detector and a Zorbax SB-C18 (4.5 mm × 250 mm) column.

3. Results and discussion

3.1. The oxidation of methyl cyclohexane under the catalysis of manganeseporphyrins

Under the catalysis of the manganeseporphyrins, the oxidation products of methyl cyclohexane were identified

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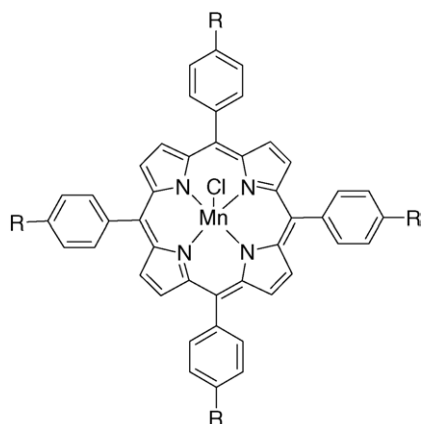


Fig. 1. Structure of T(*p*-R)MnPpCl, R = OH, OCH₃, CH₃, H, Cl.

by GC–MS and LC–MS. This reaction was shown in Fig. 2.

The products 1–5 were quantified by GC, and 6–8 by HPLC. There are three kinds of C–H bonds in methyl cyclohexane. Product 1 was obtained by the oxidation of tertiary C–H bond of methyl cyclohexane, and products 2–5 were obtained by the oxidation of secondary C–H bonds. Product 6 came from the oxidation of 2, and the products 7 and 8 were the deep oxidation products of 4 and 5 [5,18]. Therefore, products 2–8 were classified as oxidation products of secondary C–H bond. From the above analysis, it can be concluded that no primary C–H bonds oxidation reactions happened. Meanwhile, the yields of different C–H bond products were calculated by the amount of methyl cyclohexane which was converted to corresponding products, and the selectivity ratio of tertiary C–H and secondary C–H (*S*) was determined and defined as follows:

$$S = \frac{\text{the yield of all tertiary C–H bond oxidation products/the number of all tertiary C–H bonds}}{\text{the yield of all secondary C–H bond oxidation products/the number of all secondary C–H bonds}}$$

$$= \frac{\text{the yield of product 1}}{\text{the whole yield of products 2–8}} \times 10$$

There exist 1 tertiary C–H bond and 10 secondary C–H bonds in methyl cyclohexane.

3.2. The changes of selectivity over time

When the temperature was at 150 °C, the pressure at 0.8 MPa and 5 mg TPPMnCl as catalyst, the changes of the oxidation

Table 1
Effect of time on *S*

Time (min)	Yield of tertiary C–H products (%)	Yield of secondary C–H products (%)	<i>S</i>
30	0.63	1.89	3.33
60	1.36	4.19	3.25
90	2.33	7.21	3.23
120	5.45	17.04	3.20
150	5.75	17.97	3.20
180	6.21	19.38	3.20

Reaction condition: TPPMnCl, 5 mg; methyl cyclohexane, 350 mL; pressure, 0.8 MPa; temperature, 150 °C.

products of different C–H bonds of methyl cyclohexane over time were listed in Table 1.

As can be seen that the oxidation products yields of both secondary and tertiary C–H bonds increased rapidly before 120 min, and then slowed down. But *S* changed little and maintains at 3.20–3.33, which means that *S* keeps invariable when the reaction time increases. Therefore, it is reasonable to employ *S* for evaluating the effect of manganese porphyrins on the catalytic oxidation of methyl cyclohexane. Consequently, the yield of both secondary C–H products and tertiary C–H products can be calculated according to the data obtained at the moment when the reaction occurred for 120 min.

3.3. Influence of temperature on selectivity

Influence of temperature on the oxidation products of different C–H bonds was investigated. The corresponding results were

illustrated in Table 2. It can be seen when temperature increased from 130 °C to 150 °C, *S* decreased from 5.2 to 3.2, indicating that the selective oxidation of secondary C–H bonds can be enhanced by increasing of temperature. This may be caused by the activation energy of different C–H bonds. The activation energy of secondary C–H bond is relatively higher than tertiary C–H bond, therefore, secondary C–H bonds oxidation products can be more easily obtained than tertiary C–H bond under higher temperature.

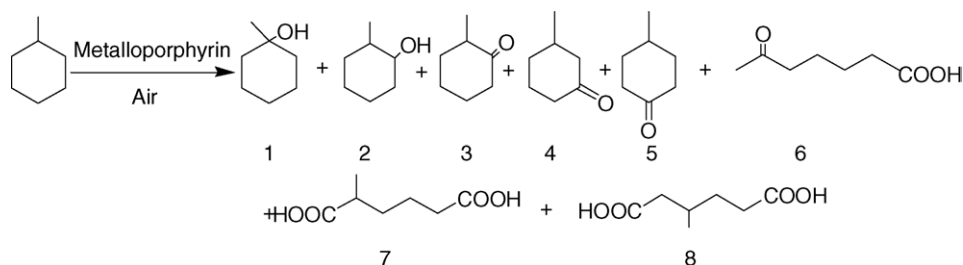


Fig. 2. Oxidation of methyl cyclohexane under the catalysis of metalloporphyrin.

Table 2
Influence of temperature on *S*

Temperature (°C)	Yield of tertiary C–H products (%)	Yield of secondary C–H products (%)	<i>S</i>
130	2.09	4.02	5.20
135	3.11	6.92	4.49
140	4.00	9.75	4.10
145	4.18	11.96	3.49
150	5.45	17.04	3.20

Reaction condition: TPPMnCl, 5 mg; methyl cyclohexane, 350 mL; pressure, 0.8 MPa; reaction time, 2 h.

Table 3
Influence of pressure on *S*

Pressure (MPa)	Yield of tertiary C–H products (%)	Yield of secondary C–H products (%)	<i>S</i>
0.6	3.44	6.89	4.99
0.8	4.00	9.75	4.10
1.0	4.06	13.09	3.10
1.2	5.84	20.85	2.80

Reaction condition: TPPMnCl, 5 mg; methyl cyclohexane, 350 mL; temperature, 140 °C; reaction time, 2 h.

3.4. Influence of pressure on selectivity

The pressure from 0.6 MPa to 1.2 MPa was investigated to reveal the relationship between *S* and the concentration of O₂ in the reaction system. Seen from Table 3, *S* decreases from 5.0 to 2.8 with the increase of pressure, which means that specific oxidation of secondary C–H bonds can be improved by the increase of pressure. Since concentration of oxygen was positively related with the pressure and the oxidation products of secondary C–H bonds could be over-oxidized to carboxylic acids, the secondary C–H bonds could be continuously oxidized with abundant oxygen. However, oxidation products of tertiary C–H bond, just like 1-methyl cyclohexanol (product 1), could not be further oxidized.

3.5. Influence of the amount of catalyst on selectivity

Table 4 shows the oxidation results of different C–H bonds when the catalyst concentration ranges from 3.0 mg to 15.0 mg.

Although the oxidation products of different C–H bonds were differed with the change of the catalyst concentration, *S* fluctuating between 2.9 and 3.2 did not altered apparently. One possible reason may be the so-called “catalyst–inhibitor trans-

Table 4
Influence of the amount of catalyst on *S*

Amount of catalysts (mg)	Yield of tertiary C–H products (%)	Yield of secondary C–H products (%)	<i>S</i>
3.0	4.72	16.07	2.94
5.0	5.45	17.04	3.20
10.0	5.92	20.43	2.90
15.0	4.09	12.78	3.20

Reaction condition: catalyst, TPPMnCl; methyl cyclohexane, 350 mL; temperature, 150 °C; pressure, 0.8 MPa; reaction time, 2 h.

Table 5
Influence of peripheral substituents of manganeseporphyrin on *S*

Metalloporphyrins	Yield of tertiary C–H products (%)	Yield of secondary C–H products (%)	<i>S</i>
T(<i>p</i> -OH)PPMnCl	0.43	2.03	2.12
T(<i>p</i> -OMe)PPMnCl	1.30	4.19	3.10
T(<i>p</i> -Me)PPMnCl	3.14	8.47	3.71
TPPMnCl	4.00	9.75	4.10
T(<i>p</i> -Cl)PPMnCl	6.52	14.16	4.60

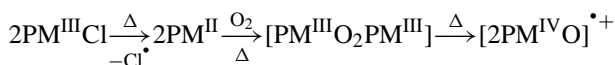
Reaction condition: catalyst, 5 mg; methyl cyclohexane, 350 mL; temperature, 140 °C; pressure, 0.8 MPa; reaction time, 2 h.

form” which causes partial deactivation of metalloporphyrin since excessive metalloporphyrin exists in the reaction system [16,19]. Therefore, the available manganeseporphyrin maintains invariably and accounts little for the change of *S*, the definite mechanism needs to be further studied.

3.6. Influence of peripheral substituents of manganeseporphyrin on selectivity

Five manganeseporphyrins with different peripheral substituents were used as catalysts to study the ratio of selectivity of different C–H bonds. Results in Table 5 show that the electron contributing groups, such as –OH, –OCH₃, etc. on the manganeseporphyrin ring assist the selective oxidation of secondary C–H bonds, While the electron withdrawing group is favorable for the selective oxidation of tertiary C–H bond.

The mechanism by which metalloporphyrins activated oxygen is proposed as follows [20–22].



The active intermediate [PM^{IV}=O]^{•+} attacking substrate led to oxidize C–H bonds [13,23]. Electron withdrawing groups on porphyrin ring could make active intermediate unstable, and strengthened its oxidizing ability to extract the hydrogen on tertiary C–H bond, which resulted in higher oxidation selectivity of tertiary C–H bond.

3.7. Preliminary mechanism analysis of selective oxidation of different C–H bonds

Present research showed that the oxidation reaction of alkanes catalyzed by metalloporphyrin is kept to the classic radical chain mechanism [9,23–25]. While at the initial stage of methyl cyclohexane aerobic oxidation, metalloporphyrin turns into high-valent oxo-metal radical cation [PM^{IV}=O]^{•+}, which is responsible for the velocity of the reaction. The selective oxidation of different C–H bond is mainly affected by two factors: activation energy and regioselectivity of different C–H bond. Obviously, the activation energy of secondary C–H bond is greater than that of tertiary C–H bond, so the factors such as temperature, catalyst activity can affect the activation energy. For the selective oxidation of secondary C–H bond, higher temperature and stronger catalyst activity is preferred. Though the pressure in the reaction system does not affect the two factors,

it can shift the equilibrium of the reaction. Therefore, it can change the oxidation selectivity of different C–H bonds. We are currently studying how the regioselectivity affects the selectivity in our laboratory, and the findings will be reported in due course.

4. Conclusion

Metalloporphyrins play important roles in the selective oxidation of methyl cyclohexane with diverse C–H bonds, so it is significant to study the factors influencing their activity. And the reaction conditions are also important factors which can influence the selective oxidation of different C–H bonds. Therefore, it is potential to get desired products by using specific catalyst and controlling the reaction conditions.

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