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# Study of the selective catalysis of metalloporphyrins for 2-methyl-butane oxidation with PhIO under mild conditions

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**Abstract**

Nine ironporphyrins and eight manganeseporphyrins were synthesized, and their selective catalysis for the oxidation of the secondary and tertiary carbon–hydrogen bonds of 2-methyl-butane with PhIO was studied. The proportion of the oxidation product of tertiary carbon–hydrogen bond to the one of secondary carbon–hydrogen bond was 3:1 when ironporphyrins were used as catalysts, and 2.3:1 when manganeseporphyrins were used as catalysts. The research showed that the substituting groups on the porphyrin rings influenced the catalytic selectivity of metalloporphyrins for the oxidation of the secondary and tertiary carbon–hydrogen bonds as well as the reaction yields. The electron-attracting groups on benzene rings of ironporphyrins increased the catalytic selectivity of ironporphyrins for the tertiary carbon–hydrogen bond oxidation and the reaction speeds, and the electron-releasing groups increased the catalytic selectivity for secondary carbon–hydrogen bond oxidation and reduced the reaction speeds. Both electron-attracting and -releasing groups on benzene rings of manganeseporphyrins enhanced the catalytic selectivity of manganeseporphyrins for the secondary carbon–hydrogen bond oxidation. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Porphyrins; Oxidation; 2-Methyl-butane; Catalysis; Selectivity

## 1. Introduction

Cytochrome P-450 monooxygenase, an only enzyme that can catalyze the oxidation of the inert carbon–hydrogen bonds under mild conditions in organisms, is able to catalyze very effectively and stereo-specially the hydroxylation and epoxidation of hydrocarbon in the metabolic system [1]. Speaking generally, the oxidation of alkane is difficult because the inactivity of carbon–hydrogen bonds of alkane chemically. But the cytochrome P-450 monooxygenase in the organism was not only able to functionallize the carbon–hydrogen bonds of alkane, but also able to catalyze the oxidation of primary carbon–hydrogen bond [2]. People have been interested in the hydrocarbon hydroxylation catalyzed very effectively and stereo-specially by cytochrome P-450 monooxygenase under mild conditions and have paid much interest to try to mimic cytochrome P-450 monooxygenase using synthetic models [3].

Metalloporphyrins were widely used as the model of cytochrome P-450 monooxygenase to catalyze the oxidation of alkane because they bear a strong resemblance to heme in both structures and catalytic property [4–9]. So far, people have already found that iron, manganese, chromium and cobalt porphyrin complexes can effectively catalyze the transfer of an oxygen atom of oxidants such as PhIO, NaClO, $H_2O_2$ and dioxygen to saturated hydrocarbons at ambient temperature and pressure [10–12].

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Alkane has the primary, secondary and tertiary carbon–hydrogen bonds. Some work [13–15] had shown that the catalytic power of metalloporphyrins for the oxidation of different carbon–hydrogen bonds of hydrocarbons was different, and that the catalytic selectivity of metalloporphyrins was related to the structures of metalloporphyrins. Although these work main used a few specified porphyrins structurally, the research results are of importance to understand the catalytic selectivity of the heme monooxygenase in biological systems.

In order to gain a systematical insight into the catalytic selectivity of metalloporphyrins for the oxidation of the different inert hydrocarbon bonds, we synthesized 17 iron- and manganeseporphyrins with different substituents on the porphyrin rings, and studied their catalytic activity for the oxidation of 2-methyl-butane with PhIO, and further explored the relationship between the structures of porphyrins and their catalytic selectivity.

## 2. Experimental

### 2.1. Instruments and reagents

The UV–VIS spectra were obtained with a Perkin-Elmer L-17 UV–VIS spectrophotometer; IR spectra were recorded on a Perkin-Elmer model 783 IR spectrophotometer. GC analysis was performed on a Shimadzu GC-16A gas phase chromatography flame ionization instrument. A Perkin-Elmer 2400 elementary analyzer and a model 5012 constant temperature water-bath were used.

Before being used, benzene and dichloromethane were dehydrated; neutral $Al_2O_3$ was baked 5 h at 100°C; pyrrole and benzaldehyde were redistilled. All reagents were analytically pure or chemically pure as received.

PhIO was synthesized by documented procedures [16], and its purity measured by iodimetry was 99%.

### 2.2. Synthesis of monometalloporphyrins

The substituted tetraphenylporphines, $RTPPH_2$, were synthesized by the direct condensation of pyrrole with the substituted benzaldehydes according to the documented procedures [17], the substituted monometalloporphyrins, $RTPPMn^{III}Cl$ and $RTPPFe^{III}Cl$, were synthesized by the reaction of the corresponding $RTPPH_2$ with metallic salts according to the documented procedures [18–19]. Test data from elemental analysis, IR and UV–VIS maximum are listed in Table 1.

Table 1
Elemental analysis, IR and UV–VIS data of compounds RTPPFeCl (1–9) and RTPPMnCl (10–17)

| No. | R | Elemental analysis (%, calculated) | | | $\lambda_{max}$ (benzene) (nm) | IR (KBr) ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| 1 | H | 75.10 (75.06) | 3.85 (4.01) | 7.90 (7.92) | 418.8, 507.2, 572.4, 652.8, 685.6 | $\upsilon_{Fe-Cl}$ 380m |
| 2 | *p*-Cl | 62.74 (62.78) | 2.80 (2.87) | 6.72 (6.66) | 420.7, 509.0, 574.8, 652.1 | $\upsilon_{Fe-Cl}$ 384m |
| 3 | *p*-Br | 51.72 (51.83) | 2.53 (2.37) | 5.67 (5.49) | 415.6, 570.5, 618.0 | $\upsilon_{Fe-Cl}$ 382m |
| 4 | *p*-I | 44.35 (43.76) | 34 (2.00) | 5.12 (4.64) | 420.8, 512.2, 549.2, 586.8, 651.2 | $\upsilon_{Fe-Cl}$ 378m |
| 5 | *p*-$CH_3$ | 75.92 (75.84) | 4.67 (4.77) | 7.83 (7.37) | 418.4, 507.6, 571.6, 653.2, 685.6 | $\upsilon_{Fe-Cl}$ 380m |
| 6 | *p*-$OCH_3$ | 69.53 (69.96) | 4.03 (4.40) | 7.33 (6.80) | 421.2, 509.2, 571.6 | $\upsilon_{Fe-Cl}$ 381m |
| 7 | *p*-$NMe_2$ | 71.05 (71.22) | 5.36 (5.53) | 12.86 (12.78) | 466.7, 396.6 | $\upsilon_{Fe-Cl}$ 383m |
| 8 | *p*-$NH_2$ | 68.93 (69.12) | 4.35 (4.23) | 14.83 (14.66) | 416.3, 567.8, 613.8 | $\upsilon_{Fe-Cl}$ 380m |
| 9 | *p*-OH | 69.05 (69.28) | 3.56 (3.68) | 14.65 (14.58) | 418.4, 332.0 | $\upsilon_{Fe-Cl}$ 379m |
| 10 | H | 75.32 (75.16) | 3.95 (4.01) | 7.80 (7.97) | 477.2, 533.6, 585.2, 620.4 | $\upsilon_{Mn-Cl}$ 320m |
| 11 | *p*-F | 68.15 (68.18) | 3.05 (3.12) | 7.14 (7.23) | 489.7, 594.4, 645.3 | $\upsilon_{Fe-Cl}$ 318m |
| 12 | *p*-Cl | 62.81 (62.85) | 2.72 (2.88) | 6.63 (6.66) | 477.6, 532.0, 585.6, 621.2 | $\upsilon_{Mn-Cl}$ 320m |
| 13 | *o*-Cl | 62.95 (62.85) | 2.50 (2.88) | 7.03 (6.66) | 478.0, 582.6, 620.0 | $\upsilon_{Mn-Cl}$ 322m |
| 14 | *o*-Br | 52.03 (51.88) | 2.25 (2.38) | 5.80 (5.50) | 477.5, 585.2, 621.4 | $\upsilon_{Mn-Cl}$ 320m |
| 15 | *p*-$CH_3$ | 75.66 (75.94) | 4.71 (4.78) | 7.43 (7.37) | 477.6, 532.8, 586.0, 622.8 | $\upsilon_{Mn-Cl}$ 319m |
| 16 | *p*-$OCH_3$ | 70.68 (70.03) | 4.31 (4.41) | 6.69 (6.81) | 479.2, 535.2, 589.6, 627.6 | $\upsilon_{Mn-Cl}$ 322m |
| 17 | *p*-(*i*-pr) | 76.96 (77.18) | 5.88 (6.01) | 6.25 (6.43) | 478.1, 534.1, 587.5, 625.0 | $\upsilon_{Mn-Cl}$ 320m |

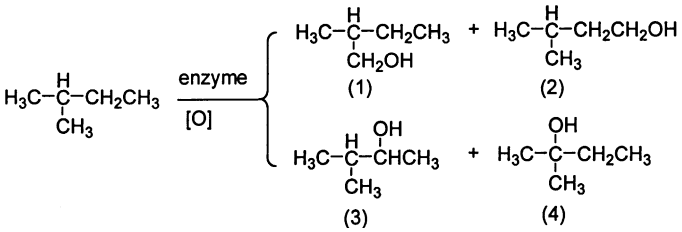
### 2.3. 2-Methyl-butane oxidation catalyzed by metalloporphyrins(1–19) with PhIO

2-Methyl-butane oxidation reported in this paper was carried out under a nitrogen atmosphere in the following procedures unless otherwise specified. A solution of PhIO (100 mg, $4.5 \times 10^{-4}$ mol), $TPPFe^{III}Cl$ (10 mg, $3.0 \times 10^{-4}$ mol) and 2-methyl-butane (0.5 ml, $4.30 \times 10^{-3}$ mol) in chlorobenzene (5 ml) was warmed to 303 K by circulation water, and then stirred 2 h by electromagnetic stirrer. The products were qualitatively analyzed by GC–MS and quantified by gas chromatography. yields calculation was based on the input moles of PhIO. The samples for dynamics analyses were regularly collected from the reaction system by micro-injector. Quantitative calculations used an internal standard method. The standard material was chlorobenzene. The chromatographic conditions were as follows: chromatographic column was thirty meters PEG-20M glass capillary column, its diameter was 0.25 mm; column temperature was 90°C; vaporization temperaturewas190°C; detector was FID; supporting gas (nitrogen) flow was 25 ml/min; hydrogen flow was 40 ml/min; air flow was 400 ml/min.

## 3. Results and discussion

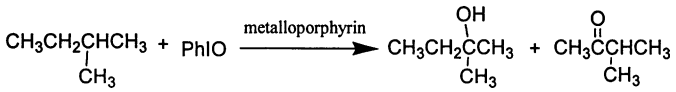
### 3.1. 2-Methyl-butane oxidation catalyzed by metalloporphyrins

2-Methyl-butane has the primary, secondary and tertiary carbon–hydrogen bonds. Catalyzed by cytochrome P-450 monooxygenase extracting from the organism, 2-Methyl-butane oxidation with PhIO gained four products.




The related ratio of the products is as following: [(1) + (2)]:(3):(4) = 6:20:74 [20].

2-Methyl-butane oxidation catalyzed by metalloporphyrins with PhIO is as following:




The reaction products are 2-methyl-2-butanol, the oxidation product of the tertiary carbon–hydrogen bond and 3-methyl-2-butanone, the oxidation product of the secondary carbon–hydrogen bond. For all oxidation experiments, the products were detected after the reactions were run for 30 min. In the absence of metalloporphyrins, neither 2-methyl-2-butanol nor 3-methyl-2-butanone was formed, indicating that metalloporphyrin acts as a catalyst in the reaction.

Catalyzed by metalloporphyrins, only 2-methyl-2-butanol and 3-methyl-2-butanone, the oxidation products of the secondary carbon–hydrogen bond and the tertiary carbon–hydrogen bond were gained, and no oxidation product of the primary carbon–hydrogen bonds was formed. This indicated that the metalloporphyrins used in these experiments could not catalyze the oxidation of the primary carbon–hydrogen bond of 2-methyl-butane. The oxidation products of the secondary carbon–hydrogen bond of 2-methyl-butane should be 3-methyl-2-butanol, but only 3-methyl-2-butanone was found. A possible reason was that PhIO oxidized 3-methyl-2-butanol into 3-methyl-2-butanone once 3-methyl-2-butanol was formed [21].

Actually, the proportion of yields between 3-methyl-2-butanone and 2-methyl-2-butanol represented the competition between the secondary carbon–hydrogen bond oxidation and the tertiary carbon–hydrogen bond oxidation in 2-methyl-butane

oxidation catalyzed by metalloporphyrins. The differences of yields between 3-methyl-2-butanone and 2-methyl-2-butanol depend on the differences of the catalytic selectivity of metalloporphyrin for the different carbon–hydrogen bond oxidation. So by comparing the yields and speeds which 3-methyl-2-butanone and 2-methyl-2-butanol was formed, we were knowable both of the catalytic selectivity of metalloporphyrin for the secondary carbon–hydrogen bond oxidation and the tertiary carbon–hydrogen bond oxidation, and of the changes of the selectivity with the changes of the structures of metalloporphyrin.

### *3.2. Catalytic selectivity of ironporphyrins for 2-methyl-butane oxidation*

For the 2-methyl-butane oxidation catalyzed by ironporphyrin RTPPFeCl with PhIO, the substituted groups R obviously affect the reaction yield, product distribution, and reaction selectivity. The results of 2-methyl-butane oxidation catalyzed by 9 different substituted RTPPFeCl after the reaction were run for 2 h were listed in Table 2.

Selectivity is calculated according to the following expression:

$$\text{selectivity} = \frac{\text{the yield of 2-methyl-2-butanol/ the number of tertiary hydrogen atoms}}{\text{the yield of 2-methyl-2-butanol/ the number of tertiary hydrogen atoms}}$$

The selectivity gained by above calculation gives expression to the differences of activity between the tertiary and secondary carbon–hydrogen bonds of 3-methyl-2-butane, and to the differences of the catalytic power of metalloporphyrins in the oxidation of the tertiary and secondary carbon–hydrogen bonds of 3-methyl-2-butane.

One can see from the Table 2 that the electron-attracting groups on porphyrin rings, such as halogen atoms, obviously increased the reaction yields, and reduced the content of secondary carbon–hydrogen bond oxidation product 3-methyl-2-butanone. The electron-releasing groups on porphyrin rings, such as methyl, methoxy, reduced the reaction yields, and increased the content of secondary carbon–hydrogen bond oxidation product 3-methyl-2-butanone. Especially, ironporphyrins with the strong electron-releasing groups on porphyrin rings, such as amino, dimethylamino, hydroxyl catalyzed secondary carbon–hydrogen bond oxidation specially, although the oxidation yields obviously decreased. This showed that the catalytic selectivity of ironporphyrins was related to the electron effect of the substituents.

### *3.3. Catalytic selectivity of manganeseporphyrins for 2-methyl-butane oxidation*

Same as the 2-methyl-butane oxidation catalyzed by ironporphyrin RTPPFeCl, the substituents R of manganeseporphyrin RTPPMnCl also affected the product distribution, the reaction yield and selectiv-

Table 2
2-Methyl-butane oxidation catalzed by ironporphyrins

| Metalloporphyrins | Product | | Total yield (%)[a] | Alkone (%) | Selectivity |
|---|---|---|---|---|---|
| | 3-Methyl-2-butanone | 2-Methyl-2-butanol | | | |
| TPPFeCl | 13.18 | 19.72 | 7.25 | 40.06 | 2.99 |
| T(*p*-Cl)PPFeCl | 18.60 | 34.63 | 11.73 | 38.70 | 3.72 |
| T(*p*-Br)PPFeCl | 16.45 | 31.75 | 10.62 | 34.13 | 3.86 |
| T(*p*-I)PPFeCl | 14.94 | 27.43 | 9.33 | 35.26 | 3.67 |
| T(*p*-$CH_3$)PPFeCl | 9.40 | 12.94 | 4.91 | 42.08 | 2.75 |
| T(*p*-$CH_3$)PPFeCl | 8.49 | 8.40 | 3.72 | 50.27 | 1.98 |
| T(*p*-$NMe_2$)PPFeCl | 6.36 | – | 1.41 | 100 | |
| T(*p*-$NH_2$)PPFeCl | 6.13 | – | 1.35 | 100 | |
| T(*p*-OH)PPFeCl | 7.81 | – | 1.72 | 100 | |

[a] Total yield is the sum of 3-methyl-2-butanone and 2-methyl-2-butanol yields based on input PhIO.

Table 3
2-Methyl-butane oxidation catalyzed by manganeseporphyrins

| Metalloporphyrins | Product ($10^{-6}$ mol) | | Total yield[a] (%) | Alkone (%) | Selectivity |
|---|---|---|---|---|---|
| | 3-Methyl-2-butanone | 2-Methyl-2-butanol | | | |
| TPPMnCl | 8.50 | 9.57 | 3.98 | 47.04 | 2.25 |
| T(*p*-F)PPMnCl | 10.91 | 14.36 | 5.57 | 43.17 | 2.63 |
| T(*p*-Cl)PPMnCl | 13.07 | 15.40 | 6.27 | 45.90 | 2.14 |
| T(*o*-Cl)PMnCl | 13.33 | 16.70 | 6.62 | 44.39 | 2.51 |
| T(*o*-Br)PPMnCl | 9.25 | 13.35 | 4.98 | 40.93 | 2.89 |
| T(*p*-$CH_3$)PPMnCl | 4.00 | 7.70 | 2.58 | 34.19 | 3.85 |
| T(*p*-$OCH_3$)PPMnCl | 3.07 | 6.54 | 2.37 | 31.95 | 4.26 |
| T(*p*-(*i*-pr))PPMnCl | 6.90 | – | 1.52 | 100 | |

[a] Total yield is the sum of 3-methyl-2-butanone and 2-methyl-2-buanol yields based on input PhIO.

ity of the 2-methyl-butane oxidation. The results of 2-methyl-butane oxidation catalyzed by nine different substituted RTPPMnCl, after the reaction were run for 2 h, were listed in Table 3.

Catalyzed by manganeseporphyrins, electron-attracting groups on porphyrin rings, such as halogen atoms, increased the total yields of the 2-methyl-butane oxidation reaction, and electron-releasing groups, such as methyl, dimethylamino and isopropyl, reduced the total yields of the oxidation. Different from the 2-methyl-butane oxidation catalyzed by the ironporphyrins, catalyzed by manganeseporphyrins, both electron-attracting groups and electron-releasing groups on porphyrin rings increased the content of secondary carbon–hydrogen bond oxidation product 3-methyl-2-butanone. This indicated that the introduction of substituents on porphyrin rings enhanced the catalytic selectivity of manganeseporphyrins for secondary carbon–hydrogen bond oxidation. Especially, after the bulky groups, such as isopropyl group was introduced on porphyrin ring, manganeseporphyrins gave expression to the catalytic specificity for the oxidation of secondary carbon–hydrogen bond of 2-methyl-butane.

Comparing Table 2 with Table 3, the oxidation yields of 2-methyl-butane catalyzed by ironporphyrins with PhIO were higher than that by manganeseporphyrins. Ironporphyrins had the better catalytic selectivity for the oxidation of tertiary carbon–hydrogen bonds, and manganeseporphyrins had the better catalytic selectivity for the oxidation of secondary carbon–hydrogen bonds.

### *3.4. Relationship between reaction yields and reaction time*

Catalyzed by ironporphyrin TPPFeCl and manganeseporphyrin TPPMnCl, the change of the yields of the 3-methyl-2-butanone and 2-methyl-2-butanol with the reaction time was, respectively, shown in the Fig. 1a and b.

Fig. 1 showed, from 15 to 120 min during the reaction, that both the 3-methyl-2-butanone yields and the 2-methyl-2-butanol yields increased with reaction time, and that there was a linear relationship between both the 3-methyl-2-butanone yields and the 2-methyl-2-butanol yields and the reaction time. The oxidation reaction revealed a zero-order feature. The kinetics experiments of the oxidations catalyzed by ironporphyrins TPPFeCl and manganeseporphyrin TPPMnCl correspond with the kinetics of the bio-oxidation reaction catalyzed by cytochrome P-450 monooxygenase [22].

Comparing Fig. 1a with b, one can find that the conversion rate of the 2-methyl-butane oxidation reaction catalyzed by TPPFeCl is greater than the one by TPPMnCl. This indicates that the TPPFeCl has better catalytic activity for 2-methyl-butane oxidation with PhIO than the TPPMnCl.

### *3.5. Analysis of 2-methyl-butane oxidation process catalyzed by metalloporphyrins*

The research of deuterated borneol and its derivatives oxidation catalyzed by cytochrome P-450

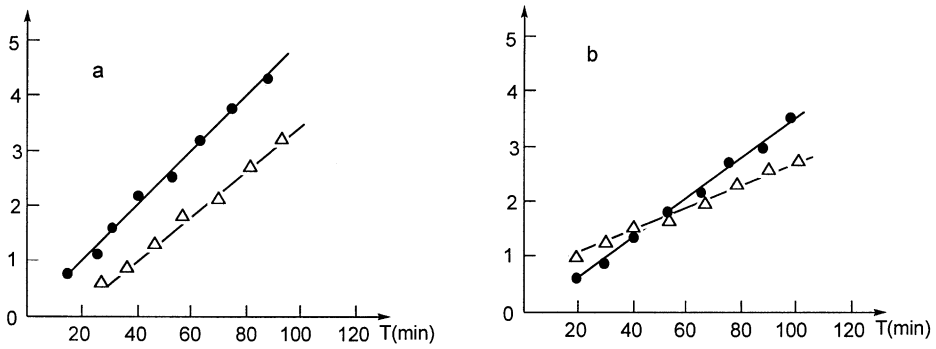
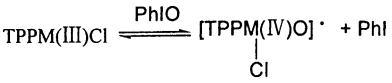



Fig. 1. Reaction yields change with the reaction time (a) catalyzed by TPPFeCl; (b) catalyzed by TPPMnCl (1) 2-methyl-2-butanol; (2) 3-methyl-2-butanone.

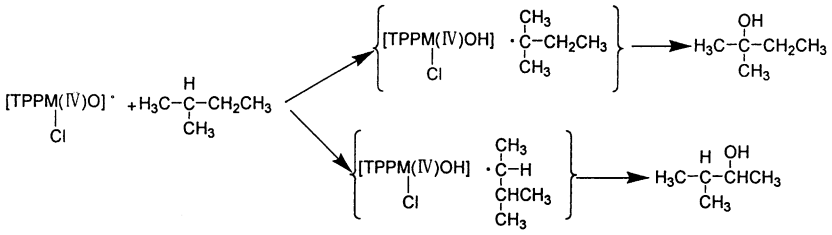
monooxygenase extracted from organisms indicated that alkane hydroxylation included two process of the formation of high valence iron–oxygen cation radical and the decomposition of radical pairs of iron–oxygen cation and alkyl radical [23]. The research of alkane hydroxylation reaction catalyzed by metalloporphyrins also indicated that the alkane hydroxylation reactions catalyzed by metalloporphyrins had the similar reaction mechanism as the same kind of reaction catalyzed by the organism enzymes [24–27].

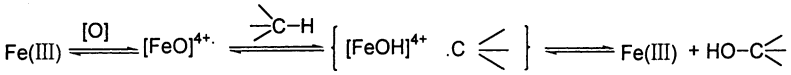
reaction mechanism as the general simulation enzyme reaction:

The first step: TPPFeCl and TPPMnCl react with PhIO to form high valence cation radical.



The second step: the high valence cation radical separately take the secondary and tertiary hydrogen atoms of 2-methyl-butane to form the radical pairs, and then decompose to form the products.





Iron–oxygen cation radical took one hydrogen atom of alkane to form alkyl radical, and then combined the alkyl radical to form the radical pairs in a cage. Finally, the collision each other of radical pairs forms the products. The collision process of the radical pairs was supposed to a cage reaction of low energy.

We think that 2-methyl-butane oxidation reaction catalyzed by metalloporphyrin with PhIO has the same

The reaction process that the high valence cation radicals take the secondary and tertiary hydrogen atoms of 2-methyl-butane is a competition process. The advantage differences between the two reactions express the reaction activity differences between the secondary carbon–hydrogen bond and tertiary carbon–hydrogen bond.

Ironporphyrin and manganeseporphyrin react with oxidant separately to form the high valence iron–oxygen cation radical and the high valence manganese–oxygen cation radical.

The stability differences between the high valence iron–oxygen cation radical and the high valence manganese–oxygen cation radical lead to the differences of their ability to take the hydrogen atom of alkane to form the radical pairs, and express the differences of the catalytic selectivity among the different metalloporphyrins. Generally speaking, the worse the stability of the high valence metal–oxygen cation radicals, the greater the reaction rate that they take the hydrogen atom to form alkane molecules, and the worse the selectivity that they react with inert carbon–hydrogen bond. For the oxidation of 2-methyl-butane catalyzed by metalloporphyrins, the stabler high valence metal–oxygen cation radicals have the smaller reaction rates and the better selectivity to take the secondary hydrogen atom of 2-methyl-butane, and worse stable high valence metal–oxygen cation radicals have the greater reaction rates and the worse selectivity to take the secondary hydrogen atom of 2-methyl-butane.

According to the atomic theory, the manganese–oxygen cation radical is more stable than the iron–oxygen cation radical. Hence, the reaction rate of 2-methyl-butane oxidation catalyzed by manganeseporphyrins is less than the one by ironporphyrins. The catalytic selectivity of manganeseporphyrin for the secondary carbon–hydrogen bond oxidation is higher, and the catalytic selectivity of ironporphyrin for the tertiary carbon–hydrogen bond oxidation is higher.

When there are the different substituents on the benzene ring of metalloporphyrin, the electron-attracting groups on the benzene ring decrease the stability of the high valence metal–oxygen cation radicals, and benefit to take the hydrogen atom of the tertiary carbon–hydrogen bond, and increase the catalytic selectivity of the oxidation of tertiary carbon–hydrogen bond of alkane. The electron-releasing groups on the benzene ring of metalloporphyrins increase the stability of the high valence metal–oxygen cation radicals, and benefit to take the hydrogen atom of the secondary carbon–hydrogen bond, and then increase the catalytic selectivity of the oxidation of secondary carbon–hydrogen bond of alkane.

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