

A new evidence of the high-valent oxo–metal radical cation intermediate and hydrogen radical abstract mechanism in hydrocarbon hydroxylation catalyzed by metalloporphyrins

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Abstract

Forty metalloporphyrins with different peripheral substituents (R) on the porphyrin ring, RTPPM^{III}Cl and [RTPPM^{III}]₂O (M = Fe, Mn), were synthesized, and were used to catalyze cyclohexane hydroxylation with iodosobenzene under mild conditions. A Hammett relationship, $\log k = \rho\sigma + c$, was shown to exist between the rate constants k of the cyclohexane hydroxylation and Hammett constants σ of substituents on the porphyrin rings. The value of the reaction constant ρ changed from 0.3 to 0.5 for the cyclohexane oxidation catalyzed by metalloporphyrins, and electron-withdrawing groups increased the reaction speeds. This means that the reaction mediator was a radical cation, and that the rate-determining step of the reaction was a radical reaction. These research results provided a new evidence for the high-valent oxo–metal radical cation intermediate and hydrogen radical abstraction mechanism in hydrocarbon hydroxylation catalyzed by metalloporphyrins. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metalloporphyrins; Catalysis; Hammett relationship

1. Introduction

Cytochrome P-450 monooxygenase with heme as an active center has been found to be one of two enzymes that can catalyze the oxidation of the inert carbon–hydrogen bond under mild conditions in organisms [1,2]. People have been interested in the hydrocarbon hydroxylation catalyzed by cytochrome P-450 monooxygenase under mild conditions and tried to understand the reaction mechanism since cy-

tochrome P-450 monooxygenase was found. Chemists have paid much interest to try to mimic cytochrome P-450 monooxygenase using synthetic metalloporphyrins because they bear a strong resemblance to heme in both structures and catalytic property. So far, they have found that iron [3–9], manganese [10–15], chromium [16–18] and cobalt [19–22] porphyrin complexes can be used as model compounds for cytochrome P-450 monooxygenase to catalyze the transfer of an oxygen atom from oxidants such as PhIO [23–28], NaClO [29–35], H₂O₂ [36–41] and dioxygen [42–47] to saturated hydrocarbons at ambient temperature and pressure, and put forward the high-valent oxo–metal radi-

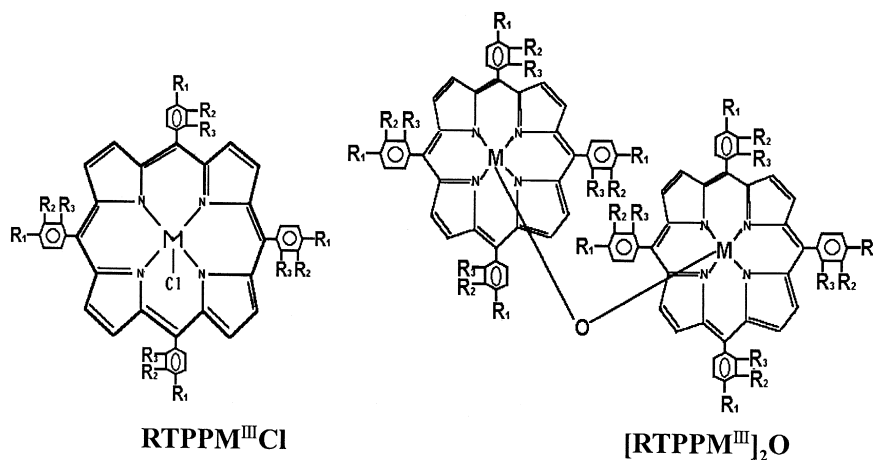
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cal cation intermediate and hydrogen radical abstraction mechanism for the hydrocarbon hydroxylation catalyzed by metalloporphyrins. These results are of importance in understanding the mechanism of the heme monooxygenase-catalyzed reaction in biological systems. In order to use the Hammett relationship to prove the high-valent oxo–metal radical cation intermediate and hydrogen radical abstraction mechanism in hydrocarbon hydroxylation catalyzed by metalloporphyrins, we synthesized 40 metalloporphyrins, shown in Fig. 1, and studied their catalysis of cyclohexane hydroxylation with PhIO.

These synthetic porphyrins included 21 monometalloporphyrin RTPPM^{III}Cl (M = Fe, Mn), which have been widely used as the

model compounds of cytochrome P-450 so far [48], and 19 μ -oxo-bismetalloporphyrin [RTPPM^{III}]₂O (M = Fe, Mn), which were recently put forward as the model compounds of cytochrome P-450 [49]. There is a different peripheral substituent R on the porphyrin ring in these compounds. The research results show that all the synthetic metalloporphyrins can catalyze cyclohexane oxidation with PhIO at ambient temperature and pressure. Moreover, there are the same kinetic relationships between the yields and the reaction time in all the cyclohexane hydroxylation catalyzed by these metalloporphyrins. For the above reaction system, it has been found that the structure of metalloporphyrins can affect their catalytic property. There are Hammett relationships between the sub-



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|--|--|--|
| 1. R ₁ =F, R ₂ =R ₃ =H, M=Fe | 2. R ₁ =Cl, R ₂ =R ₃ =H, M=Fe | 3. R ₁ =R ₂ =H, R ₃ =Cl, M=Fe |
| 4. R ₁ =Br, R ₂ =R ₃ =H, M=Fe | 5. R ₁ =I, R ₂ =R ₃ =H, M=Fe | 6. R ₁ =R ₂ =R ₃ =H, M=Fe |
| 7. R ₁ =CH ₃ , R ₂ =R ₃ =H, M=Fe | 8. R ₁ = <i>i</i> -C ₃ H ₇ , R ₂ =R ₃ =H, M=Fe | 9. R ₁ =OCH ₃ , R ₂ =R ₃ =H, M=Fe |
| 10. R ₁ =NO ₂ , R ₂ =R ₃ =H, M=Fe | 11. R ₁ =F, R ₂ =R ₃ =H, M=Mn | 12. R ₁ =Cl, R ₂ =R ₃ =H, M=Mn |
| 13. R ₁ =H, R ₂ =Cl, R ₃ =H, M=Mn | 14. R ₁ =R ₂ =H, R ₃ =Cl, M=Mn | 15. R ₁ =Br, R ₂ =R ₃ =H, M=Mn |
| 16. R ₁ =R ₂ =H, R ₃ =Br, M=Mn | 17. R ₁ =I, R ₂ =R ₃ =H, M=Mn | 18. R ₁ =R ₂ =R ₃ =H, M=Mn |
| 19. R ₁ =CH ₃ , R ₂ =R ₃ =H, M=Mn | 20. R ₁ = <i>i</i> -C ₃ H ₇ , R ₂ =R ₃ =H, M=Mn | 21. R ₁ =OCH ₃ , R ₂ =R ₃ =H, M=Mn |
| 22. R ₁ =R ₂ =R ₃ =H, M=Fe | 23. R ₁ =F, R ₂ =R ₃ =H, M=Fe | 24. R ₁ =Cl, R ₂ =R ₃ =H, M=Fe |
| 25. R ₁ =CH ₃ , R ₂ =R ₃ =H, M=Fe | 26. R ₁ = <i>i</i> -C ₃ H ₇ , R ₂ =R ₃ =H, M=Fe | 27. R ₁ =H, R ₂ =F, R ₃ =H, M=Fe |
| 28. R ₁ =H, R ₂ =Cl, R ₃ =H, M=Fe | 29. R ₁ =H, R ₂ =Br, R ₃ =H, M=Fe | 30. R ₁ =H, R ₂ =CH ₃ , R ₃ =H, M=Fe |
| 31. R ₁ =R ₂ =R ₃ =H, M=Mn | 32. R ₁ =CH ₃ , R ₂ =R ₃ =H, M=Mn | 33. R ₁ = <i>i</i> -C ₃ H ₇ , R ₂ =R ₃ =H, M=Mn |
| 34. R ₁ =F, R ₂ =R ₃ =H, M=Mn | 35. R ₁ =Cl, R ₂ =R ₃ =H, M=Mn | 36. R ₁ =R ₂ =H, R ₃ =OCH ₃ , M=Mn |
| 37. R ₁ =NMe ₂ , R ₂ =R ₃ =H, M=Mn | 38. R ₁ =H, R ₂ =Cl, R ₃ =H, M=Mn | 39. R ₁ =R ₂ =H, R ₃ =Cl, M=Mn |
| 40. R ₁ =R ₂ =H, R ₃ =Br, M=Mn | | |

Fig. 1. Structure of RTPPM^{III}Cl(1–21) and [RTPPM^{III}]₂O(22–40).

stituent constants σ of *para*- and *meta*-substituents on the benzene ring of porphyrins and the rate constants k of the reactions catalyzed by these metalloporphyrins, whether $\text{RTPPM}^{\text{III}}\text{Cl}$ or $[\text{RTPPM}^{\text{III}}]_2\text{O}$. There is also a similar result in the self-oxidation of these metalloporphyrins, which is a competitive reaction in the cyclohexane hydroxylation system. This study will further offer evidence both for determining competitive mechanisms between the reaction catalyzed by metalloporphyrins and the self-oxidation of the metalloporphyrins, and for the structure of the radical cation intermediate in the above mimicry system. The research results mean that the linear free-energy relationship, which commonly exists in chemical phenomena, might fit in with the enzyme-catalyzed reaction in the human body.

2. Experimental

2.1. Instruments and reagents

Gas chromatography was performed on a Shimadzu GC-16A coupled with a Shimadzu C-R3A reporting integrator, infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer, visible spectra were recorded on a Perkin-Elmer L-17 spectrometer. A Perkin-Elmer Model 2400 elemental analysis meter was used.

Benzene was refluxed with metallic sodium for 10 h and redistilled before used. Pyrrole was also redistilled before used. There was no impurity found in cyclohexane by GC analysis before being used. Oxidant PhIO was synthesized according to a method in the literature [50]. Its purity, measured by iodimetry, was 99%. Substituted benzaldehydes and other reagents were all of analytical or commercial chemical grade.

2.2. Synthesis of metalloporphyrin compounds (1–21)

Substituted benzaldehyde and pyrrole were refluxed in propanoic acid [51] to give the cor-

responding substituted tetraphenylporphine RTPPH_2 . RTPPH_2 reacted with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 5\text{H}_2\text{O}$ in DMF respectively to give substituted chlorotetraphenylporphinatoiron(III), $\text{RTPPF}^{\text{III}}\text{Cl}$ (1–10) and substituted chlorotetraphenylporphinatomanganese(III), $\text{RTPPMn}^{\text{III}}\text{Cl}$ (11–21) using the literature method [52]. The structures of compounds (1–21) were all characterized by elementary analysis and ultraviolet absorption spectrometry (see Table 1).

2.3. Synthesis of μ -oxo-bis[tetraphenylporphinatoiron(III)] compounds $[\text{RTPPF}^{\text{III}}]_2\text{O}$ (22–30)

Compounds (22–30) were prepared according to the following procedure: 2 g of $\text{TRPPFe}^{\text{III}}\text{Cl}$ was passed through a chromatographic column filled with 500 g Al_2O_3 using the wet method. Benzene containing 5% of $\text{C}_2\text{H}_5\text{OH}$ was used as drip washing liquid. $[\text{TRPPFe}^{\text{III}}]_2\text{O}$ was formed in the above procedure. The eluate was evaporated in vacuo. The purity of $[\text{TRPPFe}^{\text{III}}]_2\text{O}$ was checked with HPLC or IR. If the components with the retention time of 2.87 min characteristic of $\text{TRPPFe}^{\text{III}}\text{Cl}$ in HPLC or with an absorption band at 380 cm^{-1} ($\nu_{\text{Fe-Cl}}$) in IR disappear, the reaction may be thought to be complete. Otherwise, the abovementioned procedure was repeated until $\text{TPPFe}^{\text{III}}\text{Cl}$ was transformed completely into $[\text{TPPFe}^{\text{III}}]_2\text{O}$. Their elementary analysis, IR and UV–Vis data are listed in Table 1.

2.4. Synthesis of μ -oxo-bis[tetraphenylporphinatomanganese(III)] $[\text{RTPPMn}^{\text{III}}]_2\text{O}$ compounds (31–40)

Compounds (31–40) were prepared according to the following procedures: 1.0 g $\text{RTPPMn}^{\text{III}}\text{Cl}$ was placed in a reactor filled with 250 ml benzene, and then 50 ml 5% aqueous NaOH was added. After vigorously stirring the

Table 1

Elemental analysis, IR and UV–Vis data of compounds RTPPMCl (1–21) and [RTPPM]₂O (22–24)

Compounds	Elemental analysis (% , calculated)			λ_{\max} (benzene) (nm)	IR (KBr) (cm ⁻¹)
	C	H	N		
1	68.24(68.09)	3.05(3.12)	7.14(7.22)	419.5, 509.4, 575.3, 651.4	$\nu_{\text{Fe}-\text{Cl}}$ 382(m)
2	62.74(62.78)	2.80(2.87)	6.72(6.66)	420.7, 509.0, 574.8, 652.1	$\nu_{\text{Fe}-\text{Cl}}$ 384(m)
3	62.85(62.78)	2.74(2.87)	6.83(6.66)	418.5, 505.4, 576.0, 648.0	$\nu_{\text{Fe}-\text{Cl}}$ 380(m)
4	51.72(51.83)	2.53(2.37)	5.67(5.49)	415.6, 570.5, 618.0	$\nu_{\text{Fe}-\text{Cl}}$ 382(m)
5	44.35(43.76)	2.34(2.00)	5.12(4.64)	420.8, 512.2, 549.2, 586.8, 651.2	$\nu_{\text{Fe}-\text{Cl}}$ 378(m)
6	75.10(75.06)	3.85(4.01)	7.90(7.92)	418.8, 507.2, 572.4, 652.8, 685.6	$\nu_{\text{Fe}-\text{Cl}}$ 380(m)
7	75.92(75.84)	4.67(4.77)	7.83(7.37)	418.4, 507.6, 571.6, 653.2, 685.6	$\nu_{\text{Fe}-\text{Cl}}$ 380(m)
8	77.32(77.10)	5.98(6.01)	6.14(6.42)	420.8, 509.2, 572.0	$\nu_{\text{Fe}-\text{Cl}}$ 383(m)
9	69.53(69.96)	4.03(4.40)	7.33(6.80)	421.2, 509.2, 571.6	$\nu_{\text{Fe}-\text{Cl}}$ 381(m)
10	59.85(59.76)	2.80(2.71)	12.53(12.67)	421.3, 514.6, 582.6, 653.7	$\nu_{\text{Fe}-\text{Cl}}$ 380(m)
11	68.15(68.18)	3.05(3.12)	7.14(7.23)	489.7, 594.4, 645.3	$\nu_{\text{Mn}-\text{Cl}}$ 318(m)
12	62.81(62.85)	2.72(2.88)	6.63(6.66)	477.6, 532.0, 585.6, 621.2	$\nu_{\text{Mn}-\text{Cl}}$ 320(m)
13	62.53(62.85)	2.82(2.88)	6.84(6.66)	477.8, 533.1, 584.5, 620.3	$\nu_{\text{Mn}-\text{Cl}}$ 321(m)
14	62.95(62.85)	2.50(2.88)	7.03(6.66)	478.0, 582.6, 620.0	$\nu_{\text{Mn}-\text{Cl}}$ 322(m)
15	52.03(51.88)	2.25(2.38)	5.80(5.50)	477.5, 585.2, 621.4	$\nu_{\text{Mn}-\text{Cl}}$ 320(m)
16	51.53(51.88)	2.54(2.38)	5.65(5.50)	479.2, 583.2, 616.4	$\nu_{\text{Mn}-\text{Cl}}$ 323(m)
17	43.52(43.79)	1.95(2.01)	4.87(4.64)	478.3, 533.5, 589.3, 625.4	$\nu_{\text{Mn}-\text{Cl}}$ 319(m)
18	75.32(75.16)	3.95(4.01)	7.80(7.97)	477.2, 533.6, 585.2, 620.4	$\nu_{\text{Mn}-\text{Cl}}$ 320(m)
19	75.66(75.94)	4.71(4.78)	7.43(7.37)	477.6, 532.8, 586.0, 622.8	$\nu_{\text{Mn}-\text{Cl}}$ 319(m)
20	76.96(77.18)	5.88(6.01)	6.25(6.43)	478.1, 534.1, 587.5, 625.0	$\nu_{\text{Mn}-\text{Cl}}$ 320(m)
21	70.68(70.03)	4.31(4.41)	6.69(6.81)	479.2, 535.2, 589.6, 627.6	$\nu_{\text{Mn}-\text{Cl}}$ 322(m)
22	78.09(78.11)	4.23(4.17)	8.05(8.28)	407.6, 570.0, 611.2	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 895(m), 870(m)
23	69.81(70.58)	2.95(3.21)	7.74(7.49)	408.0, 570.0, 610.8	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 895(m), 875(m)
24	64.73(64.90)	2.88(2.97)	7.11(6.88)	408.0, 570.8, 611.2	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 895(m), 870(m)
25	78.23(78.68)	4.86(4.95)	7.66(7.68)	409.2, 572.8, 612.8	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 895(m), 870(m)
26	79.27(79.61)	6.25(6.20)	6.64(6.63)	409.6, 572.4, 613.6	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 895(m), 870(m)
27	70.01(70.58)	2.95(3.21)	7.61(7.49)	405.6, 568.4, 607.2	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 905(m), 880(m)
28	64.52(64.90)	2.78(2.97)	7.03(6.88)	407.6, 568.8, 608.8	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 910(m), 880(m)
29	52.95(53.26)	2.13(2.44)	6.02(5.65)	408.0, 569.4, 611.4	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 910(m), 880(m)
30	78.33(78.68)	4.85(4.95)	7.68(7.68)	406.4, 570.4, 610.4	$\nu_{\text{Fe}-\text{O}-\text{Fe}}$ 910(m), 885(m)
31	77.81(78.21)	4.18(4.18)	8.62(8.29)	616.0, 578.4, 472.9, 418.5	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 876(m), 849(m)
32	78.25(78.78)	4.80(4.96)	7.87(7.66)	618.6, 581.0, 471.6, 419.6	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 878(w), 848(m)
33	79.26(79.69)	5.87(6.21)	6.27(6.64)	621.6, 582.6, 472.0, 420.8	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 875(s), 850(s)
34	69.80(70.69)	3.27(3.24)	7.58(7.50)	615.6, 578.4, 470.4, 419.0	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 886(w), 852(s)
35	64.42(64.97)	3.05(2.97)	6.74(6.89)	616.0, 578.4, 470.2, 420.4	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 883(s), 850(s)
36	71.85(72.45)	4.47(4.56)	6.99(7.04)	627.6, 586.0, 472.6, 421.8	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 880(m), 849(s)
37	72.85(73.59)	5.63(5.70)	12.85(13.21)	618.0, 572.8, 474.8, 438.4	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 878(s), 846(s)
38	64.63(64.97)	3.14(2.97)	6.53(6.89)	615.6, 578.0, 470.2, 420.6	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 887(m), 850(m)
39	64.35(64.97)	3.27(2.97)	7.03(6.89)	655.2, 586.8, 511.8, 471.6	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 881(s), 845(w)
40	52.90(53.32)	2.32(2.44)	6.14(5.65)	474.7, 419.6	$\nu_{\text{Mn}-\text{O}-\text{Mn}}$ 883(m), 847(w)

reactants for 3 h, 300 ml water was added. Benzene was evaporated under vacuum. The crude product [RTPPMn^{III}]₂O gained by crystallization was washed with water until the filter liquor became neutral. [RTPPMn^{III}]₂O was dried in air and recrystallized with absolute anhydrous benzene and cyclohexane. IR, UV–Vis and elemental analysis data of [RTPPMn^{III}]₂O (31–40) are listed in Table 1.

2.5. Cyclohexane monooxygenation

Except where special explanation is given, all cyclohexane hydroxylations were carried out according to the following procedure: 4.5×10^{-4} mol of PhIO and 3.0×10^{-5} mol metalloporphyrin (metal atom as the standard) were put into a 25-ml double-layer reactor through which constant-temperature water could flow through.

After air had been removed out of the reactor with N₂, 5 ml cyclohexane and 5 ml of solvent benzene were put into the reactor. Then an electromagnetic stirrer was started, and the reaction carried out. The products were analyzed by GC, and quantified by internal standard method. The standard substance was chlorobenzene. When the quantity of products did not increase further in the GC analysis, the ultimate yield was determined based on the quantity of PhIO added. Kinetic analysis was made by measuring samples that were taken directly from the reaction system with a mini-injector.

2.6. Kinetic determination for the self-oxidation of metalloporphyrins

PhIO was dissolved in benzene to obtain a saturated solution; its concentration was measured by iodimetry. Metalloporphyrin was quantitatively weighed, then dissolved and diluted to the order of 10^{-5} mol l⁻¹ with benzene. Absorption spectrometry was used to measure the change of the absorbency of the metalloporphyrin during the reaction of metalloporphyrins with PhIO at 25°C.

3. Results and discussion

3.1. Linear free-energy relationship in cyclohexane hydroxylation catalyzed by metalloporphyrins

Catalyzed by compounds 1–40, PhIO oxidizes cyclohexane into cyclohexanol and cyclohexanone at ambient temperature and pressure. The yield of cyclohexanol changes with the change in reaction time, which agrees with the kinetic relationship in the reaction catalyzed by an enzyme [53]. The linear relationship between the yield (%) of cyclohexanol and the reaction time (t) in cyclohexane monooxygenation

catalyzed by RTPPF^{III}Cl with different peripheral substituent R on porphyrin ring is shown in Fig. 2.

According to kinetic analysis, linear slopes in Fig. 2 represent the rate constants of the reactions. The research shows that the reaction rates of cyclohexane hydroxylation not only change with the change of metal atoms in metalloporphyrins and structures of metalloporphyrins, but also change with the change of peripheral substituents on the porphyrin ring in the same pattern of metalloporphyrins. The reaction yields (%), the rate constant k and productive selectivity in cyclohexane hydroxylation is listed in Table 2.

The relationships between the reaction rate constant k and the substituent constant σ for cyclohexane hydroxylation catalyzed by *para*- and *meta*-substituents agree with linear free-energy relationship [54] (Fig. 3): $\log k = \rho\sigma + c$.

Their mathematical equations are listed in Table 3.

In Hammett equations, which show the linear free-energy relationship, all the reaction constants ρ are positive. Their values change from 0.33 to 0.53 with the change of pattern of metalloporphyrins, but the differences in numbers are not large. This indicates a similar reaction mechanism and the same reaction intermediate in cyclohexane hydroxylation catalyzed by

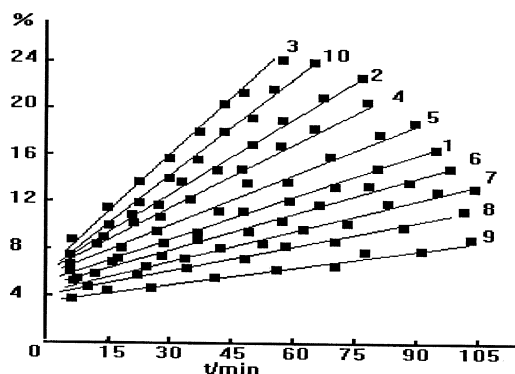


Fig. 2. Cyclohexanol yield (%) versus reaction time (t) relationship in cyclohexane hydroxylation catalyzed by metalloporphyrins.

Table 2

Reaction yields (%), the rate constant k and productive selectivity of cyclohexane hydroxylation catalyzed by different metalloporphyrins

Metalloporphyrin		Substituent constant σ	Yield (%)	$k \times 10^6$ (mol min ⁻¹)	$\log(k \times 10^6)$	Alcohol: ketone	
Pattern	Substituent R						
RTPPF ^{III} Cl	<i>p</i> -F	0.06	22	12.1	1.08	9.4	
	<i>p</i> -Cl	0.23	34	15.0	1.18	7.1	
	<i>o</i> -Cl		46	53.1	1.73	14.3	
	<i>p</i> -Br	0.23	33	14.8	1.17	7.3	
	<i>p</i> -I	0.18	29	14.2	1.15	9.7	
	H	0.00	21	11.5	1.06	6.3	
	<i>p</i> -Me	-0.17	28	9.8	0.99	7.6	
	<i>p</i> -(<i>i</i> -Pr)	-0.15	35	9.6	0.98	8.3	
	<i>p</i> -OCH ₃	-0.27	31	8.2	0.92	9.4	
	<i>p</i> -NO ₂	0.78	42	25.1	1.40	5.8	
	RTPPMn ^{III} Cl	<i>p</i> -F	0.06	33	10.9	1.04	3.0
		<i>p</i> -Cl	0.23	34	13.9	1.14	2.8
<i>p</i> -Br		0.23	33	13.7	1.14	2.7	
<i>p</i> -I		0.18	34	13.2	1.12	2.7	
<i>m</i> -Cl		0.37	33	16.5	1.22	2.8	
<i>o</i> -Cl			39	22.5	1.35	3.7	
<i>o</i> -Br			38	19.7	1.30	3.6	
H		0.00	29	10.3	1.01	2.2	
<i>p</i> -CH ₃		-0.17	34	8.7	0.94	2.7	
<i>p</i> -(<i>i</i> -Pr)		-0.15	35	10.4	1.02	2.6	
<i>p</i> -OCH ₃		-0.27	36	7.5	0.88	2.7	
[RTPPF ^{III}] ₂ O		<i>m</i> -Br	0.39	39	13.5	1.13	5.9
	<i>m</i> -Cl	0.37	37	14.1	1.15	5.9	
	<i>m</i> -F	0.34	36	13.7	1.14	5.9	
	<i>p</i> -Cl	0.23	33	12.6	1.10	6.0	
	<i>p</i> -F	0.06	30	11.1	1.04	5.9	
	H	0.00	29	10.7	1.03	5.7	
	<i>m</i> -CH ₃	-0.07	28	10.2	1.01	5.8	
	<i>p</i> -(<i>i</i> -Pr)	-0.15	29	9.0	0.96	5.7	
	<i>p</i> -CH ₃	-0.17	26	9.5	0.98	6.0	
	[RTPPMn ^{III}] ₂ O	<i>m</i> -Cl	0.37	46	22.1	1.35	3.1
		<i>p</i> -Cl	0.23	48	17.2	1.24	2.5
		<i>p</i> -F	0.06	46	14.1	1.15	2.7
H		0.00	47	12.7	1.11	2.6	
<i>p</i> -(<i>i</i> -Pr)		-0.15	47	9.4	0.97	2.6	
<i>p</i> -CH ₃		-0.17	46	10.2	1.01	2.7	
<i>p</i> -OCH ₃		-0.27	45	8.3	0.92	2.7	
<i>p</i> -NMe ₂		-0.83	8.5	5.8	0.76	^a	
<i>o</i> -Cl			55	24.2	1.39	5.0	
<i>o</i> -Br			53	21.8	1.34	5.3	

^aTrace ketone.

these metalloporphyrins. The values of the reaction constant k for porphyrins with the same metal atom are nearer than those for porphyrins with different metal atoms, which means that there might be a tiny difference between the reaction mechanism catalyzed by iron porphyrins and that catalyzed by manganese porphyrins.

3.2. Linear free-energy relationship in self-oxidation of metalloporphyrins

The linear relationship between the yield (%) of cyclohexanol and the reaction time (t) in cyclohexane hydroxylation catalyzed by metalloporphyrin 1–40 exists only during 90–120 min of the early reaction stage, then this linear

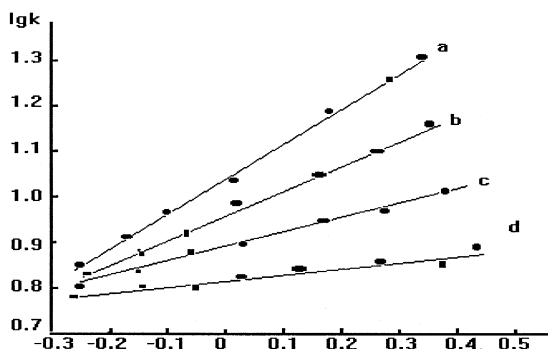


Fig. 3. Hammett relationship between rate constant k and substituent constant σ for substituent on porphyrin ring in cyclohexane hydroxylation catalyzed by different metalloporphyrins. (a) For $[\text{RTPPMn}^{\text{III}}]_2\text{O}$; (b) for $\text{RTPPFel}^{\text{III}}\text{Cl}$; (c) for $\text{RTPPFel}^{\text{III}}\text{Cl}$; (d) for $[\text{RTPPFel}^{\text{III}}]_2\text{O}$.

relationship deviates gradually when the reaction time is prolonged. This relationship between the reaction yields and reaction time in the cyclohexane hydroxylation agrees with the result reported in the literature [4]. This phenomenon shows that cyclohexane monooxygenation and self-oxidation of metalloporphyrins under the action of PhIO take place simultaneously. The latter reaction causes metalloporphyrins to lose their catalytic activity. The above relationship between the reaction yields and the reaction time is the result of competition between the two reactions with each other. The kinetic property of the self-oxidation of metalloporphyrins under the action of PhIO is found to be related to both the structures of the metalloporphyrin and the metal atom in metalloporphyrin. The studies prove that this is a second-order reaction for iron-porphyrin, $\text{RTPPFel}^{\text{III}}\text{Cl}$, and a first-order reaction for manganese porphyrin, $\text{RTPPMn}^{\text{III}}\text{Cl}$ or μ -oxo-bisporphyrinatoiron, $[\text{RTPPFel}^{\text{III}}]_2\text{O}$. The differences among the kinetic properties in the self-oxidation of the different metalloporphyrins show that there are some differences in the reaction mechanisms of their self-oxidation. The rate constants in self-oxidation of some metalloporphyrins, measured by spectrophotometry, are listed in Table 4.

Just as cyclohexane hydroxylation is catalyzed by metalloporphyrins, there is also linear free-energy relationship in the self-oxidation of metalloporphyrins (Table 5).

The above linear free-energy relationships show that self-oxidation of such monometalloporphyrins as $\text{RTPPFel}^{\text{III}}\text{Cl}$ and $\text{RTPPMn}^{\text{III}}\text{Cl}$ is sensitive to substituents on porphyrin rings. All substituents accelerate the reactions, whether electron-releasing groups or electron-attracting groups, suggesting a U-shaped Hammett correlation. However, the self-oxidation of μ -oxo-bisporphyrinatoiron, $[\text{RTPPFel}^{\text{III}}]_2\text{O}$, is not sensitive to substituents on porphyrin rings. Electron-attracting substituents slightly favor the reaction. Comparing the above results with Table 2, it has been shown that the effect of substituents on the rates in self-oxidation of metalloporphyrins agrees with the effect of substituents on the yields in cyclohexane monooxygenation catalyzed by metalloporphyrins.

3.3. Hydroxylation mechanism

So far all the abovementioned studies show that the active species formed in hydrocarbon hydroxylation catalyzed by monometalloporphyrin is a radical cation of a high-valence metalloporphyrin, $[\text{PM}^{\text{V}}-\text{O}]^+$ ($\text{M} = \text{Fe}, \text{Mn}$). In this reaction, metalloporphyrin reacts first with the oxidant PhIO to form the radical cation intermediate, then this intermediate abstracts a hydrogen atom from hydrocarbon to form a product alcohol [55–62]. In this work, the values of the reaction constant ρ obtained by

Table 3
Linear free-energy relationship in cyclohexane hydroxylation catalyzed by metalloporphyrins

Metalloporphyrin	Hammett relationship	Relative coefficient r
$\text{RTPPFel}^{\text{III}}\text{Cl}$	$\log k = 0.46\sigma - 5.03$	0.9963
$[\text{RTPPFel}^{\text{III}}]_2\text{O}$	$\log k = 0.34\sigma - 5.00$	0.9927
$\text{RTPPMn}^{\text{III}}\text{Cl}$	$\log k = 0.47\sigma - 4.98$	0.9978
$[\text{RTPPMn}^{\text{III}}]_2\text{O}$	$\log k = 0.53\sigma - 4.90$	0.9972

Table 4
Rate constant of self oxidation of some metalloporphyrins

Substituent	Substituent constant σ	RTPPF ^{III} Cl		[RTPPF ^{III}] ₂ O		[RTPPMn ^{III}] ₂ O	
		$k_2 \times 10^3$ (l mol ⁻¹ min ⁻¹)	log k_2	$k_1 \times 10^2$ (min ⁻¹)	–log k_1	$k_1 \times 10^2$ (min ⁻¹)	–log k_1
H	0.00	2.727	3.4354	2.745	0.5614	2.711	0.5668
<i>p</i> -F	0.06			2.841	0.5465		
<i>p</i> -Cl	0.23	6.786	3.8316	3.159	0.5004	4.122	0.3849
<i>p</i> -Br	0.23	6.770	3.8306				
<i>p</i> -I	0.18	5.3375	3.7274				
<i>p</i> -CH ₃	0.17	5.294	3.7237	2.378	0.6238	6.035	0.2193
<i>p</i> -(<i>i</i> -Pr)	0.15	5.580	3.7466	1.816	0.7409	6.400	0.1938
<i>p</i> -OCH ₃	0.27	7.237	3.8596	5.335	0.2729	5.335	0.2729
<i>m</i> -F	0.34			3.426	0.4652		
<i>m</i> -Cl	0.37			3.551	0.4497	4.901	0.3098
<i>m</i> -Br	0.39			3.551	0.4497		
<i>m</i> -CH ₃	–0.07			3.713	0.4303		
<i>o</i> -Cl		0.903	2.9557	2.642	0.5781	4.189	0.3779

Hammett relationship changed from 0.3 to 0.5 for the cyclohexane oxidation catalyzed by metalloporphyrins. This means that the reaction is the radical cation mechanism. The fact that electron-withdrawing groups increase the reaction speeds agrees with the fact that the rate-determining step is hydrogen radical abstraction. The plots in Fig. 2 have a good linear relationship up to 24% conversion of the PhIO and this can be satisfactorily explained in terms of the radical cation and hydrogen radical abstraction mechanism [63]. Furthermore, there are the same linear free-energy relationships and the approaching values of reaction constant ρ in reactions catalyzed by monometalloporphyrins or μ -oxo-bismetalloporphyrins, which shows that there are similar intermediates and mechanisms

in the reactions catalyzed by them. However, the facts reported in the literature [64,65] and the research results show that the catalytic process of iron porphyrins is not the same as that of the manganese porphyrins. Based on the facts reported in the literature and the results in this work, a reaction mechanism can be proposed for the reaction systems consisting of metalloporphyrins, PhIO and hydrocarbons, as shown in Fig. 4.

There are the same linear free-energy relationships between the self-oxidation of metalloporphyrins and hydrogen radical abstraction in hydroxylation, which show that self-oxidation of metalloporphyrins and hydrogen radical abstraction in the system of the cyclohexane hydroxylation are two competing reactions via the

Table 5
Linear free-energy relationship in self-oxidation of metalloporphyrins

Metalloporphyrin	Hammett relationship	Relative coefficient r
RTPPF ^{III} Cl	log $k_2 = 1.7106\sigma + 3.4326$ (electron-attracting substituent)	0.9989
	log $k_2 = -1.5734\sigma + 3.4396$ (electron-releasing substituent)	0.9981
[RTPPF ^{III}] ₂ O	log $k_1 = 0.3973\sigma - 0.5682$	0.9942
RTPPMn ^{III} Cl	log $k_1 = 0.7025\sigma - 0.5668$ (electron-attracting substituent)	0.9987
	log $k_1 = -2.4870\sigma - 0.5668$ (electron-releasing substituent)	0.9990

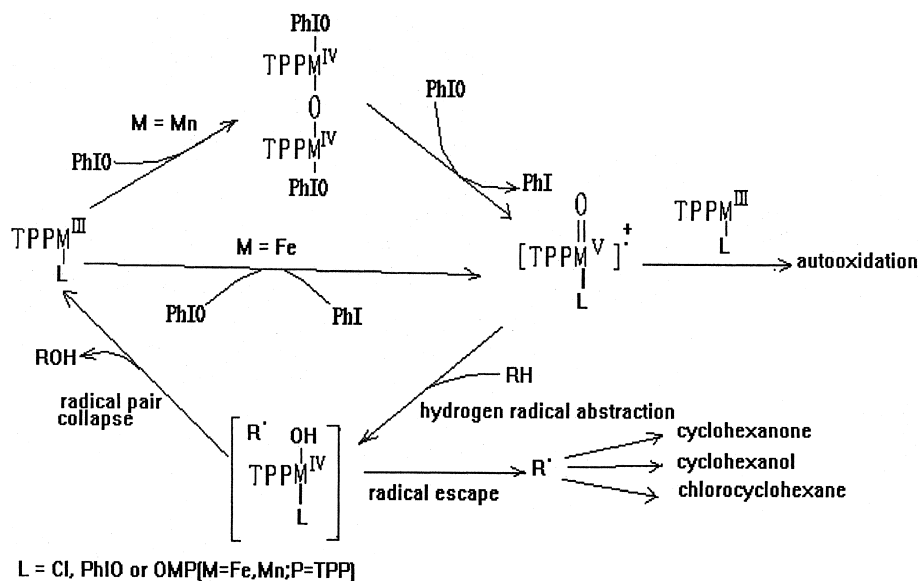


Fig. 4. Mechanism of hydrocarbon hydroxylation catalyzed by metalloporphyrins.

same active intermediate. The values of the reaction constant ρ in cyclohexane hydroxylations catalyzed by the different metalloporphyrins are slightly different, which means that all hydroxylations have undergone the same rate-determining steps of reaction in the process. However, the rate-determining steps of reaction in the self-oxidations of different metalloporphyrins might be different, which can be shown from the differences in the kinetic property and the linear free-energy relationship among the self-oxidations of the different metalloporphyrins, and are also proved by the different *ortho*-effects (shown in Table 4) in the reaction.

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