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Comparative study on heme-containing enzyme-like catalytic activities of water-soluble metalloporphyrins

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Abstract

This paper reported the heme-containing enzyme-like catalytic activities of 15 water-soluble metalloporphyrins (M-Ps) produced from three metal ions (Fe, Mn and Co) and five porphophine ligands, i.e. porphyrin IX, *meso*-tetrakis(*p*-sulfonatophenyl) porphophine ($TPPS_4$), *meso*-tetrakis(4-carboxy-phenyl)porphophine (TCPP), *meso*-tetrakis[4-(*N*-trimethyl)aminophenyl]-porphophine (TTMAPP) and *meso*-tetrakis(4-*N*-methylpyridinium)porphophine (TMPyP). Their catalytic activities of catalase, peroxidase and cytochrome P-450 on the typical reactions were systematically studied and compared. The results indicated that the metalloporphyrins with Fe and Mn as central ions show high catalytic activities of catalase and peroxidase at pH range of 10.5–11.5, and among them Fe-TMPyP and Fe-TTMAPP have the highest catalytic capability, while all Co-porphyrins have weak activities. Interestingly, only Mn-TMPyP of the 15 metalloporphyrins shows relatively high cytochrome P-450-like activity. The presence of imidazole has enhancement effects to different extent on the peroxidase-like activities of these metalloporphyrins and negligible effects on catalase-like activities.

Keywords: Metalloporphyrin; Biomimetic catalysis; Peroxidase; Catalase; Cytochrome P-450

1. Introduction

Heme-containing enzymes such as catalase, peroxidase and cytochrome P-450 utilize oxygen and its partially reduced forms in a variety of enzymatic reactions such as the oxidation of substrates (catalase and peroxidase) and the incorporation of oxygen atoms into organic substrates (cytochrome P-450) [1–3]. Because of the important roles of these enzymes in biochemistry, numerous studies have been performed on the mimic of heme-containing enzymes [4,5].

Since hemin, a naturally occurring metalloporphyrin (M-P), is a common prosthetic group of heme-containing enzymes, many M-Ps that have different ligand structures and central metal ions have been synthesized to imitate heme-containing enzymes [6–11]. Furthermore, in order to increase the catalytic capability and selectivity of biomimetic enzymes (also called artificial enzymes), the effect of axial ligand has been studied [12–16]. M-Ps with axial ligands have been found to have higher catalytic activities and selectivity than those without axial ligands.

Heme-containing enzymes have the same prosthetic group, so the reason that they show various specificity is because of the presence of different apoproteins, and, therefore, is irrelative to the prosthetic

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group. Apoproteins show no catalytic activities independently, and their function lies only in modulating the substrate specificity, chemical selectivity, activating mode of oxidant, and oxidation rate of prosthetic group. Therefore, analogous with the active center of all heme-containing enzymes, M-P should show more or less all kinds of catalytic activities of heme-containing enzymes, and the activities depend on the structure of the porphyrin and central metal ions. In previous reports, usually only one kind of catalytic activity of M-Ps was studied, while their other enzyme-like catalytic activities were neglected. Although catalase-like and peroxidase-like activities of some M-Ps have been studied [17], no study was conducted on all kinds of activities of the complex in a single report.

Therefore, the purpose of this paper is to estimate systematically the catalase-, peroxidase- and cytochrome P-450-like catalytic activities of a series of water-soluble M-Ps, in order to get some useful information about the effects of porphyrin structure, central metal ions as well as axial ligand on the enzyme activity and specificity. The reactions utilized in this study were decomposition of hydrogen peroxide, oxidation of homovanillic acid (HVA) with hydrogen peroxide, and oxidation of styrene with oxone. These were typical reactions catalyzed by catalase, peroxidase and cytochrome P-450, respectively.

2. Experimental

2.1. Instruments

UV–VIS spectra were recorded on a Varian Cary 1E Spectrophotometer (USA). All fluorescence data were obtained from a Perkin-Elemer LS-50B luminescence spectrometer (USA). Gas chromatographic analyses were carried out on a Shimadzu GC-9A (Kyoto, Japan) equipped with SE-30 capillary column (0.25 mm × 21 m), FID detector and HP 3394 integrator. The oxidation products of styrene were characterized by a HP 5971 GC–MS (USA).

2.2. Materials

Porphyrin IX, pyrrole and horseradish peroxidase (HRP, E.C. 1.11.1.7, 242 U/mg) were purchased from Sigma (St. Louis, USA), and 4-carboxybenzaldehyde and 4-pyridinecarboxaldehyde obtained from Acros (Pittsburgh, USA). Styrene, methyl iodide, benzaldehyde, 4-*N*,*N*′-dimethylaminobenzaldehyde and hydrogen peroxide were supplied by Beijing Chemical Plant (Beijing, China), HVA from Kanto Chemical (Japan). Other chemicals were of analytical grade. *Meso*-tetrakis(*p*-sulfonatophenyl)porphophine ($TPPS_4$), *meso*-tetrakis(4-carboxy-phenyl)porphophine (TCPP), *meso*-tetrakis[4-(*N*-trimethyl)aminophenyl] porphophine (TTMAPP) and *meso*-tetrakis-(4*N*-methylpyridinium)porphophine (TMPyP) were synthesized according to the literature procedures [18–21], and then metalloporphyrins were prepared as described in the literature [22]. The stock solutions of M-Ps (1.0×10^{-4} M) were prepared in deionized water. A working solution of H_2O_2 was freshly prepared by appropriate dilution of a stock solution, which was standardized by potassium permanganate method. The buffer solutions of Na_2HPO_4–NaH_2PO_4 (PBS) and $NaHCO_3$–Na_2CO_3 of specified pH values were used to control the acidities of reaction medium.

2.3. Procedures

2.3.1. Measurement of catalase-like activity

Buffer solution (3.80 ml) and 100 μl M-P of 1.0×10^{-4} M were mixed. Then, 100 μl H_2O_2 of 5.0×10^{-3} M was added under stirring. At the reaction time of 2 min, 100 μl of the mixed solution was taken out and placed into a mixture of 1.70 ml PBS (0.2 M, pH 7.0), 100 μl HRP of 0.15 mg/ml and 100 μl HVA of 2.0×10^{-3} M. After 30 min, the fluorescence intensity was measured at the emission wavelength of 425 nm with excitation at 315 nm. The slit widths for excitation and emission were both 5 nm. From the fluorescence intensity the percentage of H_2O_2 decomposed can be calculated.

2.3.2. Measurement of peroxidase-like activity

Buffer solution (1.70 ml), 100 μl HVA of 1.0×10^{-3} M and 100 μl H_2O_2 of 1.0×10^{-4} M were, in turn, added in a quartz cell with 10 mm long light path. Then, 100 μl M-P solution of 2.0×10^{-6} M was added under stirring to initiate the reaction. The kinetic curve was recorded at the excitation and emission wavelengths of 315 and 425 nm, respectively.

2.3.3. Measurement of cytochrome P-450-like activity

Styrene solution (2.0 ml) of 0.05 M in acetonitrile and 1.0 ml M-P solution of 1.0×10^{-4} M were mixed together. Then, 1.0 ml oxone solution of 0.1 M in 0.2 M PBS (pH 6.8) was added under stirring. The reaction products were analyzed with GC by direct injection of 2.0 ml of the reaction mixture at a reaction time of 10 min and their structures were confirmed by GC–MS.

3. Results and discussion

3.1. Catalase-like activity of metalloporphyrins

The concentration of H_2O_2 in our experiment is very low, so it is difficult to be determined by simple titration (e.g. potassium permanganate and cerium(IV) sulfate titration. Enzymatic H_2O_2 assay is very commonly method to determine the H_2O_2 concentration and it is with very low determination limit [23]. We designed a simple procedure described in Section 2 to quantify H_2O_2 undecomposed in the presence of M-P, so that the reaction rate or percentage of H_2O_2 decomposition could be calculated, and further the catalase-like catalytic activity of M-P could be estimated. The influences of pH on the decomposition rate of H_2O_2 in the presence of M-Ps were studied and the results were depicted in Fig. 1. Clearly, both negatively charged M-P (Fe-TCPP) and positively charged M-P (Fe-TTMAPP) showed similar activity–pH profiles. Their highest activities appeared at pH range of 10.5–11.5. The low activity of M-Ps in stronger alkaline media is probably due to the dissociation of H_2O_2, which has a pK_a of 11.75. The activity of M-Ps may involve the participation of hydroxyl ion, which maybe the reason why they show low activity in acidic and neutral pH. The relative catalase-like activities of 15 M-Ps in the presence and absence of imidazole were measured at pH 10.5. Table 1 summarized the results. It is obvious that the order of catalase-like activity for the M-Ps with same central ion is: TMPyP $\approx$ TTMAPP $>$ TCPP $\approx$ $TPPS_4$ $>$ porphyrin IX; for the M-Ps with the same porphyrin ligand, the order is Fe $>$ Mn $>$ Co. The presence of imidazole has some effects on the catalase-like activity of some M-Ps, but the effects are much weaker than those on peroxidase-like activity. A comparison experiment was carried out, which showed H_2O_2 was stable in the pH range of 7–12 within 2 min and in H_2O_2 determination solution (pH = 7.0), the decomposition of H_2O_2 by M-Ps can be negligible. Therefore, the method used for catalase activity is receivable.

3.2. Peroxidase-like activity of metalloporphyrins

The reaction rates of the oxidation of HVA with H_2O_2 in the presence of M-Ps at different pH were

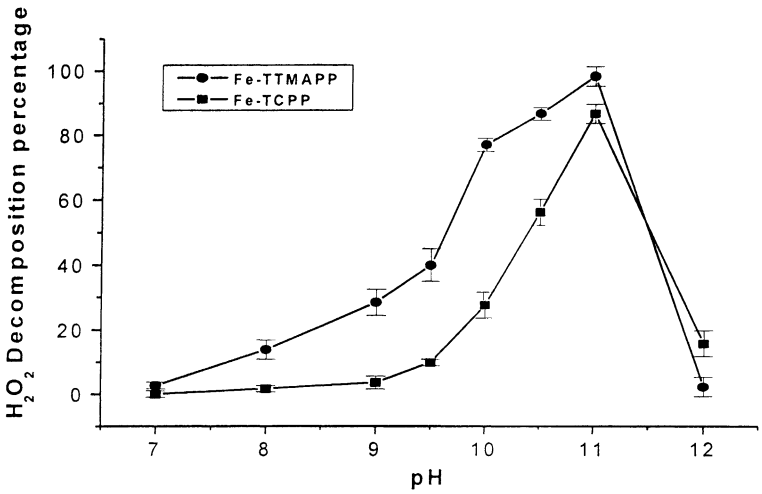

Fig. 1. Effect of pH on the decomposition rate of H_2O_2 in the presence of Fe-TCPP and Fe-TTMAPP. c (M-P) $= 2.5 \times 10^{-5}$ M and c (H_2O_2) $= 1.25 \times 10^{-3}$ M. The reactions were at room temperature and data were based on three replicate measurements.

Table 1
The reaction rate of H_2O_2 decomposition catalyzed by metalloporphyrins in the absence and presence of imidazole[a]

Metalloporphyrin	Reaction rate (10^{-9} mol/min)	
	Absence of imidazole	Presence of imidazole
Mn-$TPPS_4$	97.5 ± 4.4	79.2 ± 4.4
Fe-$TPPS_4$	116 ± 5	120 ± 3
Co-$TPPS_4$	19.6 ± 6.3	30.2 ± 2.8
Mn-TCPP	87.8 ± 5.4	98.7 ± 2.6
Fe-TCPP	209 ± 1	219 ± 3
Co-TCPP	22.4 ± 4.0	22.9 ± 7.4
Mn-porphyrin IX	11.8 ± 3.8	14.2 ± 7.2
Hemin	37.9 ± 3.6	48.6 ± 2.5
Co-porphyrin IX	14.0 ± 3.3	15.7 ± 8.4
Mn-TTMAPP	199 ± 4	166 ± 3
Fe-TTMAPP	246 ± 1	234 ± 5
Co-TTMAPP	23.0 ± 4.6	7.0 ± 3.2
Mn-TMPyP	192 ± 4	245 ± 2
Fe-TMPyP	263 ± 3	245 ± 7
Co-TMPyP	16.9 ± 1.1	14.9 ± 2.0

[a] c (M-P) $= 2.5 \times 10^{-5}$ M, c (H_2O_2) $= 1.25 \times 10^{-3}$ M, c (M-P)/c (imidazole) = 1 :1000. The reaction was at room temperature and at pH 10.5. The data listed were based on three replicate measurements.

measured, and the results were displayed in Fig. 2. The figure reflected the dependence of peroxidase-like activity on acidity. Both anionic and cationic M-Ps show similar dependence. The activity increases along with the increment of pH, and reaches the highest catalytic activity at range of 10.5–11.5 and then decrease remarkably when pH is higher. The change trend is very similar to that of catalase probably also due to the same reason.

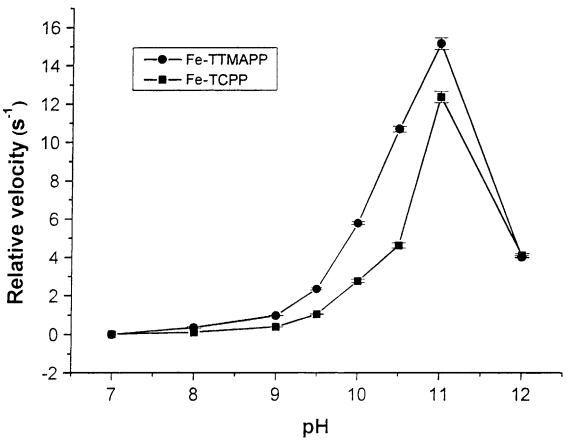

Fig. 2. Effect of pH on the initial rate of homovanillic acid oxidation by H_2O_2 in presence of metalloporphyrins. c (M-P) $= 1.0 \times 10^{-7}$ M, c (HVA) $= 5.0 \times 10^{-5}$ M, c (H_2O_2) $= 5.0 \times 10^{-6}$ M. The reactions were at room temperature and data were based on three replicate measurements.

Table 2 summarized the relative reaction rates of HVA oxidation with H_2O_2 in presence of metalloporphyrins. These data indicated that some metalloporphyrins have peroxidase-like catalytic effectiveness. It is very clear that for the M-Ps with same central ion, the order of peroxidase-like activity is TMPyP ≈ TTMAPP > TCPP ≈ $TPPS_4$ > porphyrin IX, and for the M-Ps with the same porphyrin structure, the order is Fe > Mn > Co. Furthermore, imidazole shows great influence on this catalytic reaction. The much different effects of imidazole on catalase- and peroxidase-like activities can be attributed to the different structure of apoproteins of these enzymes around the active center. In peroxidase, the imidazole of histidine residue is involved in axial coordination and activation of the center ion. Therefore, the presence of imidazole showed the enhancement effect on

Table 2
The initial rates of metalloporphyrin-catalyzed oxidation of homovanillic acid by H_2O_2 in the absence and presence of imidazole[a]

Metalloporphyrin	Relative reaction rate (fluorescence intensity (s))	
	Absence of imiadzole	Presence of imiadzole
Mn-$TPPS_4$	0.24 ± 0.03	0.69 ± 0.01
Fe-$TPPS_4$	1.24 ± 0.02	1.54 ± 0.02
Co-$TPPS_4$	Extremely slow	–[b]
Mn-TCPP	0.27 ± 0.06	0.59 ± 0.03
Fe-TCPP	3.80 ± 0.03	5.58 ± 0.28
Co-TCPP	Extremely slow	–[b]
Mn-porphyrin IX	0.15 ± 0.01	0.40 ± 0.02
Hemin	0.44 ± 0.01	1.20 ± 0.05
Co-porphyrin IX	Extremely slow	–[b]
Mn-TTMAPP	2.81 ± 0.01	3.76 ± 0.01
Fe-TTMAPP	12.00 ± 0.38	14.00 ± 0.59
Co-TTMAPP	Very slow	–[b]
Mn-TMPyP	5.11 ± 0.22	11.28 ± 2.12
Fe-TMPyP	13.13 ± 0.21	15.34 ± 0.34
Co-TMPyP	Very slow	–[b]

[a] c (M-P) $= 1.0 \times 10^{-7}$ M, c (HVA) $= 5.0 \times 10^{-5}$ M, c (H_2O_2) $= 5.0 \times 10^{-6}$ M, c (M-P)/c (imidazole) = 1 :1000. The reaction was at room temperature and at pH 10.5. The data were based on three replicate measurements.

[b] Insignificantly different from that in the absence of imiadzole.

peroxidase-like activity of the M-Ps. For catalase, the axial ligand is not histidine. Thus, the presence of imidazole in M-Ps solution does not show evident influence on their catalase-like activity.

3.3. Cytochrome P-450-like activity of metalloporphyrins

Previous researches indicated that in aqueous solution, M-Ps cannot catalyze the epoxidation of olefins by hydrogen peroxide [24,25]. Based on the fact that at low pH some substances with C=C bond can be epoxidized by H_2O_2 in the presence of some M-Ps [26], we studied the Mn-TMPyP-catalyzed oxidation of allyl alcohol and styrene by H_2O_2 in aqueous solution and water–acetonitrile solution. No oxidation product was observed either in the presence or absence of imidazole. Therefore, we chose oxone, another oxidant, as molecular oxygen donor and explored the epoxidation of styrene in the presence of M-Ps in water–acetonitrile (1:1, v/v) solution. Acetonitrile was used not only to increase the solubility of styrene, but also to increase the stability of the M-P, since such a catalyst in water solution containing oxone shows much faster decomposition rate (by observing the disappearance of the solution color) than in water–acetonitrile (1:1) system. Oxone can oxidize imidazole. Therefore, its effect on the cytochrome P-450-like activity was not studied in this work.

The data listed in Table 3 showed that except for Mn-TMPyP, all tested water-soluble M-Ps are not effective mimics of cytochrome P-450 with oxone as an oxidant in water–acetonitrile solution. The conversion rates are all lower than 10%. Although Mn-TMPyP was found to give out a total conversion of 96%, its specificity was not good enough. The kinetics of styrene oxidation in the presence of Mn-TMPyP was studied, and the result was shown in Fig. 3. Clearly, the styrene can be converted to three kinds of products in 10 min. The selectivity for phenylacetaldehyde is relatively high. The much higher activity of Mn-TMPyP than other M-Ps is interesting and worthy of further study. We also noticed that iron porphyrin complex showed high cytochrome P-450 activity in previous

Table 3
The conversion rate of oxidation of styrene by oxone in the presence and absence of metalloporphyrin[a]

Metalloporphyrin	Total conversion rate (%)	Products yield (%)		
		Benzaldehyde	Phenylacetaldehyde	Phenyloxirane
Mn-TPPS$_4$	2.1 ± 0.4	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.2
Fe-TPPS$_4$	–[b]	–[b]	–[b]	–[b]
Co-TPPS$_4$	1.4 ± 0.1	0.6 ± 0.1	0.3 ± 0.1	0.5 ± 0.1
Mn-TCPP	2.5 ± 0.6	0.5 ± 0.1	1.1 ± 0.2	0.9 ± 0.4
Fe-TCPP	–[b]	–[b]	–[b]	–[b]
Co-TCPP	2.0 ± 0.4	0.8 ± 0.1	0.4 ± 0.0	0.8 ± 0.2
Mn-porphyrin IX	1.6 ± 0.1	0.4 ± 0.1	0.7 ± 0.0	0.5 ± 0.1
Hemin	–[b]	–[b]	–[b]	–[b]
Co-porphyrin IX	6.4 ± 0.4	2.5 ± 0.3	1.5 ± 0.3	2.4 ± 0.1
Mn-TTMAPP	17.4 ± 1.8	1.1 ± 0.2	8.7 ± 1.2	7.6 ± 0.3
Fe-TTMAPP	0.9 ± 0.1	0.3 ± 0.0	0.3 ± 0.1	0.3 ± 0.0
Co-TTMAPP	5.1 ± 0.3	1.9 ± 0.2	1.1 ± 0.0	2.1 ± 0.2
Mn-TMPyP	96.0 ± 0.8	6.1 ± 0.4	55.4 ± 2.2	34.4 ± 2.9
Fe-TMPyP	3.5 ± 0.2	0.3 ± 0.1	0.8 ± 0.1	2.3 ± 0.2
Co-TMPyP	7.5 ± 0.3	2.7 ± 0.1	1.9 ± 0.2	2.9 ± 0.3
None	–[b]	–[b]	–[b]	–[b]
None[c]	0.8 ± 0.1	0.2 ± 0.0	0.3 ± 0.1	0.3 ± 0.0
None[d]	2.2 ± 0.1	0.60 ± 0.1	0.6 ± 0.1	1.0 ± 0.2

[a] c (M-P) $= 2.5 \times 10^{-5}$ M, c (styrene) $= 0.025$ M, c (oxone) $= 0.025$ M. The reaction was at room temperature and the data were obtained based on three replicate measurements. Unless otherwise mentioned the reaction time was 10 min.

[b] Very low and not quantified.

[c] Reaction time of 1 h.

[d] Reaction time of 3 h.

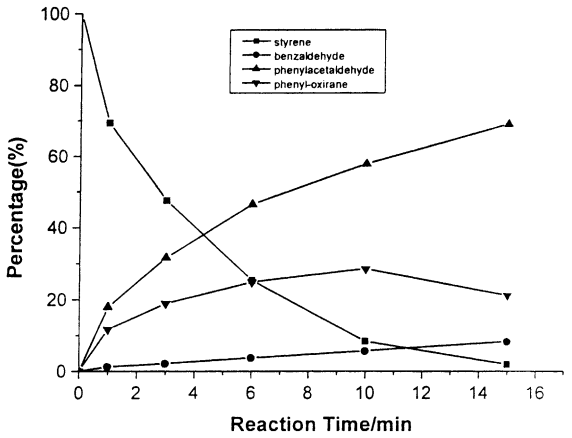

Fig. 3. The percentages of reactant and products in the Mn-TMPyP-catalyzed oxidation of styrene by oxone. c (M-P) $= 2.5 \times 10^{-5}$ M, c (styrene) $= 0.025$ M, c (oxone) $= 0.025$ M. The reactions were at room temperature.

studies [27]. However, in present study their activities are much lower than that of Mn-TMPyP. This is probably due to the use of different oxidants or different porphyrin structures. The latter effect is evident for Mn-porphyrin complex (Table 3).

4. Conclusion

The step of the forming an active intermediate, M-P *p*-cationic radical species is the decisive step in the oxidation reaction catalyzed by M-P acting as a heme-containing enzyme. While H_2O_2 is applied as an oxidant in the reaction catalyzed by M-P, it bonds with M-P at first, then transfer oxygen to the M-P to form a metal-oxo porphyrins *p*-cationic radical species [28]. The existence of hydroxyl ion is in favor of the forming of such an active intermediate. If pH is too high (higher than pK_a of H_2O_2, 11.75), the dissociation of H_2O_2 will be unfavorable for the forming of the active intermediate. Such an active intermediate can react with a substrate (organic substrate or hydrogen peroxide) very quickly and then return to original state. So, we can conclude that when M-Ps are used as mimics of heme-containing enzymes, if the oxidants are same, they should express the same order activity catalase and peroxidase-like activities. Equally important is that axial ligand imidazole shows different modulation effect on catalase- and peroxidase-like activities, which is in good agreement with the fact that these enzymes have a different environment around the active center—porphyrin IX.

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