

Oxidation of styrene by various oxidants with different kinds of metalloporphyrins

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Abstract

In $\text{CH}_3\text{CN}:\text{H}_2\text{O} = 1:1$ (v/v) medium, the oxidation of styrene by water-soluble oxidants (KHSO_5 , NaClO , NaIO_4 or H_2O_2) catalyzed by metalloporphyrins (MPs) with various structures and central ions was investigated. The effect of imidazole and pyridine was also studied. The results indicated that the oxidation of styrene catalyzed by MPs is related to the pH of reaction medium, structure and central ions of MPs, oxidants and axial ligands. In neutral medium, MPs showed higher activity and yield of epoxide compared with that in acidic medium. For different MPs, phenyl-substituted manganese porphyrins can effectively catalyze KHSO_5 and NaClO to oxidize styrene and pyridine-substituted manganese porphyrin can effectively catalyze KHSO_5 and NaIO_4 to oxidize styrene. But all MPs studied cannot effectively catalyze H_2O_2 to oxidize styrene. For different central metal ions, KHSO_5 is effective for manganese and cobalt porphyrins, NaClO is effective for manganese porphyrins and NaIO_4 is effective for iron porphyrins. Imidazole can markedly enhance the activity of MPs when KHSO_5 , NaIO_4 and H_2O_2 were used as oxidants and inhibit the activity of MPs when NaClO was used as oxidant. Pyridine can markedly enhance the activity of MPs when KHSO_5 and NaClO were used as oxidants, but no effect was found when NaIO_4 and H_2O_2 were used as oxidants. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Reaction mechanisms of metalloporphyrins (MPs) with various oxidants have received considerable attention since they are relevant to the catalytic mechanisms of heme enzymes, such as peroxidases, catalases and cytochrome P-450s, all of which contain iron(III) protoporphyrin IX (hemin) as their active centers [1,2]. Though the structures of oxidants are different, it is generally considered that in the catalytic cycle, these oxidants transfer an oxygen atom

to the central ion of MPs to form a high-valent metal oxo porphyrin π -cation radical species, which is the only active intermediate responsible for the oxygenation of hydrocarbons [1,2]. A number of high-valent iron oxo and manganese oxo porphyrin complexes have been prepared at low temperature, characterized with variety of spectroscopic methods, and directly used in the reactivity studies of oxygen atom transfer reactions such as olefin epoxidation and alkane hydroxylation [3–5]. However, recent research indicated that under some reaction conditions, MPs also catalyze oxidant to oxidize the substrates though other intermediates and the occurrence of this phenomenon were to a great degree decided by reaction medium, reaction temperature and property of MPs

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themselves [6–9]. In our previous paper, we have studied the catalytic properties of 15 water-soluble MPs with emphasis on multi-enzyme activities related to porphyrin structure, central ions as well as axial ligand [10]. In the present paper, we report our further investigation with emphasis on the influence of different oxidants, which is related to the porphyrin structures, central ions and axial ligand. The oxidants selected include KHSO_5 , NaIO_4 , NaClO and H_2O_2 .

2. Experiment

2.1. Instruments

UV–Vis spectra were recorded on a Varian Cary 1E Spectrophotometer (USA). Gas chromatographic analyses were carried out on a Shimadzu GC-9A (Kyoto, Japan) equipped with SE-30 capillary column (0.25 mm \times 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

4-pyridinecarboxaldehyde and oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) were obtained from Acros (Pittsburgh, USA). Pyrrole was purchased from Sigma (St Louis, USA). Benzaldehyde, 4-*N,N'*-dimethylaminobenzaldehyde, styrene, methyl iodide, NaClO , NaIO_4 , H_2O_2 , imidazole, pyridine and CH_3CN were supplied by Beijing Chemical Plant (Beijing China). The solution of KHSO_5 , NaClO , NaIO_4 and H_2O_2 were all 0.2 M water solution, and freshly prepared before use. Purified styrene (0.1 M) was prepared in CH_3CN . Pyridine and imidazole were 0.04 M CH_3CN solutions. Porphyrin ligands (tetrakisphenylporphyrin (TPP), meso-tetrakis(*p*-sulfonatophenyl)porphophine (TPPS₄), meso-tetrakis[4-(*N*-trimethyl)aminophenyl]porphophine (TTMAPP) and meso-tetrakis(4-*N*-methylpyridinium)porphophine (TMPyP)) and corresponding metal complexes are the same as those used in previous report [10]. The stock solutions of MPs (5.0×10^{-4} M) were prepared with deionized water, except for MnTPP that was prepared in CH_3CN due to its low solubility in water.

2.3. Procedures

Under room temperature, 1.0 ml styrene solution of 0.1 M, MP solution of 1.0×10^{-4} M (1.0 ml) and 1.0 ml acetonitrile (or pyridine acetonitrile solution of 0.04 M or imidazole acetonitrile solution of 0.04 M) were mixed together. Then, 1.0 ml oxidant solution of 0.1 M was added under stirring. The reaction products were analyzed with GC by direct injection of 2.0 μl of the reaction mixture at a certain reaction time and the product structures were confirmed by GC–MS. The reaction time for KHSO_5 was 30 min and for the other oxidant system it was 2 h.

3. Results and discussion

3.1. Effect of pH on the catalytical activity and selectivity of MPs

The oxidation of styrene in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (v/v = 1:1) catalyzed by MPs with various oxidants afforded a complex mixture of phenyl-oxirane, phenylacetaldehyde and benzaldehyde. Because the reaction was performed in aqueous medium, pH will have some effect on the activity and selectivity. Some studies about this had been reported in the previous work [11,12]. In present study, we choose MnTPPS₄– KHSO_5 system to study the effect of pH. As KHSO_5 is not stable at alkaline solution, only two pH values, 3.0 and 7.0, were studied. As shown in Fig. 1, both the total conversion rate and selectivity are higher at pH 7.0 than those at pH 3.0. Interestingly, no benzaldehyde was found at pH 7.0, probably due to the low activity of the MPs intermediate at this pH, since the forming of benzaldehyde needs breaking of C–C bond. Another possibility is that proton may be involved in the forming of benzaldehyde. This result was coincident with that reported previously [12]. Since higher activity and selectivity were found to be in neutral medium, all the experiments hereafter were performed in neutral medium. The total conversion rate, which is roughly proportional to the percentage of phenyl-oxirane in the products mixture, was used as a parameter to show the catalytical activities of MPs under different conditions. The focus of this study is on the effect of structure of porphyrin ligands, central ions, oxidants and axial ligands on the activity of MPs, so the total conversion

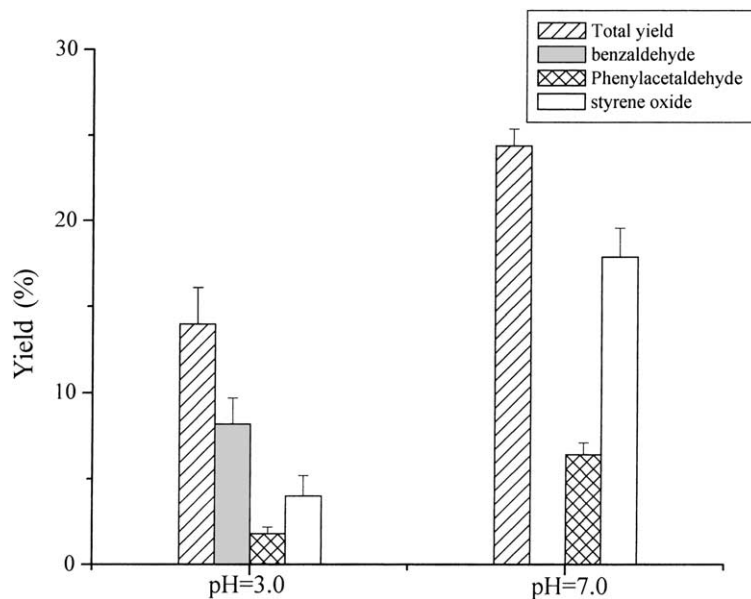


Fig. 1. Effect of pH on oxidation of styrene by KHSO_5 catalyzed by MnTPPS_4 .

rate was used as the standard of the catalytical activity.

3.2. Effect of various oxidants on the catalytical activity of Mn-porphyrins of different structures

The influence of various oxidants on the catalytical activities of MPs in oxidation of styrene was studied since the activation of MPs is closely related to the

oxidants. Mn-porphyrins of different structures are selected for this study. Fig. 2 clearly showed that all the MP systems showed substantial catalytical activities though in different extent that is evidently oxidant co-related. For all MPs, the system of KHSO_5 with an O–O structure showed high conversion rate. This is probably due to the asymmetric structure of O–O bond in the KHSO_5 , which is in favor of heterolytic cleavage to form the active intermediate. MPs of MnTPP or

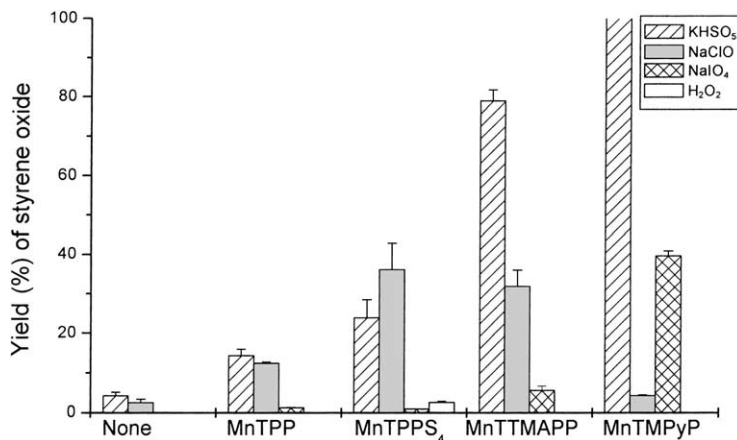


Fig. 2. Oxidation of styrene by KHSO_5 , NaClO , NaIO_4 and H_2O_2 catalyzed by manganese MPs with different substituted ligands.

its derivatives with a substituent at the *para*-position of the phenyl ring in MnTPP, such as MnTPPS₄ (a negatively charged ligand) and MnTTMAPP (a positively charged ligand), showed similar activity, i.e., the systems with KHSO₅ and NaClO as oxidants give the high conversion rate. However, when MnTMPyP was used high total conversion rates were observed with KHSO₅ and NaIO₄ as oxidants. Compared with others, MnTMPyP is quite different in its ligand structure or electronic structure. For all the MPs, H₂O₂ is not an effective oxidant. Therefore, only a proper matching of MP and oxidant will result in effective catalyzed reaction.

3.3. Effect of various oxidants on catalytic activity of MPs with different central metal ions

The key of the forming active intermediate is the bonding of the central ion and oxidant and the cleavage of the O–X (X stands for O, Cl, I and so on) bond. Therefore, the nature of central ions must have a great effect on the catalytic activity of MPs. As shown in Fig. 3, the total conversion rate is both highly MP and oxidant dependent. For MnTTMAPP, both KHSO₅ and NaClO were the effective oxidants; and NaIO₄ was effective for FeTTMAPP, while KHSO₅ was effective for CoTTMAPP. CuTTMAPP could

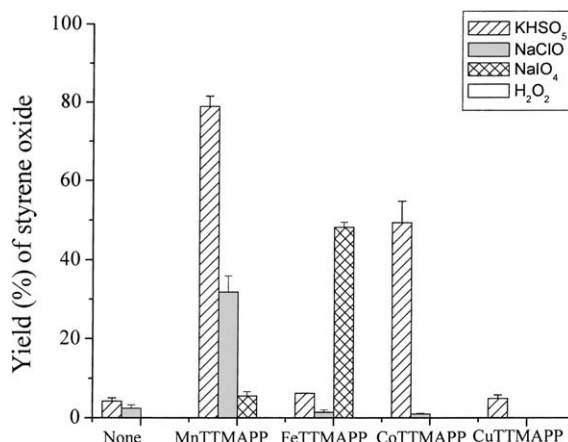


Fig. 3. Oxidation of styrene by KHSO₅, NaClO, NaIO₄ and H₂O₂ catalyzed by various MPs with TTMAPP as ligand.

not catalyze any oxidant to oxidize styrene and even quenches the oxidation of styrene when NaClO is used as oxidant. Once again, H₂O₂ is not a suitable oxidant for all the catalyst systems.

3.4. Effect of various oxidants on catalytic activity of MPs with different axial ligands

Commonly, nitrogenous organic base ligands have clear enhancement on oxidation reactions catalyzed by

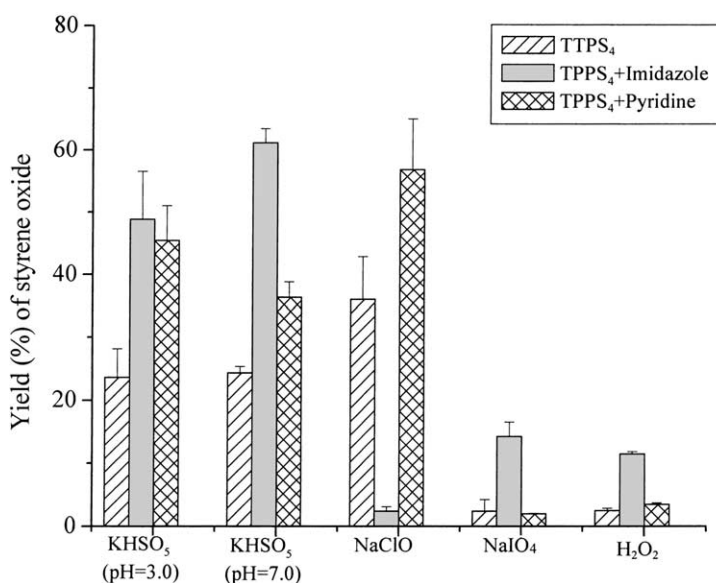


Fig. 4. Effect of imidazole and pyridine on the oxidation of styrene by KHSO₅, NaClO, NaIO₄ and H₂O₂ with MnTPPS₄ as catalyst.

MPs. There are two reasons: (1) ligand can bond central ions of MP at axial position direction, and display the effect of axial ligand in nature enzyme; (2) ligands can also display the action of acid–base catalyst and promote the cleavage of O–X (X = O, Cl, I, and so on) bond in oxidants forming active intermediate at distal site. Imidazole and pyridine are commonly used effective organic base ligands in the previous study, so in our experiment we have chosen them as axial ligands. In the present study, we studied the effect of imidazole and pyridine on oxidation of styrene catalyzed by MnTPPS₄ with various oxidants. KHSO₅ can oxidize imidazole and pyridine, and they are seldom used as axial ligands when KHSO₅ is used as oxidant. Fig. 4 showed that in CH₃CN–H₂O medium, both imidazole and pyridine could increase the total conversion in either acidic or neutral medium. In the neutral medium, imidazole and pyridine mainly acted as axial ligands and in the acidic medium they may act as distal acid–base catalyst. Only proper combination of axial ligands and oxidant will produce efficient oxidation of styrene. As shown in Fig. 4, when KHSO₅ and H₂O₂ were used, both imidazole and pyridine showed clear enhancement effect on oxidation reaction catalyzed by MPs. When NaOCl was used, significant inhibition effect was observed with imidazole as axial ligand and enhancement effect was obtained with pyridine as axial ligand. While NaIO₄ was used as oxidant, imidazole showed enhancement and pyridine did not show any obvious effect on the reaction. These mysterious enhancement or inhibition effect on the reaction is reaction mechanism related, and further investigation is required to answer why the opposite effect was found.

4. Conclusions

The results above indicated that the activity and selectivity of MPs are greatly influenced by the structures of porphyrin ligand, central ions, oxidants, axial ligands and the nature of reaction medium. MPs showed higher activity and yield of epoxide in neutral medium than in acidic medium. For the oxidation of

styrene, phenyl-substituted manganese porphyrins are effective with KHSO₅ and NaClO as oxidants and pyridine-substituted manganese porphyrin is effective with KHSO₅ and NaIO₄ as oxidants. However, all MPs studied show low activity when H₂O₂ was used as oxidant. For the same porphyrin ligand, KHSO₅ is effective for manganese and cobalt porphyrins. NaClO is an effective oxidant for manganese porphyrins while NaIO₄ is effective for iron porphyrins. When different oxidants were used, imidazole and pyridine displayed different effect on the activity of the MPs. In summary, only proper combination of MP, oxidant and axial ligand will effectively oxidize styrene.

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