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Journal of Molecular Catalysis A: Chemical 147 (1999) 173–178

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Amino acid Schiff base complex catalyst for effective oxidation of olefins with molecular oxygen

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Abstract

The amino acid Schiff base manganese complex (Sal–Phe–Mn) was prepared with L-phenylalanine, salicylaldehyde and $Mn(OAc)_2 \cdot 4H_2O$. The ligand and the complex were characterized by the infrared spectra, small area X-ray photoelectron spectroscopy, and ICP-AES. In the presence of the manganese complex, cyclohexene was effectively oxidized by molecular oxygen without reductant. The major products of the reaction were 2-cyclohexen-1-ol (–OH), 2-cyclohexen-1-one (C=O) and 2-cyclohexen-1-hydroperoxide (–OOH), which was different with typical oxidation of cyclohexene. The influence of reaction temperature and additive for oxidation had been studied. The selectivity of 2-cyclohexen-1-hydroperoxide varied with reaction time and different additives. The mechanism of cyclohexene oxidation had also been discussed.

Keywords: Aerobic oxidation; Amino acid Schiff base manganese complex; Cyclohexene

1. Introduction

The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors, like dioxygen, hydrogen peroxide, alkylhydroperoxide, sodium hypochlorite or iodosobenzene into various organic molecules, under mild conditions, remains a difficult challenge in the fields of chemical and biological catalysis [1]. The oxidation of hydrocarbons by transition metal complexes has been studied extensively [2–5]. The current progress of the research on synthetic metalloporphyrin catalysts has led to the development of several systems that are able to reproduce the heme-enzyme mediated oxygenation and oxidation reactions, at least in terms of reaction types, mechanisms and often rates [6,7]. However, in olefin epoxidations or alkane hydroxylation, the oxygen source has mainly come from H_2O_2, alkylhydroperoxide, NaOCl or PhIO. When dioxygen was used as an oxidant, in most cases, the reductant should be added into the reactive system. Halogenated iron porphyrins can catalyze oxidation of hydrocarbons by molecular oxygen without reductant [8]. When cobalt Schiff base complex [9,10] or bis(1,3-diketonato) metal complex [11] was used as catalyst in the oxidation of organic substrates by dioxygen, the reductant, such as isobutyraldehyde, isovalveraldehyde, acetaldehyde, or ethyl 2-oxocyclo-

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1381-1169/99/$ - see front matter
PII: S1381-1169(99)00143-0

pentanecarboxylate was necessary in the catalytic system. In this paper, we found that cyclohexene could be effectively oxidized by molecular oxygen catalyzed by amino acid Schiff base complexes. The allylic hydroperoxide was obtained as an important product, which suggested a clear allylic pathway of oxidation of cyclohexene.

2. Experimental

2.1. Materials and equipment

L-phenylalanine and salicylaldehyde were both purchased from Aldrich. Cyclohexene was purified by fractionating distillation just before use. All other reagents commercially available, such as ethyl alcohol, metals and salts were of the highest grade and were used as received.

The metal contents were analyzed on a model ARL-3520 Inductively Coupled Plasmas Atomic Emission Spectrometry of USA. XPS (small area X-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System, Power Source By MgK_{α} line and Ag $3d_{5/2}$ FWHM ≤ 0.48 eV. IR spectra were recorded in KBr disks with an Alpha-centauri FT-IR spectrophotometer. The reaction products of oxidation were determined and analyzed by using Shimadzu QP-1000A GC/MS system, GL-16A gas chromatograph with a 5 m $\times$ 3 mm OV-17 column, 80°C–200°C (10°C/min), Inj. 220°C (Dect. 220°C). The products were determined by comparing with the standard mass spectrometry of organic compounds and fragmentation pattern.

2.2. Synthesis of amino acid Schiff base manganese complexes (Sal–Phe–Mn)

Ten millimoles of L-phenylalanine and 10 mmol of sodium hydroxide were stirred in 75 ml 95% EtOH. When the L-phenylalanine and NaOH were dissolved, 75 ml of the alcohol which dissolved 10 mmol of salicylaldehyde was added. After stirring for 15 min, the solution became yellow. In stirring, 75 ml of the solution of $Mn(OAc)_2 \cdot 4H_2O$ (10 mmol) was slowly added. The color of solution changed to deep yellow, and the solution was continuously stirred for 2 h. Left out for a night, the complex settled out. The precipitate of manganese complex was collected by filtration, washed with a small amount of water and ethanol, respectively, and dried under vacuum.

2.3. Oxidation of cyclohexene

Typical procedure: a glass flask is charged with Sal–Phe–Mn (1 mg) and cyclohexene (1 ml). The dry oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The gas outlet tube was closed. The reactor was put into a heating bath whose temperature was 70°C, and stirring was started. The consumption of oxygen was measured and calculated by gauge glass. After reacting for 12 h, the products were analyzed by gas chromatograph, GC/MS system.

3. Results and discussion

3.1. Characterization

IR spectra (Table 1) show that asymmetric stretching vibration absorption band (ν_{as}) of COO appear at 1613 cm^{-1}, $\nu_{sCOO}-$ at 1409 cm^{-1}, $\nu_{C=N}$ at 1632 cm^{-1}, and ν_{Ph-O} at 1250 cm^{-1} for amino acid Schiff base ligand (Sal–Phe). The stretching vibrations of C=N, COO and Ph–O bonds of complex (Sal–Phe–Mn) are different because the backbones are influenced by the metal ion. The Mn–N bond and Mn–O bond appear in the complex.

In order to confirm the structure of the ligand (Sal–Phe) and the coordination of the complex

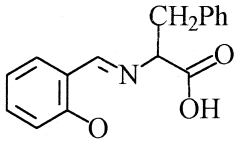
Table 1
The IR data of the amino acid Schiff base (Sal–Phe) and its complex (Sal–Phe–Mn) (KBr, cm^{-1})

Compound	$\nu_{C=N}$	ν_{asCOO}	ν_{sCOO}	ν_{Ph-O}	ν_{Mn-N}	ν_{Mn-O}
Sal–Phe	1632	1613	1409	1250	–	–
Sal–Phe–Mn	1628	1602	1388	1244	532	436

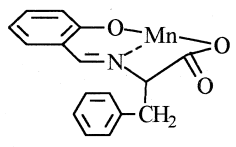
Table 2
The XPS data of the amino acid Schiff base (Sal–Phe) and its complex (Sal–Phe–Mn)

Compound	Binding energy (eV)			
	$C_{1S_{1/2}}$	$O_{1S_{1/2}}$	$N_{1S_{1/2}}$	$Mn_{2p3/2}$
Sal–Phe		531.6		
	288.6; 284.6	532.8/531.6/531.1 (1/1/1)	400.0	–
$Mn(OAc)_2$	–	–	–	640.6
Sal–Phe–Mn		532.3		
	288.6; 284.6	532.5/531.7/530.8 (1/1/1)	398.9	641.8

(Sal–Phe–Mn), the small area X-ray photoelectron spectroscopy data were measured (Table 2). It shows that the chemical shift of binding energy of carbon is less than 0.2 eV. The chemical shifts of nitrogen and metallic element are more than 0.5 eV. The carbon peaks in the ligand and the complex could be divided into two peaks. One (288.6 eV) is afforded the carbon of carboxyl group. The oxygen peak in the complex could be divided into three peaks. Comparing with the ligand, the chemical shifts of each $O_{1S_{1/2}}$ in complexes are different. The atomic concentration of the complex showed the ratio of Mn:N:O ≅ 1:1:4, which indicated that a water molecular was in the complex. The result of ICP-AES showed that the manganese content of the complex is 16.11%, which conformed to the formula of Sal–Phe–Mn ($C_{16}H_{13}NO_3Mn \cdot H_2O$, Mn = 16.17%). The structure of amino acid Schiff base and its complex (Sal–Phe–Mn) could be confirmed.



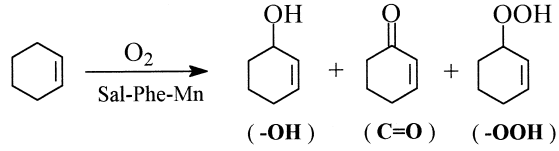
Sal-Phe



Sal-Phe-Mn

3.2. Oxidation of cyclohexene

In the presence of the amino acid Schiff base manganese complex (Sal–Phe–Mn), cyclohexene oxidation by dioxygen was investigated by monitoring the O_2 consumption. The component products were analyzed in the period of reaction or after the reaction by the gas chromatograph and the GC-MS system. The structures were determined by comparing with the standard mass spectrometry of organic compounds and fragmentation pattern. The major products of the reaction were 2-cyclohexen-1-ol (–OH), 2-cyclohexen-1-one (C=O) and 2-cyclohexen-1-hydroperoxide (–OOH).



As shown in Fig. 1, at 343 K, when the consumption of dioxygen was more than 20 ml, the total selectivity for the major products was more than 80%. The side product was cyclohexene oxide, and its selectivity was between 3% and 4%.

3.2.1. Effect of temperature

The catalytic activity of Sal–Phe–Mn was investigated as a function of temperature. The consumption of dioxygen with 2 mg Sal–Phe–Mn as a function of time at 313, 323, 333, and 343 K are shown in Fig. 2. It is clear that higher

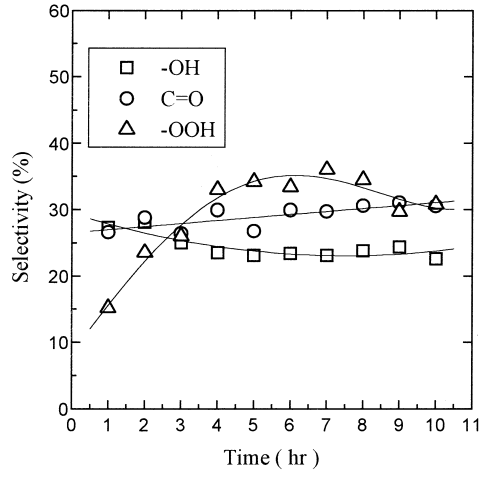


Fig. 1. Relationship between the selectivity of the major products and reaction time (Cat: 2 mg; cyclohexene: 3 ml; 343 K).

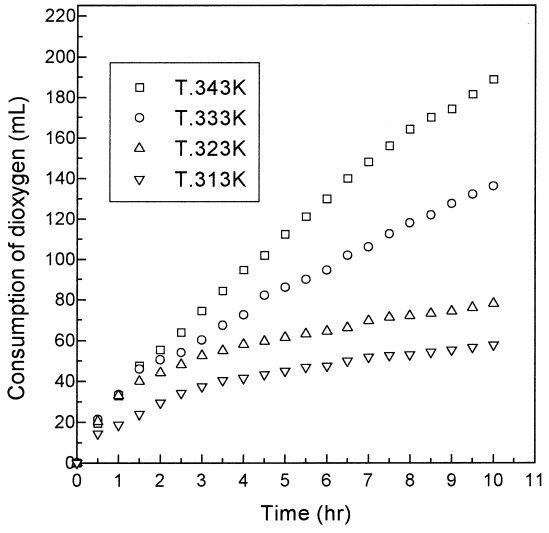


Fig. 2. Relationship between consumption of O_2 with reaction time catalyzed by Sal–Phe–Mn in different temperature (Cat: 2 mg; Sub: cyclohexene (2 ml)).

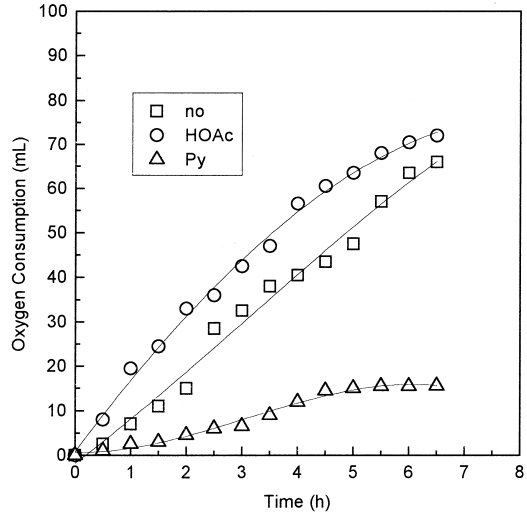


Fig. 3. Effect of the additive (5%) in the oxidation of cyclohexene (1 ml) in the presence of Sal–Phe–Mn (1 mg) at 343 K.

the reaction temperature, the faster the oxygen consumption. The steady reaction rate, conversion and selectivity at the end of the reaction are collected in Table 3. At 343 K, the rate of cyclohexene oxidation is 2.8 times than that of 313 K. At 333 K, the rate is 1.7 times than that of 323 K. When the reaction temperature or time increased, the reaction rate or conversion of cyclohexene increased quickly. But the selectivity of 2-cyclohexen-1-hydroperoxide (–OOH) decreased. It is indicative of a free radical reaction pathway.

3.2.2. Effect of the additive

The catalytic activity of Sal–Phe–Mn was investigated in the presence or absence of the additive. As shown in Fig. 3, at 343 K, in the presence of acetate acid, rapid oxygen consumption was observed. The cyclohexene oxidation rate was 1.1 times that of no additive. The selectivity of 2-cyclohexen-1-hydroperoxide (–OOH) was only half of that of no additive, and the selectivity of 2-cyclohexen-1-ol (–OH) and 2-cyclohexen-1-one (C=O) increased 63% and 38%, respectively.

When the pyridine was added into the oxidation system, the rate of O_2 consumption decreased quickly. The rate was only 24% that of no additive. The selectivity of 2-cyclohexen-1-hydroperoxide (–OOH) was 81% that of no additive. The 2-cyclohexen-1-one (C=O) increased 23% while the 2-cyclohexen-1-ol (–OH) was similar with no additive.

Table 3
Product distribution and rate of oxidation of cyclohexene (2 ml) in the presence of Sal–Phe–Mn at various temperatures

Temperature (K)	Time (h)	$\Delta n(O_2)$[a] (mmol)	Conv.[b] (%)	Selectivity (%)		Rate[c] ($\times 10^{-5}$ mol/min)
				S (total)	*S* (–OOH)	
313	10	2.58	12.3	99.7	44.5	0.43
323	11	3.58	33.1	92.7	47.3	0.54
333	14	7.73	58.5	79.9	40.7	0.92
343	14	10.06	74.8	75.1	29.6	1.20

[a]Amount of oxygen reacted.
[b]Conversion of cyclohexene, analyzed by GC.
[c]Rate is the steady oxygen consumption rate.

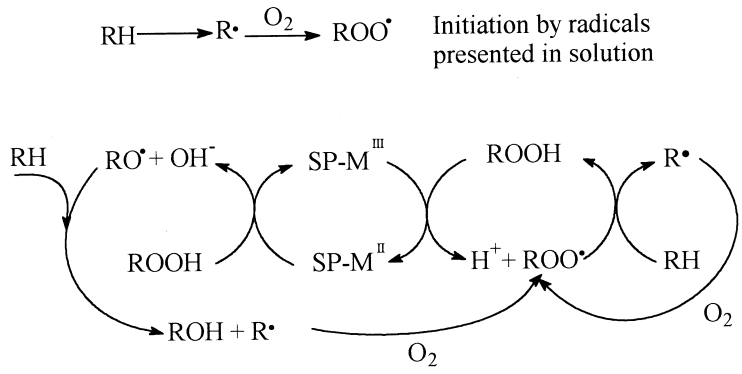


Fig. 4. The allylic peroxide decomposition mechanism for dioxygen reactions with metal complex (SP-M = Sal–Phe–Mn). Initiated by radicals in solution, the peroxides thereby generated are catalytically decomposed by the manganese complex. These radicals can then propagate the reaction further.

3.3. Mechanism of oxidation of cyclohexene

In order to explain the highly catalytic activity of highly halogenated porphyrin complexes, such as octabromotetra(pentafluorophenyl) porphyrin ferric complex (Fe(TFPPBr$_8$)Cl), for the oxidation of *iso*-butane to *t*-butanol by molecular oxygen, Grinstaff et al. [7] and Labinger [12] have proposed a radical-chain mechanism. This mechanism was also available for explaining highly catalytic activity of Fe(TFPPBr$_8$)Cl in the oxidation of cyclohexene with dioxygen [13]. In the presence of Sal–Phe–Mn, cyclohexene oxidation to a mixture of 2-cyclohexen-1-ol (–OH), 2-cyclohexen-1-one (C=O) and 2-cyclohexen-1-hydroperoxide (–OOH)(Fig. 1), and a little of cyclohexene oxide was observed. The product distribution and activity varied with reaction time, temperature and the additive. Considering the similarity of the major products in two catalytic oxidation system, especially the appearance of hydroperoxide in Sal–Phe–Mn system, it is likely that they carry out the same radical chain mechanism, as shown in Fig. 4 (SP-M = Sal–Phe–Mn).

Initiated by radicals presented in solution, the concentration of 2-cyclohexen-1-hydroperoxide

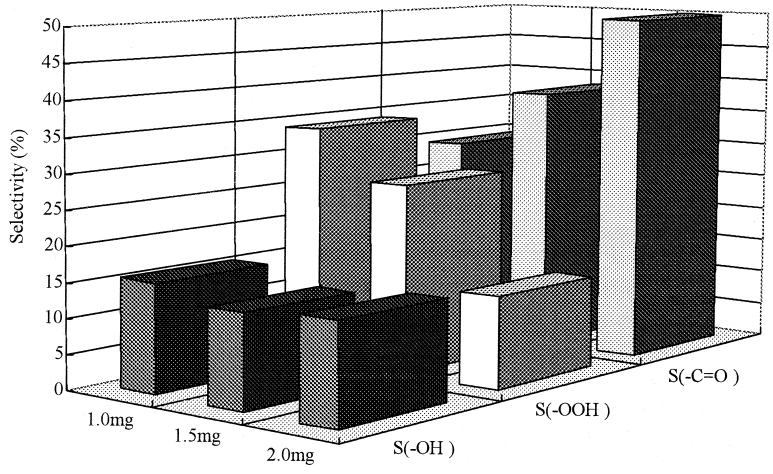


Fig. 5. Effect of the catalyst amount on oxidation of cyclohexene (1 ml) at 343 K.

(–OOH) increased quickly at the first 5 h, and then it was catalytically decomposed by the manganese complex. Therefore, the selectivity of hydroperoxide decreased after the increase in reaction time or temperature (Fig. 1, Table 3). When the acetic acid was added into the oxidation system, the rate of reaction increased and the selectivity of hydroperoxide decreased because the proton can prompt decomposition of hydroperoxide. Since the nitrogen of pyridine easily coordinate with center metal of amino acid Schiff base complexes as the fourth ligand [14], adding the pyridine into the system made the catalytic activity of manganese complex decrease quickly (Fig. 3).

At 343 K, the rate of oxidation increases with the increase of the substrate amount (cyclohexene). It is not evident that by using more catalyst, the rate will increase. But the selectivity of hydroxide decreases with the increase in the catalyst amount (Fig. 5). It indicated that as the amount of the complex increases, the decomposition of 2-cyclohexen-1-hydroperoxide becomes more rapid.

4. Conclusion

It was demonstrated that the amino acid Schiff base manganese complex (Sal–Phe–Mn) is an effective catalyst for cyclohexene oxidation by O_2 without reductant. The major products of the reaction were 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-cyclohexen-1-hydroperoxide. Adding acetate acid made catalytic activity increase, and the pyridine made catalytic activity drop. The mechanism of oxidation is a radical chain mechanism, which is similar with the system in the presence of highly halogenated porphyrins ferric complexes. This kind of catalyst is a potentially important catalyst in cyclohexene oxidation or similar oxidation processes of hydrocarbons.

Acknowledgements

We wish to thank the National Natural Sciences Foundation of China and the Gansu Bureau of Environmental Protection for financial support.

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