

Polymer-Bound Schiff-Base Complex Catalyst for Effective Oxidation of Olefins with Molecular Oxygen

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ABSTRACT: Polymer-bound Schiff-base ligand (PS–SalPhe) was prepared from polystyrene-bound salicylaldehyde and phenylalanine, and its complex (PS–SalPhe–M) (M = Co, Mn) was also synthesized. The polymer ligand and its complex were characterized by infrared spectra, small area X-ray photoelectron spectroscopy, and ICP–AES. In the presence of the complex, cyclohexene can be effectively oxidized by molecular oxygen without a reductant. The major products of the reaction are 2-cyclohexen-1-ol (—OH), 2-cyclohexen-1-one (C=O), and 2-cyclohexen-1-hydroperoxide (—OOH), which is different from the typical oxidation of cyclohexene. The mechanism of cyclohexene oxidation is also discussed. Long-chain linear aliphatic olefins, such as 1-octene, 1-decene, 1-dodecene, and 1-tetradecene, can be directly oxidized by molecular oxygen catalyzed by PS–SalPhe–M (M = Mn, Co), which yields the 1,2-epoxy alkane. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1138–1143, 2000

Key words: oxidation; polymer; Schiff-base complex; cyclohexene; linear aliphatic olefins; epoxidation

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.^{1–4} Synthetic metal complexes, such as metalloporphyrins, phthalocyanines, and metal–Salen, for the catalytic oxidation of hydrocarbons, mimicking the action of cytochrome P-450-based enzymes, has

been studied extensively.^{5,6} The main drawback for practical use of protein-free metalloporphyrins is their potential self-destruction by oxidative degradation. Therefore, efforts have been made to circumvent this problem. There are two typical methods: One is extensive halogenation of the macrocycle in order to enhance both the stability and the catalytic activity of the complexes.^{7,8} The other is consumption of a reductant such as isobutyraldehyde, isovalveraldehyde, acetaldehyde, or ethyl 2-oxocyclopentanecarboxylate, for inhibiting degradation of the catalyst in a catalytic system.^{9–11} It was also found that the stability of the metal-complex catalyst may be improved by polymerization of the complexes or by being bonded on the polymer.^{12,13}

For the potentially practical use of the catalytic systems in oxidation, research emphasis should

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be directed to the use of cheap, easily accessible, and environmentally friendly oxidants such as molecular oxygen or hydrogen peroxide. The Schiff-based complexes are relatively more easily prepared than are the metal-porphyrin complexes. In this article, it is shown that olefins could be effectively oxidized by molecular oxygen catalyzed by polymer-bound Schiff-base complexes, which are environmentally friendly when catalyzed. Allylic hydroperoxide was obtained as an important product, which suggested a clear allylic pathway for the oxidation of cyclohexene.

EXPERIMENTAL

Materials and Equipment

Both phenylalanine and 2,4-dihydroxybenzaldehyde were obtained from Aldrich Co. (Milwaukee, WI) and used without further purification. Olefins were purified by distillation just before use. Other reagents, such as ethanol and metals salts, were used as received.

The metal contents were detected on an American ARL-3520 inductively coupled plasma atomic emission spectrometry. Small-area X-ray photoelectron spectroscopy (XPS) data were recorded using the PHI-5702 Multi-Technique System, with the power source of MgK α line and Ag 3d_{5/2}, fwhm \leq 0.48 eV. IR spectra were recorded with an Alpha-centauri FTIR spectrophotometer (KBr disks). The reaction products of oxidation were determined and analyzed using a Shimadzu GC-16A gas chromatograph, QP-1000A GC/MS system, and a GC-IR system (HP 5890 GC and Bio-Rad 65A FTS IR system).

Synthesis of Polymer-bound Schiff Base (PS-SalPhe)

Synthesis of Polymer-bound Salicylaldehyde (PS-Sal)

Twenty grams of crosslinked chloromethyl polystyrene (crosslinked: 6%, Cl content: 0.1 mol) was added in 200 mL of acetone. In an argon atmosphere, the solution of 2,4-dihydroxybenzaldehyde (14 g, 0.1 mol) in acetone (50 mL) was added to the above mixture accompanied by stirring. Next, 13.8 g (0.1 mol) of anhydrous K₂CO₃ and 1.66 g of KI was added. The reaction mixture was stirred and refluxed for 10 days in the presence of argon. Cooling to room temperature, the product of the polymer was filtrated and washed with

water until no K₂CO₃ and KI was present, then washed with alcohol until no 2,4-dihydroxybenzaldehyde was in the filtrate. After being dried under a vacuum, 28 g of the pink polymer (PS-Sal) was obtained (yield of 82%).

Synthesis of Polymer-bound Salicylaldehyde (PS-SalPhe)

Phenylalanine, 0.05 mol, was added to 200 mL of a mixture of ethanol and water (1:1); then, 4 g (0.1 mol) of NaOH was added. The mixture was stirred until the phenylalanine and NaOH dissolved. PS-Sal, 14 g, was added to the above solution and the mixture was stirred at 60°C for 24 h. The polymer-bound Schiff-based ligand (PS-SalPhe) was filtrated and washed with water and then ethanol. After being dried under a vacuum, the yellow polymer-bound Schiff base (PS-SalPh) was obtained.

Synthesis of the Polymer-bound Schiff-based Complexes (PS-SalPhe-Mn)

Mn(OAc)₂ · 4H₂O, 10 mmol, was dissolved in 30 mL of 95% EtOH. The polymer-bound Schiff base ligand (3.5 g) was added. The mixture was stirred for 24 h at room temperature. The polymer-bound Schiff-based manganese complex (PS-SalPhe-Mn) was collected by filtration, washed with a small amount of water and then ethanol, and dried under a vacuum.

Procedure of Oxidation: Typical Oxidation Procedure of Cyclohexene

A glass flask was charged with PS-SalPhe-Mn (5 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. After closing the gas outlet tube, the reactor was put into a heating bath, the temperature of which was kept at 70°C, and stirring was begun. The consumption of oxygen was measured and calculated by a gauge glass. After reacting for 12 h, the reaction products were analyzed using a Shimadzu GC-16A gas chromatograph with a 5 m \times 3-mm OV-17 column, Shimadzu QP-1000A GC/MS system, and a GC-IR system (HP 5890 GC and Bio-Rad 65A FTS IR system; interface: GC/C 32 GC-IR; column: SE54 (25 m \times 0.32 mm); FID; inj. 260°C, dect. 260°C; init. temp. 100°C, init. time: 3 min, rate 10°C/min, final temp. 220°C; flow: 1.41 mL/

Table I XPS Data of the Amino Acid Schiff Base (PS-SalPhe) and Its Complex (PS-SalPhe-Mn)

Compound	Binding Energy (eV)			
	C _{1s1/2}	O _{1s1/2}	N _{1s1/2}	Mn _{2p3/2}
PS-SalPhe	388.6; 284.6	531.6	400.0	
Mn(OAc) ₂	—	—	—	640.6
PS-SalPhe-Mn	387; 284.6	532.3	399.6	642.0
Co(OAc) ₂	—	—	—	779.6
PS-SalPhe-Co	284.6	532.3	399.0	781.4

min). The oxidation procedure of the linear aliphatic olefins was similar to the above process.

Characterization of the Polymer-bound Schiff-based Ligand and Its Complexes

IR spectra showed that the asymmetric stretching vibration absorption band (ν_{as}) of COO appeared at 1680 cm^{-1} ; of $\nu_{s\text{COO}}$, at 1410 cm^{-1} ; of $\nu_{\text{C=N}}$, at 1625 cm^{-1} ; and of $\nu_{\text{Ph-O}}$, at 1257 cm^{-1} for the polymer-bound Schiff-base ligand (PS-SalPhe). The stretching vibrations of the C=N, COO, and Ph-O bonds of the complex (PS-SalPhe-M) are different from those of PS-SalPhe because the macrocycle backbones are influenced by the metal ion. The Mn-N bond and Mn-O bond of the complexes appeared near 548 and 461 cm^{-1} , respectively.

To confirm the structure of the ligand (PS-SalPhe) and the coordination of the complex (PS-SalPhe-Mn), the XPS data were measured. They showed (Table I) that the chemical shift of the binding energy of carbon is less than 0.2 eV . The chemical shifts of nitrogen and the metallic element are more than 0.4 eV . The carbon peaks in the ligand and the complex could be divided into two peaks: One (388.6 eV) is attributed the carbon of the carboxyl group. Compared with the ligand,

the chemical shifts of each O_{1s1/2} in the complexes are different. The atomic concentration of the complex showed the ratio of Mn:N:O $\approx 1:1:4$, which indicated that a water molecule was present in the complex. The results of ICP-AES showed that the manganese content of the complex is $9.1 \times 10^{-2}\text{ mmol g}^{-1}\text{ cat}^{-1}$ and the cobalt content of the complex is $8.8 \times 10^{-2}\text{ mmol g}^{-1}\text{ cat}^{-1}$.

RESULTS AND DISCUSSION

Oxidation of Cyclohexene

In the presence of the polymer-bound Schiff-base manganese complex (PS-SalPhe-Mn), cyclohexene oxidation was investigated by monitoring the O₂ consumption. The component products were analyzed during the reaction or after the reaction by the gas chromatograph and the GC-MS system. The structures were determined by comparison with the standard mass spectrometry of organic compounds and the 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**). Table II shows the product distribution in the oxi-

Table II Product Distribution in Oxidation of Cyclohexene in the Presence of PS-SalPhe-M (M = Mn,Co)

Catalyst	Time ^a (h)	Conversion (%)	Selectivity (%)		
			S(—OH)	S(C=O)	S(—OOH)
PS-SalPhe-Mn	10 ^b	59%	21.0	36.7	23.0
PS-SalPhe-Co	13 ^c	49%	16.1	41.2	8.8

^a Temperature: 343 K .

^b Substrate: 2 mL .

^c Substrate: 1 mL .

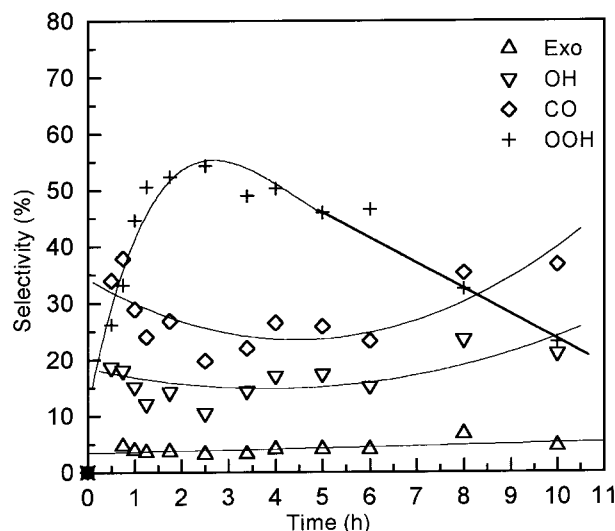
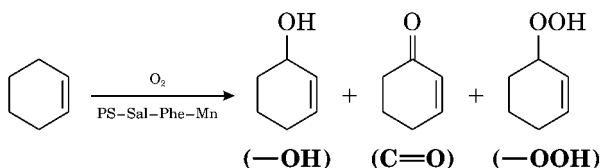


Figure 1 Relationship between the selectivity of the products and reaction time catalyzed by PS-SalPhe-Mn. Cat: 5 mg; cyclohexene: 2 mL; 343 K.

dation of cyclohexene in the presence of PS-SalPhe-M (M = Mn, Co).

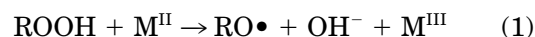


As shown in Figure 1, in the presence of PS-SalPhe-Mn, the product distribution varied with the reaction time. The selectivity for 2-cyclohexen-1-hydroperoxide (—OOH) increased rapidly in the beginning of the reaction. After 3 h, the selectivity for (—OOH) decreased along with slowly increasing of the selectivity for 2-cyclohexen-1-ol (—OH), 2-cyclohexen-1-one (C=O). The side product was cyclohexene oxide, and its selectivity was between 3–4.5%.

The major products in this catalytic oxidation system are similar to those of the highly halogenated porphyrins complexes,^{7,14,15} especially the appearance of hydroperoxide in the PS-SalPhe-Mn system. It is likely that they operate by the same radical-chain mechanism, which is shown in Figure 2, which allows the radical-chain mechanism to be explained more easily. In Figure 2, R is 2-cyclohexenyl. Combining the results with those of the references, the mechanism is proposed as follows: Initiated by radicals present in the solution, cyclohexene may dissociates its al-

lylic C—H bond into the 2-cyclohexen-1-yl radical. In the propagation steps, the allylic radicals react with oxygen to form 2-cyclohexen-1-hydroperoxide (—OOH), which abstracts a hydrogen from cyclohexene to regenerate the 2-cyclohexen-1-yl radical. The concentration of 2-cyclohexen-1-hydroperoxide (—OOH) increased quickly for the first 3 h and then it was catalytically decomposed by the manganese complex (PS-SalPhe-Mn). Therefore, the amount of hydroperoxide decreased with increasing reaction time. The amount of 2-cyclohexen-1-ol (—OH), 2-cyclohexen-1-one (C=O) increased slowly as the amount of hydroperoxide decreased, which shows that 2-cyclohexen-1-ol (—OH), 2-cyclohexen-1-one (C=O) comes from hydroperoxide.

The variation in selectivity for products with the cobalt complex (PS-SalPheCo) can be explained by change in the catalytic activity of the central metal ion. Being catalyzed by the cobalt complex, the following reaction of the allylic peroxide decomposition was faster than that of the manganese complex (PS-SalPheMn):



By adding a small amount of acid, such as HOAc, the oxidation reaction would be faster than in Eq. (1), which would make more M^{III} complex in the catalytic system.

As a by-product, the selectivity for cyclohexene oxide is between 3 and 4.5%. However, no cyclohexene oxide is present in the beginning 0.5 h, which may suggest that cyclohexene oxide comes from the reaction of 2-cyclohexen-1-hydroperoxide with the double bond of cyclohexene.

Aerobic Epoxidation of Linear Aliphatic Olefins

The linear aliphatic olefins **1**, such as 1-octene, 1-decene, or 1-dodecene, can be directly oxidized

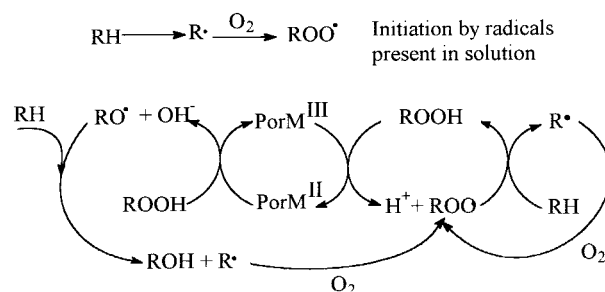



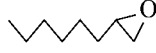






Figure 2 Allyl peroxide decomposition mechanism for O_2 reactions with PS-SalPheM.

Table III PS-SalPhe-M-catalyzed Aerobic Epoxidation of Linear Aliphatic Olefins

Substrate	Catalyst	Time (h)	Conversion (%)	Product	Selectivity (%)
	PS-SalPhe-Mn	21.0	21.0		63.0
	PS-SalPhe-Co	26.5	71.3		53.8
	PS-SalPhe-Mn	10	10.1		65.1
	PS-SalPhe-Mn	21.0	31.8 ^a		73.1

Conditions: substrate: 1.00 mL; catalyst: 5 mg; reaction temperature: 100°C.

^a Reaction temperature: 120°C.

by molecular oxygen in the presence of PS-SalPhe-M without any reductants or solvents, which produces the 1,2-epoxy alkane **2**:

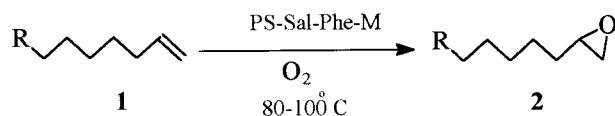


Table III shows the results of aerobic epoxidation catalyzed by PS-SalPhe-M. In general, the selectivity of 1,2-epoxy alkane was from 70 to 50%. When the conversion of linear aliphatic olefins is increased by extending the reaction time or increasing the oxidation temperature, the selectivity of 1,2-epoxides will decrease.

The oxidation reaction did not occur when the temperature for 1-octene was lower than 80°C; for 1-decene, lower than 90°C; for 1-dodecene, lower

than 95°C; and for 1-tetradecene, lower than 100°C. In most of the common solvents, such as alcohol, acetonitrile, methylene dichloride, and cyclohexane, the epoxidation also did not occur because their boiling temperatures are not higher than 80°C.

Some linear aliphatic olefins, such as 1-C₃H₁₆, 1-C₁₀H₂₀, 1-C₁₂H₂₄, and 1-C₁₄H₂₈, were smoothly epoxidized, but 1-hexene had been evaporated to dryness before it was oxidized by oxygen at 60°C. The induced period for 1-C₁₂H₂₄ was 3 h, and for 1-C₁₄H₂₈, 4 h. The selectivity of 1,2-epoxy alkane was also stable in the period of oxidation. The mechanism of the above aerobic epoxidation needs to be studied in the future.

Aerobic Oxidation of Styrene

When the polymer complexes were used in the oxidation of styrene (**3**), the major product comes from oxidative C=C cleavage of the olefinic moiety with the formation of phenyl aldehyde (**4**), and the selectivity for epoxy (**5**) is low (Table IV).

Table IV PS-SalPhe-M-catalyzed Aerobic Oxidation of Styrene

Catalyst	Time (h)	Conversion (%)	Selectivity (%)	
			4	5
PS-SalPhe-Co	13	9	90	3
PS-SalPhe-Mn	13	24	83	9

Condition: sub: 2 mL; cat: 2 mg.

CONCLUSIONS

The polymer-bound Schiff-base manganese complex is a new catalyst for the oxidation of cyclohexene, linear aliphatic olefins, and styrene by O₂ without a reductant. The major products of the reaction for cyclohexene were 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 2-cyclohexen-1-hydroperoxide. The mechanism of oxidation is a radical-chain mechanism. This kind of catalyst is a potentially important catalyst in cyclohexene and chain linear aliphatic olefin oxidation or similar

oxidation processes of hydrocarbons. In summary, the advantage of PS–SalPhe–M is that it is easily prepared and does not use reductants in the epoxidation of long-chain linear aliphatic olefins. They are environmentally more attractive than is oxidation based on stoichiometric amounts of H_2O_2 , NaIO_4 , $\text{Pb}(\text{OAc})_4$, RuO_4 , NaClO , or KMnO_4 .

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