

# Heterogeneous catalytic aerobic oxidation behavior of Co–Na heterodinuclear polymeric complex of Salen-crown ether

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## Abstract

A new kind of Co–Na heterodinuclear polymer complex based on Salen Schiff base and crown ether has been successfully prepared by condensation polymerization. Its catalytic behavior for aerobic oxidation of cyclohexene, alkylbenzenes and linear aliphatic olefins was studied in the absence of any solvents or reducing agents under mild conditions. The oxidation of cyclohexene catalyzed by the above catalyst proved to be a simple and efficient method for obtaining 2-cyclohexen-1-one (C=O) and 2-cyclohexen-1-ol (–OH) in a high selectivity. Kinetics of the oxidation was also investigated. The results showed that the aerobic oxidation of cyclohexene catalyzed by Salen-crown ether heterodinuclear polymer complex follows a radical chain aerobic oxidation mechanism. This oxidation system is also efficient in the oxidation of alkylbenzenes and linear aliphatic olefins, which afforded corresponding benzylic oxidation products and epoxides, respectively.

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**Keywords:** Co–Na heterodinuclear polymer Schiff base complex; Oxidation

## 1. Introduction

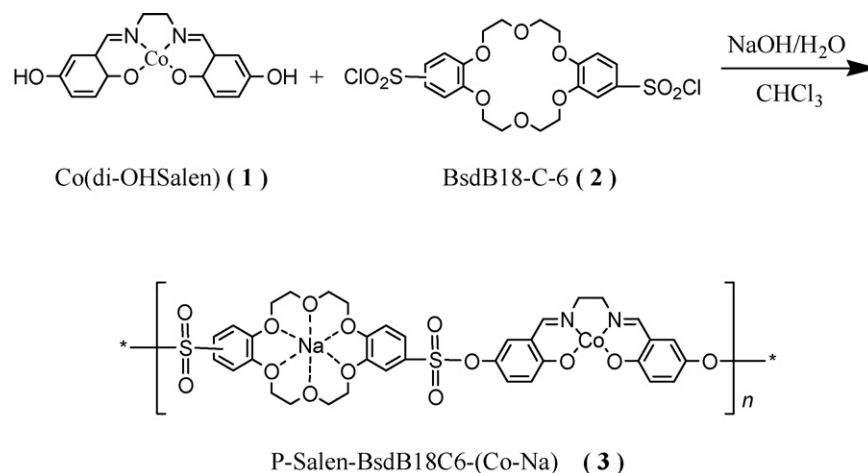
Oxidative functionalization of hydrocarbons into useful organic compounds is of an immense interest in the area of transition metal complexes mediated reactions over the past decades [1,2]. In this regard, metalloporphyrins have been used extensively owing to their direct relationship to enzymatic oxidation with cytochrome P-450 [3–5]. Parallel to the porphyrin chemistry, the same catalytic reactions are mimicked by various transition metal complexes, in particular Schiff base complexes, because of cheap and easy synthesis, and chemical and thermal stability of them [6–9].

Catalytic oxidation of hydrocarbons have been carried out using a variety of oxidants such as PhIO, NaOCl, H<sub>2</sub>O<sub>2</sub>, alkyl hydroperoxides, percarboxylic acids, magnesium monoperoxophthalate and molecular oxygen. Among these oxygen donors, molecular oxygen is becoming an increasingly important oxidant both in industry and academic research. As a cheap,

environmentally clean and readily available oxidant, molecular oxygen has received much attention in the recent years. One of the most interesting trends are known as the direct reaction of hydrocarbons with molecular oxygen catalyzed by halogenated metalloporphyrins with electron withdrawing groups, such as the Lyon's system [10,11]. However, there are only a few papers concerning the catalytic oxidation of hydrocarbons with molecular oxygen in the presence of Salen Schiff base as catalyst without the use of sacrificial co-reductant [12]. One reason is that the Salen Schiff base complexes with low molecular weight are easy to be degraded or dimerized to  $\mu$ -oxy-metal species, which leads to deactivation of the catalytic species. In order to overcome the above problems, two strategies are commonly employed. One is to anchor the catalyst to an inert organic or inorganic solid supports. The other is to encapsulate the catalyst in microporous solids such as zeolite. The proportion of active metal sites is often low in the polymer-supported systems, and catalytic activity is also low.

In order to isolate catalytic active centers of complex catalysts without decreasing the proportion of active metal sites, the polymeric metal complexes were employed, such as polymeric porphyrin complexes [13], coordination polymers

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Scheme 1. Preparation of the heterodinuclear Salen-crown ether polymeric complex.

and polynuclear Schiff base complexes [14]. It has been revealed that the heterogenization of homogeneous catalysts is a good way to render them practicable and improve stability and selectivity because of polymer environment. They can also be recovered and reused. Therefore, application of polymer complexes in organic transformation has been receiving attention.

Recently, a few papers have reported that benzo-crowned Schiff base complexes showed significantly improved dioxygen affinities and biomimetic catalytic performance compared to the uncrowned analogues. Co-complexation of a hard cation close to the transition-metal center is believed to play an important role in perturbing its oxygen-binding properties [15–17]. However, to our knowledge, there are no reports about the polymer Salen Schiff bases complexes which combine crown ethers in the polymer chain. After successfully synthesizing Co–Na heterodinuclear Salen-crown ether polymeric complexes [P-SalPhen-dSdB18C6-(Co–Na)] which derived from the condensation of 2,4-dihydroxybenzaldehyde with bis(chlorosulfonyl)dibenzo-18-crown-6 [18], we have also synthesized the heterodinuclear Salen-crown ether polymeric complex [P-Salen-BsdB18C6-(Co–Na)] by condensation polymerization of 2,4-dihydroxybenzaldehyde with ethylenediamine and bis(chlorosulfonyl)dibenzo-18-crown-6 (Scheme 1). Herein, details of preparation, characterization and catalytic oxidation behavior of this new heterodinuclear polymeric complex [P-Salen-BsdB18C6-(Co–Na)] are reported. It is shown that this complex catalyzes efficiently the oxidation of cyclohexene, alkylbenzenes and linear aliphatic olefins with molecular oxygen without any solvents or reducing agents.

## 2. Experimental

### 2.1. Materials

Both dibenzo-18-crown-6 and 2,4-dihydroxybenzaldehyde were obtained from Aldrich. Cyclohexene was purified by fractional distillation just before use. Other reagents and metals salts were commercially available.

### 2.2. Physical measurements

IR spectra were recorded in KBr disks with an Alpha-centauri FT-IR spectrophotometer. XPS (small area X-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System (Power Source by Mg K $\alpha$  line and Ag 3d<sub>5/2</sub> FWHM  $\leq$  0.48 eV). The thermal analysis was recorded on a Shimadzu DT-40 Thermal Analyzer (10 °C/min). Scanning electron micrograph (SEM) was obtained using a Hitachi S-450 scanning electron microscope. The oxidation reaction products were determined and analyzed by a Shimadzu GC-16A gas chromatograph-QP-1000A GC/MS system.

### 2.3. Synthesis

#### 2.3.1. Synthesis of Co(di-OHSalen) (1)

The Co(di-OHSalen) (1) was synthesized using Co<sup>2+</sup> as template. Firstly, 2,4-dihydroxybenzaldehyde (1.38 g, 10 mmol) and ethylenediamine (0.3 g, 5 mmol) were dissolved in propanol with stirring, and then the solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.225 g, 5 mmol) in 10 mL of water was added. Under N<sub>2</sub>, the mixture was stirred at 60 °C for 8 h. The product was filtered and washed by H<sub>2</sub>O and alcohol three times, respectively. After vacuum drying, the reddish brown powder was obtained with a yield of 76%.

#### 2.3.2. Synthesis of bis(chlorosulfonyl)dibenzo-18-crown-6 (2)

Bis(chlorosulfonyl)dibenzo-18-crown-6 (2) was prepared from dibenzo-18-crown-6 [19,20]. The reagent of HSO<sub>3</sub>Cl (23.3 g, 0.2 mol) was added dropwise to the chloroform solution of dibenzo-18-crown-6 (3.6 g, 0.01 mol) cooled in an ice-bath under Ar. The reaction mixture was stirred for 9 h at room temperature, and then poured into ice. Then the organic phase was dried by CaCO<sub>3</sub>. After filtration, the filtrate was evaporated in vacuum to dryness and recrystallized from ethyl acetate/acetonitrile to provide white powder, yield of 54%.

#### 2.3.3. Synthesis of P-Salen-BsdB18C6-(Co–Na) (3)

The P-Salen-BsdB18C6-(Co–Na) (3) was successfully synthesized using interfacial condensation polymerization [21].

Owing to the phase transfer ability of crown ether, the condensation polymerization and coordination of sodium ion occurred at the same time at a high rate. The chloroform solution of bis(chlorosulfonyl)dibenzo-18-crown-6 (0.557 g, 1 mmol) was added dropwise into the NaOH solution (0.4 mol/L, 5 mL) of Co(di-OHSalen) (0.357 g, 1 mmol) with vigorously stirring. After the reaction for 2 h at room temperature, the crude product was isolated by filtration, and washed separately with H<sub>2</sub>O and acetone. The black polymer complex (**3**) was obtained with a yield of 82% after vacuum drying.

#### 2.4. Procedure of oxidation

The oxidation of organic substrate by atmospheric pressure of molecular oxygen was carried out using a straightforward apparatus. In a typical oxidation reaction, 2 mL of substrate and given amount of catalyst (P-Salen-BsdB18C6-(Co-Na)) were added to a glass reactor (10 mL). The reactor was filled with molecular oxygen using the gauge glass, and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The mixture was heated to a constant temperature in an oil bath and stirred with a magnetic stirring bar. The consumption of oxygen was measured and calculated by the gauge glass. At the end of the reaction time, liquid samples were removed from the reactor vessel and analyzed by GC and GC-MS techniques.

### 3. Results and discussion

#### 3.1. Characterization

##### 3.1.1. The IR spectra

The IR spectrum of P-SalEten-bSdB18C6-(Co-Na) was measured and compared with that of the monomer [22]. The absorption of S=O double bond of symmetrical stretching vibration appeared at 1118 cm<sup>-1</sup>, and the asymmetrical stretching vibration at 1362 cm<sup>-1</sup>. The stretching vibrations of C=N and Ph-O bond appeared at 1630 and 1227 cm<sup>-1</sup>, respectively. The weak absorption peaks at 466 and 527 cm<sup>-1</sup> are attributed to the Co-N and Co-O bonds, respectively. The -CH<sub>2</sub>-O-CH<sub>2</sub>- absorption peaks shifted from 1268, 1174 and 1088 cm<sup>-1</sup> to 1263, 1180 and 1036 cm<sup>-1</sup>, respectively, indicating that sodium ion is coordinated to oxygen in crown ether.

##### 3.1.2. X-ray photoelectron spectroscopy

In order to confirm the coordination of polymer ligand with cobalt and sodium ions, the Co-Na heterodinuclear polymer complex (P-Salen-BsdB18C6-(Co-Na)) and monomer (Co(di-OHSalen)) were characterized by XPS [23]. It was found that the binding energies of Co(2p<sub>1/2</sub>) and Co(2p<sub>3/2</sub>) of P-Salen-BsdB18C6-(Co-Na) were 795.5 and 780.6 eV, respectively, and those of Co(di-OHSalen) were 796.1 and 780.2 eV, respectively. In P-Salen-BsdB18C6-(Co-Na), the Co<sub>2p</sub> binding energies of the complex increased by 0.5 eV compared with those of the cobalt acetate (Co(2p<sub>1/2</sub>): 795.0 eV, Co(2p<sub>3/2</sub>): 779.6 eV). These results indicate that the charge on the cobalt atoms decreased when the complex was formed. Furthermore, compared to the binding energy of Na(2s<sub>1/2</sub>) of NaCl, the chemical shift of that of

P-SalPhen-bSdB18C6-(Co-Na) was about 0.7 eV from 1072.5 to 1071.8 eV. All these results indicate that cobalt and sodium ion were successfully introduced into the framework of the polymer.

The contents of C, H and N was measured with the elemental analyzer, being found to be C% (45.5), H% (4.0), N% (3.1). They were similar to the calculated values of unit formula (P-SalPhen-bSdB18C6-(Co-Na): C<sub>36</sub>H<sub>34</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>CoNaCl + 3H<sub>2</sub>O): C% (45.3), H% (4.2), N% (2.9). It also showed that water molecule was absorbed on to the polymeric metal complex.

##### 3.1.3. Scanning electron microscopy

The morphologies and surface image of the monomer and P-Salen-BsdB18C6-(Co-Na) were further examined with scanning electron microscopy. Fig. 1 reveals their surface images. It shows that monomer was crystal and the polymer complex was different from the monomer.

##### 3.1.4. Thermal stability of the polymeric Schiff base complexes

Thermal stability of the P-Salen-BsdB18C6-(Co-Na) was studied using TG-DTA analysis, which showed that the polymer complex decomposed above 300 °C.

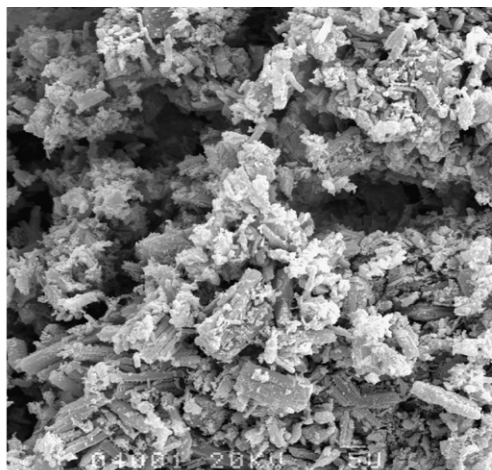
#### 3.2. Oxidation of cyclohexene by O<sub>2</sub>

Cyclohexene (**4**) was chosen as a model substrate because both allylic oxidation and epoxidation are possible. It was found that oxidation preferentially happened in the activated allylic C-H bond, which afforded 2-cyclohexene-1-one (C=O) (**5**), 2-cyclohexene-1-ol (-OH) (**6**) and 2-cyclohexen-1-hydroperoxide (-OOH) (**7**). Only a little cyclohexene epoxide was formed (Scheme 2).

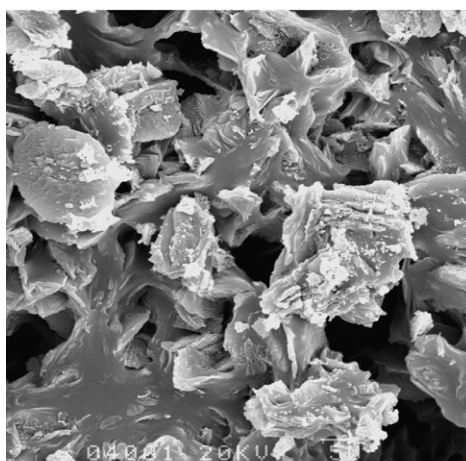
In order to understand how the products are formed and changed, the oxidation of cyclohexene with molecular oxygen was performed without any solvents or additional additives. The distribution of products in the period of the catalytic oxidation is demonstrated in Fig. 2. The contribution of the epoxide was not taken into account because its yield was very low. In the first instance, owing to the presence of high concentration of 2-cyclohexen-1-hydroperoxide (-OOH), the total selectivity for 2-cyclohexen-ol (-OH) and 2-cyclohexen-1-one (C=O) was relatively low. But the total selectivity for alcohol (-OH) and ketone (C=O) increased slowly along with decreasing selectivity for 2-cyclohexen-1-hydroperoxide. After the reaction for 8 h, hydroperoxide (-OOH) was decomposed completely. The selectivity for alcohol (-OH) was always higher than that of ketone (C=O). It can be deduced that 2-cyclohexen-ol (-OH) and 2-cyclohexen-1-one (C=O) as main products of the reaction derived from the decomposition of 2-cyclohexen-1-hydroperoxide (-OOH), and its mechanism is consistent with the classic Haber-Weiss radical-chain sequence mechanism which we will discuss later.

##### 3.3. Kinetics study of the oxidation of cyclohexene

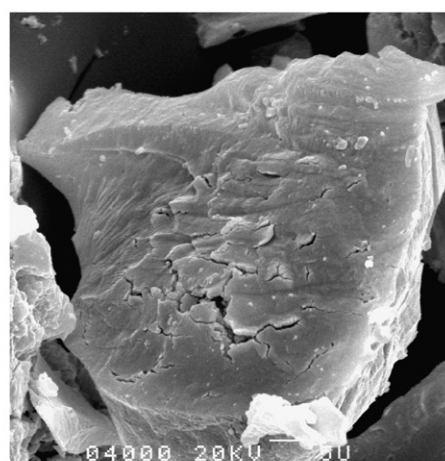
A further series of experiments was carried out in order to test the effect of temperature, substrate ratio and additives on



Co(di-OHSalen) ( 1 )



BsdB18C6 ( 2 )



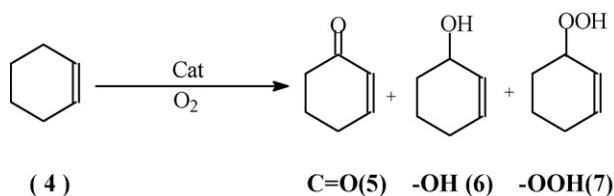
P-Salen-BsdB18C6(Co-Na) ( 3 )

Fig. 1. Images of monomer and polymer complex under scanning electron microscopy.

the catalytic oxidation of cyclohexene by the polymer complex (P-Salen-BsdB18C6-(Co-Na)).

### 3.3.1. Effect of temperature

The oxidation of cyclohexene was found to be very slow at room temperature (25 °C). It was also difficult to initiate the reaction if the temperature was below 50 °C. Better results of catalytic oxidation are obtained in the temperature range of 50–80 °C. Fig. 3 shows the relationship between the conversion and the reaction time at different reaction temperatures. It shows that the conversion increased substantially with increasing temperature from 50 to 70 °C. It is interesting to note that



Scheme 2. Aerobic oxidation of cyclohexene catalyzed by P-Salen-BsdB18C6-(Co-Na).

the selectivity was effected by temperature (Fig. 4). At 50 °C, the selectivity for 2-cyclohexen-1-one (C=O), 2-cyclohexen-ol (-OH) and 2-cyclohexen-1-hydroperoxide (-OOH) was 23.4, 25.2 and 46.5%, respectively. At 70 °C, the total selectivity for

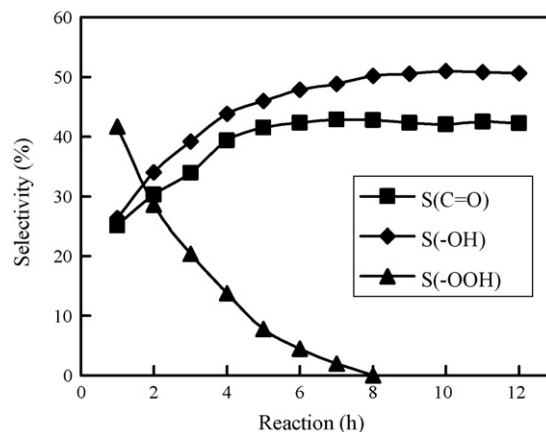


Fig. 2. Oxidation products distribution with reaction time. Conditions: Cyclohexene, 2 mL; Cat., 1.0 mg; Temp., 70 °C, 1 atm O<sub>2</sub>.

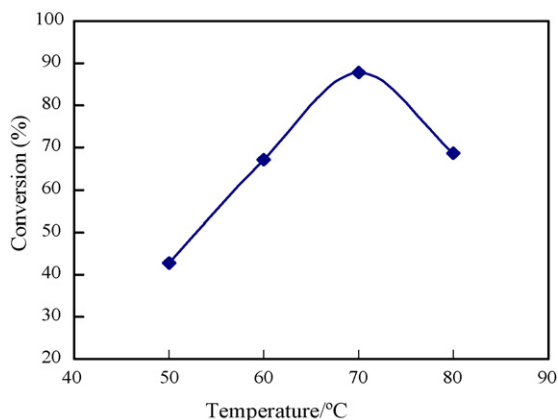


Fig. 3. Effect of temperature on catalytic activity of the polymer complex. Conditions: Cyclohexene, 2 mL; Cat., 1.0 mg; 1 atm O<sub>2</sub>; 12 h.

–OH and C=O increased to 92.8%, and –OOH nearly disappeared, which indicated that raising the reaction temperature promoted the decomposition of hydroperoxide and facilitate reaction. So it is necessary to raise the reaction temperature in order to initiate the reaction to afford 2-cyclohexen-1-one (C=O) and 2-cyclohexen-ol (–OH) in high concentrations. But the reaction rate decreased when the temperature was higher than 70 °C. Cyclohexene is easy to be vaporized if the temperature is higher than 70 °C. Then the catalytic active center is difficult to establish contact with the substrate and oxygen together, resulting in low catalytic activity. Furthermore, we studied the catalytic activity of monomer cobalt complex Co(di-OHSalen) in the oxidation of cyclohexene at optimum temperature; the conversion was less than 65%. The selectivities were as follows: C=O (38.5%), –OH (49.2%), epoxide (6.8%). Namely, the catalytic activity of Co(di-OHSalen) was lower than that polymeric metal complex (P-Salen-BsdB18C6-(Co–Na)), while it was similar in the selectivity for the polymer complex.

### 3.3.2. Effect of the amount of catalyst used on the reactivity

The oxidation was carried out at 70 °C by varying the amount of catalyst. The results are shown in Table 1. It was observed

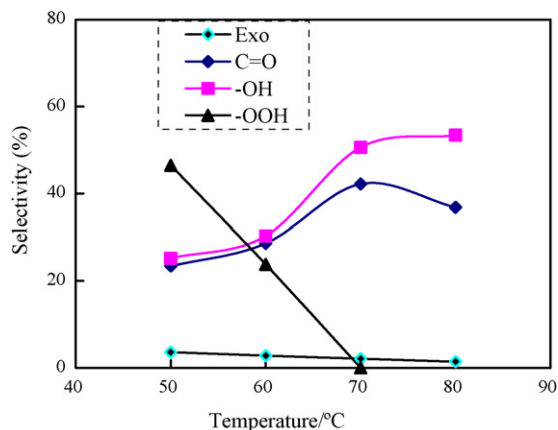


Fig. 4. Effect of temperature on product selectivity. Conditions: Cyclohexene, 2 mL; Cat., 1.0 mg; 1 atm O<sub>2</sub>; 12 h.

Table 1  
Effect of the amount of catalyst on aerobic oxidation of cyclohexene

Amount of catalyst (mg)	Conversion (%)	Selectivity (%)			
		Exo	C=O	–OH	–OOH
0.5	82.8	5.6	39.5	42.5	8.6
1.0	87.8	2.1	42.2	50.6	–
1.5	91.4	1.8	41.4	51.3	–
2.0	86.2	1.6	40.1	52.8	–

Conditions: Cyclohexene, 2 mL; 1 atm O<sub>2</sub>; 70 °C; 12 h.

the conversion of cyclohexene increased from 82.8 to 91.4% when the amount of catalyst was increased from 0.5 to 1.5 mg. Further increasing the amount of catalyst, however, resulted in the decrease in the conversion to 86.2%. This phenomena may be due to fast decomposition of 2-cyclohexen-1-hydroperoxide (–OOH) acting as radical intermediate in the presence of excess of the catalyst.

### 3.3.3. Effect of the additives

The catalytic activity of P-Salen-BsdB18C6-(Co–Na) is sensitive to additives. We investigated the effect of three types of additives, organic acid, base and co-reductant (Fig. 5). When a trace of acetic acid (0.1 mL) was added to the oxidation system, the rapid oxygen consumption was observed at the beginning of oxidation. But the reaction rate decreased quickly after 8 h. The conversion was only 72.5%, and the selectivity for 2-cyclohexen-1-ol (–OH) increased slightly. This indicates that acetic acid caused decomposition of the catalyst. The pyridine made the catalytic efficiencies very low (52.5% conversion), which is attributed to the donor nitrogen atom of pyridine with high ability to coordinate with center metal of transition metal complex, inducing a significant decrease in the redox potentials [24]. To our surprise, the addition of isobutanol as co-reductant could not prompt the activity of the catalyst and the conversion decreased to 77.8%. It indicates that the presence of isobutanol maybe causes a kinetic barrier for the approach of active intermediate species toward the catalytically active center.

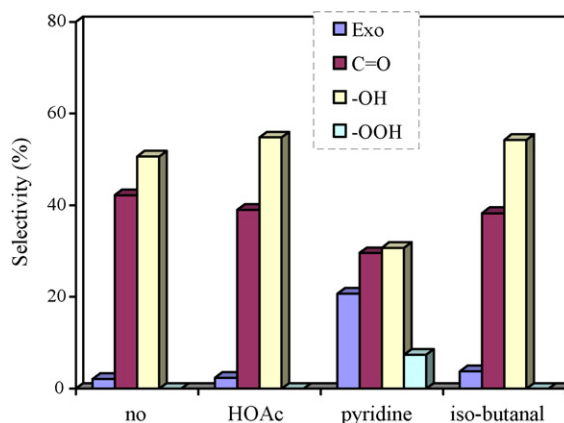


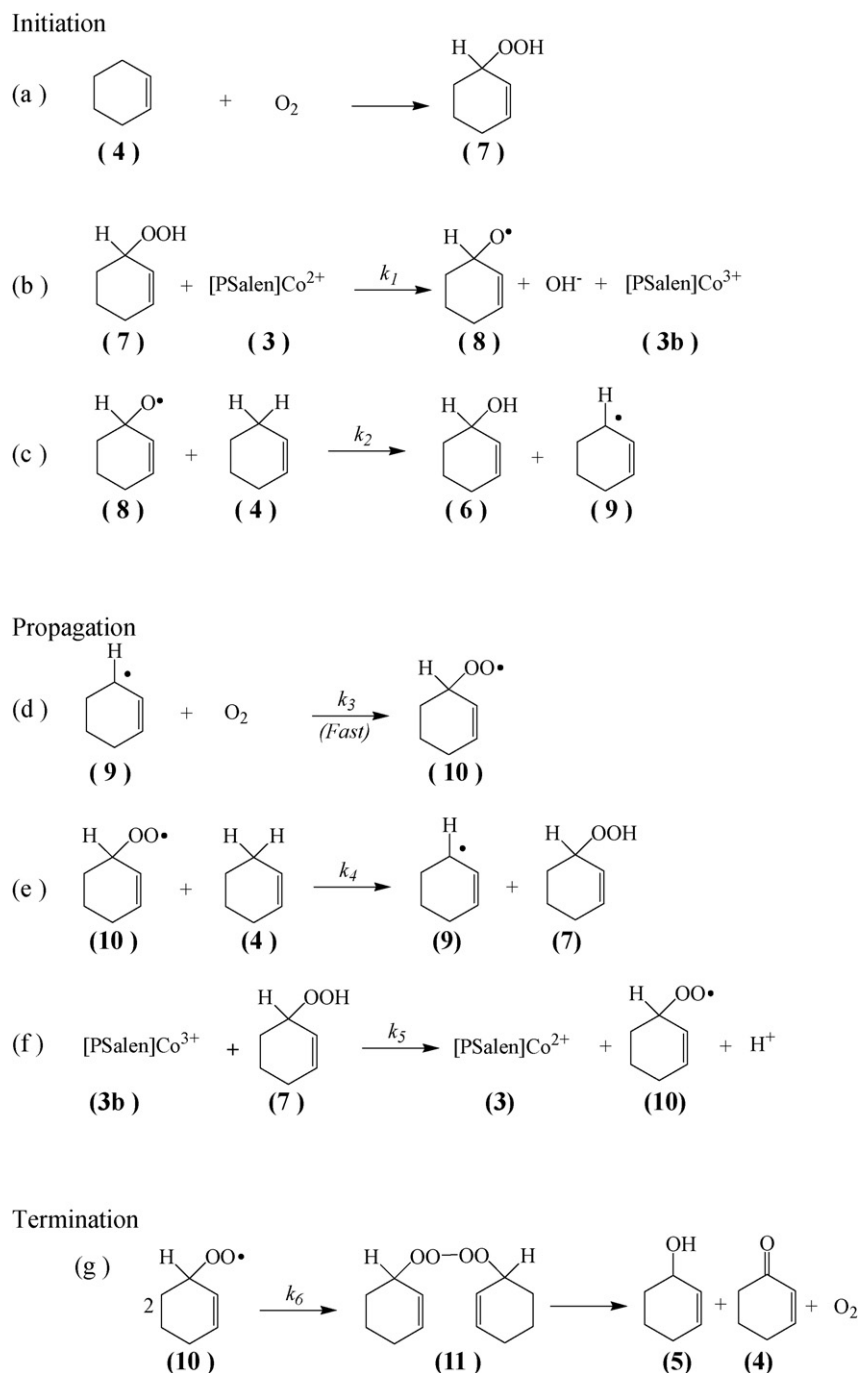
Fig. 5. Effect of the additives on the product selectivity. Conditions: Sub., 2 mL; Cat., 1.0 mg; additive, 0.1 mL; 1 atm O<sub>2</sub>; 70 °C; 12 h.

#### 4. Mechanism

The aerobic oxidation of alkanes and alkenes catalyzed by halogenated porphyrin has been studied in detail [10,25]. It has been concluded that the reaction involves the formation and decomposition of alkyl peroxide and carries on a radical-chain sequence mechanism. Subsequently, a series of Salen derivatives bearing electronegative substituents and their corresponding iron(III) complex was examined on catalytic properties in the oxidation of cyclohexene using molecular oxygen as oxidant [12]. The results indicated that all the observations

for Salen Schiff base complex point to the same radical chain auto-oxidation mechanism as previously established for the metalloporphyrin-catalyzed oxidation of different hydrocarbons, where the primary role of the metal is to catalytically decompose the hydroperoxide by alternate reduction and oxidation.

In order to obtain more evidence to confirm that the aerobic oxidation of cyclohexene catalyzed by P-Salen-BsdB18C6-(Co-Na) is also a radical chain aerobic oxidation mechanism, we investigated the effects of radical initiator and inhibitor on the catalytic reaction. An induction period was observed during the early stages, where negligible conversion is obtained.



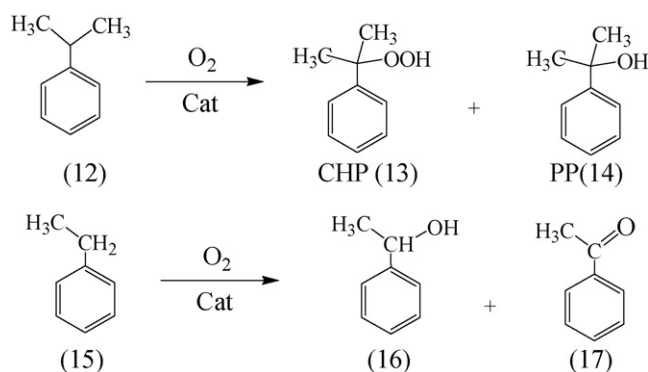
Scheme 3. The classic Haber–Weiss radical-chain sequence mechanism of which applied to aerobic oxidation of cyclohexene catalyzed by PSalenCo.

It represents the time required for the formation of the free radicals in the oxidation of cyclohexene catalyzed by P-Salen-BsdB18C6-(Co-Na) in the absence of any radical initiators. Addition of *tert*-butyl hydroperoxide (about 0.05 mL) substantially accelerated the oxidation during early stages of reaction. It indicates that the peroxide (–OOH) served only to shorten the induction period. Conversely, the oxidation was inhibited, or stopped completely if appropriate radical traps were added to the reaction system. If 10 mg of hydroquinone, free-radical trap, was added into the oxidation system with P-Salen-BsdB18C6-(Co-Na), the induction period elongated to about 4 h (versus ca. 0.5 h under normal conditions), and the conversion of cyclohexene was only 12.4% after 12 h. The oxidation was stopped completely if the amount of hydroquinone exceeded 20 mg. The same phenomena were observed by addition of asafetida and thiourea. Overall, the results of these inhibitor studies are consistent with the radical-chain autoxidation pathway [12,26].

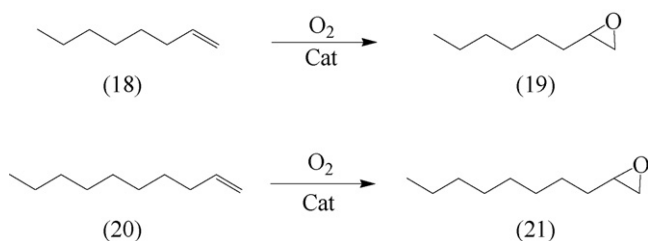
Following the classic Haber–Weiss radical-chain sequence mechanism [27–29], the aerobic oxidation of cyclohexene catalyzed by P-Salen-BsdB18C6-(Co-Na) [Abbr. as PSalenCo] is proposed as Scheme 3. The main function of catalyst [PSalenCo] is to serve as electron-transfer chain initiator,  $\text{Co}^{2+}/\text{Co}^{3+}$ , step (b), and resultant alkylhydroperoxide oxidizer ( $\text{Co}^{3+}/\text{Co}^{2+}$ ), step (f). In contrast to base, acid can promote the decomposition of hydroperoxide. In steps (a) and (b), adding acetic acid can accelerate the reaction rate at the beginning of oxidation and make the selectivity for 2-cyclohexen-1-ol (–OH) raise slightly. As the reaction rate decreased with the time owing to the decrease in substrate amount in the process of oxidation, we considered that the concentration of substrate in the reaction mixture dominates over the reaction rate in the propagation period (step e). The chain termination is dominated by the classic Russell tetraoxide intermediate pathway, step (g). In this pathway, two cyclohexenyl peroxy radicals combine to the resultant tetraoxide intermediate. Then it is decomposed to 2-cyclohexen-1-ol (–OH) and 2-cyclohexen-1-one (C=O). Based on this mechanism, the yield of 2-cyclohexen-1-ol (–OH) is higher than that of 2-cyclohexen-1-one (C=O), which is consistent with our results. The alkyl hydroperoxide decomposition mechanism does not directly address the origin of epoxides, which may be formed via different mechanisms.

#### 4.1. Catalytic aerobic oxidation of alkylbenzenes

The possibility of oxidizing primary alkyl substituents attached to an aromatic framework was examined by studying the catalytic oxidation of toluene, ethylbenzene and cumene (Scheme 4). Under dioxygen, the reaction mainly took place on the benzyl carbon of the alkylbenzenes. In the catalytic oxidation of cumene (**12**) the conversion was 59.1% and the products selectivity for cumene hydroperoxide (CHP) (**13**) and 2-phenyl-2-propanol (PP) (**14**) were 37.5 and 56.8%, respectively. The oxidation of ethylbenzene (**15**) was carried out in similar conditions. The conversion was 24.6% with product of  $\alpha$ -methyl benzyl alcohol (**16**) (60.7%) and of acetophenone (**17**) (38.3%). But toluene cannot be oxidized. Furthermore, we monitored the molecular oxygen adsorption rate and found the reaction rate of



Scheme 4. Aerobic oxidation of alkylbenzene catalyzed by P-Salen-BsdB18C6-(Co-Na). Conditions: Sub., 2 mL; Cat., 1.0 mg; 110 °C; 1 atm  $\text{O}_2$ ; 12 h.



Scheme 5. Aerobic oxidation of linear aliphatic olefins catalyzed by P-Salen-BsdB18C6-(Co-Na). Conditions: Sub., 2 mL; Cat., 1.0 mg; 1 atm  $\text{O}_2$ ; 12 h; 100 °C for (**18**) and 110 °C for (**19**).

cumene was always higher than that of ethylbenzene. The induction period in the oxidation of ethylbenzene was about 2 h. However, it was very short for cumene. These results indicate that methyl groups substituted for the benzylic hydrogens can stabilize the benzyl radical which can induce radical propagation.

#### 4.2. Catalytic oxidation of linear aliphatic olefins

The activity of the P-Salen-BsdB18C6-(Co-Na)/ $\text{O}_2$  system towards linear aliphatic olefins was examined using 1-octene, 1-decene and 1-dodecene as substrate without any solvents or sacrificial reductants. In the case of linear aliphatic olefins, the allylic hydrogen was not predominantly active. Therefore, epoxide was formed. Compared to cyclohexene and alkylbenzenes, the lower activity and selectivity were obtained. 1-Octene (**18**) and 1-decene (**20**) showed 31.4 and 22.7% conversion with 56.1 and 82.0% of selectivity for corresponding epoxides (**19**, **21**), respectively. However, only trace quantity of 1,2-epoxide was detected for 1-dodecene. It suggested that the longer the alkyl chain of olefin, the more obstructed the access to the active center of catalyst (Scheme 5).

## 5. Conclusions

A new kind of heterodinuclear polymer complex based on Salen Schiff base and crown ether is successfully synthesized and applied to catalytic aerobic oxidation of hydrocarbons, which utilizes molecular oxygen as the oxidant at atmospheric pressure and mild temperature in the absence of any solvents

or the sacrificial co-reductants. High conversions for cyclohexene are observed and the high selectivity for allylic oxidation products shows the attack of the activated C–H bond predominates over that of the C–C bond. Furthermore, kinetics study and the effect of radical initiator and inhibitor attest to a free radical mechanism. This oxidation system is also efficient in the oxidation of alkylbenzenes and linear aliphatic olefins. The alkylbenzenes are more reactive than the terminal olefins.

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