

Synthesis and study of binuclear calix[4]arene Schiff base Co(II) complexes as catalyst in the presence of PhIO for the catalytic oxidation of olefin

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Abstract The binuclear Co(II) complexes of calix[4]arene substituted 2-vanillin (R_1) and 2-hydroxy naphthalaldimine (R_2), Schiff bases (Co_2L^1 and Co_2L^2) have been synthesized, characterized and employed as models to mimic monooxygenase in the catalytical oxidation of olefins. The kinetic mathematical model (oxygen rebound mechanism) for olefin cleavage catalyzed by the complexes has been proposed. The results show that, compared to the calix[4]arene-free analogous, the mono and multinuclear complexes of calix[4]arene Schiff bases as catalyst exhibit high activity in the olefin catalytic oxidation.

Keywords Calix[4]arene Schiff base · Binuclear Co(II) complexes · Catalytic oxidation · Olefin

Introduction

Molecular oxygen would be the most desirable oxidant in organic synthesis in terms of costs and environmental considerations. Efforts have long been focused on the development of O_2 -mediated oxidation methods [1–3]. Cobalt Schiff base complexes are often described as good epoxidation catalysts, due to their high activity and selectivity [4]. However, for its practical application, the catalyst should be easy to synthesize and stored display high reactivity (turnover frequency), selectivity, and durability (turn over number), using reasonably priced and environment friendly [5–7]. For a number of years, we have studied the reactions of iodosylbenzene with olefins

catalyzed by metal ions and complexes of ligands other than porphyrins [8, 9]. The method is mild and is an environment friendly process. However, the cost of porphyrin is high. It was also found that Schiff base complexes are effective catalysts for aerobic oxidation of olefins [10]. Parallel to the porphyrin chemistry, the same catalytic reactions are mimicked by various transition metal complexes, in particular Schiff base complexes, because of their cheap and easy synthesis and chemical and thermal stability [11–14].

A number of previous works on phase transfer catalysis showed that cyclodextrins and cyclodextrin based calix[4]arene catalysts [15–19], which combine the properties of phase transfer agent and metal complex with the function of molecular recognition, can change the reaction selectivity and can increase the activity of catalysts. There are very limited studies on the oxidation of an olefin catalyzed by calix[4]arene metal complexes. Recently, a few papers have been reported where in calix[4]arene complexes have been used as oxidation catalyst and in alkene epoxidation [20, 21]. However, to our knowledge, there are no reports on the calix[4]arene Schiff base complexes and their catalytic oxidation study. In the present work, solid complexes of calix[4]arene Schiff bases (2-vanillin and 2-hydroxy naphthaldehyde) with the metal Co(II), were prepared and were used as catalyst for the oxidation of the olefins, e.g. styrene and cyclohexene.

Experimental

Materials

All the chemicals used were of A.R. Grade of Aldrich and E. Merck unless otherwise specified. Iodosylbenzene was

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prepared by the method reported by Lucas et al. [22]. The substrates, styrene, cyclohexene and oxidation products benzaldehyde, styrene oxide, cyclohexene oxide, cyclohexene-1-one were obtained from Aldrich.

Physical measurement

The spectra were scanned on Hitachi Model UV-3210 spectrophotometer. Discover BenchMate system-240V (CEM Corporation) microwave synthesizer was used for synthesis. The FT-IR spectra were recorded as KBr pellet on Bruker Tensor-27. The MALDI-TOF MS was run on a Micromass TofSpec 2E instrument, using a nitrogen 337 nm laser (4 ns pulse). ^1H NMR spectra was scanned on 400 MHz FT-NMR Bruker Avance-400 and ^{13}C NMR spectra was recorded on a Bruker DPX-300 spectrometer with tetramethylsilane (TMS) as internal standard in deuterated DMSO. Gas chromatographic/mass spectrometric (GC/MS) analyses were carried out using a Shimadzu GC-17A series gas chromatograph equipped with a SG BP 1 column (0.32 mm $\times$ 30 m) and helium as carrier gas and mass spectrometric detection was performed on QP5050 series A mass spectrometer. The electron spin resonance spectra were recorded using tetracyano ethylene (TCNE) as a reference standard which has $g = 2.00277$ on E112 ESR Spectrometer.

Synthesis of ligand

p-Tert-butylcalix[4]arene (**1**) was synthesized by microwave technique developed in our laboratory. The synthesis of the intermediates, debutylated calix[4]arene [23], azocalix[4]arene [24] and tetraaminocalix[4]arene [25] were according to the literature methods.

Microwave-assisted synthesis of 5,11,17,23-tetra-butyl-25,26,27,28 tetrahydroxyl calix[4]arene **1**

For the microwave synthesis of **1** (Scheme 1), 10 g of *p*-tert-butylphenol was mixed with NaOH (0.05 g, 1.2 mmol) dissolved 0.5 mL of water and 6.2 mL 37% formaldehyde solution and was heated in a Discover BenchMate system-240V (CEM Corporation) microwave at 300 W output power for 5 min to give a yellow solid. To this was added 7 mL of diphenyl ether and 1 mL toluene and the mixture was heated at 300 W output power for 15 min to obtain corresponding calix[4]arene. The purity was checked by TLC and the results of mp, FT-IR, ^1H NMR, ^{13}C NMR and MS were compared with standard sample.

Synthesis of calix[4]arene Schiff bases

Tetraaminocalix[4]arene (10 mmol) and aldehydes (40 mmol) (Scheme 2) in anhydrous ethanol (100 mL)

were stirred for 2 h under N_2 atmosphere. The yellow precipitate was filtered and recrystallized from ethanol and chloroform.

Calix[4]arene Schiff base, H_4L^1 Yield 2.5 g (83%), m.p. 120 °C. Anal. calc. for $\text{C}_{60}\text{H}_{52}\text{N}_4\text{O}_{12}$: C, 70.58; H, 5.13; N, 5.49%. Found: C, 70.61, H, 5.12; N, 5.47%. FT-IR (KBr) ν : 3221 cm^{-1} (–OH), 2958 cm^{-1} , 1603 cm^{-1} (CH=N). ^1H NMR (CDCl_3) δ 9.5 (s, 4H, Ar OH) 13.9 (s, 4H, Ar OH) 8.52 (s, 4H, Ar CH=N) 2.52 (s, 8H, CH_2) 7.15 (m, 12H, ArH) 7 (m, 8H, ArH) 3.83 (s, 12H, CH_3). ^{13}C NMR (CDCl_3) δ 160 (CH=N), 159, 151, 149, 144.7, 128.9, 127.8, 124.1, 119.6, 118.1 and 113 (ArC), 56.2 (–OCH₃), 13.0 (–CH₂–). MALDI-TOF MS (m/z) 1022(M + 1).

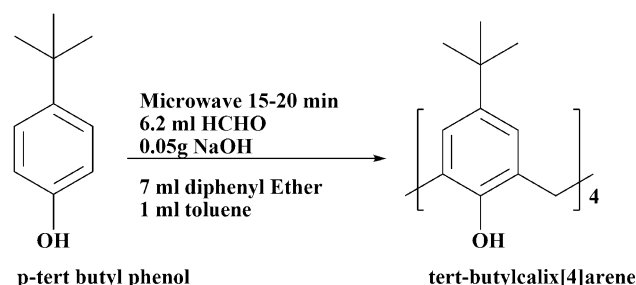
Calix[4]arene Schiff base, H_4L^2 Yield 2.5 g (83%), m.p. 205 °C. Anal. calc. for $\text{C}_{72}\text{H}_{52}\text{N}_4\text{O}_8$: C, 78.53; H, 4.76; N 5.09%. Found: C, 78.40; H, 4.79; N, 5.19%. FT-IR (KBr) ν : 3166 cm^{-1} (–OH), 1904 cm^{-1} , 1671 (CH=N) cm^{-1} . ^1H NMR (CDCl_3) 9.85 (s, 4H, Ar OH) 12.65 (s, 4H, Ar OH) 9.33 (s, 4H, Ar CH=N) 2.58 (s, 8H, CH_2) 7.83 (m, 24H, ArH) δ 7.02 (m, 8H, ArH). ^{13}C NMR (CDCl_3) δ 153.8 (CH=N), 172, 157, 145.1, 135.8, 129.1, 128.0, 127.8, 125.2, 124.9, 122, 118.6 and 116.4 (Ar C), 13 (–CH₂–). MALDI-TOF MS (m/z) 1103(M+).

Synthesis of calix[4]arene Schiff base metal complexes

A solution of H_4L^1 or H_4L^2 (1.0 mmol) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol) in anhydrous ethanol (30 mL) was stirred for 2 h under N_2 at 80 °C, then the mixture was cooled and filtered, washed with methanol to give metal complexes, and the pure product was obtained after recrystallization from ethanol (95%).

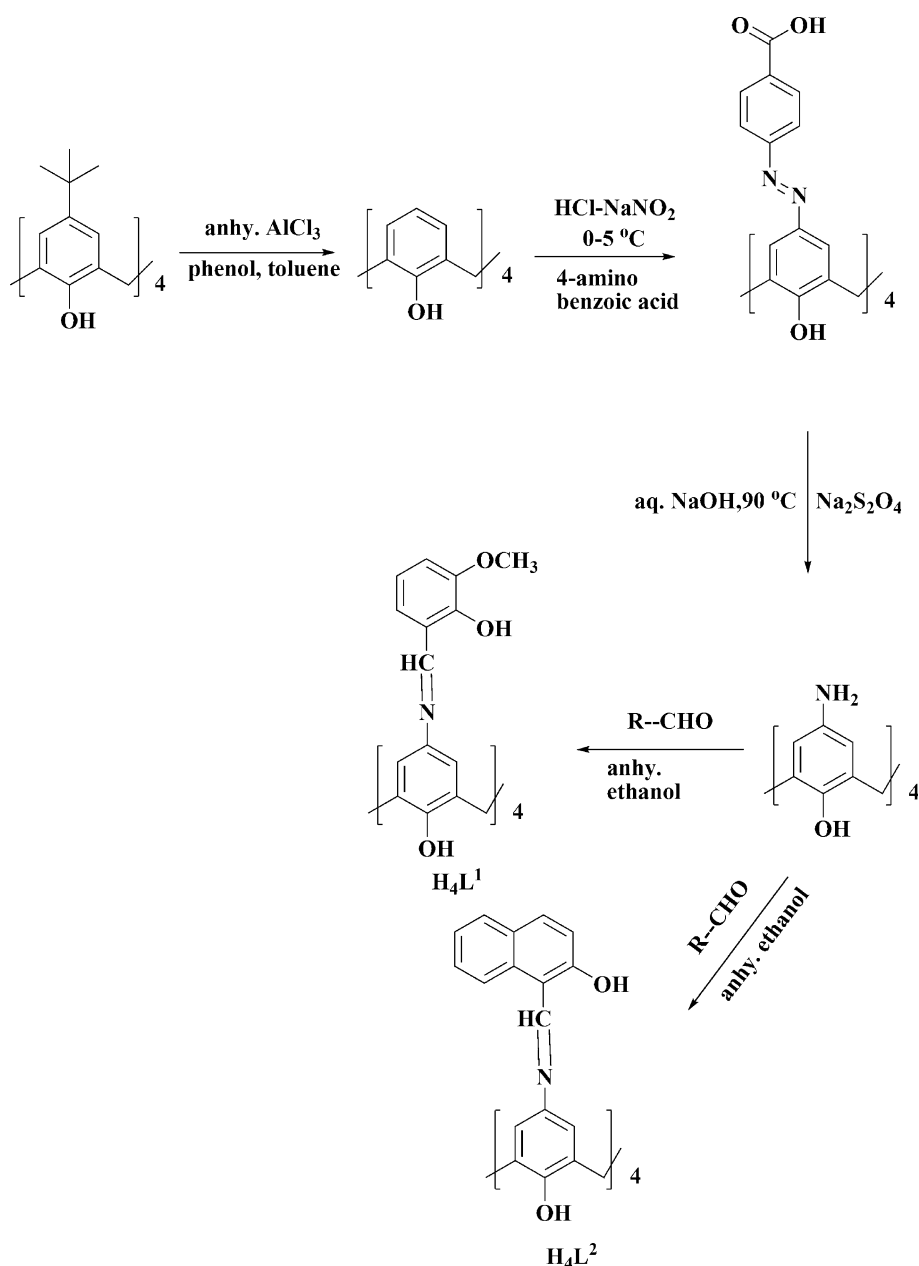
Co_2L^1 : dark brown, yield 77%, m.p > 223 °C. Anal. calc. for $\text{C}_{60}\text{H}_{48}\text{N}_4\text{O}_{12} \text{Co}_2$ Calcd: C, 70.58; H, 5.13; N, 5.49; M, 9.14%. Found: C 70.12, H 5.43, N 5.59, M 9.20%. FT-IR (KBr) ν : 3445 (–OH) cm^{-1} 1635 (–CH=N) cm^{-1} . MALDI-TOF MS (m/z) 1135(M + 1).

Co_2L^2 : dark brown, yield 77%, m.p > 245 °C. Anal. calc. for $\text{C}_{72}\text{H}_{48}\text{N}_4\text{O}_8 \text{Co}_2$: C, 78.53; H, 4.76; N, 5.09; M,



Scheme 1

Scheme 2



8.10% Found: C 78.10, H 4.89, N 5.29, M 7.28%. FT-IR (KBr) ν : 3245 ($-OH$) cm^{-1} , 1685 ($-CH=N$) cm^{-1} . MALDI-TOF MS (m/z) 1220 ($M + 1$).

Oxidation of olefins

All the reactions were carried out in a Schlenk tube under dinitrogen atmosphere. Styrene (2.5 mmol), catalyst (0.01 mmol) dissolved in a water-dioxane mixture (2:6 v/v) and chlorobenzene (internal standard) were mixed and the reaction mixture was de-aerated by flushing N_2 for 10 min. Iodosyl benzene (90.5 mmol) was then added and the reaction mixture was stirred for about 4 h. 2 μL aliquots were withdrawn from the

reaction mixture and analysed by gas chromatography. The reaction mixture was extracted with 3×20 mL dichloromethane, followed by the separation of the organic phase. The organic phase was washed with saturated $FeSO_4$ solution, dried over magnesium sulfate, evaporated and analysed by GC using the internal standard method. After 4 h there is no further increase in the yield of epoxide which indicates that the reaction is complete. Authenticated standard samples were used for the identity of the products; the total conversion and product distribution were evaluated with calibration curves, which were obtained by injecting known amount of authenticated standard. Products were identified by comparison with standard samples and by GC/MS.

Procedure for kinetic studies

Styrene and cyclohexene were used as the substrate for kinetic studies with complexes Co_2L^1 and Co_2L^2 as catalyst. All the kinetic studies were carried out at $25 \pm 1^\circ\text{C}$ using a thermostat. In one set of experiments various amounts of olefin (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 mmol) were taken keeping all the other factors constant. In another set, catalyst amount was similarly varied. Addition of PhIO was considered as zero time. Stirring was stopped for 1–2 min and aliquots (1 μL) were withdrawn every 15 min for GC analysis.

Initial rate for the reaction in all the kinetic studies was calculated by graphical method. Log [initial rate] was then plotted against log [catalyst] or log [olefin] using linear regression. The slope of the straight line thus obtained yielded the order of the reaction with respect to catalyst or alkene.

Result and discussion

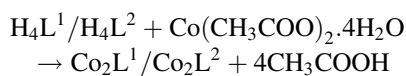
Physical characterization of calix[4]arene Schiff base and Co complexes

The synthesis scheme of calix[4]arene Schiff base is given in Scheme 2. The spectroscopic methods (FTIR, ^1H NMR, ^{13}C NMR and MALDI-TOF MS) have been employed to elucidate the structures of the compounds (H_4L^1 and H_4L^2). FTIR data show that the investigated bonds, which can be assigned to the stretching of imine ($\text{C}=\text{N}$) of both compounds were observed at the frequencies of $1593\text{--}1642\text{ cm}^{-1}$. The bands appearing at $3165\text{--}3425\text{ cm}^{-1}$ in the spectra of compounds can be ascribed to the presence of hydroxy ($-\text{OH}$) group.

^1H NMR data of the compounds showed a peak due to the presence of azomethine proton ($\text{CH}=\text{N}$) at the chemical shift $\delta = 8.52\text{--}9.35$ ppm. While the multiplet owing to the presence of aromatic protons was observed within the range of $\delta = 7.1\text{--}7.80$ ppm, the phenolic protons was observable within the range of $\delta = 9.45\text{--}13.92$ ppm.

^{13}C NMR data of the compounds showed a peak due to the presence of azomethane carbon ($\text{CH}=\text{N}$) observable at the chemical shift $\delta = 162$ and 151 ppm. The aromatic carbon showed peaks observable at $\delta = 171\text{--}114.3$ ppm; aliphatic carbon at $\delta = 57.4$ ppm and methylene bridge carbon showed peak at $\delta = 13.0$ ppm. The percentage of C, H and N from the analysis conform the calculated value. The percentage of metal was studied by AAS.

The synthesis scheme of Co complexes with the ligand is as given in the following equation:



The probable structures of Co(II) complexes are given in Figs. 1 and 2.

Thermal stability of calix[4]arene Schiff base complexes

Thermal stability of the calix[4]arene Schiff bases was studied using TG-DTA analysis, which showed that the complexes are stable and decomposed above 300°C .

ESR studies

The electron spin resonance spectra for the paramagnetic complexes were recorded using tetracyano ethylene (TCNE) as a reference standard which has $g = 2.077$. The ESR spectra of the complexes were recorded at room temperature in Table 1.

Oxidation of olefins

- (i) Oxidation of styrene and cyclohexene with Cobalt complexes of calix[4]arene Schiff bases are shown in Figs. 3 and 4.
- (ii) *Effect of the binuclear complexes on catalytic oxidation of styrene and cyclohexene* In order to investigate the effect of calix[4]arene ring on the catalytic oxidation performance of Co(II) Schiff base complexes, the oxidation of styrene and cyclohexene using PhIO as oxidant was chosen as a model reaction. The dioxygen affinities of Co(II) complexes were influenced greatly by the structure of the Schiff base. Calix[4]arene ring will probably favours oxygen molecule to approach the coordination center of Co(II) complexes and stabilize the bond of $\text{Co}=\text{O}$ for its hydrophobicity of outer ethylene group and orderly arrangement of inner oxa atom. $(\text{Co}_2)\text{L}^1$ and $(\text{Co}_2)\text{L}^2$ show more excellent catalytic oxidation performance in selectivities for styrene oxide compared to the other

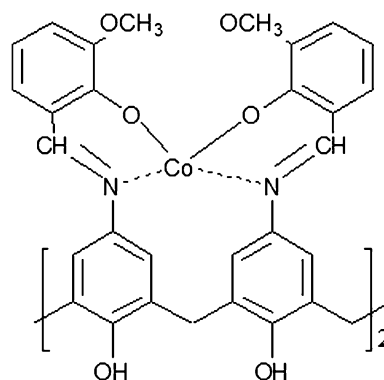


Fig. 1 Structure of Co_2L^1

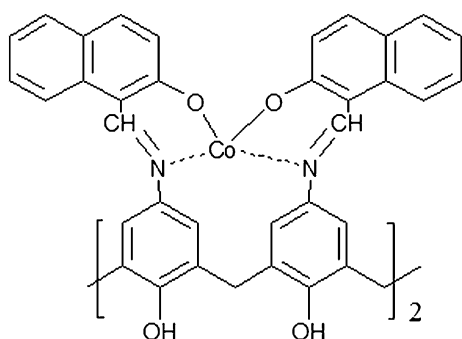


Fig. 2 Structure of Co_2L^2

Table 1 ESR spectral data of the complexes

Compound	Polycrystalline state (298 K Compound)					
	$g_{\parallel}$	$g_{\perp}$	g_{av}	G	$A_{\perp}$	$A_{\parallel}$
Co_2L^1	2.27	2.02	2.070	2.93	150	27
Co_2L^2	2.20	2.09	2.077	2.87	155	29

complexes reported [26] in the literature because of the presence of two metal centers.

- (iii) *Selection of single oxygen donor* The chemical catalytic oxidation with dioxygen requires the presence of a reducing agent in large excess (e.g. hydride [27], H_2/Pt [28], Zinc [29]) as well as a proton donor (CH_3COOH).

So far the most efficient catalytic method for olefin oxidation had been with ‘single-oxygen donors’ such as H_2O_2 or alkyl hydro peroxides, but with these reagents, the most selective reaction was observed when run in anhydrous conditions [30]. Concentrated solutions of these oxidants were sensitive to radical-chain decomposition [31]. NaOCl

is also known as a strong oxidant but it could not provide a good chemical model of P-450 enzyme, whereas Iodosylbenzene had given similar result as given by NaOCl and also it gave easy way to understand the Cytochrome P-450 enzyme model [32–34].

The oxidation of olefin is due to the macrocyclic effect of calix[4]arene rings that probably facilitates the oxygen molecules to approach the coordination center of $\text{Co}(\text{II})$ complexes and form the $\text{Co}=\text{O}$ bond through the hydrophobicity of the outer ethylene group and the orderly arrangement of the inner oxygen atoms. Moreover, the calix[4]arene ring’s special conformation in $(\text{Co})_2\text{L}^1$ and $(\text{Co})_2\text{L}^2$ can offer large steric hindrance, and possibly favor the formation of the active $\text{Co}=\text{O}$ and stabilize the species.

Catalytical reaction

- (i) *Oxidation of olefin with different manganese complexes of calix[4]arene Schiff bases* Oxidation of olefin with different Co complexes of calix[4]arene Schiff bases are shown in Tables 2 and 3 and the oxygen rebound mechanism are shown in Fig. 5.
- (ii) *Influence of olefin concentration on the selectivity of the reaction* The selectivity of this reaction was highly dependent of the initial concentration of olefin where the ratio catalyst/olefin is kept constant in Fig. 6. For a ratio of 0.4%, the selectivity increases from 40 to 100% by changing the olefin concentration from 0.5 to 3.5 mmol. At 2.5 mmol the conversion was completed within 4 h and the selectivity of styrene oxide reaches 99%. So the increase in olefin concentration up to 2.5 mmol leads to an efficient catalytical oxidation of styrene.

Fig. 3 Catalytic oxidation of styrene

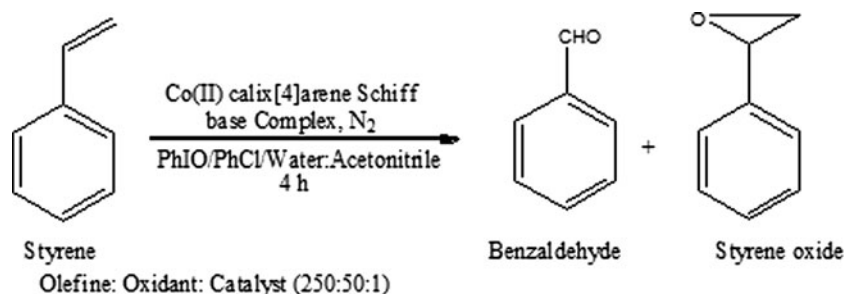
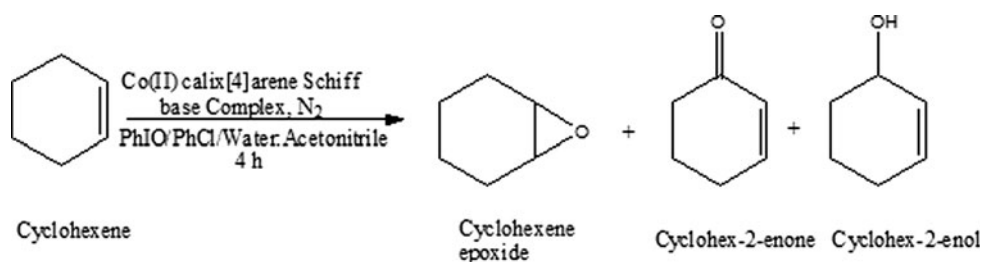


Fig. 4 Catalytic oxidation of cyclohexene



(iii) *Influence of the concentration of PhIO* The influence of catalyst concentration has been studied in the oxidation of 2.5 mmol of styrene in the presence of Co_2L^1 in Fig. 7 shows the cyclohexene epoxide formation for three different catalyst/olefin ratios: 0.25, 0.4 and 2.5% (0.0006–0.06 mmol of catalyst). The oxidation selectivity was nearly the same in all cases (70–80%). The main effect observed with an increase in catalyst/olefin ratio was the increase of the reaction rate. For small amount of complex (less

than 0.01 mmol), the conversion was not completed, most likely the formation of $\text{Co}=\text{O}$ of the catalyst after 6–8 h influence the concentration of PhIO

The influence of the concentration of PhIO had been studied in the oxidation of 2.5 mmol of styrene in the presence of Co_2L^1 in Fig. 8 shows the Styrene oxide formation for three different concentration of PhIO. The main effect observed with an increase in the concentration of PhIO was the increase of the reaction rate.

Table 2 The catalytical oxidation of styrene by Co(II) Schiff base complexes

Catalyst	Substrate	Product	Conversion ^a	TOF ^b	Epoxide yield	Selectivity ^c	Time (h)
Co_2L^1	Styrene	Styrene oxide	77	0.76	76	98.7	4
Co_2L^2	Styrene	Styrene oxide	74	0.73	73	98.6	4

Reaction was carried out at room temperature with Co(II) complex catalyst (0.01 mmol), the PhIO (0.1 mmol), styrene (2.5 mmol)

^a Conversion determined by GC using an internal standard

^b Turnover frequency is calculated by the expression $[\text{product}]/[\text{catalyst}] \times \text{time s}^{-1}$

^c Selectivity $[\text{epoxide yield (\%)/conversion (\%)}] \times 100$

Table 3 The catalytical oxidation of cyclohexene by Co(II) Schiff base complexes

Catalyst	Substrate	Product	Conversion ^a	TOF ^b	Epoxide yield	Selectivity ^c	Time(h)
Co_2L^1	Cyclohexane	Cyclohexane epoxide	90	0.90	87	96.66	4
Co_2L^2	Cyclohexane	Cyclohexane epoxide	96	0.96	82	85.41	4

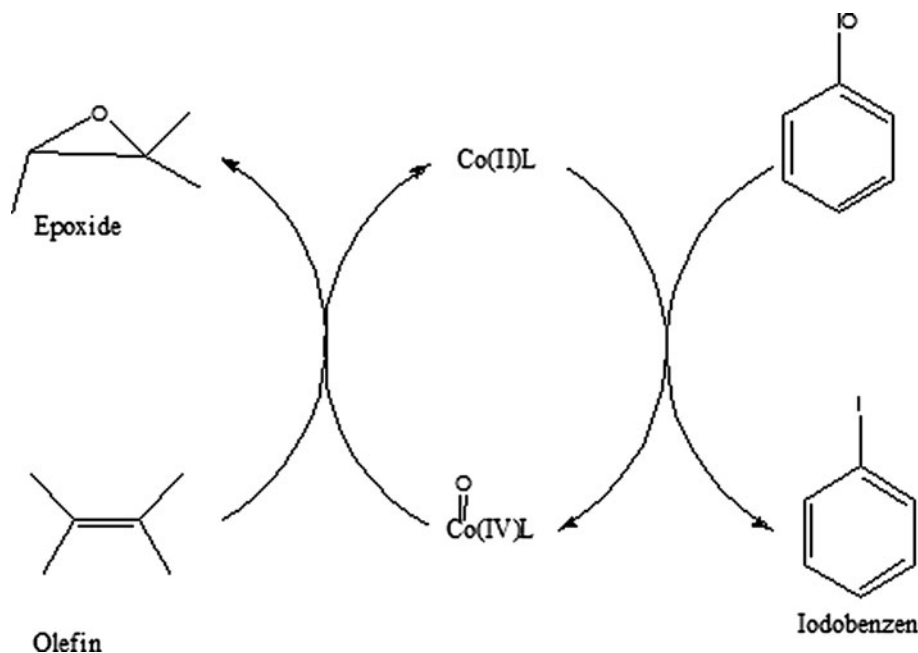
Reaction was carried out at room temperature with Co(II) complex catalyst (0.01 mmol), the PhIO (0.1 mmol), cyclohexene (2.5 mmol)

^a Conversion determined by GC using an internal standard

^b Turnover frequency is calculated by the expression $[\text{product}]/[\text{catalyst}] \times \text{time s}^{-1}$

^c Selectivity $[\text{epoxide yield (\%)/conversion (\%)}] \times 100$

Fig. 5 Oxygen rebound mechanism of Co(II) calix[4]arene Schiff base



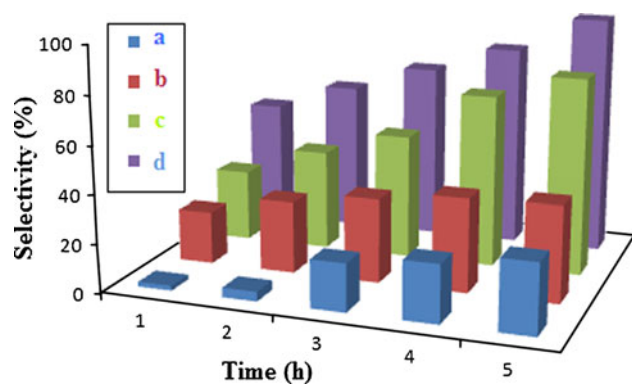


Fig. 6 Styrene oxidation at different initial concentration *a* 0.5 mmol, *b* 1.5 mmol, *c* 2.5 mmol, *d* % styrene oxide

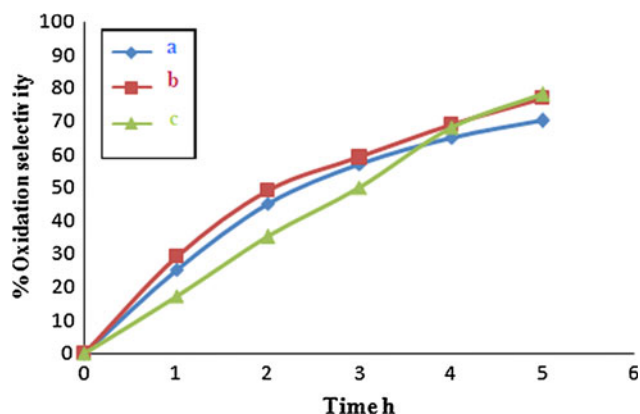


Fig. 7 Influence of the catalyst concentration of styrene oxidation *a* 2.5%, *b* 0.4%, *c* 0.25% PhIO

Kinetic study

The kinetic studies using different concentrations of styrene and cyclohexene using Co_2L^1 and Co_2L^2 as catalysts ($25 \pm 1^\circ\text{C}$) showed that the reaction was zero order with respect to alkene (slope = 0.1). This is expected, since a large excess of the alkene was being used, the reaction becomes virtually independent of the alkene concentration. Studies using various concentration was of fractional order with respect to the catalyst concentration (slope = 0.5). This supports the suggested reaction mechanism. Apparently, rate of the reaction does not depend directly on the concentration of the catalyst but is dependent on the

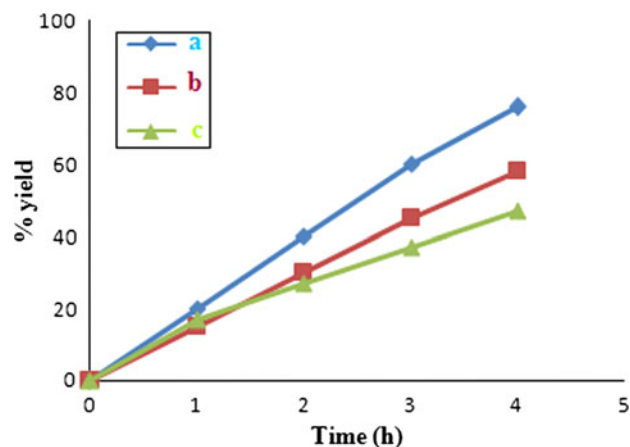


Fig. 8 Influence of concentration of PhIO on styrene oxidation *a* 0.2 mmol, *b* 0.4 mmol, *c* 0.6 mmol

intermediate $\text{Co}=\text{O}$ formed by the reaction of metal centre with the oxidant. Hence, order of the reaction is fraction with respect to catalyst concentration.

Catalyst reuse and stability

The stability of catalyst was studied in repeated epoxidation reactions. The epoxidation of styrene and cyclohexene was used for studying of catalyst reuse and stability. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration, washed with water and acetonitrile, and reused. After the use of catalyst for four consecutive times, the epoxide yield was 94%.

Comparison with the calix[4]arene-free analogous

The present method was compared with the other recently reported methods in Table 4. It was found that the time taken for conversion is very less compared to the other methods with an increase in the yield.

Conclusion

In conclusion, this study demonstrates the highly selective oxidation of styrene to styrene epoxide and cyclohexene to

Table 4 Comparison of present method with the other reported methods

Number	Name of the catalyst	Time (h)	Epoxide yield%	Reference
1	Mn(III) salen complexes	20	58	[35]
2	SalCo-NaB18C6	12	65	[36]
3	Cr(III)-binaphthyl Schiff base complexes	14	54	[37]
4	Present work	4	85	–

cyclohexene epoxide which has been successfully carried out in the presence of calix[4]arene Schiff base Co(II) complexes as catalyst. In the presence of catalytic amount of cobalt calix[4]arene Schiff base complexes, Iodosylbenzene is a good source of oxygen for olefin epoxidation. This new catalytic method of epoxidation occurs in mild conditions and is useful for selective oxidation.

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