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Epoxidation of alkenes using cost-effective green oxidant under eco-friend reaction condition

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The catalytic properties of the mononuclear non-heme iron(III) complexes with N_4-donor ligands containing N,N′-bis(2-pyridylmethyl)-diamine moiety (diamines used are, 1,2-cyclohexanediamine in complex **1** and ethane-1,2-diamine in complex **2**) have been investigated in the epoxidation of alkenes using green and environmentally benign hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (^{t}BuOOH) as terminal oxidants at room temperature. The analysis of the results obtained in the oxidation of cyclohexene suggests the involvement of radical-based pathway in the catalytic epoxidation reaction. The catalytic efficiency in terms of the yield of the oxidation products is found to be strongly dependent on the nature of the diamine moiety in the catalyst and the oxidant.

Keywords: Iron complexes, catalysis, alkenes, epoxidation, hydrogen peroxide, *tert*-butyl hydroperoxide.

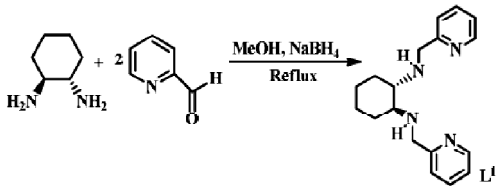
Introduction

Epoxidation of alkenes deserves special attention not only from an academic viewpoint, but also from an industrial perspective as epoxides are useful intermediates in various organic syntheses and are widely used as raw materials for epoxy resins, paints, food additives and surfactants[1]. Consequently, the epoxidation of alkenes has received great attention. Nature has evolved several iron-containing metalloenzymes to carry out alkene epoxidation selectively under very mild conditions[2]. Metalloporphyrins have always enjoyed a special preference as synthetic models for the reaction site of cytochrome P-450[3]. Numerous reports on metalloporphyrin-catalyzed epoxidation of alkenes with different terminal oxidants have appeared in the literature[4]. Apart from metalloporphyrins, metalloenzymes containing non-heme iron centres have been shown to promote novel oxidative chemistry[5]. Inspired by these iron-containing oxygenases, much effort has been invested in developing new families of non-heme iron catalysts[6]. Furthermore, developing systems using environmentally friendly conditions and cost effective terminal oxidants remains as an important challenge. Hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (^{t}BuOOH) have some advantages compared with conventional epoxidation reagents peracid, because they are cheaper, more environmentally clean and more readily available. Therefore, researchers have tried very hard recently to study the catalytic epoxidation of alkenes using green H_2O_2 and ^{t}BuOOH as terminal oxidants under eco-friend reaction conditions[7]. In this paper we wish to report the catalytic property of mononuclear non-heme iron(III) complexes containing N_4-donor ligands towards epoxidation of alkenes with mild and green H_2O_2 and ^{t}BuOOH at room temperature. The comparison between H_2O_2 and ^{t}BuOOH as the terminal oxidants in the alkene epoxidation reaction has also been studied.

Results and discussion

Synthesis and characterization:

The ligands L^1 and L^2 were synthesized according to the literature procedure[8]. Synthesis of the ligands involves the condensation of pyridine-2-carboxaldehyde and corresponding diamine (1,2-cyclohexanediamine in L^1 and ethane-1,2-diamine in L^2) in dry methanol at 60°C for 2 h followed by reduction with $NaBH_4$ by refluxing the reaction mixture for 16 h (Scheme 1). The synthesized ligands were characterized by IR and ^{1}H NMR spectroscopic techniques. The spec-



Scheme 1. Synthesis of ligand, L^1.

tral data of both the ligands are provided in the experimental section and are in good agreement with the reported data[9].

Synthesis and storage of non-heme iron(II) catalysts invariably require moisture and air-free conditions and are generally performed in inert gas-filled glove boxes. Therefore, straightway use of iron(III) catalysts for epoxidation of alkenes with green and environmentally benign oxidants provide an useful alternative in terms of the development of cost-effective catalytic system. Hence, an attempt was made to synthesize iron(III) catalysts for the epoxidation of alkenes under mild conditions. This has been achieved successfully by the reaction of equimolar amounts of L^1 and anhydrous $FeCl_3$ in methanol medium at room temperature in good yields. On cooling, shinning crystals of mononuclear iron(III) complex **1** precipitated from the reaction mixture. Iron(III) complex of ligand L^2, **2**, was prepared according to the literature procedure[10]. The structure of the complexes **1** and **2** is shown in Fig. 1.

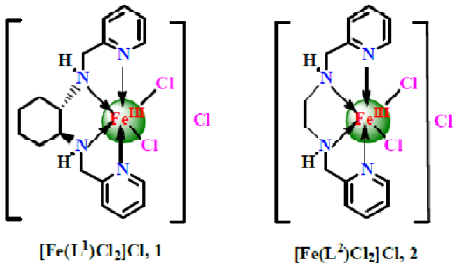


Fig. 1. Structure of mononuclear iron(III) complexes.

The synthesized complexes were characterized well by UV-Visible spectral data, and elemental microanalyses. In acetonitrile solution, both the complexes exhibit absorption bands in the region 250–400 nm. The intense band near 255 nm for both the complexes is due to the $\pi \rightarrow \pi^*$ transition within the pyridine moiety[11]. The bands near 290 nm(sh) and a broad band near 360 nm for both the complexes are assigned to the chloro-to-iron(III) charge transfer transition[11a,12]. The elemental analyses data also supports the formation of mononunclear iron(III) complex with Fe-Cl bonds.

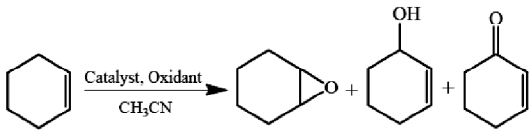
Catalytic epoxidation of alkenes:

The catalytic activity of non-heme mononuclear iron(III) complexes was evaluated in the epoxidation of alkenes using environmentally benign H_2O_2 and ^{t}BuOOH as oxidants. Cyclohexene, cyclooctene, 1-octene, norbornene and dihydronaphthalene were used as substrates with a ratio of catalyst:oxidant:substrate equal to 1:10:1000. Oxidation reactions were carried out in acetonitrile medium at room temperature under argon atmosphere as described in details in Experimental Section.

Oxidation of cyclohexene:

Under the reaction conditions employed, both the complexes **1** and **2** catalyzed the oxidation of cyclohexene by H_2O_2 and ^{t}BuOOH as oxidants. Cyclohexene, which is susceptible to allylic oxidation, forms 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the oxidation products along with cyclohexene oxide (Scheme 2). The product distributions are summarized in Table 1. All the reactions were carried out at least thrice, and the yields reported represent the average obtained.

With H_2O_2 as oxidant and employing complex **1** as catalyst, oxidation of cyclohexene afforded 2-cyclohexene-1-one as the major product with the selectivity of 73% together with 2-cyclohexene-1-ol with 20% selectivity. A little amount of



Scheme 2. Oxidation of cyclohexene.

Table 1. Oxidation of cyclohexene at room temperature

Entry	Catalyst	Oxidant	Yield (%)[a]	Product selectivity (%)[b]		
				Epoxide	Cyclohexene-1-ol	Cyclohexene-1-one
1	Complex **1**	H_2O_2	36	11	19	70
2	Complex **2**	H_2O_2	27	11	15	74
3	Complex **1**	^{t}BuOOH	47	–	17	83
4	Complex **2**	^{t}BuOOH	42	–	19	81

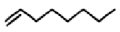
[a]Yields are based on oxidant concentration. [b]Selectivity is percentage expressed with respect to total yield.

the epoxide was also detected with very low selectivity of 7%. Total yield of the oxidation products was 36% based on H_2O_2. Under the same conditions, cyclohexene conversion decreased to 27% when complex **2** was used as catalyst. However, the selectivity of the products was almost remains as with complex **1** as catalyst. On the other hand, ^tBuOOH as oxidant enhanced the formation of corresponding alcohols and ketones with a combined yield of 42–47% with higher selectivity towards 2-cyclohexene-1-one (Table 1, entries 3 and 4). No epoxide formation was detected using ^tBuOOH as terminal oxidant. It was also found that cyclohexene was not oxidised in the absence of catalyst under the similar reaction conditions showing that complexes **1** and **2** have significant contribution in the oxidation reaction. The observation that allylic oxidation products are the main component of the observed reaction yield indicates that the oxidation process occurs via a radical mechanism[13].

Epoxidation of other alkenes:

The reactivity of iron complexes was further investigated in the epoxidation of other alkenes, such as cyclooctene, 1-octene, norbornene and dihydronaphthalene, using green H_2O_2 and ^tBuOOH as the oxidants at room temperature. The obtained catalytic results are summarized in Table 2.

Table 2. Oxidation of alkenes by mild H_2O_2 and ^tBuOOH at room temperature

Entry	Substrate	Catalyst	Product	Yield (%)[a]	
				H_2O_2	^tBuOOH
1		Complex **1**	Cyclooctene	13	6
2		Complex **2**	oxide	7	3
3		Complex **1**	1,2-	16	19
4		Complex **2**	Epoxyoctane	17	18
5		Complex **1**	Exo-epoxide	55	25
6		Complex **2**		39	35
7		Complex **1**	Oxide	65	60
8		Complex **2**		36	29

[a]Yields are based on oxidant concentration.

Cis-cyclooctene as substrate afforded *cis*-cyclooctene epoxide with 7–13% yield based on H_2O_2 catalyzed by both the complexes (Table 2, entries 1 and 2). Under the similar reaction conditions, ^tBuOOH as oxidant provided lower epoxidation yield of 3–6%. Like cyclohexene, here also, complex **2** was found to be less active as epoxidation catalyst. Catalytic epoxidation of 1-octene was also attempted (Table 2, entries 3 and 4). The results are almost similar to those described for epoxidation of cyclooctene, although the product yields (17–19%) were significantly higher for 1-octene using both the oxidants. No dependence on the nature of the ligand moiety in the catalyst is observed in the epoxidation of 1-octene. Norbornene is regiospecifically oxidised to its *exo*-epoxide with 55% yield by $1/H_2O_2$ system. However, the conversion decreased to 25% when ^tBuOOH was used as oxidant. On the other hand, complex **2** as catalyst provided 39% epoxide with H_2O_2 and 35% with ^tBuOOH.

The present catalytic system is also effective in catalyzing the epoxidation of dihydronaphthalene at room temperature (Table 2, entries 5 and 6). Complex **1** catalyzed the oxidation of dihydronaphthalene with the yield of 60–65% using both the oxidants; however, complex **2** as catalyst provided lower yield (29–36%) of oxidised product. Here also complex **1** appeared as better catalyst than complex **2**. Thus, at room temperature, **1**/oxidant exhibited better catalytic activity than **2**/oxidant towards epoxidation reaction under the given reaction conditions.

Experimental

Materials:

All the chemicals used for the synthesis, alkene substrates and the internal standard (pentafluoroiodobenzene) were purchased from Sigma-Aldrich and were used as received without further purification. Cyclohexene was distilled under argon and passed through a silica gel column prior to reaction. The active oxygen contents of the oxidants, H_2O_2 (as ~30% solution in water) and ^tBuOOH (as ~70% solution in water) were determined iodometrically prior to use. The solvents used for the catalytic experiments were distilled under argon and stored over molecular sieves (4 Å).

Physical methods:

UV-Visible spectral measurements were done with JASCO V-530 spectrophotometer. The infrared spectra were recorded on KBr disc in a JASCO 5300 FT-IR spectrophotometer. The ^1H NMR analyses were undertaken on a Bruker spectrometer operating at 400 MHz. ESI-MS spectra were obtained on Agilent 6520 Q-TOF mass spectrometer. Magnetic susceptibility measurements were carried out using MSB mk1-Sherwood magnetic susceptibility balance. Elemental microanalyses (C, H and N) were done by Perkin-Elmer

(Model 240C) or Heraeus Carlo Erba 1108 elemental analyzer. The product analyses were done by Perkin-Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column).

Synthesis of the ligands:

Synthesis of N,N′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (L^1):

The ligand was synthesized according to the literature procedure[8]. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, 2H, Py, *J* 4 Hz), 7.61 (m, 2H, Py), 7.37 (d, 2H, Py, *J* 8 Hz), 7.2 (m, 2H, Py), 4.04 and 3.84 (d, 2×2H, *J* 16 Hz), 3.03 (s, 2H, NH), 2.35 (m, 2H, CyH), 2.12 (m, 2H, CyH), 1.7 (m, 2H, CyH), 1.2 (m, 4H, CyH).

Synthesis of N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine (L^2):

The procedure employed for L^1 was also used for the preparation of L^2. Ethylenediamine was used in the place of *trans*-1,2-diaminocyclohexane. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, 2H, Py, *J* 4 Hz), 7.7 (m, 2H, Py), 7.41 (d, 2H, Py, *J* 8 Hz), 7.23 (m, 2H, Py), 4.12 (s, 4H), 3.36 (s, 2H, NH), 3.13 (s, 4H).

Synthesis of the catalysts:

*Synthesis of $[Fe(L^1)Cl_2]Cl$ (**1**):*

A methanolic solution (5 mL) of anhydrous $FeCl_3$ (0.1624 g, 1 mmol) was added to a solution of L^1 (0.296 g, 1 mmol) in methanol (10 mL) with stirring at room temperature. After stirring for 1 h, the solution was cooled. The yellow precipitate obtained was filtered off, washed with diethylether and then dried. The complex was recrystallized from acetonitrile as shining crystals. Yield: 70%. Anal. Calcd. for $C_{18}H_{24}Cl_3FeN_4.2H_2O$: C, 43.71; H, 5.71; N, 11.33. Found: C, 43.38; H, 5.41; N, 11.15%.

*Synthesis of $[Fe(L^2)Cl_2]Cl$ (**2**):*

This compound was prepared according to the literature procedure[10]. To an aqueous solution (8 mL) of L^2.4HCl (0.388 g, 1 mmol) was added $FeCl_3.6H_2O$ (0.270 g, 1 mmol) with stirring. After 10 min, sodium acetate (0.408 g, 3 mmol) was added to the yellow solution. The yellow solid that precipitated was filtered off and air dried. The complex was recrystallized from acetonitrile as yellow needles. Yield: 74%. Anal. Calcd. for $C_{14}H_{18}Cl_3FeN_4$: C, 41.57; H, 4.49; N, 13.85. Found: C, 41.14; H, 4.48; N, 13.65%.

Catalytic oxidation of alkenes:

Catalytic epoxidation reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction, 0.7 mM of catalyst and 700 mM of substrate were dissolved in 2 mL of argon-saturated acetonitrile. The oxidation reaction was initiated by adding 7 mM of oxidant and the contents were stirred at room temperature by using magnetic bar for 3 h. The product analysis was done by injecting 1 μL aliquot from the reaction vial into a capillary column of a preheated GC after addition of pentafluoroiodobenzene (PFIB) as internal standard. The identification and quantification of the products were done from the response factors of standard product samples.

Conclusions

Mononuclear non-heme iron(III) complexes was synthesized with N_4-donor ligands containing N,N′-bis(2-pyridylmethyl)-diamine moiety and anhydrous $FeCl_3$ in good yields.

The synthesized complexes have been characterized by elemental as well as by spectroscopic analyses. Epoxidation of a series of alkenes has been achieved at room temperature by the synthesized complexes **1** and **2** with environment friendly H_2O_2 and ^{t}BuOOH as oxidants under eco-friend reaction condition. ^{t}BuOOH as oxidant provided lower oxidation yields in comparison to H_2O_2; nevertheless it slightly favours the formation of alcohols and ketones versus epoxide in the oxidation of cyclohexene. Formation of allylic oxidation products over epoxide in the cyclohexene oxidation using both the oxidants suggest radical based reaction pathway.

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