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cis-Dihydroxylation of electron deficient olefins catalysed by an oxo-bridged diiron(III) complex with H_2O_2

Ambica Kejriwal[a], Sachidulal Biswas[a], Achintesh N. Biswas[b], Pinaki Bandyopadhyay[a,*]

[a] Department of Chemistry, University of North Bengal, Raja Rammohunpur, Siliguri 734013, India
[b] Department of Chemistry, Siliguri College, Siliguri 734001, India

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ABSTRACT

Room temperature oxidation of olefins catalysed by a symmetrical (μ-oxo)(μ-hydroxo)diiron(III) complex (**1**) based on the amino pyridyl ligand bpmen (bpmen = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridyl methyl)ethane-1,2-diamine) with hydrogen peroxide under the conditions of limiting substrate is described. Excellent substrate conversions have been achieved under ambient reaction conditions. The olefin oxidation efficacy of the **1**/H_2O_2 system has been found to get improved in presence of acetic acid. The catalytic system has been shown to oxidise electron-deficient olefins to the corresponding *cis*-diols, while epoxidation is favoured in case of electron-rich olefins. The μ-oxo diiron(III) core of the catalyst **1** has been found be regenerated after the catalytic turnovers. Addition of a second batch of substrate and oxidant at the end of the olefin oxidation results in the formation of almost identical amounts of epoxides/diols. Moreover, the regenerated catalyst exhibits a significantly higher preference towards the oxidation of electron-deficient olefins.

1. Introduction

Oxidative transformation of olefins into epoxides and *cis*-diols constitutes a key chemical process in synthetic organic chemistry [1–4]. Over the decades, considerable progress has been made in this area and several catalytic systems based on first-row transition metal complexes have been developed [5–12]. In particular, mononuclear non-heme iron(II) complexes based on tripodal pyridylamine ligands [13–15] (Scheme 1) have emerged as useful catalysts for the oxidation of olefins with mild hydrogen peroxide as the oxidant. These catalysts have been purposely developed to mimic iron enzymes such as methane monooxygenase, rieske dioxygenase etc. [16]. Based on their pattern of reactivity, the iron(II)-catalysts have been categorised into two classes, *viz.*, Class A & Class B catalysts [17]. Class A catalysts prefer electron-rich olefins and oxidize them into epoxides and *cis*-diols. In contrast, Class B catalysts preferentially react with electron-deficient olefins. Moreover, the diols derived in reactions catalysed by the latter have been found to incorporate both the O-atoms from H_2O_2 [17]. So far, significant progress on the mechanistic details on the reactivity of the Class A catalysts has been made, wherein an electrophilic $Fe^{V}(O)(OH)$ species, generated from the heterolytic OO bond cleavage of $Fe^{III}OOH$, has been implicated to be the active oxidant [18–21]. However, little is known about the modus operandi of the Class B catalysts. Formation of a high-spin $Fe^{III}OOH$ species with a strong OO bond has been suggested in this case. It is unclear whether the high-spin $Fe^{III}OOH$ species performs the *cis*-dihydroxylation directly or the putative oxoiron(V) intermediate formed *via* OO heterolysis of $Fe^{III}OOH$ is the active oxidant.

Several diiron catalytic systems have also been examined for olefin oxidation [22]. However, a vast majority of the oxo-bridged diiron complexes based on similar nitrogen rich ligands have exhibited rather sluggish oxidative reactivity [23–26] Moreover, during the course of the catalytic reactions, the diiron catalysts have found to dissociate to monoiron complexes [26]. In an effort to overcome this problem, Kodera et al. have recently developed a dinucleating ligand (6-HPA, Scheme 1) by introducing a -(CH_2CH_2)- spacer in between two tris(2-pyridylmethyl) amine (TPA). The (μ-oxo) diiron(III) complex of the dinucleating pyridyl ligand (6-HPA) was shown to be stable in solution and also during catalytic reactions with H_2O_2 [27,28]. In presence of excess cyclooctene and 150 equiv. of H_2O_2 (*w.r.t.* the catalyst), the diferric catalytic system yields 105 turnovers of epoxide accounting for 70% of the oxidant.

Therefore, development of model systems with diiron core has to rely on the use of suitable ligand platform capable of stabilizing the dinuclear structure in solution. The catalytic results of the diiron complexes based on tripodal TPA ligand encouraged us to explore

* Corresponding author. Fax: +91 353 2699001.
E-mail address: pbchem@rediffmail.com (P. Bandyopadhyay).

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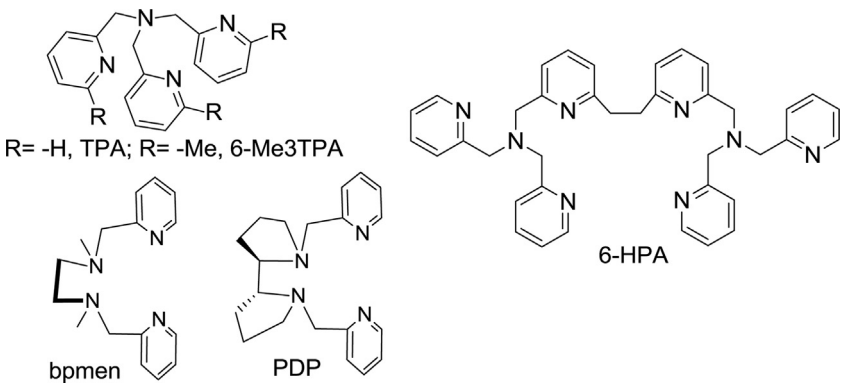
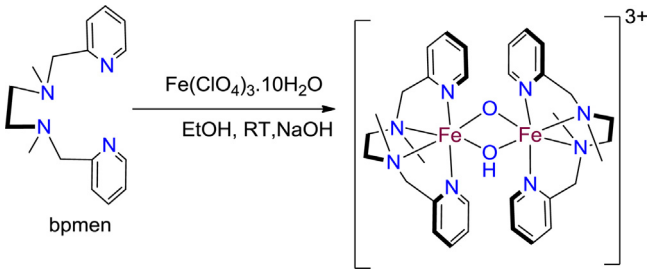


Scheme 1. Polydentate ligands used in non-heme iron catalysed alkene oxidation reactions.



Scheme 2. Synthesis of (μ-oxo)(μ-hydroxo) bridged diiron(III) complex (**1**) containing bpmen ligand.

the catalytic potential of the oxobridged diiron(III) complex (**1**) of a linear aminopyridyl ligand, bpmen (Scheme 2, bpmen = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl) ethane-1,2-diamine).

The mononuclear iron(II) complex of the ligand, $[Fe^{II}(bpmen)]^{2+}$ (**2**) has previously been reported to be an excellent catalyst for epoxidation of olefins with H_2O_2 at room temperature [29]. The mononuclear complex (**2**) exhibits high reactivity towards electron-rich olefins and can be categorised as a Class A catalyst. Interestingly, ^{1}H NMR and EPR studies on the catalytic system **2**/H_2O_2 by Talsi et al. indicated the presence of the μ-oxo diiron(III) complex as the predominant species in acetonitrile solution [30,31]. At low temperature, the authors observed EPR signals characteristic of low-spin ferric hydroperoxo intermediates as well as a binuclear $Fe^{III}Fe^{IV}$ complex with localised antiferromagnetically coupled $S = 3/2$ Fe^{III} and $S = 1$ Fe^{IV} centres [30]. The binuclear $Fe^{III}Fe^{IV}$ complex has been found to decay five times faster in presence of cyclohexene indicating that the species is involved in epoxidation of olefins by **2**/H_2O_2. Although epoxidizing ability of similar diiron species based on TPA ligand has already been established, the results disagree with the sluggish catalytic behaviour of μ-oxo diiron(III) complex based on bpmen ligand and H_2O_2 towards olefins [14,15]. Thus, the nature of the active species of **1**/H_2O_2 and **2**/H_2O_2 is far for being settled.

Very recently, we have shown that the diiron(III) complex (1) can catalyze aromatic hydroxylation of benzene and alkylbenzenes with hydrogen peroxide as the terminal oxidant [32]. In this case, compelling evidences supporting the involvement of electrophilic high-valent oxoiron species as the true oxidant are obtained. Encouraged by these results, herein, we set out to explore the catalytic reactivity of the (μ-oxo)(μ-hydroxo) diiron(III) complex, $[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2]$ (**1**) [33,34] towards olefins with benign hydrogen peroxide as the terminal oxidant. The substrate-scope of **1**/H_2O_2 and the effect of acetic acid on olefin oxidation have been evaluated. Moreover, catalytic reactions have been performed under substrate limiting condition in order to demonstrate its suitability in preparative scale organic synthesis.

2. Experimental

2.1. Materials

All reagents and chemicals were purchased from Sigma–Aldrich and were used without further purification unless noted otherwise. 2-Picolyl chloride, *N*,*N*′-dimethylethylenediamine and $Fe(ClO_4)_3$, xH_2O were purchased from Sigma–Aldrich. HPLC grade Acetonitrile (S.D. Fine Chem. Ltd., India) and ethanol (E. Merck, India) were used as received. H_2O_2 (as ~30% solution in water) was used as received and the exact active oxygen content of the oxidant was determined iodometrically prior to use.

2.2. Synthesis of the ligand

The ligand, *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine) (bpmen) was synthesised following the literature method [34]. 1H NMR (300 MHz, $CDCl_3$): $\delta = 2.27$ (s, 6H, —N—CH_3), 2.66 (s, 4H, —CH_2—CH_2—), 3.69 (s, 4H, N—CH_2—Py), 7.1–8.54 (m, 8H, Py ring) (Figs. S1 and S2, ESI).

2.3. Synthesis of the catalyst

The synthesis of the metal complex was carried out according to the published procedure [33]. ESI-MS: *m*/*z*: 392 (100%) $[M\text{-}2ClO_4]^{+2}$ (Fig. S3, ESI). Anal. Calcd. (found) for $C_{32}H_{45}N_8Fe_2Cl_3O_{14}$: C, 39.07 (38.39); H, 4.61 (4.81); N, 11.39 (11.26). UV–vis (in acetonitrile): λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 377 (4720), 430(2060) (sh), 479 (660) 512(580), 555(720).

2.4. Physical methods

UV–vis spectra were recorded on Agilent 8453 Spectrophotometer. Elemental Microanalysis (CHN) was done in Vario EL-III elementary analyser. The ^{1}H NMR spectrum was recorded on a Bruker spectrometer operating at 300 MHz. The product analyses were done by PerkinElmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column). ESI-MS data were collected on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. EPR spectra in the X-band were recorded with a JEOL Model JES-FA200 spectrometer.

2.5. Reaction conditions for catalytic experiments using limiting substrates

2.5.1. Method A

A total of 150 μL of a 0.5 M H_2O_2 solution (diluted from a 30% H_2O_2 solution) in CH_3CN was delivered all at once in air to a CH_3CN solution (2.0 mL) containing catalyst **1** (1.25 mM, 5 mol%) catalyst

Table 1
Oxidation of *tert*-butyl acrylate by [$Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2$] (**1**) and H_2O_2 at room temperature.

Entry	Cat:Sub:HOAc:H_2O_2	Method[a]	Diol (%)[b]	Epoxide (%)[b]	TON
1	1:20:0:30	A	17	06	4.6
2	1:20:1:30	A	25	04	5.8
3	1:20:0:30	B	28	08	7.2
4	1:20:1:30	B	60	04	12.8
5	1:40:1:60	B	55	05	12
6	1:60:1:90	B	45	06	10.2
7	1:100:1:150	B	17	02	3.8
8	3:100:3:150	C	64	07	14.2
9	1:20 × (2):2:30 × (2)	D	64	04	13.6
10	1:20 × (3):3:30 × (3)	D	69	04	14.6

[a] Method A: 37.5 mM (1.5 equiv. *w.r.t.* substrate) was added all at once; Method B: 37.5 mM (1.5 equiv. *w.r.t.* substrate) was delivered by a syringe pump over 15 min at a rate of 0.6 mL/h; Method C: Three iterative additions of **1** (3 mol%), AcOH (3 mol%) and H_2O_2 (0.5 equiv. *w.r.t.* substrate). Method D: Additional aliquots of H_2O_2 (37.5 mM, 1.5 equiv. *w.r.t.* substrate) and substrates were delivered at the end of the reactions.
[b] Yields are based on the substrate concentration. See Section 2 for details.

and 25 mM olefin substrate. The final ratios of the catalyst, substrate and the oxidant are given in Table 1 in the main text. In various experiments, acetic acid (1 equiv. *w.r.t.* the catalyst) was added to the initial solution prior to the addition of oxidant. The solution was stirred for 5 min. In all cases, the resulting solutions were treated with acetic anhydride (1.0 mL) together with 1-methylimidazole (0.1 mL) to esterify the diol products. Iodopentafluorobenzene was added as an internal standard. Organic products were extracted with $CHCl_3$, and the solution was washed with 1 M H_2SO_4, sat. $NaHCO_3$, and H_2O. The organic layer was dried with $MgSO_4$ and the solution was subjected to GC analysis. The products were identified by comparison of their GC retention times with those of authentic compounds. The product analysis was done by PerkinElmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) by injecting 1 μL aliquot from the reaction vial taken after addition of pentafluoroiodobenzene (PFIB) as internal standard. All experiments were run at least in duplicate, the reported data being the average of these reactions. GC chromatograms containing the assignment of peaks for substrate, main products and internal standard, along with peak area data are compiled in Supporting information.

2.5.2. Method B

A total of 150 μL of a 0.5 M H_2O_2 solution (diluted from a 30% H_2O_2 solution) in CH_3CN was delivered by a syringe pump over a period of 15 min (rate: 0.6 mL/h) to an acetonitrile solution (2.0 mL) containing catalyst **1**(1.25 mM) and 25 mM olefin substrate. The reaction mixture was further stirred for 15 min. Identification and quantification of the products were performed according to the procedure outlined in Method A.

2.5.3. Method C

A 10 mL vial was charged with the following: catalyst (2.5 μmol), substrate (250 μmol), and acetic acid (1 equiv. *w.r.t* catalyst) and a magnetic stir bar. The vial was placed on a stir plate and stirred vigorously at room temperature. A solution of H_2O_2 (250 μL) was added dropwise *via* syringe pump over 15 min. After stirring for 15 min, a solution of catalyst (2.5 μmol), and acetic acid (2.5 μmol) was added *via* syringe. This was followed by H_2O_2 (250 μL) with the aid of syringe pump over 15 min. After being stirred for 15 min a third addition was performed in the same manner for a total of 7.5 μmol of catalyst, 7.5 μmol AcOH, and 1.5 equiv. H_2O_2. Each addition was allowed to stir for 15 min, for a total reaction time of 45 min.

2.5.4. Method D

Same as Method B except that additional aliquots of oxidant and substrate were delivered *via* syringe pump at the end of the catalytic reactions. Identification and quantification of the products were performed according to the procedure outlined in Method A.

2.6. Competitive olefin oxidation reactions

Three substrates were selected for pairwise competition experiments, where equimolar amounts of two different substrates were oxidised according to the procedure outlined in Method B (see above). The results of the competitive olefin oxidation reactions are compiled in Table S1.

2.7. Reactions performed with the regenerated catalyst (1′)

A total of 150 μL of a 0.5 M H_2O_2 solution (diluted from a 30% H_2O_2 solution) in CH_3CN was delivered by syringe pump over 15 min at 25 °C in air to a CH_3CN solution (2.0 mL) containing iron 1.25 mM catalyst and 1 equiv. acid with respect to catalyst. The final ratio is catalyst: acid: oxidant = 1:1:30. After 15 min of stirring, equimolar (25 mM) amounts of cyclooctene and *tert*-butyl acrylate was added. After the addition, 1 equiv. of acid (1.25 mM) and 150 μL of a 0.5 mM H_2O_2 solution (diluted from a 30% H_2O_2 solution) in CH_3CN was delivered by syringe pump over 15 min. The solution was further stirred for 15 min. After that, it was treated with acetic anhydride (1 mL) and 1-methylimidazole (0.1 mL) to esterify the diol products and followed work up under the normal catalytic condition explained above.

3. Results and discussion

3.1. Olefin oxidation catalysed by the (μ-oxo) diiron(III) complex (1) with H_2O_2

The oxo-bridged diiron(III) complex (**1**) has been found to be fairly stable in anhydrous acetonitrile at 25 °C as no significant electronic spectral change of **1** is observed. The stability of the μ-oxo-diiron motif in 'neat' acetonitrile appeared promising and prompted us to explore the reactivity of the (μ-oxo) diiron(III) complex [$Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2$] (**1**) towards olefin oxidation with H_2O_2 at room temperature. To assess the potential of **1**/H_2O_2, *tert*-butyl acrylate, a prototype of electron-deficient alkenes, is chosen as the model substrate. So far, only a handful of catalytic systems have shown to be efficient in catalysing *cis*-dihydroxylation of electron-poor olefins with H_2O_2 [13]. An efficient manganese based catalytic system for selective *cis*-dihydroxylation of electron deficient olefins with H_2O_2 has been reported by Saisaha et al. [35]. The manganese catalyst, prepared *in situ* by the reaction of a Mn(II) salt, pyridine-2-carboxaldehyde, a base and a ketone has exhibited high selectivity towards *cis*-dihydroxylation. An iron(III) catalyst based on a macrocyclic tetraza ligand has been shown to effec-

tive in catalyzing *cis*-dihydroxylation of electron poor olefins with oxone as the terminal oxidant [12]. Apart from these examples, a vast majority of catalysts based on inexpensive first-row transition metal catalysts have exhibited only modest reactivity towards olefin *cis*-hydroxylation [13].

The results encouraged us to explore the catalytic reactivity of the diiron(III) catalyst (**1**) towards electron-poor olefins. The catalytic reactions have been performed in acetonitrile medium by both syringe-pump as well as all-at-once addition of H_2O_2 (Table 1). Oxidation of *tert*-butyl acrylate in presence of catalytic amount of $Fe(NO_3)_3.9H_2O$ is found to yield only a trace amount of epoxide under the present experimental condition. Moreover, no oxidation products are obtained when the reaction is carried out without any metal catalyst. However, as shown in Table 1, using 5 mol% catalyst **1**, oxidation of *tert*-butyl acrylate affords the 17% *syn*-diol and 6% epoxide in acetonitile at room temperature (298 K) (Entry 1, Table 1). When the reaction is carried out in presence of one-equivalent acetic acid (*w.r.t.* **1**), modest improvement of substrate conversion is observed (Entry 2, Table 1). In order to further improve the catalyst turnovers and substrate conversion, H_2O_2 (1.5 equiv. *w.r.t.* the substrate) has been delivered over a period of 15 min at a rate of 0.6 mL/h. Under the syringe pump addition protocol, significant improvement substrate conversion (Entry 4, Table 1) is observed and the corresponding *syn*-diol is obtained as the major product. However, increasing the amount of substrate under identical reaction condition has been found to result in poor substrate conversion. As shown in Table 1, employing a catalyst:substrate:HOAc:H_2O_2 of 1:100:1:150, only 17% *syn*-diol and 2% epoxide are obtained indicating significant catalyst deactivation. In order to overcome it, three iterative additions of the catalyst **1,** HOAc and the oxidant H_2O_2 has been designed. Under iterative addition protocol, yield of the diol increases up to 64% (Entry 7 & 8, Table 1). It is noteworthy in this regard that oxidation of *tert*-butyl acrylate catalysed by the monomeric iron(II) complex of bpmen [(bpmen)$Fe^{II}(OTf)_2$] [19,28,36]. and H_2O_2 has been shown to afford both epoxide and diol with a slight preference for the diol product over epoxide (epoxide/diol = 1:1.5). Furthermore, addition of acetic acid dramatically improved epoxide selectivity (epoxide/diol = 5:1). Therefore, in order to have further insight into the catalytic reactivity of complex **1**, attempts have also been made to assess the amount of catalytically reactive species at the end of the reaction. Thus, after delivering H_2O_2 (75.0 μmol, 1.5 equiv. *w.r.t.* the substrate) in acetonitrile medium containing 5 mol% (2.5 μmol) of **1** and HOAc, followed by stirring the reaction mixture for an additional 15 min, a second aliquot of both the substrate, acid and oxidant have been added in an identical fashion. Interestingly, the catalytic system has been found to exhibit almost identical catalytic reactivity (Entry 9, Table 1). The reactivity remains unchanged even after the third addition of substrate, acid and oxidant indicating almost complete regeneration of the oxidizing species at the end of each catalytic cycle.

The role of the acidic additives in the catalytic olefin oxidation by **1**/H_2O_2 is also evaluated. The formation of *cis*-diol product has been found to get suppressed in oxidation of *tert*-butyl acrylate by **1**/H_2O_2 in presence of mineral acids such as HCl and HNO_3 (Table S3, Supporting information). Since no direct relationship between the catalytic reactivity of **1**/H_2O_2 and pK_a of the additives can be highlighted, it is believed that the catalytic reactivity is augmented due to the binding of acetic acid in equilibrium condition.

The substrate scope of the present catalytic system has also been examined and the results are summarised in Table 2. In all catalytic reactions, the ratio of catalyst:substrate:HOAc:H_2O_2 of (1:20:1:30) has been maintained and the oxidant is delivered over a period of 15 min (see Section 2 for details). For the electron deficient olefins, *cis*-diols are obtained as the major product with modest yields. Oxidation of dimethyl fumarate afforded the *cis*-diol product, *d/l*-dimethyl tartarate as the major product with high diol selectivities, *viz.*, diol/epoxide ratio of 7.5 which shoots up to 22 in presence of 2.5 μmol acetic acid in acetonitrile at room temperature (Entries 1 & 2, Table 2). Oxidation of ethyl crotonate yielded a mixture of *cis*-diol and epoxides with higher selectivity for the diol (D/E of 4.0, Entry 5, Table 2). In presence of acetic acid, a clear preference for the formation of *cis*-diol product, as evident from a D/E value of 14.3, is observed (Entry 6, Table 2). Oxidation of other electron-deficient olefins, *viz.*, acrylonitrile, diethyl maleate and 2-cyclohexene-1-one also exhibited similar product profile under identical reaction condition (Table 2). Oxidation of methyl cinnamate under similar reaction condition results in the formation of diols and epoxide with somewhat lower yields (Entry 7 & 8, Table 2). In this case, preliminary studies have indicated a competitive oxidation of the phenyl ring of the substrate by **1**/H_2O_2(AcOH) [32], which, in turn, rationalizes the lower yield of the products derived from the C=C oxidation. Oxidation of electron-rich olefins by **1**/H_2O_2 exhibits a complete reversal in product profile with epoxides as the major products with minor amounts of *cis*-diols. The electron-rich *cis*-cyclooctene has been converted to the cyclooctane oxide in 60% yield. A small amount of the corresponding *cis*-diol product (10%) has also been obtained (Entry 13, Table 2).

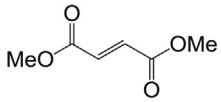
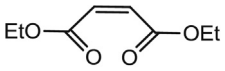
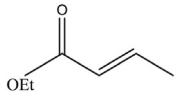
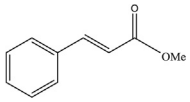
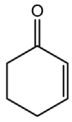
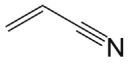
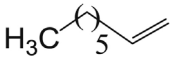
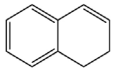
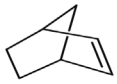
Addition of **1** equiv. of acetic acid prior to the addition of the substrate results in considerable increase in the product yield (87%) based on the initial substrate concentration (Entry 14, Table 2). In case of oxidation of 1-octene by **1**/H_2O_2, overall yield of oxygenates reaches 50% with an epoxide/*cis*-diol ratio of 4.0. Moreover, combined yields of epoxide and *cis*-diol as well as the epoxide selectivity have been found to increase in presence of one equivalent of AcOH (Entries 15 & 16, Table 2). Olefin epoxidation catalysed by **1**/H_2O_2 has exhibited a modest degree of retention of configuration in case of *cis*-stilbene, a 1,2-disubstituted alkene. Oxidation of *cis*-stilbene under identical reaction condition yielded the corresponding epoxide with 50% retention of configuration. However, in presence of one equivalent AcOH, the epoxide product was formed with more than 80% retention of configuration (Table 2). Such a high degree of stereo-retention further supports the involvement of a metal-based oxidant in the present oxidizing system [37].

The epoxidizing ability of **1**/H_2O_2 has been compared with the best known iron-based epoxidation catalysts in order to assess its potential for the application in preparative scale organic synthesis.

The catalytic reactions were performed in acetonitrile medium using a large excess of the olefin (1000 equiv./catalyst) and by all-at-once addition of H_2O_2 (100 equiv./catalyst). Under the reaction condition cyclooctene has been found to be converted into a mixture of epoxide and *cis*-diol in 40% and 5% yields respectively. Furthermore, the catalytic efficacy of complex **1** increased considerably upon addition of 1 equiv. acetic acid prior to the addition of H_2O_2 (Table 3). In presence of acid turnover number (TON) based on complex **1** reached 65 and only a trace amount (2%) of *cis*-diol was obtained. As shown in Table 3, epoxidizing ability of **1**/H_2O_2/AcOH is comparable to that obtained with the (μ-oxo) diiron(III) complex of a dinucleating pyridyl ligand (6-HPA) reported recently by Kodera et al. under similar reaction condition. In this case, 70% of the oxidant has been accounted for the products. In comparison, 65% of the total H_2O_2 has been shown to be converted into mainly epoxides during oxidation of *cis*-cyclooctene by the present catalytic system.

In order to evaluate the nature of oxidant in the present catalytic system, competitive olefin oxidation reactions under similar reaction condition were performed. Equimolar amounts of a pair of olefin substrates have been oxidised by **1**/H_2O_2 either in presence & in absence of AcOH. The results are presented in Fig. 1 and Table S1. For instance, when *cis*-cyclooctene and *tert*-butyl acrylate are used as substrates, cyclooctene oxidation yields 55% products (epoxide/diol = 4.5:1) while only 4% oxygenates (epoxide/diol = 1:3) are

Table 2
Oxidation of olefins by $[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2]$ (**1**) and H_2O_2 in acetonitrile at room temperature[a].

Entry	Substrate	HOAc (equiv.)	Yield[b] (%)	Diol[b] (%)	Epoxide[b] (%)	D/E	TON
1		–	34	30	04	7.5	6.8
2		1.0	46	44	02	22	9.2
3		–	12	10	2	5	2.4
4		1.0	36	33	3	11	7.2
5		–	25	20	5	4	5.0
6		1.0	46	43	3	14.33	9.2
7		–	12	9	3	3	2.4
8		1.0	26	21	5	4.2	5.2
9		–	9	6	3	2	1.8
10		1.0	20	14	4	3.5	4.0
11		–	19	16	03	5.33	3.8
12		1.0	40	39	01	39	8.0
13		–	70	10	60	0.167	14.0
14		1.0	87	03	84	0.036	17.4
15		–	50	10	40	0.25	10.0
16		1.0	66	04	62	0.065	13.2
17		–	30	10	20	0.5	6.0
18		1.0	38	08	30	0.267	7.6
19		–	38	12	26	0.46	7.6
20		1.0	38	08	30	0.267	7.6
21		–	75	–	50 (*cis*) 25(*trans*)	–	15.0
22		1.0	78	–	70 (*cis*) 08(*trans*)	–	15.6

[a] H_2O_2 was delivered by syringe pump over 15 min at a rate of 0.6 mL/h and 15 extra minutes of stirring were allowed before workup.
[b] Yields are based on substrate concentration.

Table 3
Oxidation of cyclooctene catalysed by non-heme iron catalysts with H_2O_2 as the oxidant.

Catalyst	Equiv. H_2O_2[a]	Equiv. AcOH	Yield (%)[b]	Products (TON)[c]	Ref.
$[(6\text{-HPA})Fe^{III}{}_2O]$	150	–	70	Epoxide (105) *Cis*-diol (03)	[27]
$[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2]$ (**1**)	100	–	45	Epoxide (40) *Cis*-diol (05)	This work
	100	1.0	65	Epoxide (63) *Cis*-diol (02)	This work
$[Fe^{II}(bpmen)]^{2+}$	300	12000	90	Epoxide (187)	[19]
$[Fe^{II}(TPA)]^{2+}$	300	12000	90	Epoxide (185)	[19]

[a] Equivalent of H_2O_2 *w.r.t.* the catalyst.
[b] Based on initial concentration of the oxidant.
[c] TON = amountof products/amount of the catalyst.

obtained from *tert*-butyl acrylate oxidation. Moreover, in presence of AcOH, catalyst **1** favoured the oxidation of electron-rich cyclooctene by a factor of 10.75 (Fig. 1). The results are indicative

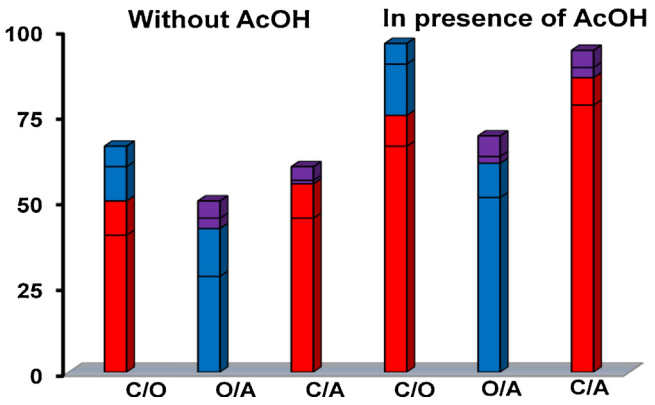


Fig. 1. Competitive experiments for the oxidation of different olefin pairs by **1**/H_2O_2. C = cyclooctene (red), O = 1-octene (blue), A = *tert*-butyl acrylate (purple). See Supporting information for further details. Lower blocks represent the amount of epoxide formed while the upper blocks represent the amount of *cis*-diol formed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

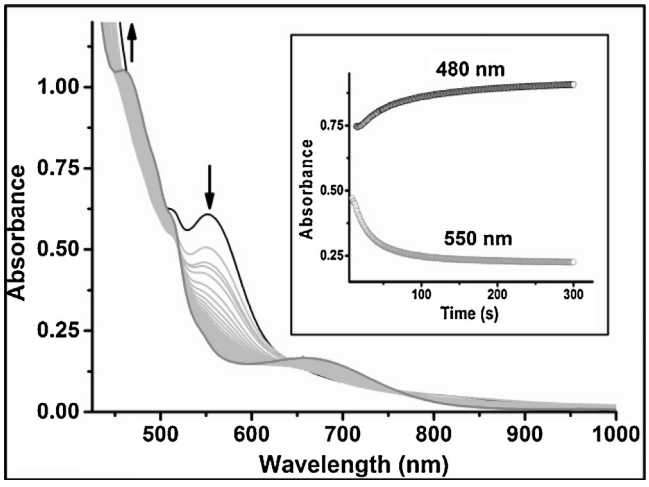


Fig. 2. UV–vis spectral changes obtained upon the addition of H_2O_2 (30 mM) to a solution of complex **1** (1 mM) and *tert*-butyl acrylate (20 mM) in neat acetonitrile at 298 K. Inset: change of absorbance of the 480 and 550 nm bands monitored with time.

of the formation of an electrophilic oxidant in the present oxidizing system [18,19].

During the course of the evaluation of the catalytic efficacy of **1**/H_2O_2, compelling evidences indicated that the initial catalyst **1** and the regenerated catalyst (**1′**) at the end of the reaction exhibit distinct reactivity patterns. In order to showcase the reactivity difference, **1′** was generated *in situ* by the reaction of **1** (2.5 μmol) and H_2O_2 (75 μmol) in acetonitrile and an equimolar mixture of *cis*-cyclooctene and *tert*-butyl acrylate (50 μmol each) is introduced as substrates. Unlike catalyst **1**, the regenerated catalyst has exhibited a significant preference towards the oxidation of electron-poor acrylate. Product analysis reveals the formation of 87% oxygenates from cyclooctene oxidation (epoxide/diol = 28) and 44% oxygenates from acrylate oxidation [38]. The regenerated catalyst favours oxidation of *cis*-cyclooctene over acrylate by a factor of only 2.0 (Table S2, ESI.).

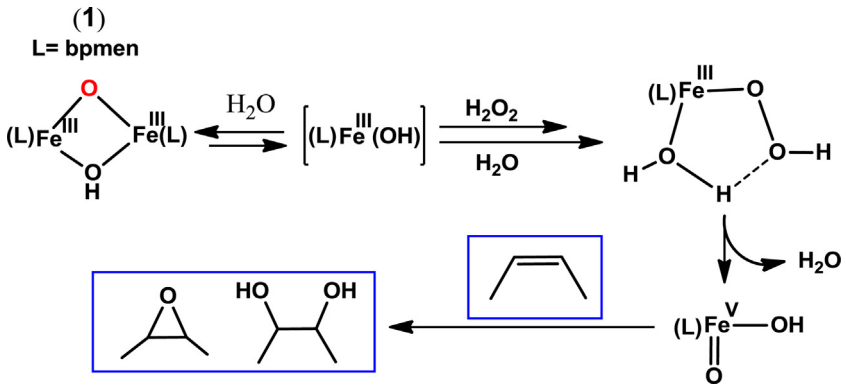
Comparing this to the result obtained by **1**/H_2O_2 (*vide supra*), significantly higher preference towards the oxidation of electron deficient olefins by **1′** is observed. The results clearly point out that the key oxidizing species responsible for olefin oxidation is less electrophilic in nature compared to that involved in the parent catalyst (Fig. 2).

3.2. Mechanistic aspects

So far, a number of nonheme iron(II) complexes have been shown to catalyze epoxidation and *cis*-dihydroxylation of olefins with H_2O_2 as the terminal oxidant [3,13,17–19]. Depending on the nature of ligands, several high-valent oxo-iron intermediates have been suggested as the key intermediate. In particular, a putative oxoiron(V) intermediate, *cis*-HO–Fe^{V} = O has been invoked as the active oxidant in *cis*-hydroxylation of olefins [39,40]. Indeed, such species has recently been detected by variable temperature mass spectrometry [41].

In contrast, a $Fe^{III}(\eta^2$-OOH) has been suggested as the active oxidant in case of olefin *cis*-dihydroxylation catalysed by Rieske dioxygenases [42,43]. Very recently, Talsi et al. have provided convincing EPR evidence supporting the formation of a formal oxoiron(V) species from dinuclear iron(III) complexs (bearing aminopyrine ligands TPA* and PDP*, TPA* = tris(3,5-dimethyl-4-methoxypyridyl-2-methyl) amine, PDP* = bis(3,5-dimethyl-4-methoxypyridyl-2-methyl)-(S,S)-2,2'-bipyrrolidine) with H_2O_2 and acetic acid [44]. In presence of acetic acid, the dinuclear iron(III) complexes are shown to get converted into monomeric ferric complexes of the type $[(L)Fe^{III}(\kappa^2$-$(OC(O)CH_3))]^{2+}$, which, reacts with H_2O_2 to generate formally oxoiron(V) intermediate [either(L)Fe^{V} = O or $(L^{\bullet+})Fe^{IV}$ = O]. The putative species is claimed to be the active oxidant in olefin oxidation. Given the structural similarity of bpmen ligand with PDP*, formation of putative oxoiron(V) species in the present case cannot be overruled. This prompted us to examine the fate of the oxo-bridged diiron(III) complex (**1**) at the end of the catalytic reactions. Thus, the oxidation of *tert*-butyl acrylate by **1**/H_2O_2 in acetonitrile at 298 K is monitored by UV–vis spectroscopy. Electronic spectrum of complex **1** in neat acetonitrile exhibits a weak absorption at 550 nm, which is a signature of the Fe(III)-(μ-O)-Fe(III) core originating from $^6A_1 \rightarrow (^4A_1, {}^4E)$ transition. Upon addition of excess H_2O_2 to complex **1**, the intensity of the 550 nm absorption decreases rapidly followed by the appearance of new absorption features around 350, 430 and 512 nm (Fig. S4, ESI). The final electronic spectrum is then compared with that of the starting complex (**1**) (Fig. S4). The spectrum of the regenerated catalyst resembles that of $[(bpmen)(H_2O)Fe(\mu$-$O)Fe(OH)(bpmen)]^{3+}$ [45], previously observed by Poussereau et al. upon addition of water to an acetonitrile solution of complex **1**. The rate of formation of the open core oxo-bridged diiron(III) complex has been found to increase in presence of AcOH (Fig. S5, ESI).

The electronic spectral changes can be rationalised in terms of rapid rupture of μ-oxo diiron core to generate a monoiron species, which ultimately converts to the thermodynamically more stable Fe(III)-(μ-O)-Fe(III) complex. Additional supports for this hypothesis have been obtained from EPR studies. The starting diiron(III) complex (**1**) is EPR silent. However, after the addition of 10 equiv. of H_2O_2 to an acetonitrile solution of complex **1** (1 mM) at room temperature and freezing the mixture at −78 °C, the EPR spectrum (Fig. S6, ESI) exhibits a signal at $g = 4.23$, which can be tentatively assigned to a high-spin mononuclear iron(III) complex. Moreover, the spectrum also indicates the presence of at least two $S = 1/2$ species in the mixture (Fig. S6, ESI). The resonances at $g_1 = 2.15$, $g_2 = 2.15$ and $g_3 = 2.08$ can be rationalised either by considering the formation of a low-spin ferric hydroperoxo intermediate or a binuclear $Fe^{IV}Fe^{III}$ complex with antiferromagnetically coupled Fe^{III} ($S = 3/2$) and a low-spin Fe^{IV} ($S = 1$) unit [30,31]. At this point, unambiguous assignment of the EPR signals could not be made due to rather low concentration of this species (<5% of the total iron concentration in the sample). The second set of signals appears at $g_1 = 2.06$, $g_2 = 2.01$ and $g_3 = 1.96$. It is noteworthy that an $S = 1/2$ EPR signal similar to the latter has recently been detected by Talsi et al. in reactions between structurally related oxo-bridged diiron(III) complex and H_2O_2 at low temperature [44]. The authors have



Scheme 3. Proposed mechanism for the olefin oxidation by **1**/H_2O_2.

assigned this signal to a highly reactive formally oxoiron(V) intermediate. Therefore, it is reasonable to believe that in the present case, a putative oxoiron(V) species may serve as one of the active intermediates. Formation of appreciable amounts of *cis*-diols in alkene oxidation catalysed by **2**/H_2O_2 is also in agreement with this hypothesis. Both the sets of resonances have been found to decay with time and ultimately yield an EPR silent species, presumably the open core Fe(III)-(μ-O)-Fe(III) species (**1′**). Formation of the monoiron species during catalysis has also been supported by the *in situ* ESIMS analysis. ESI-MS spectrum obtained after the addition of H_2O_2 to an acetonitrile solution of **1** (Fig. S7, ESI) exhibited prominent peaks at m/z = 342 and 361, which can be tentatively assigned to the $[(bpmen)Fe^{III}(O)]^+$ and $[\{(bpmen)Fe^{III}(O)(OH_2)\}+H^+]$.

We have also scrutinised whether the catalytic reactivity of complex **1** is due to the *in situ* generated (μ-oxo)(μ-acetato) diiron(III) complex as previously reported by Jacobsen et al. [29]. Independently synthesised (μ-oxo)(μ-acetato) diiron(III) (**3**) has been found to be inefficient in catalysing olefins under similar reaction condition as only traces of epoxide from *cis*-cyclooctene have been obtained. Even in presence of excess acetic acid, **3**/H_2O_2 exhibits poor oxidative reactivity towards olefins. The present results corroborates with the previous results, wherein the (μ-oxo) diiron(III) complex of bpmen is reported to be catalytically inactive towards hydrocarbons [46].

The mechanism of olefin oxidation by the present catalytic system is not completely clear to us. However, based on the experimental findings the sequence shown in Scheme 3 seems reasonable.

The diiron(III) complex (**1**) reacts with the oxidant(H_2O_2) to generate a high-spin mononuclear iron(III) complex, $[(bpmen)Fe^{III}(OH)]^{2+}$. This is followed by the formation of the ferric hydroperoxo species, $[Fe^{III}(OOH)(H_2O)]^+$ (not detected at room temperature). Heterolytic cleavage of the OO bond of the ferric hydroperoxo generates the *cis*-HO-Fe^V=O oxidant capable of oxidizing olefins into epoxides and *cis*-diols. Finally, Fe^{III}-OH iron(III) species combine to form the open core Fe(III)-(μ-O)-Fe(III) complex, $[(bpmen)(H_2O)Fe(\mu\text{-}O)Fe(OH)\ (bpmen)]^{3+}$ (**1′**), which reacts with additional H_2O_2 to drive further oxidation of olefinic substrates.

4. Conclusions

In summary, the (μ-oxo) diiron(III) complex $[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(bpmen)_2]$ (**1**) has emerged as an useful catalyst with H_2O_2 in epoxidation of olefins under conditions of limiting substrates at room temperature. Excellent substrate conversions have been obtained in presence of acetic acid. The catalytic system has been shown to epoxidize electron-rich olefins, whereas *cis*-dihydroxylation is favoured in case of electron-deficient olefins. Infact, unlike the nonheme diiron(III) catalysts explored so far, the present catalytic system exhibits very high selectivity in *cis*-dihydroxylation of electron-deficient olefins under ambient reaction condition. The (μ-oxo) diiron(III) complex has been found to dissociate in solution to form monoiron species, which are believed to mitigate olefin epoxidation with hydrogen peroxide. The (μ-oxo) diiron(III) has been found to regenerate at the end of catalytic turnovers. Interestingly, the open-core oxo-bridged diiron(III) complex has been found to be catalytically potent. The regenerated complex (**1′**) shows a greater preference in *cis*-dihydroxylation of electron-deficient alkenes than the parent catalyst. To the best of our knowledge, the present catalytic system is the only diiron(III) complex that can catalysed *cis*-dihydroxylation of electron deficient olefins with mild H_2O_2 as the terminal oxidant at room temperature. Given the easy preparation and handling of the diiron(III) catalyst as well as the atom-economy of the process, the present catalytic system appears promising for the application in synthetic organic chemistry.

Acknowledgements

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Appendix A. Supplementary data

^{1}H NMR spectra of the ligand and the main products formed in catalytic olefin oxidation, results of competitive olefin oxidation and the GC chromatograms.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.11.023.

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