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Reductive Activation of O_2 by Bioinspired Fe-Complex for Catalytic Epoxidation Reactions

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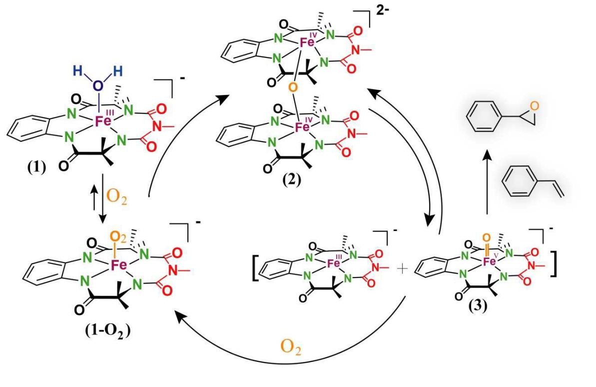
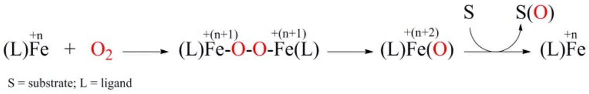
Aerobic epoxidation of olefins catalyzed by iron complexes without the use of sacrificial coreductant are unknown. We report the reductive activation of O_2 by the bioinspired $[(bTAML)Fe^{III}(H_2O)]^-$ (1) complex to catalyze epoxidation of alkenes with TONs up to 80. Spectroscopic and kinetic evidence indicates involvement of the $Fe^V(O)$ as the active oxidant during the reaction.

Epoxides represent an extremely important class of chemicals both to synthetic chemists as well as chemical industries. Traditionally, epoxides are synthesized by intramolecular etherification of intermediate chlorohydrins formed by the reaction of alkenes with hypochlorous acid or by the reaction of peracids with alkenes. Safety and environmental concerns have led to the development of catalytic epoxidation methods using alkyl hydroperoxides and hydrogen peroxide.[1] The major limitation of peroxide based oxidants are their sensitive nature towards self-decomposition and subsequently catalyzing radical-chain reaction at higher concentrations. More efficient and greener approach would be the catalytic oxygen atom transfer from dioxygen to alkenes resulting in the formation of epoxides as is observed in monooxygenases such as cytochrome P450. The stoichiometry of this reaction requires two electrons from an exogenous source which is typically a coenzyme.[2] Thus, most functional mimics of cytochrome P450 which catalyse epoxide formation have employed reduced oxygen species such as peroxides as terminal oxidants.[3] Epoxide formation via reductive activation of dioxygen by metal complexes have been reported but each require the consumption of at least stoichiometric amounts of a reducing agent (hydride, H_2/Pt, ascorbic acid etc.).[4] Even the use of inexpensive electron and proton source is unsatisfactory for the large scale synthesis of epoxides. It is however possible to conceive dioxygenase activity for metal complexes, especially with the cheap and environmentally friendly metal Fe, for oxidation reactions, without the use of sacrificial reductant as shown below.



Scheme 1 Aerobic catalytic epoxidation with **1**.



$$(L)\overset{+n}{Fe} + O_2 \longrightarrow (L)\overset{+(n+1)}{Fe}\text{-}O\text{-}O\text{-}\overset{+(n+1)}{Fe}(L) \longrightarrow (L)\overset{+(n+2)}{Fe}(O) \xrightarrow{S \rightarrow S(O)} (L)\overset{+n}{Fe}$$

S = substrate; L = ligand

Few such efforts have been reported in the literature for iron-heme,[5] iron-nonheme[6] and Fe-TAML[7] complexes. Electron withdrawing porphyrin complexes have been shown to be an active catalyst for the hydroxylation of light alkanes by O_2 under mild conditions (1 atmosphere O_2, 25 °C).[5(b)] However, mechanistic studies indicate a radical-chain autoxidation pathway which results in poor selectivity.[8] A mononuclear non-heme iron complex, $[Fe^{II}(TMC)(CF_3SO_3)_2]$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), activates dioxygen for the catalytic aerobic oxidation of triphenyl phosphine, thioanisole and benzyl alcohol.[9] Fe-TAMLs have been shown to activate O_2 to form the corresponding room temperature stable $[\{(TAML)Fe\}_2^{IV}\text{-}\mu\text{-}Oxo]^{2-}$ dimer (TAML = tetraamido macrocyclic ligand). This dimer was reactive at elevated temperatures but its reactivity was only limited to oxidation of benzyl alcohol.[7] However, due to the inability of these complexes to form a reactive high valent mononuclear iron-oxo complex by reductive activation of O_2, they remained catalytically inactive for reactions such as the epoxidation of alkenes to epoxides. It should however be noted that such

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aerobic epoxidation of olefins using a ruthenium porphyrin complex, $Ru^{IV}(TMP)(O)_2$ {TMP = 5, 10, 15, 20-(tetramesityl)porphyrin}, without any coreductant was reported in 1985.[10] Subsequently, epoxidation with other ruthenium complexes and a ruthenium substituted polyoxometalate, $\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$ has also been observed.[11] Although in a biomimetic approach a plethora of model iron complexes have been generated to activate molecular oxygen, none of them are proven as a potential epoxidation catalyst where molecular oxygen can be used as a terminal oxidant without the use of coreductant.[12]

We have recently shown that Fe-complexes of biuret-modified TAML (bTAML) can be transformed to the corresponding $[\{(bTAML)Fe\}_2{}^{IV}\text{-}\mu\text{-}Oxo]^{2-}$ dimer (**2**) by reaction with 0.5 equiv. of NaOCl. Dimer **2** is a competent oxidant for both epoxidation of alkenes and hydroxylation of alkanes unlike the prototype Fe-TAML reported earlier by Collins.[13] Mechanistic studies indicate that this dimer (**2**) exists in equilibrium with the starting $[(bTAML)Fe^{III}]^-$ complex and the corresponding $[(bTAML)Fe^{V}(O)]^-$ complex (**3**) which upon reaction with alkenes and alkanes results in the quantitative regeneration of the starting Fe^{III} complex (**1**) at the end of the reaction.[13(b),13(d)] Since such μ-Oxo-$Fe_2{}^{IV}$ dimers can also be quantitatively generated from the reaction of Fe^{III}-TAML and O_2, we hypothesized that a catalytic epoxidation of alkenes can be performed only with complex **1** and O_2 as has been shown in Scheme 1. In this work we report for the first time the catalytic epoxidation of alkenes by Fe-Complex using O_2 as the oxidant in the absence of any addded sacrificial reductant.

We first investigated the reductive activation of O_2 by $[(bTAML)Fe^{III}(H_2O)]^-$ (**1**) using UV-vis spectroscopy. When solid complex **1** was added to dichloromethane (DCM; CH_2Cl_2) under air, a reddish color solution was observed which displayed an absorbance at 412 nm. Over time (~10 min) the color of the solution changed to dark brown and new spectral features having a broad peak between 850-1050 nm was observed (Fig. 1B). This solution having dark brown color has been previously characterized as the dimer **2** using ^1H NMR and EPR.[13(b)] This dimer **2** has also been independently synthesized earlier by the comproportionation reaction of $[(bTAML)Fe^{III}(Cl)]^{2-}$ and $[(bTAML)Fe^{V}(O)]^-$.[13(b)] Since the O-atom in dimer **2** was derived from molecular oxygen (shown earlier for related Fe-TAMLs and other iron-complexes[7,14]), we hypothesized that the reddish color solution observed upon dissolution of solid **1** in DCM under air was likely a dioxygen adduct of $[(bTAML)Fe]^-$ (**1-O_2**). To test this hypothesis, the reddish colored solution having a UV-vis spectral feature at 412 nm was freshly prepared and purged with argon (Ar) for 15 minutes. It was observed that spectral feature at 412 nm disapeared and a new peak at 375 nm appeared which remained unchanged over several hours upon rigorous exclusion of O_2 (Fig. 1A). The solution having an absorption maxima at 375 nm was also independently prepared by preparing a solution of **1** in DCM with rigorous exclusion of air. Upon opening this solution to air, the specral features changed, first with the appearaence of peak at 412 nm which then subsequently formed the dimer **2** as shown below (Fig. 1). Hence, the reactivity of **1** with O_2 to form a dimer complex **2** quantitatively was similar to what has been previously reproted for Fe-heme and Fe-TAML. However, unlike other systems, this dimer with bTAML ligand has been shown to be reactive with alkenes to form the corresponding epoxide under single turnover conditions and the parent Fe^{III} complex (**1**) is quantitatively generated at the end of the reaction.[13(d)] We therefore attempted the catalytic epoxidation of alkenes with **1** as the catalyst and O_2 as the terminal oxidant without the use of any sacrificial reductant.

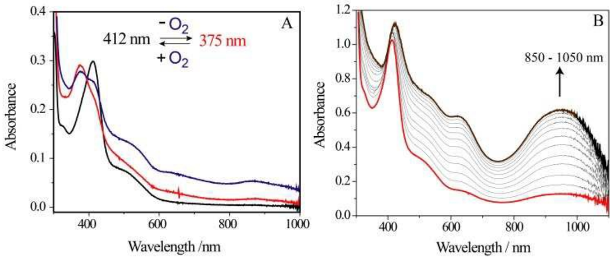

Fig. 1 (A) UV–vis spectral changes for reversible O_2 binding with complex **1** in DCM at room temperature (25 °C); (B) UV-vis spectral scan for the formation of dimer complex **2** by reaction of complex **1** (3×10^{-4} M) in DCM with air (10 min reaction time, 25 °C and atmospheric pressure).

To a solution of styrene (40 mM, 1 equiv.) was added complex **1** (0.006 equiv.; 0.25 mM) in 5 mL DCM and the reaction mixture was stirred at room temperature (RT, 25 °C) under air for 20 hours. At the end of the reaction, analysis of product showed formation of styrene oxide (2 mM, TON 8, TON = turnover number; moles of product divided by moles of catalyst **1**) with no other side products. We attempted to increase the product yield by carrying out the reaction at 5 bar O_2 pressure *via* increasing the reaction rate. A five fold increase of styrene oxide formation (10 mM, TON 40) was observed at 5 bar O_2 pressure. Upon further increasing the O_2 pressure to 10 bar and 20 bar, a decrease in the TON (34 and 26 respectively) was observed (Table S1, ESI[†]). Although high selectivity towards the formation of styrene oxide was observed (<10% side products), moderate yields of styrene oxide obtained led us to investigate the fate of the catalyst at the end of the reaction. It was observed that the color of the reaction mixture turned purple after completion of reaction and UV-vis of this spent reaction mixture showed formation of a monomeric Fe^{IV} complex reminiscent of $[(bTAML)Fe^{IV}(Cl)]^-$ which has been independently synthesized by us (Fig. S1, ESI[†]). Analysis of the spent reaction mixture by UV-vis and HR-MS showed the presence of $[(bTAML)Fe^{IV}(Cl)]^-$ complex (Fig. S2, ESI[†]). We hypothesized that this monomeric $[(bTAML)Fe^{IV}(Cl)]^-$ complex was formed from either reaction of $Fe^{V}(O)$ (**3**) (which exists in equilibrium with the dimer complex **2**) with DCM (Fig. S3, ESI[†]) or by a radical chain reaction, where Cl radical can react with complex **1**. Thus, likely inactivation pathway of catalyst during epoxidation reaction is DCM solvent mediated.

In order to avoid the catalyst deactivation reaction described above, we investigated the use of 1, 2-dichlorobenzene (DCB) as an alternative solvent. DCB is unreactive towards $Fe^{V}(O)$, and also has the necessary properties of hydrophobicity required for O_2 activation. Since

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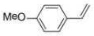
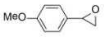
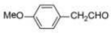
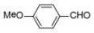
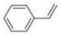
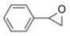
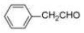
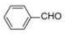
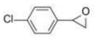
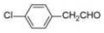
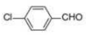
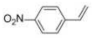
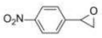
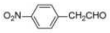
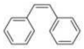
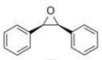
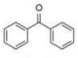
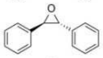
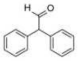
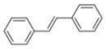
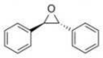
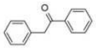
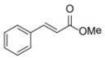
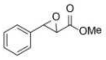
complex **1** was fairly insoluble in 1, 2-dichlorobenzene at room temperature (25 °C), an elevated temperature of 50 °C was used to increase its solubility during the reaction. Using DCB as the solvent at 50 °C under atmospheric pressure of air, epoxidation of styrene resulted in styrene oxide with moderate yields (10 mM, TON 41). For the electron rich alkene 4-methoxystyrene, the amount of epoxide obtained doubled to 20 mM (TON: 80; Table 1, Entry 1) while with electron deficient alkene like methyl *trans*-cinnamate, a very small yield of the epoxide product was obtained (TON: 0.4; Table 1, Entry 8). The selectivity of the catalyst towards oxidation of C=C bond over C-H bond was observed in the case of norbornene. This is in line with what was observed for reactions of norbornene with $Fe^V(O)$.[13(d)] A low yield of epoxide product was obtained with *trans*-stilbene (TON = 2.4; Table 1, Entry 7) in comparison to *cis*-stilbene (TON = 12; Table 1, Entry 6). The most probable reason for the reduced yield of epoxide with *trans*-stilbene is its sterically bulky nature which hinders the approach of the iron-oxo intermediate towards the C=C bond.

Table 1 Epoxidation of different alkenes by complex **1** and O_2 in DCB at 50 °C.

Entry	Substrate	Product	TON	Other products	TON
1.			80 (5)		Trace
					3.9
2.			41 (3)		1.6
					1.9
3.			39 (3)		3.9
					2.1
4.			32 (3)		2.9
5.			29 (3)		0.9
6.			09 (1)		0.9
			03 (0.2)		1.1
7.			2.4 (0.2)		0.6
8.			0.4 (0.1)		

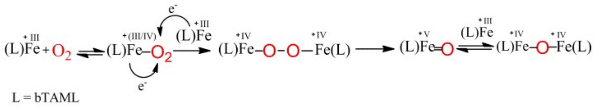
Reaction conditions: Complex 1 (0.25 mM), substrate (40 mM), air (atmospheric pressure), temperature 50 °C, 20 hours; TON = moles of product/moles of catalyst **1**; values in parentheses represents possible error (±) in TON determination.

In order to understand the effect of electronic environment associated with the substituent on styrene, different para-substituted styrene derivatives showed enhanced rate of epoxide formation for electron donating substituents than electron withdrawing para substituents. A relatively small hammett ρ value of –0.87 was obtained for styrene and its para-substituted analogue (Fig. S4, ESI†), indicating the electrophilic nature of the terminal oxidant. In case of *cis*-stilbene, a mixture of both *cis* and *trans* configured epoxides were observed which points to the formation of a radical intermediate where it would allow C-C bond rotation to give the stereoisomers. Such isomerization was also observed for the epoxidation of *cis*-stilbene with $Fe^V(O)$.[13(d)] All these observations point out the involvement of a high valent electrophilic iron-oxo intermediate reminiscent of $Fe^V(O)$.

To convincingly demonstrate that the O-atom present in the epoxide resulted from O_2, epoxidation reactions were carried out with $^{18}O_2$. An incorporation of ~35% ^{18}O label was observed in the product styrene oxide (Fig. S5, ESI†). The low incorporation of ^{18}O atom is due to the exchange of O-atom of $Fe^V(^{18}O)$ with $H_2{}^{16}O$ present in the reaction mixture and this is aided by long reaction times required for the reaction of styrene with **2**. As a consequence, the remaining 65% styrene oxide showed ^{16}O incorporation. In fact, when $^{18}O_2$ was used for the sulfoxidation reaction of thioanisole, where the reaction rates are much faster, ~70% incorporation of labelled ^{18}O was observed in the product (Fig. S6, ESI†). Similar observations have been reported in related systems.[15,9,7(a)] We also carried out epoxidation reaction in the presence of small amounts of $H_2{}^{18}O$ in air. Here ~45% of the labelled ^{18}O was incorporated in the product (Fig. S7, ESI†). As a control, the reaction of complex **1** and styrene in O_2 free environment with $H_2{}^{18}O$ in DCM showed no product formation over a period of 20 hrs. These evidences clearly indicate molecular dioxygen as the O-atom source for the epoxide formation with complex **1** and the operation of an electrophilic high-valent iron-oxo as the active intermediate for the epoxidation reaction.

The progress of the reaction in DCB was similar to what was observed in DCM. Reaction of complex **1** with O_2 in DCB resulted in the formation of dimer complex **2**. However, at the end of the reaction no purple solution of inactive $[(bTAML)Fe^{IV}(Cl)]^-$ complex was observed. Instead, a yellow precipitate was observed which was isolated by filtration. This precipitate was insoluble in DCM or any non-coordinating solvent, but it became solubilized upon addition of a coordinating additive (acetonitrile, methanol etc.). The UV-vis and HR-MS of the acetonitrile solution of this precipitate was identical to the solution of $(bTAML)Fe^{III}$ complex in acetonitrile (Fig. S8 and S9, ESI†). This indicates that no chemical change of the complex took place during the reaction and the complex structure remained intact. The likely reason for precipitation could be aggregation of complex $(bTAML)Fe^{III}$ *via* binding of ligand amide O-atom to the electrophilic Fe^{III} center in the absence of a coordinating ligand. When acetonitrile was removed from this solution, the solid left back was reused to catalyze aerobic epoxidation in DCB.

We propose that upon solubilizing **1** in a hydrophobic and non-cordinating solvent like DCB, the axial H_2O is replaced by O_2. This is indicated from our UV-vis studies (Fig. 1) and supported by literature reports on related complexes.[7] The Fe-O_2 adduct reacts with a second molecule of iron complex to form a peroxobridged iron dimer $Fe^{IV}OOFe^{IV}$ (which remain undetected). Subsequent homolytic cleavage of O-O bond in $Fe^{IV}OOFe^{IV}$ results in formation of the putative $Fe^V(O)$ which immediately comproportionates with the parental Fe^{III} complex to form the dimer complex **2** (Scheme 2). Kinetic studies on the formation of $Fe^{IV}OFe^{IV}$ from Fe-O_2 indicate a second order dependency on catalyst concentration which partly supports this mechanism (Fig. S10, ESI†).



Scheme 2 Proposed mechanism for the formation of **2** by reaction of complex **1** and O_2.

Unlike previous reports with iron-heme and Fe-TAML complexes, this iron(IV) dimer **2** has limited stability in presence of substrate like alkene or alkanes, since it rests in an equilibrium with the Fe^{V}(O) and Fe^{III} complex. Kinetic evidence for epoxidation reaction indicates presence of such an equilibrium.[13(d)] In addition, when this dimer was incubated with a nitro substituted $[(NO_2\text{-bTAML})Fe^{III}(Cl)]^{2-}$ complex,[16] the scrambling of O-atom from **2** was observed by high-resolution mass spectrometry (HR-MS) analysis (Fig. S11, ESI[†]) which substantiates our hypothesis. Upon addition of alkene, the Fe^{V}(O) reacts with alkene to form epoxide and regenerates the starting Fe^{III} complex, which again reacts with another O_2 molecule to start the cycle once again. This catalytic cycle continues until the catalyst precipitates out from the solution. We believe that complex **1** functions like a dioxygenase, where both the O-atoms of O_2 molecule are utilized for substrate oxidation. Such atom-economical use of O_2 is clearly superior to monooxygenases where one O-atom inserts into the organic substrate while the other O-atom is reduced to H_2O in the presence of coreductant.

In summary, monomeric Fe^{III}-bTAML complex **1** is competent to activate molecular dioxygen (O_2) to generate a dimeric complex **2** which is reactive towards alkenes. The catalytic use of O_2 by a monomeric iron-complex towards epoxidation reaction without the use of any coreductant is unprecedented. Above investigations indicate the involvement of a high valent Fe^{V}(O) species during the reaction of complex **1** and O_2 with alkene; although we are currently unable to spectroscopically observe this intermediate under the reaction conditions. Further investigations for understanding the binding of O_2 with monomeric iron(III) centre and sequential steps for the dimer formation are being carried out in our laboratory.

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