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Efficient epoxidation of olefins by H_2O_2 catalyzed by iron "helmet" phthalocyanines†

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High yields of epoxides were obtained in the oxidation of a large range of olefins using 1.2–2 equiv. of H_2O_2 in the presence of iron helmet phthalocyanines. The involvement of high-valent iron oxo species was evidenced using cryospray mass spectrometry.

Clean oxidation of hydrocarbons using hydrogen peroxide under mild conditions continues to be a challenge in catalysis. The selective epoxidation of olefins with high efficiency in terms of the H_2O_2 amount is particularly difficult to achieve. Bio-inspired macrocyclic complexes have been extensively investigated as catalysts for mild oxidation. Application of metal complexes on porphyrin,[1] phthalocyanine,[2] corrole[3] and corrolazine[4] platforms as bio-inspired catalysts for various oxidation reactions has been well-documented. Such a variety of supporting ligands having different properties allows obtaining a very different reactivity of the corresponding complexes in catalysis. The catalytic activities of the complexes can be further tuned by introducing electron-withdrawing substituents at the periphery of the macrocyclic ligand.[1b] Another possible approach is to modify the parent ring system of the supporting ligands thus obtaining new complexes. Indeed, significant progress has been achieved in the preparation of numerous confused porphyrinoids *via* fusion, expansion and contraction, resulting in a great variety of structures.[5] As for the phthalocyanine core, only a few cases of modification of the parent phthalocyanine ring have been described.[6–9] Expanded phthalocyanines with two Mo or W central ions and four isoindole units have been prepared under conditions typical for phthalocyanine formation.[6] However, the catalytic properties of confused or modified macrocycles have rarely been explored.

Our research group has been involved in the development of the catalytic chemistry of metal phthalocyanine complexes.[2a,10] In particular, we have found that μ-nitrido diiron phthalocyanines are efficient catalysts for oxidation,[11] oxidative dehalogenation[12] and C–C bond formation.[13] The exceptional catalytic properties of μ-nitrido diiron complexes[14] prompted us to initiate a project on the search of novel binuclear structures as potential catalysts. During preparation of binuclear complexes based on iron tetra-*tert*-butylphthalocyanine we have found that the resulting materials contained small amounts of brown admixture which showed a significant activity in the epoxidation of olefins by H_2O_2. Spectroscopic analyses using CSI-MS, UV-vis and EPR methods indicated the formation of a bicyclic pentadentate 14,28-[1,3-diimino-6-*tert*-butylisoindolinato]-tetra-*tert*-butylphthalocyaninatoiron(III) complex (**1-Fe**, Fig. 1).

This kind of modified phthalocyanine complex was described for the first time by McGaff and co-workers using an unsubstituted phthalocyanine core.[8b] X-ray structure of the 14,28-[1,3-diiminoisoindolinato]phthalocyaninatoiron(III) (**2-Fe**, helmet phthalocyanine) showed a strong distortion of the phthalocyanine plane and a short Fe–N_{axial} bond of 1.866 Å. DFT calculations

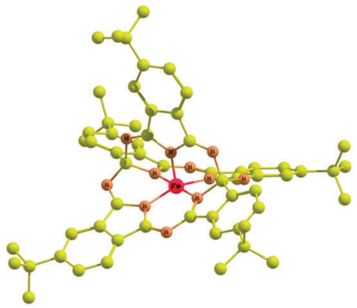

Fig. 1 Optimized DFT structure of one positional isomer of the 14,28-[1,3-diimino-6-*tert*-butylisoindolinato]tetra-*tert*-butylphthalocyaninatoiron(III) complex (**1-Fe**). Synthesized **1-Fe** represents a mixture of positional isomers. Hydrogen atoms are omitted for clarity.

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Table 1 Epoxidation of cyclohexene by H_2O_2 catalyzed by iron helmet phthalocyanine complexes[a]

Entry	Catalyst (mol%)	Substrate (M)	Conversion (%) (time (h))	Selectivity (%)
1	**1-Fe** (1)	0.1	25 (2)	74
2	**1-Fe** (1)	0.3	27 (2)	74
3[b]	**1-Fe** (1)	0.3	20 (2)	75
4[b]	**1-Fe** (3)	0.1	85 (2)	84
5	**2-Fe** (1)	0.1	85 (2)	89
6	**2-Fe** (1)	0.3	97 (2)	92
7	**2-Fe** (0.5)	0.3	56 (2.5)	86
8[c]	**2-Fe** (0.1)	1	18 (0.3)	65

[a] Reaction conditions: MeCN, $[H_2O_2]:[\text{cyclohexene}] = 2:1$, air, 25 °C. [b] Under argon. [c] $[H_2O_2]:[\text{cyclohexene}] = 1.2:1$.

show that the substituted helmet complex is also distorted and the substituents can create some hindrance around the metal site that might be useful for catalysis. The typical feature for the phthalocyanine Q-band in the UV-vis spectrum was absent owing to the interruption of conjugation in the macrocyclic ring.[8b] The same feature was observed for **1-Fe**. McGaff and co-workers have shown interesting catalytic properties of **2-Fe** in the oxidation of cycloalkanes by H_2O_2.[8c] This result has prompted us to prepare unsubstituted **2-Fe** and to examine the two helmet complexes in epoxidation of olefins.

Initial experiments were performed using cyclohexene as a model substrate with 1.2–2 equiv. of H_2O_2 at 25 °C (Table 1). While both **1-Fe** and **2-Fe** complexes provided epoxides with a good selectivity, **2-Fe** exhibited a higher conversion, most probably due to a higher stability. Similar results were obtained under air and argon suggesting that O_2 was not involved in the reaction. Under optimal conditions (1 mol% **2-Fe** and 0.3 M substrate), cyclohexene was oxidized to epoxide with 97% conversion and 92% selectivity at room temperature (Table 1, entry 6). The yields of cyclohexene-2-ol and cyclohexene-2-one were 4% and 1%, respectively. Noteworthily, this reaction is very efficient in terms of oxidant utilization: only 2 equiv. of H_2O_2 was used.

When ^{t}BuOOH was used as the oxidant under conditions of entry 7, Table 1, cyclohexene-2-one was obtained in 65% selectivity and 83% conversion. Thus, the selectivity of olefin oxidation can be controlled by the appropriate choice of the oxidant.

The scope of the **2-Fe**–H_2O_2 system was evaluated in the oxidation of various olefins (Table 2).

Table 2 Epoxidation of olefins using the **2-Fe**–H_2O_2 system[a]

Entry	Substrate	Conversion (%) (time (h))	Selectivity (%)	TOF[b] (h^{-1})
1	Cyclohexene	97 (2)	92	212
2	Cyclooctene	100 (0.5)	90	207
3	α-Pinene	100 (1)	60	157
4	β-Pinene	100 (1.5)	71	148
5	Limonene	72 (1)	95[c]	143
6	Norbornene	14 (3)	100	27
7	1-Octene	13 (0.5)	95	140
8	*trans*-5-Decene	100 (0.5)	96	234
9	Styrene	100 (0.5)	95	184
10	*trans*-β-Methylstyrene	100 (0.17)	91	1070
11	4-Methylstyrene	100 (0.33)	95	470
12	4-*tert*-Butylstyrene	100 (0.5)	95	335
13	4-Chlorostyrene	100 (0.5)	95	421
14	4-Fluorostyrene	100 (0.5)	95	175

[a] Reaction conditions: MeCN, 1 mol% **2-Fe**, 0.3 M olefin, $[H_2O_2]:[\text{olefin}] = 2:1$, air, 25 °C. [b] The aliquots of the reaction mixture were withdrawn every 6 min and analyzed using GC. The reactions were stopped at the reaction time when no further substrate conversion occurred. The turnover frequency (TOF) was determined from the initial rate of the substrate consumption, mmol of substrate/mmol of catalyst per hour. [c] 1,2-Epoxide (55%), 8,9-epoxide (30%), bis-epoxide (10%).

The catalytic system was very efficient for the epoxidation of cyclic and linear olefins except for terminal 1-octene (Table 2, entry 7) and norbornene (Table 2, entry 6). The reason for the relative inertness of norbornene is not yet clear. Note that McGaff and co-workers observed a much lower activity of the **2-Fe**–H_2O_2 system in the oxidation of indan ($BDE_{C\text{–}H}$ = 82 kcal mol^{-1}) as compared to the oxidation of cyclohexane ($BDE_{C\text{–}H}$ = 99 kcal mol^{-1}).[8c] One might propose that a saddle distortion of the **2-Fe** molecule could make an approach of sterically demanding substrates like norbornene or indan more difficult. Styrenes bearing electron-donating and electron-withdrawing substituents provided epoxides with 95% yields. Importantly, no appreciable formation of benzaldehyde (1–2%), a typical by-product in epoxidation of styrenes, was observed. The catalytic system **2-Fe** (1 mol%)–H_2O_2 (0.2 M) showed epoxidation of 0.1 M *cis*-stilbene (60% conversion, 95% selectivity after 2 h) with high stereoselectivity. *cis*-Epoxide and *trans*-epoxide were obtained in a 96 : 4 ratio.

A high selectivity of oxidation of olefins to epoxides and the absence of influence of oxygen on the reaction as well as a high stereoselectivity of *cis*-stilbene epoxidation suggest the involvement of iron-centered oxo species. Such high-valent iron oxo complexes showing epoxidizing activity are well-documented entities in the cases of porphyrin, corrole, and non-heme ligands.[1–4,15] However, the corresponding phthalocyanine-based species have often been postulated as active species but have never been characterized. Only recently, we have prepared the first high-valent oxo complex on the flat phthalocyanine platform.[10d] To explore a possibility of the formation of **2-Fe** oxo species we have conducted a cryospray mass spectrometry study of interaction of **2-Fe** with H_2O_2.

It should be noted that all **1-Fe** and **2-Fe** species exhibit a strong tendency for protonation most probably owing to basicity of imine nitrogen atoms. **2-Fe** showed a strong signal at m/z = 711 attributed to monoprotonated $[\mathbf{2\text{-}Fe} + H]^+$ species. Due to electron-donating *tert*-butyl substituents, the **1-Fe** complex was even more protonated under cryospray MS conditions. Signals at m/z = 992 and m/z = 993 corresponding to doubly and triply protonated **1-Fe** species were observed. Because of less complicated protonation behaviour, **2-Fe** was chosen for cryospray MS study of the interaction with H_2O_2. After testing several solvents, including CH_2Cl_2, CH_3CN, CH_3OH, DMF, acetone and their mixtures, a CH_3OH–acetone mixture (80 : 20 v/v) was found to be the most suitable solvent in which **2-Fe** showed a lesser protonation tendency and sufficient stability of formed oxo species. H_2O_2 was added to a 10^{-6} M **2-Fe** solution at −45 °C or −60 °C. The resulting mixture was incubated at low temperature for 2–3 min and MS analysis was

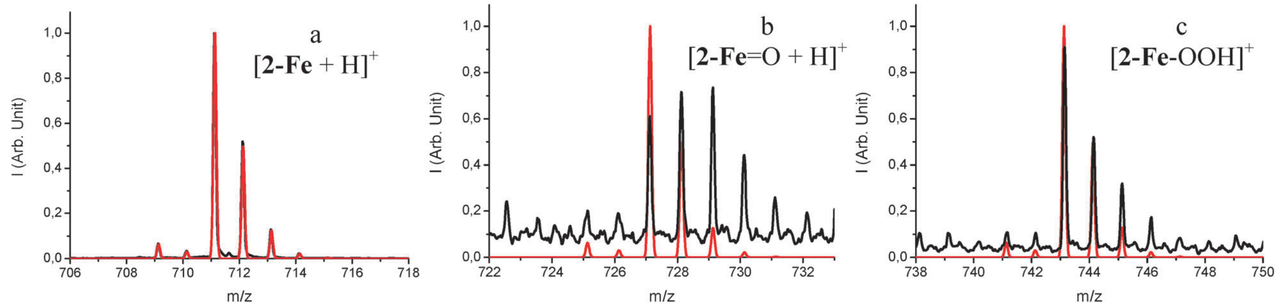
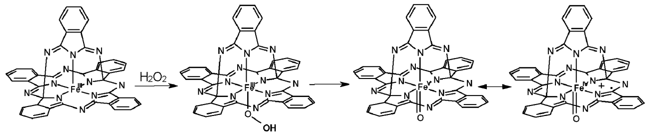


Fig. 2 Positive ion CSI MS study of the reaction of **2-Fe** and H_2O_2 at −40 °C. Experimental (black) and simulated (red) isotopic distribution patterns of molecular peaks of (a) [**2-Fe** + H]$^+$, (b) [**2-Fe**=O + H]$^+$ and (c) [**2-Fe**−OOH]$^+$.



Scheme 1 Proposed mechanism for the formation of high-valent iron oxo helmet phthalocyanine species.

rapidly performed at −40 °C in the positive detection mode. Along with the signal of the starting complex at *m/z* = 711 (for [**2-Fe** + H]$^+$) signals at *m/z* = 727 and *m/z* = 743 corresponding to [**2-Fe**=O + H]$^+$ and [**2-Fe**−OOH]$^+$, respectively, were observed (Fig. 2). While experimental isotopic distribution patterns of molecular peaks of [**2-Fe** + H]$^+$ and [**2-Fe**−OOH]$^+$ species are identical to theoretical ones, the comparison of experimental and simulated molecular peak clusters of oxo species suggests a contribution of several protonated forms. The experimental isotopic distribution pattern of the molecular peak of the oxo complex can be simulated suggesting the presence of ∼55% of monoprotonated and ∼45% of diprotonated species. The transient nature of this signal is compatible with the proposed structure of high-valent iron oxo species capable of performing the selective epoxidation of olefins. A possible mechanism of formation of this species is proposed in Scheme 1.

In conclusion, we have shown highly efficient mild epoxidation of a range of olefins by H_2O_2 mediated by iron helmet phthalocyanines for the first time. The hydroperoxo and high-valent iron oxo species based on the modified phthalocyanine core were detected for the first time. The latter was proposed to be involved in the selective epoxidation of olefins.

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