2: L-Aspartic acid (asp) (1 mmol) was added to an aqueous solution of $Dy(ClO_4)_3$ under stirring and heating at 80 °C, then 0.1 M aqueous NaOH was added to adjust the pH to 6.5. The precipitate formed due to the partial hydrolysis of Ln^{3+} ions was filtered off and the filtrate was allowed to stand at room temperature. Colorless block-shaped crystals were obtained after one month. Yield: 34 % based on the aspartic acid. Elemental analysis calcd for $C_{12}H_{54}Cl_2Dy_4N_3O_{42}$ (%): N 2.57, C 8.82, H 3.31; found: N 2.16, C 7.49, H 3.22.

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[9] Crystal structure analysis data: compound **1**: $[Gd_4(Hpro)_4(pro)_2(\mu_3\text{-}OH)_4(H_2O)_7](ClO_4)_6 \cdot 6H_2O$, $M_r = 2216.72$, rhombohedral, $R3$, $a = b = c = 12.8953(15)$ Å, $\alpha = \beta = \gamma = 100.663(17)^\circ$, $V = 2016.8(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.825$ Mg m^{-3}, $\mu = 3.545$ mm^{-1}, $GOF = 1.083$, $F(000) = 1086$, $R1 = 0.0683$, $wR2 = 0.1876$, 317 parameters, 4130 reflections $[I > 2\sigma(I)]$. The intensity data was collected at 294 K on a Rigaku RAXIS IIc imaging-plate diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min} = 3^\circ$, $2\theta_{max} = 55^\circ$, 34 oscillation frames in the range of 0–180°, exposure 8 min per frame). A self-consistent semiempirical absorption correction based on Fourier coefficient fitting was applied using ABSCOR. Compound **2**: $C_{12}H_{54}Cl_2Dy_4N_3O_{42}$, $M_r = 1633.48$, orthohombic, $P2_12_12_1$, $a = 14.011(3)$, $b = 18.822(4)$, $c = 23.421(5)$ Å, $V = 6176(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.757$ Mg m^{-3}, $\mu = 4.958$ mm^{-1}, $F(000) = 3124$, $GOF = 1.013$. The data were collected on a Nonius Kappa CCD with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXL 97 program. $R1 = 0.0497$, $wR2 = 0.1354$, 483 parameters, 12942 reflections $[I > 2\sigma(I)]$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-141086 (**1**) and CCDC-141085 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Remarkable Anionic Axial Ligand Effects of Iron(III) Porphyrin Complexes on the Catalytic Oxygenations of Hydrocarbons by H_2O_2 and the Formation of Oxoiron(IV) Porphyrin Intermediates by *m*-Chloroperoxybenzoic Acid**

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The reactions of iron(III) porphyrin complexes with various oxidants such as peroxy acids and hydroperoxides have been extensively studied for the past two decades, with the intention of elucidating the mechanisms of O–O bond activation and developing biomimetic oxygenation reactions.[1] Since hydrogen peroxide (H_2O_2) is a biologically important and environmentally clean oxidant, use of the oxidant in catalytic oxygenation of hydrocarbons by iron porphyrin complexes has attracted much attention in the communities of bioinorganic and oxidation chemistry.[1] Traylor et al. reported for the first time that the reactions of iron porphyrins with H_2O_2 in a protic solvent such as CH_3OH generate oxoiron(IV) porphyrin cation radical complexes $[Fe^{IV}(porp)^{+\bullet}(O)]$ that epoxidize olefins to give the corresponding oxide products.[2] We and Mansuy et al. also showed recently that highly electron-deficient iron porphyrin complexes react with H_2O_2 to form intermediates that are capable of oxygenating olefins and unactivated alkanes in aprotic solvent.[3, 4]

Another oxidant that has been widely used in the mechanistic studies of O–O bond activation by iron(III) porphyrin complexes is peroxy acids such as *m*-chloroperoxybenzoic acid (*m*-CPBA).[1] It is generally believed that iron porphyrins react with peroxy acids to form $[Fe^{IV}(porp)^{+\bullet}(O)]$ by O–O bond heterolysis in polar solvents such as CH_2Cl_2.[5] As far as we have been able to discern, there is no report that shows that both heterolysis and homolysis can occur concurrently in the *m*-CPBA reactions in polar solvent. Herein, we report two novel results that were obtained using an electron-deficient iron(III) porphyrin complex containing different anionic axial ligands: the remarkable anionic axial ligand effects on 1) the catalytic epoxidation and hydroxylation of hydrocarbons by

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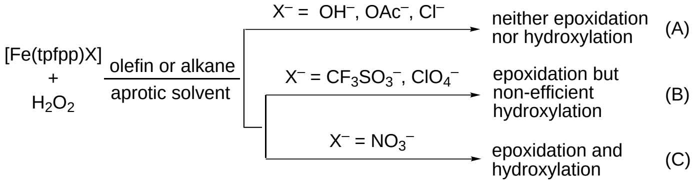
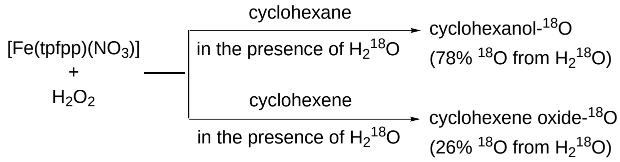
aqueous 30 % H_2O_2 in aprotic solvent and 2) the formation of two distinct oxoiron(IV) porphyrin intermediates in *m*-CPBA reactions in polar solvent.

When the catalytic oxygenations of olefins and alkanes by H_2O_2 were carried out in the presence of [Fe(tpfpp)X] (tpfpp = *meso*-tetrakis(pentafluorophenyl)porphinato dianion) in a solvent mixture of CH_3CN and CH_2Cl_2, no or only trace amounts of oxygenated products such as epoxides and alcohols were formed in the reactions where X^- in [Fe(tpfpp)X] was OH^-, $CH_3CO_2^-$, and Cl^- (see Table 1 and Scheme 1, pathway A). However, when the identical reactions were carried out with [Fe(tpfpp)X] complexes containing different anionic axial ligands such as $CF_3SO_3^-$, ClO_4^-, and NO_3^-, the formation of epoxide and alcohol products was observed (see Table 1). In the epoxidation of cyclohexene, high yields of cyclohexene oxide were formed with trace amounts of allylic oxidation products (Table 1, entry 1). Also, *cis*-stilbene was predominantly oxidized to *cis*-stilbene oxide with trace amounts of *trans*-stilbene oxide and benzaldehyde formation (Table 1, entry 2). These results indicate that Fenton-type oxidation reactions were not involved in the olefin epoxidation reactions.[6] More interestingly, in the hydroxylation of alkanes, the [Fe(tpfpp)(NO_3)] complex yielded alcohols as the major products with high alcohol to ketone ratios (Table 1, entries 3 and 4; also see Scheme 1, pathway C).[7] The kinetic isotope effect (k_H/k_D) was determined to be 4.3 ± 0.3 in the competitive hydroxylation of cyclohexane and [D_{12}]cyclohexane by [Fe(tpfpp)(NO_3)] and H_2O_2 at 20 °C.[3a]



Scheme 1. A schemtic diagram showing the anionic axial ligand effect on the epoxidation and hydroxylation of hydrocarbons by [Fe(tpfpp)X] and H_2O_2.

We then studied the hydroxylation of cyclohexane and the epoxidation of cyclohexene by [Fe(tpfpp)(NO_3)] and H_2O_2 by using isotopically labeled water ($H_2{}^{18}O$) to gain a better understanding of the nature of reactive intermediates responsible for the oxygenations of alkanes and olefins.[8] The percentages of ^{18}O incorporated from $H_2{}^{18}O$ into cyclohexanol (20 % yield based on H_2O_2 used) and cyclohexene oxide (55 % yield based on H_2O_2 used) were 78 ± 4 % and 26 ± 3 %, respectively (Scheme 2). These results demonstrate that the reactive species, which was formed in the reaction of [Fe(tpfpp)(NO_3)] and H_2O_2 carried out in the presence of water, was an oxoiron(IV) porphyrin cation radical complex [$Fe^{IV}(tpfpp)^{+\bullet}(O)$] (**1**).[8] We also suggest that the different amounts of ^{18}O incorporation into the cyclohexanol and cyclohexene oxide is due to the fact that oxygen transfer from the intermediate to organic substrates competes with the oxygen exchange between the intermediate and labeled water.[8b, 9] Thus, the reactivity of iron porphyrin catalysts in epoxidation and hydroxylation reactions is markedly influenced by the nature of anionic axial ligands, and the catalytic efficiency of the [Fe(tpfpp)X] complexes decreases in the order: $X^- = NO_3^- > CF_3SO_3^-, ClO_4^- \gg OAc^-, Cl^- \geq OH^-$.



Scheme 2. Results of ^{18}O-labeled water experiments in the oxygenation of cyclohexane and cyclohexene by [Fe(tpfpp)(NO_3)] and H_2O_2.

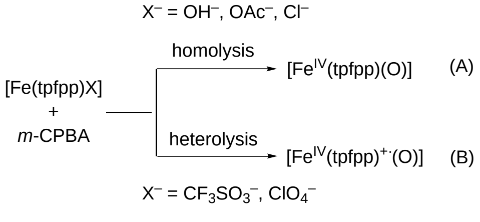
The anionic axial ligand effect was also observed in the reactions of [Fe(tpfpp)X] and *m*-CPBA carried out in polar

Table 1. Effect of anionic axial ligands of [Fe(tpfpp)X] on the catalytic epoxidation and hydroxylation of hydrocarbons by H_2O_2.[a,b]

Entry	Substrate	Products	Yields of products[c] [%]					
			$X^- = OH^-$	OAc^-	Cl^-	$CF_3SO_3^-$	ClO_4^-	NO_3^-
A. Epoxidation of olefins								
1	cyclohexene	cyclohexene oxide	< 2	< 2	< 2	65 ± 5	68 ± 5	78 ± 6
		cyclohexenol	0	3 ± 3	0	3 ± 2	4 ± 2	6 ± 4
		cyclohexenone	0	3 ± 3	0	2 ± 2	2 ± 2	5 ± 3
2	*cis*-stilbene	*cis*-stilbene oxide	< 2	9 ± 2	14 ± 2	78 ± 5	76 ± 5	74 ± 5
		trans-stilbene oxide	0	0	0	3 ± 1	3 ± 1	3 ± 1
		benzaldehyde	2 ± 1	2 ± 1	2 ± 1	3 ± 1	3 ± 1	3 ± 1
B. Hydroxylation of alkanes								
3	cyclohexane	cyclohexanol	< 1	< 1	< 1	6 ± 1	6 ± 1	30 ± 2
		cyclohexanone	0	0	0	1 ± 1	1 ± 1	1 ± 1
4	[D_{12}]cyclohexane	[D_{12}]cyclohexanol	< 1	< 1	< 1	3 ± 1	3 ± 1	17 ± 2
		[D_{10}]cyclohexanone	0	0	0	0	0	0
C. Fe^{III}/Fe^{II} redox potential[d]								
5			–[e]	– 0.44	– 0.44	– 0.12	– 0.11	– 0.15

[a] See Experimental Section for detailed reaction procedures. [b] All reactions were run at least in triplicate, and the data reported represent the average of these reactions. Although the yields and product distributions obtained in the oxygenation reactions were not affected by molecular oxygen, all the reactions were performed under argon atmosphere at room temperature. All iron porphyrin complexes used in this study were obtained from Mid-Century Chemicals and used without further purification. [c] Based on the amounts of H_2O_2 used. [d] In volts versus Fc/Fc^+ couple. [e] No clear reversible cathodic and anodic peaks were obtained.

solvent. As mentioned above, it is generally believed that the reactions of iron(III) porphyrin complexes with *m*-CPBA in polar solvent generate [Fe^{IV}(porp)$^{+\bullet}$(O)] by O–O bond heterolysis.[5] However, when [Fe(tpfpp)X] complexes containing OH$^-$, OAc$^-$, and Cl$^-$ as axial ligands were allowed to react with *m*-CPBA in a solvent mixture of CH_2Cl_2 and CH_3CN at –60 °C, the formation of [Fe^{IV}(tpfpp)(O)] (**2**) was observed (Scheme 3, pathway A; also see Figure 1 A for the UV/Vis spectrum of 2-Cl (i.e. [Fe^{IV}(tpfpp)(O)] generated from [Fe(tpfpp)Cl]) as a representative of the spectra of all other compounds).[10] In contrast, when the identical reactions were carried out with [Fe(tpfpp)X] (X$^-$ = $CF_3SO_3^-$ and ClO_4^-) complexes, [Fe^{IV}(tpfpp)$^{+\bullet}$(O)] (**1**) was formed by O–O bond heterolysis (Scheme 3, pathway B; also see Figure 1 B, UV/Vis spectrum of **1**-CF_3SO_3 (i.e., [Fe^{IV}(tpfpp)$^{+\bullet}$(O)] generated from [Fe(tpfpp)CF_3SO_3]).[11] On the basis of these results, we conclude that the mechanism of O–O bond cleavage of *m*-CPBA by electron-deficient iron porphyrin complexes is significantly affected by the nature of the anionic axial ligands and that both heterolysis and homolysis can occur in the reactions of iron porphyrin complexes with *m*-CPBA even in polar solvent.[12]



Scheme 3. Dependence of heterolytic versus homolytic O–O bond cleavage of *m*-CPBA on the anionic axial ligands of [Fe(tpfpp)X] in polar solvent.

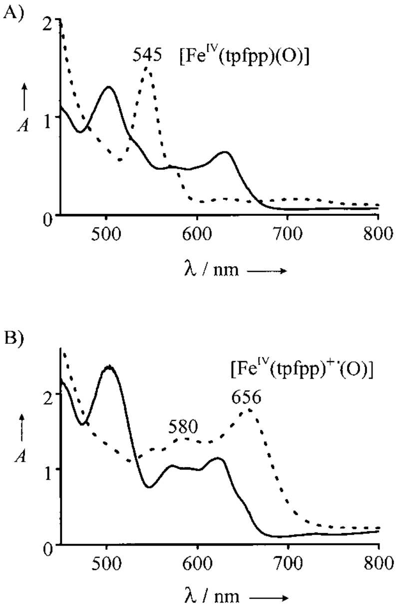


Figure 1. UV/Vis spectra of A) [Fe(tpfpp)Cl] (solid line) and **2**-Cl (dotted line) and B) [Fe(tpfpp)(CF_3SO_3)] (solid line) and **1**-CF_3SO_3 (dotted line).[10a)]

Then, what is the effect of the anionic axial ligands on the activation of H_2O_2 and the mechanism of O–O bond cleavage of *m*-CPBA? It is well-known that the types and rates of O–O bond cleavage of [(porp)Fe^{III}–OOR] species are significantly affected by the electronic properties of axial ligands bound to the iron(III) ion in heme enzymes and iron porphyrin models.[13] In addition, the reactivities of oxoiron(IV) porphyrin cation radical [Fe^{IV}(porp)$^{+\bullet}$(O)] and iron(III) peroxo porphyrin intermediates [Fe^{III}(porp)(O_2^-)] are shown to be greatly influenced by the electronic nature of axial ligands bound to the iron porphyrin intermediates.[13–15] Therefore, it may be suggested that the anionic axial ligand effect observed in this study is due to the difference of the electron-donating ability of the anionic axial ligands. In fact, the electron-donating ability of the anionic axial ligands has been determined from the NMR and resonance-Raman studies of [Fe(tmp)X] (X$^-$ = Cl$^-$, OAc$^-$, $CF_3SO_3^-$, and ClO_4^-; tmp = *meso*-tetramesitylporphinato dianion) complexes and their oxidized derivatives, [(tmp)$^{+\bullet}$Fe^{IV}=O(X)].[16] On the basis of the NMR and resonance-Raman spectral features, the axial ligands bound to the [Fe(tmp)X] complexes were grouped into two sets: one set with stronger electron donors such as Cl$^-$ and OAc$^-$ and another set with weaker electron donors such as $CF_3SO_3^-$ and ClO_4^-. We also found in the present study that the anionic axial ligands of [Fe(tpfpp)X] are divided into two groups, on the basis of Fe^{III}/Fe^{II} reduction potentials (Table 1, entry 5) and the reactivity patterns of the [Fe(tpfpp)X] complexes: one group with stronger electron donors such as Cl$^-$ and OAc$^-$ and another group with weaker electron donors such as $CF_3SO_3^-$, ClO_4^-, and NO_3^-. Interestingly, the [Fe(tpfpp)X] complexes with the axial ligands of weaker electron donors (i.e., $CF_3SO_3^-$, ClO_4^-, and NO_3^-) give high yields of oxygenated products in the H_2O_2 reactions and form **1** in the *m*-CPBA reactions, whereas the iron porphyrins with the axial ligands of stronger electron donors (i.e., Cl$^-$ and OAc$^-$) yield low or no oxygenated products in the H_2O_2 reactions and form **2** in the reactions of *m*-CPBA.[17] Although we propose at this moment that the electron-donating ability of the anionic axial ligands is a key factor in controlling the catalytic activity of [Fe(tpfpp)X] complexes in the H_2O_2 reactions and the formation of oxoiron(IV) porphyrin intermediates in the *m*-CPBA reactions, more detailed studies are in progress to gain a better understanding of the exact roles of the anionic axial ligands.

Experimental Section

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.

All reactions were carried out at room temperature under argon. Catalytic epoxidation of olefins: H_2O_2 (0.05 mmol, diluted in CH_3CN (0.3 mL)) was slowly added over a period of 20 min to a stirred solution containing [Fe(tpfpp)X] (1×10^{-3} mmol) and olefin (2 mmol) in a solvent mixture (2.2 mL) of CH_3CN and CH_2Cl_2 (1:1). The reaction mixture was stirred for 10 min and directly analyzed by GC for cyclohexene and by HPLC for *cis*-stilbene. Product yields were determined by comparison with standard curves of known authentic samples.

Catalytic hydroxylation of alkanes: H_2O_2 (0.02 mmol, diluted in CH_3CN (0.5 mL)) was slowly added over a period of 1 h to a stirred solution containing [Fe(tpfpp)X] (1×10^{-3} mmol) and alkane (1 mmol) in a solvent mixture (1 mL) of CH_3CN and CH_2Cl_2 (3:1). The reaction mixture was further stirred for 5 min and directly analyzed by GC. The competitive hydroxylation of cyclohexane and [D$_{12}$]cyclohexane was performed with a mixture of cyclohexane (0.3 mmol) and [D$_{12}$]cyclohexane (1 mmol).

Labeled water ($H_2{}^{18}O$) experiment: H_2O_2 (0.04 mmol, diluted in CH_3CN (0.5 mL)) was slowly added over a period of 1 h to a stirred solution containing [Fe(tpfpp)(NO_3)] (1×10^{-3} mmol), substrate (1 mmol), and $H_2{}^{18}O$ (50 µL, 95% ^{18}O enriched) in a solvent mixture (1 mL) of CH_3CN and CH_2Cl_2 (3:1). The reaction mixture was further stirred for 5 min and directly analyzed by GC/MS. The ^{16}O and ^{18}O compositions in cyclohexanol and cyclohexene oxide were determined by the relative abundances of mass peaks at *m*/*z* 57 and 59 for cyclohexanol and at *m*/*z* 83 and 85 for cyclohexene oxide. Control reactions, performed by stirring cyclohexanol-^{16}O or cyclohexene oxide-^{16}O in a solution containing [Fe(tpfpp)(NO_3)] and $H_2{}^{18}O$, showed that the oxygen of the products did not exchange with labeled water under the reaction conditions.

Electrochemical measurements: All electrochemical experiments were performed under an N_2 atmosphere in a glove box using a BAS 50W voltammetric analyzer. The cyclic voltammetric measurements were carried out in a solvent mixture of CH_3CN/CH_2Cl_2 (1:1) containing iron porphyrin (0.2 mM) and tBu$_4$NPF$_6$ (40 mM) as a supporting electrolyte in one compartment. The working electrode was a glassy carbon disk and the counter electrode was a platinum wire. The potential was measured by using a Ag/Ag$^+$ (0.01 M) reference electrode and reported versus a Fc/Fc$^+$ couple. The cyclic voltammograms were run at a scan rate of 50 mV s^{-1}.

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[10] a) Reaction conditions: *m*-CPBA (1.5×10^{-3} mmol and 3×10^{-3} mmol for [Fe(tpfpp)Cl] and [Fe(tpfpp)(CF_3SO_3)] reactions, repectively, diluted in a solvent mixture (50 µL) of CH_3CN and CH_2Cl_2 (1:1)) was introduced into a 0.1-cm UV cell containing [Fe(tpfpp)X] (5×10^{-4} mmol and 1×10^{-3} mmol for [Fe(tpfpp)Cl] and [Fe(tpfpp)(CF_3SO_3)], respectively) in a solvent mixture (0.5 mL) of CH_3CN and CH_2Cl_2 (1:1) at -60 °C. Spectral changes were directly monitored by UV/Vis spectroscopy (Hewlett Packard 8453 spectrophotometer equipped with *Optostat* variable-temperature liquid-nitrogen cryostat (Oxford Instruments)). b) Further evidence that **2** was formed in the reaction of [Fe(tpfpp)Cl] and *m*-CPBA was the silent EPR spectra and the appearance of a β-pyrrole hydrogen resonance signal at $\delta = 4.0$ at -50 °C.

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Dynamics of Hole Trapping by G, GG, and GGG in DNA**

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Oxidative damage to DNA by ionizing radiation, carcinogenic agents, and photosensitizers occurs predominately at guanine (G) bases,[1, 2] a result which can be rationalized by the hierarchy of in vitro oxidation potentials of the isolated nucleobases ($G < A \ll C,T$).[3] Strand cleavage reactions, induced, for instance, by piperidine treatment,[4] have shown consistently that multiple guanine tracts in DNA are more susceptible to oxidative damage than isolated guanine bases.

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