

2: L-Aspartic acid (asp) (1 mmol) was added to an aqueous solution of Dy(ClO₄)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 Ln³⁺ 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 C₁₂H₃₄Cl₂Dy₄N₃O₄₂ (%): N 2.57, C 8.82, H 3.31; found: N 2.16, C 7.49, H 3.22.

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Remarkable Anionic Axial Ligand Effects of Iron(III) Porphyrin Complexes on the Catalytic Oxygenations of Hydrocarbons by H₂O₂ 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 (H₂O₂) 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 H₂O₂ in a protic solvent such as CH₃OH generate oxoiron(IV) porphyrin cation radical complexes [Fe^{IV}(porp)⁺⁺(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 H₂O₂ 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)⁺⁺(O)] by O–O bond heterolysis in polar solvents such as CH₂Cl₂.^[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

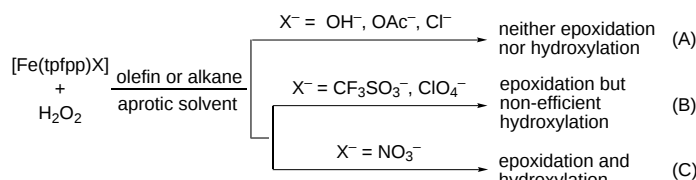
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- [9] Crystal structure analysis data: compound **1**: [Gd₄(Hpro)₄(pro)₂(μ₃-OH)₄(H₂O)](ClO₄)₆·6H₂O, *M*_r = 2216.72, rhombohedral, *R*₃, *a* = *b* = *c* = 12.8953(15) Å, *α* = *β* = *γ* = 100.663(17)°, *V* = 2016.8(4) Å³, *Z* = 1, *ρ*_{calcd} = 1.825 Mg m⁻³, *μ* = 3.545 mm⁻¹, *GOF* = 1.083, *F*(000) = 1086, *R*₁ = 0.0683, *wR*₂ = 0.1876, 317 parameters, 4130 reflections [*I* > 2σ(*I*)]. The intensity data was collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using MoK_α radiation (*λ* = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA (2θ_{min} = 3°, 2θ_{max} = 55°, 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**: C₁₂H₃₄Cl₂Dy₄N₃O₄₂, *M*_r = 1633.48, orthorhombic, *P*2₁2₁2₁, *a* = 14.011(3), *b* = 18.822(4), *c* = 23.421(5) Å, *V* = 6176(2) Å³, *Z* = 4, *ρ*_{calcd} = 1.757 Mg m⁻³, *μ* = 4.958 mm⁻¹, *F*(000) = 3124, *GOF* = 1.013. The data were collected on a Nonius Kappa CCD with MoK_α radiation (*λ* = 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. *R*₁ = 0.0497, *wR*₂ = 0.1354, 483 parameters, 12942 reflections [*I* > 2σ(*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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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 $[\text{Fe}(\text{tpfpp})\text{X}]$ (tpfpp = *meso*-tetrakis(pentafluorophenyl)porphyrinato 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 $[\text{Fe}(\text{tpfpp})\text{X}]$ was OH^- , CH_3CO_2^- , and Cl^- (see Table 1 and Scheme 1, pathway A). However, when the identical reactions

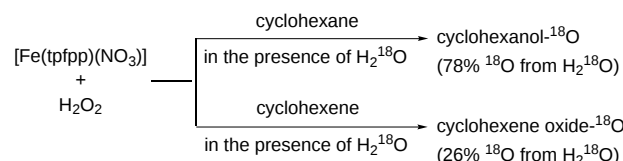


Scheme 1. A schematic diagram showing the anionic axial ligand effect on the epoxidation and hydroxylation of hydrocarbons by $[\text{Fe}(\text{tpfpp})\text{X}]$ and H_2O_2 .

were carried out with $[\text{Fe}(\text{tpfpp})\text{X}]$ 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 $[\text{Fe}(\text{tpfpp})(\text{NO}_3)]$ 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 ($k_{\text{H}}/k_{\text{D}}$) was deter-

mined to be 4.3 ± 0.3 in the competitive hydroxylation of cyclohexane and $[\text{D}_{12}]$ cyclohexane by $[\text{Fe}(\text{tpfpp})(\text{NO}_3)]$ and H_2O_2 at 20°C .^[3a]

We then studied the hydroxylation of cyclohexane and the epoxidation of cyclohexene by $[\text{Fe}(\text{tpfpp})(\text{NO}_3)]$ 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 $78 \pm 4\%$ and $26 \pm 3\%$, respectively (Scheme 2). These results demonstrate that the reactive



Scheme 2. Results of ^{18}O -labeled water experiments in the oxygenation of cyclohexane and cyclohexene by $[\text{Fe}(\text{tpfpp})(\text{NO}_3)]$ and H_2O_2 .

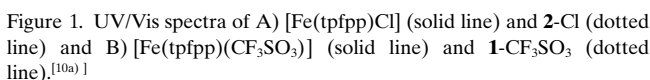
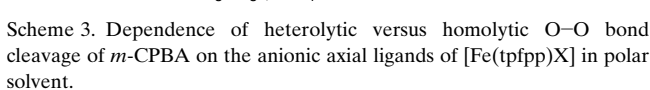
species, which was formed in the reaction of $[\text{Fe}(\text{tpfpp})(\text{NO}_3)]$ and H_2O_2 carried out in the presence of water, was an oxoiron(IV) porphyrin cation radical complex $[\text{Fe}^{\text{IV}}(\text{tpfpp})^+\cdot(\text{O})]$ (**1**).^[8] We also suggest that the different amounts of ^{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 $[\text{Fe}(\text{tpfpp})\text{X}]$ complexes decreases in the order: $\text{X}^- = \text{NO}_3^- > \text{CF}_3\text{SO}_3^-, \text{ClO}_4^- \gg \text{OAc}^-, \text{Cl}^- \geq \text{OH}^-$.

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

Table 1. Effect of anionic axial ligands of $[\text{Fe}(\text{tpfpp})\text{X}]$ 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 ₃ SO 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	<i>cis</i> -stilbene	<i>cis</i> -stilbene oxide	< 2	9 ± 2	14 ± 2	78 ± 5	76 ± 5	74 ± 5
		<i>trans</i> -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.



Complexes of metal cations with organic ligands are

All reactions were carried out at room temperature under argon. Catalytic

Catalytic hydroxylation of alkanes: H_2O_2 (0.02 mmol, diluted in CH_3CN)

further stirred for 5 min and directly analyzed by GC. The competitive hydroxylation of cyclohexane and [D₁₂]cyclohexane was performed with a mixture of cyclohexane (0.3 mmol) and [D₁₂]cyclohexane (1 mmol).

Labeled water (H₂¹⁸O) experiment: H₂O₂ (0.04 mmol, diluted in CH₃CN (0.5 mL)) was slowly added over a period of 1 h to a stirred solution containing [Fe(tpfp)(NO₃)] (1 × 10⁻³ mmol), substrate (1 mmol), and H₂¹⁸O (50 µL, 95% ¹⁸O enriched) in a solvent mixture (1 mL) of CH₃CN and CH₂Cl₂ (3:1). The reaction mixture was further stirred for 5 min and directly analyzed by GC/MS. The ¹⁶O and ¹⁸O 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-¹⁶O or cyclohexene oxide-¹⁶O in a solution containing [Fe(tpfp)(NO₃)] and H₂¹⁸O, 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 N₂ atmosphere in a glove box using a BAS 50W voltammetric analyzer. The cyclic voltammetric measurements were carried out in a solvent mixture of CH₃CN/CH₂Cl₂ (1:1) containing iron porphyrin (0.2 mM) and *t*Bu₄NPF₆ (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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Dynamics of Hole Trapping by G, GG, and GGG in DNA**

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Bernd Giese,* and Maria E. Michel-Beyerle*

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 ≪ 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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