## Metalloporphyrin/Iodine(III)-Cocatalyzed Oxygenation of Aromatic Hydrocarbons

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Abstract: Hypervalent iodine species have a pronounced catalytic effect on the metalloporphyrinmediated oxygenations of aromatic hydrocarbons. In particular, the oxidation of anthracene to anthraquinone with Oxone readily occurs at room temperature in aqueous acetonitrile in the presence of 5-20 mol% of iodobenzene and 5 mol% of a watersoluble iron(III)-porphyrin complex. 2-tert-Butylanthracene and phenanthrene also can be oxygenated under similar conditions in the presence of 50 mol% of iodobenzene. The oxidation of styrene in the presence of 20 mol% of iodobenzene leads to a mixture of products of epoxidation and cleavage of the double bond. Partially hydrogenated aromathydrocarbons (e.g., 9,10-dihydroanthracene, ic 1,2,3,4-tetrahydronaphthalene, and 2,3-dihydro-1Hindene) afford under these conditions products of oxidation at the benzylic position in moderate yields. The proposed mechanism for these catalytic oxidations includes two catalytic redox cycles: 1) initial oxidation of iodobenzene with Oxone producing the hydroxy(phenyl)iodonium ion and hydrated iodosylbenzene, and 2) the oxidation of iron(III)porphyrin to the oxoiron(IV)-porphyrin cation-radical complex by the intermediate iodine(III) species. The oxoiron(IV)-porphyrin cation-radical complex acts as the actual oxygenating agent toward aromatic hydrocarbons.

**Keywords:** catalysis; hypervalent iodine; iodine; oxidation; porphyrinoids

The catalytic properties of transition-metal porphyrins, phthalocyanines, and related compounds in the biomimetic oxygenations of organic substrates are well-documented in the literature.<sup>[1]</sup> Various terminal oxidants (e.g., O<sub>2</sub>, hydrogen peroxide and organic peroxides) have been used in these oxygenations. In 1979 Groves and co-workers reported that iodosylbenzene,  $(PhIO)_n$ , is the most efficient source of oxygen in the oxygenation of hydrocarbons in the presence of iron-(III) porphyrin complexes,<sup>[2a]</sup> and since then iodosylarenes and other hypervalent iodine reagents have been widely used as stoichiometric oxidants in the reactions mimicking natural oxidations performed by the hemecontaining cytochrome P-450 class of enzymes.<sup>[1,2]</sup>

It is generally agreed that the intermediate high valent metal oxo-complexes are responsible for the oxygen transfer from (PhIO)<sub>n</sub> to the organic substrate. However, the details of the initial interaction of iodine(III) species with the metal complex are still unclear. In particular, it has been shown that iodosylbenzene reacts with metalloporphyrins with the formation of unstable adducts, which can serve as the actual oxidants in catalytic oxygenations and thus explain the unusual reactivity of hypervalent iodine reagents as terminal oxidants.<sup>[3]</sup> Herein we report our study on the catalytic application of iodine(III) species in the metalloporphyrin-mediated oxygenation of aromatic hydrocarbons with Oxone  $(2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2 \text{SO}_4)$  as terminal oxidant. The results of this study indicate that hypervalent iodine species have a pronounced catalytic effect on the biomimetic iron(III) porphyrin-mediated oxygenations of aromatic hydrocarbons.

Our approach involves the use of iodine(III) species, generated *in situ* from iodobenzene and Oxone in aqueous acetonitrile, as the efficient source of oxygen in the oxygenation of aromatic hydrocarbons in the presence of water-soluble metalloporphyrin complexes 1 (Figure 1). At the initial stage of our study, we have investigated and optimized a water-based oxidizing system utilizing metalloporphyrin catalysts and a water-soluble stoichiometric hypervalent iodine oxidant that can be generated from iodoben-zene and Oxone in aqueous solutions.

First of all, several preliminary experiments were performed in order to identify the most active catalyst 1 and to ensure that Oxone alone cannot serve as a source of oxygen in the metalloporphyrin-mediated oxygenations (Table 1). We have tested the catalytic





Figure 1. Water-soluble metalloporphyrin complexes 1.

activity of water-soluble metalloporphyrins **1a–f** using the water-soluble oligomeric iodosylbenzene sulfate **2** as a terminal stoichiometric oxidant in the oxygenation of anthracene **3**.<sup>[4]</sup> Reagent **2** was generated *in situ* from (diacetoxyiodo)benzene and sodium bisulfate (Scheme 1) according to the known procedure.<sup>[5]</sup> The results of these oxidations (Table 1, entries 1–7) clearly indicate that Fe(III)-porphyrin **1a** is the most active catalyst under these conditions (entry 2), while the Zn(II)-porphyrin **1f** does not show any catalytic effect as expected from the inability of Zn(II) to participate in oxygen-transfer processes. Based on these results, we have used the Fe(III)-porphyrin complex **1a** in all following experiments.

In the next set of preliminary experiments, we have tested the ability of Oxone to serve as a source of oxygen in the metalloporphyrin-mediated oxygenations. In particular, separate experiments have shown

**Table 1.** Catalytic effect of metalloporphyrins 1 and PhI on the oxygenation of anthracene 3 to anthraquinone 4.<sup>[a]</sup>

Entry	Catalyst <sup>[b]</sup>	Oxidant <sup>[c]</sup>	PhI (mol%)	Time [h]	Yield of <b>4</b> [%]
1	none	2	0	3	8
2	1a	2	0	1	100, <sup>[d]</sup> 88 <sup>[e]</sup>
3	1b	2	0	3	5 <sup>[d]</sup>
4	1c	2	0	5	48 <sup>[d]</sup>
5	1d	2	0	3	85 <sup>[d]</sup>
6	1e	2	0	3	5 <sup>[d]</sup>
7	1f	2	0	3	2 <sup>[d]</sup>
8	1a	Oxone	0	1	0 <sup>[d]</sup>
9	1a	Oxone <sup>[f]</sup>	0	24	$1.5^{[d]}$
10	none	Oxone	20	24	0 <sup>[d]</sup>
11	1a	Oxone	20	1	100 <sup>[d]</sup>
12	1a	Oxone	10	1	39 <sup>[d,g]</sup>
13	1a	Oxone	5	1	35 <sup>[d,g]</sup>

<sup>[a]</sup> All reactions were performed at room temperature in MeCN/H<sub>2</sub>O (1:1 v/v) under stirring.

<sup>[b]</sup> 5 mol% of catalyst  $\hat{\mathbf{1}}$  were used.

- [c] 2 mol equiv. of reagent 2 (6 equiv. of active O) or 8.2 mol equiv. of Oxone (16.4 equiv. of active O) were used.
  [d] CC right
- <sup>[d]</sup> GC yield.
- [e] Isolated yield.
- <sup>[f]</sup> NBu<sub>4</sub>HSO<sub>4</sub> (20 mol%) as a phase-transfer catalyst was added.
- <sup>[g]</sup> Also contains unreacted **3**.



**Scheme 1.** Metalloporphyrin-catalyzed oxygenations using iodosylbenzene sulfate **2** as a stoichiometric oxidant.

that the treatment of anthracene **3** with complex **1a** (5 mol%) and 8.2 mol equiv. of Oxone in a 1:1 mixture acetonitrile-water does not lead to any significant oxidation of the substrate (entry 8, Table 1). The addition of a phase-transfer catalyst, NBu<sub>4</sub>HSO<sub>4</sub>, to improve the solubility of Oxone in acetonitrile, also did not have any noticeable effect (entry 9).

Based on the optimized reaction conditions for the metalloporphyrin-catalyzed oxygenation in aqueous solution, we have developed a Fe(III)-porphyrin/ iodine(III) co-catalytic system utilizing iodobenzene, PhI, as a pre-catalyst. The actual source of oxygen in the metalloporphyrin-mediated oxygenations shown in Scheme 1 are the iodine(III) species formed in aqueous solution upon dissociation of the oligomeric iodosylbenzene sulfate 2. A previously reported mass spectrometry study of the aqueous solution of 2 has shown that these species are represented mainly by hydroxy(phenyl)iodonium ion, PhI+OH, and hydrated iodosylbenzene, PhI(OH)2.<sup>[5a,b]</sup> We have found that the same iodine(III) species can be generated in solution by simple treatment of iodobenzene with Oxone aqueous acetonitrile at room temperature in (Scheme 2).

The presence of the  $[PhIO + H]^+$  and  $[PhI(OH)_2 + H]^+$  species in such solutions (Scheme 2) is supported by mass spectrometry (see Experimental Section). Based on this observation, we have tested the metalloporphyrin/PhI-cocatalyzed oxygenations and were pleased to find that the oxidation of anthracene **3** to anthraquinone **4** selectively proceeds in aqueous acetonitrile at room temperature in the presence of Fe-(III)-porphyrin **1a** (5 mol%) and PhI (20 mol%) with Oxone as terminal oxidant (Table 1, entry 11). The use of smaller amounts of PhI led to a lower conversion (Table 1, entries 12 and 13). In the absence of

2PhI + 2KHSO<sub>5</sub> (Oxone) 
$$\xrightarrow{\text{MeCN-H}_2\text{O}, \text{ r.t.}}_{-K_2\text{SO}_4} \xrightarrow{\text{OH}}_{\text{Ph}-i^+} \xrightarrow{\text{OH}}_{+} \xrightarrow{\text{OH}}_{+}$$

**Scheme 2.** Active iodine(III) species generated in solution by treatment of iodobenzene with Oxone.



Scheme 3. Fe(III)-porphyrin-catalyzed and iodine(III)-mediated oxygenations using Oxone as a stoichiometric oxidant.

catalyst **1** this system does not lead to any significant oxidation of the substrate (Table 1, entry 10).

In order to demonstrate the general character of this catalytic reaction, we performed the iodine(III)mediated oxidation of aromatic hydrocarbons 5 and 7 in the presence of Fe(III)-porphyrin 1a (Scheme 3). Compared to the oxidation of anthracene 3, the reaction of 2-tert-butylanthracene 5 was slower, probably due to steric hindrance caused by the tert-butyl group. However, the use of larger amounts of PhI (50 mol%) allowed us to reach a 100% conversion in 3 h at room temperature. The GC analysis of the reaction mixture indicated the presence of a single product of oxidation, 2-tert-butylanthraquinone 6, along with some iodobenzene. The pure 2-*tert*-butylanthraquinone **6** was isolated from the reaction mixture by preparative TLC chromatography on silica gel as yellow needles in 80% yield and identified by comparison with an authentic sample. The previously reported oxidation of 2-tert-butylanthracene using stoichiometric oxidant 2 in the Fe(III)-phthalocyanine-catalyzed oxygenations in toluene proceeded more slowly (20 h at room temperature) and afforded 2-tert-butylanthraquinone 6 in 72% isolated yield.<sup>[4a]</sup> Phenanthrene 7 is even less reactive, producing phenanthrene-9,10-dione 8 under these conditions only in 14% yield after 7 days at room temperature. The low reactivity of phenanthrene is in agreement with the previously reported Fe(III)-phthalocyanine-catalyzed oxygenations using oxidant 2.<sup>[4b]</sup>

Preliminary studies have shown that the Fe(III)porphyrin/PhI catalytic system can be effectively applied toward the oxidation of alkenes; however, these reactions in general lack selectivity. In particular, the oxidation of styrene in the presence of 20 mol% of iodobenzene proceeds with 99% conversion after 1 hour leading to a mixture of products of epoxidation, ring hydroxylation, and cleavage of the double bond (Table 2, entry 1). No oxidation of styrene is observed under these conditions in the absence of PhI even after 24 h. The formation of epoxides in moderate yields in the reaction of alkenes with iodosylbenzene in the presence of iron-porphyrin complexes was previously reported in the literature.<sup>[2a]</sup> Partially hydro-

**Table 2.** Oxidation of styrene, partially hydrogenated aromatic hydrocarbons, and adamantane using Fe(III)-porphyrin/PhI catalytic system.<sup>[a]</sup>



- <sup>[a]</sup> All reactions were performed at room temperature in MeCN/H<sub>2</sub>O (1:1 v/v) using 5 mol% of catalyst 1a, 20 mol% of PhI and 8.2 mol equiv. of Oxone; product composition after 1 h of reaction is shown.
- <sup>[b]</sup> Product composition and yields were determined by GC-MS.
- <sup>[c]</sup> For all substrates, no significant oxidation was observed in the absence of PhI.

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genated aromatic hydrocarbons (e.g., 9,10-dihydroanthracene, 1,2,3,4-tetrahydronaphthalene, and 2,3-dihydro-1*H*-indene) afford under these conditions products of oxidation at the benzylic position in moderate to low conversions (Table 2, entries 2–4). The oxidation of adamantane under these conditions proceeds very slowly (entry 5, 2% conversion after 1 hour). The previously reported oxidation of adamantane using Fe(III)-porphyrin and stoichiometric iodosylbenzene afforded 1-adamantanol in 12% yield; the lower yields of the less reactive hydrocarbons were explained by oxidative degradation of the catalyst.<sup>[2a]</sup>

Our results clearly indicate that PhI has a pronounced catalytic effect on the metalloporphyrinmediated oxygenations and thus support previous observations about the high reactivity of iodine(III) species as the source of oxygen.<sup>[2,3]</sup> It was suggested previously that a direct transfer of oxygen from iodosylbenzene to an organic substrate is possible in the presence of transition metal ions,<sup>[6]</sup> which may activate an iodine(III) species as a Lewis acid.<sup>[6a]</sup> The results of our study support the special role of iodine-(III) in these oxygenations; however, the observation that Zn(II)-porphyrin **1f** does not show any catalytic effect (Table 1, entry 7) indicates that the high valent metal oxo-complexes are responsible for the oxygen transfer to the substrate.

A simplified mechanism for these catalytic oxidations is shown in Scheme 4 that includes two catalytic redox cycles. We propose that the intermediate iodine(III) species are responsible for the oxidation of the Fe(III)-porphyrin to the oxo-Fe(IV)<sup>+</sup>-porphyrin complex. The oxoiron(IV) porphyrin complex acts as the actual oxygenating agent according to the previously discussed mechanisms.<sup>[1-3]</sup> Our results are in agreement with previous observations<sup>[3]</sup> that iodosylbenzene can react with metalloporphyrins with the formation of highly reactive adducts, which can serve as the actual oxidants in catalytic oxygenations.

In conclusion, the results of our study indicate that hypervalent iodine species have a pronounced catalytic effect on the iron(III) porphyrin-mediated oxygenations of aromatic hydrocarbons. This effect should be taken into consideration by researchers utilizing iodo-



P = porphyrin

**Scheme 4.** Tandem catalytic cycles for the Fe(III)-porphyrin/ iodine(III)-cocatalyzed oxygenation of aromatic hydrocarbons.

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sylbenzene as a common source of oxygen in the reactions mimicking natural oxidations performed by cytochrome P-450 class of enzymes. At the same time, this new catalytic system can serve as a basis for new efficient synthetic methodologies. The new metalloporphyrin/iodine(III)-cocatalyzed oxygenations complement the recently reported iodine(V)/Ru(III)-cocatalyzed benzylic oxidations<sup>[7]</sup> and bring a new dimension to the emerging field of hypervalent iodine catalysis.<sup>[8,9]</sup>

### **Experimental Section**

#### **General Methods**

All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. GC-MS analysis was carried out with an HP 5890A Gas Chromatograph using a 5970 Series mass selective detector. Mass spectrometric (ESI-MS) analyses were obtained at the University of Minnesota Minneapolis Mass Spectrometry Facility, using a BioTOF II mass spectrometer.

#### Typical Procedure for Metalloporphyrin-Catalyzed Oxygenation of Anthracene using Iodosylbenzene Sulfate 2 (*in situ*) as a Stoichiometric Oxidant

A solution of anthracene **3** (0.05 mmol) in a 1:1 mixture of acetonitrile/water (2 mL) was mixed with the appropriate catalyst **1** (0.0025 mmol, 0.05 mol equiv.), (diacetoxyiodo)-benzene (0.25 mmol, 5 mol equiv.), and sodium bisulfate (0.25 mmol, 5 mol equiv.), with stirring, at room temperature. Samples of the reaction mixture (100  $\mu$ L) were collected every hour, filtered through 2–3 cm of silica gel suspended in a Pasteur pipette, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and analyzed using GC-MS.

# Fe(III)-Porphyrin/PhI-Cocatalyzed Oxygenation of Anthracene

A solution of anthracene **3** (89 mg, 0.5 mmol) in a 1:1 mixture of acetonitrile/water (2 mL) was mixed with Fe(III) porphyrin **1a** (22 mg, 0.025 mmol), iodobenzene (20 mg, 0.1 mmol), and Oxone (2.52 g, 4.1 mmol), with stirring, at room temperature. The reaction mixture (100  $\mu$ L samples) was analyzed using GC-MS. Upon completion of the reaction, the reaction mixture was concentrated and separated using TLC plate and ethyl acetate/hexane (2:3 v:v) mixture as the eluent to afford analytically pure anthraquinone **4**; yield: 59.4 mg (57%).

# Fe(III)-Porphyrin/PhI-Cocatalyzed Oxygenation of 2-*tert*-Butylanthracene

A solution of 2-*tert*-butylanthracene **5** (117 mg, 0.5 mmol) in a 1:1 mixture of acetonitrile/water (2 mL) was mixed with Fe(III) porphyrin **1a** (22 mg, 0.025 mmol), iodobenzene (51 mg, 0.25 mmol), and Oxone (2.52 g, 4.1 mmol), with stirring, at room temperature. The reaction mixture (100  $\mu$ L





Figure 2. ESI mass spectrum of PhI-Oxone<sup>®</sup> mixture in aqueous acetonitrile.

samples) was analyzed using GC-MS every hour. Upon completion of the reaction, the reaction mixture was concentrated and products were separated using TLC plate and ethyl acetate/hexane (2:3 v:v) mixture as the eluent to afford analytically pure 2-*tert*-butylanthraquinone as yellow needles; yield: 107 mg (80%), mp 103–104 °C.<sup>[10]</sup>

Fe(III)-Porphyrin/PhI-Cocatalyzed Oxygenation of Phenanthrene

A solution of phenanthrene **7** (0.05 mmol) in a 1:1 mixture of acetonitrile/water (2 mL) was mixed with Fe(III) porphy-

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rin 1a (0.0025 mmol, 0.05 mol equiv.), iodobenzene

(0.025 mmol, 0.5 mol equiv.), and Oxone (0.41 mmol, 8.2

mol equiv.), with stirring, at room temperature. Samples of

the reaction mixture (100 µL) were collected every hour, fil-

tered through 2-3 cm of silica gel suspended in a Pasteur

pipet, washed with a mixture of ethyl acetate and hexane

(2:3 v:v), and analyzed using GC-MS.

### Fe(III)-Porphyrin/PhI-Cocatalyzed Oxidations of Styrene, 9,10-Dihydroanthracene, 1,2,3,4-Tetrahydronaphthalene, 2,3-Dihydro-1*H*-indene, and Adamantane (Table 2)

A solution of the organic substrate (0.05 mmol) in a 1:1 mixture of acetonitrile/water (2 mL) was mixed with Fe(III) porphyrin **1a** (0.0025 mmol, 0.05 mol equiv.), iodobenzene (0.01 mmol, 0.2 mol equiv.), and Oxone (0.41 mmol, 8.2 mol equiv.), and stirred at room temperature for 1 hour. The reaction mixture was filtered through 2–3 cm of silica gel suspended in a Pasteur pipet, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and analyzed using GC-MS.

### Mass Spectra of Aqueous Mixture PhI-Oxone

A solution of Oxone and iodobenzene in a 1:1, 8:1 and 16:1 ratio in a 1:1 mixture of acetonitrile/water (2 mL) was stirred at room temperature. Samples of the reaction mixture were collected every hour and analyzed by MS. A typical mass spectrum is shown in Figure 2.

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