



## Binuclear iron(III) phthalocyanine( $\mu$ -oxodimer)/tetrabutylammonium oxone: a powerful catalytic system for oxidation of hydrocarbons in organic solution

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### ABSTRACT

Binuclear iron(III) phthalocyanine-( $\mu$ -oxodimer) complex was tested in catalytic oxygenation reactions of several hydrocarbons using tetrabutylammonium oxone as the oxidant in dichloromethane solution at room temperature. Results of the study demonstrate that this is an extremely powerful catalytic system for oxidative conversion of aromatic hydrocarbons (anthracene, 2-*tert*-butylantracene, 2-methylnaphthalene, 9,10-dihydroanthracene, 1,2,3,4-tetrahydronaphthalene, indane, ethylbenzene, toluene, and benzene) to the respective *p*-quinones in high yields in 5–30 min. Under these conditions, adamantane is oxidized with 71% conversion after 10 min affording a mixture of 1-adamantanol, 2-adamantanone, 1-hydroxy-2-adamantanone, and 4-protoadamantanone.

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Transition-metal porphyrins, phthalocyanines, and related compounds are widely used as catalysts in the reactions mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.<sup>1</sup> It was demonstrated recently that porphyrin and phthalocyanine iron  $\mu$ -oxo-,<sup>2a-c</sup> and  $\mu$ -nitridodimers,<sup>2d-f</sup> which were earlier considered as catalytically inactive compounds, in many cases have high catalytic activity in different oxidation reactions. Most commonly, hydrogen peroxide, organic peroxides, and iodosylbenzene are used as terminal oxidants in the transition-metal porphyrin-type catalyzed reactions.<sup>1</sup> In particular, iodosylbenzene,<sup>3</sup> 2-iodylbenzoate ester,<sup>4a,4b</sup> and oligomeric iodosylbenzene sulfate ( $\text{PhIO}_3\text{SO}_3$ ,<sup>3g,4b-d</sup> have been demonstrated to be efficient sources of oxygen in these reactions. It was also shown that the oxidative activity of a porphyrin (or phthalocyanine) based catalytic system strongly depends on the nature of the terminal oxidant. In our recent studies of hypervalent iodine reagents as terminal oxidants in the iron(III) phthalocyanine( $\mu$ -oxodimer)-catalyzed oxygenations,<sup>4c</sup> we have found that the catalytic systems utilizing oligomeric iodosylbenzene sulfate are significantly more reactive compared to the systems based on traditional two-electron transfer oxidants, such as iodosylbenzene or hydrogen peroxide. In the present work, we report preliminary results on the iron(III) phthalocyanine( $\mu$ -oxodimer) **1** (Fig. 1) catalyzed oxygenations using one of the most powerful oxidants, tetrabutylammonium oxone [approximate composition  $2\text{Bu}_4\text{NHSO}_5 \cdot \text{Bu}_4\text{NHSO}_4 \cdot (\text{Bu}_4\text{N})_2\text{SO}_4$ ],<sup>5</sup> which has excellent solubility in non-polar organic solvents and thus allowing catalytic reactions in solution under homogeneous conditions.

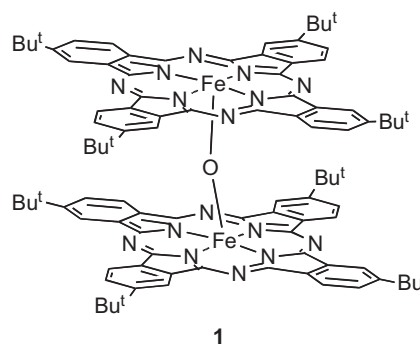


Figure 1. Iron(III) phthalocyanine-( $\mu$ -oxodimer) **1**.

Complex **1** was synthesized using direct high-temperature reaction between 4-*tert*-butylphthalonitrile and iron(II) acetate as described previously,<sup>6</sup> while tetrabutylammonium oxone was prepared by simple treatment of commercial Oxone® ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ) with tetrabutylammonium bisulfate.<sup>5a</sup> The results of catalytic oxidation of anthracene **2**, 2-*tert*-butylantracene **4**, 2-methylnaphthalene **6**, 9,10-dihydroanthracene **11**, 1,2,3,4-tetrahydronaphthalene **12**, indane **16**, ethylbenzene **20**, toluene **22**, benzene **24**, and adamantane **26** using tetrabutylammonium oxone and catalyst **1** are summarized in Table 1.

All oxidation reactions were carried out in dry dichloromethane using two times excess of tetrabutylammonium oxone (6 mol equiv of active oxygen per one molecule of substrate) with 0.05 equiv of the catalyst **1**. Samples of the reaction mixture

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**Table 1**  
Catalytic oxidation of organic substrates using tetrabutylammonium oxone as the stoichiometric oxidant<sup>a</sup>

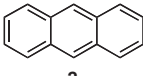
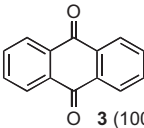
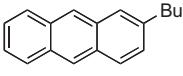
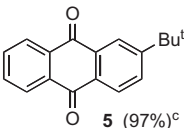
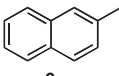
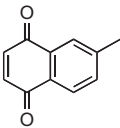
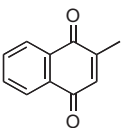
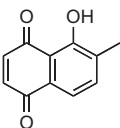
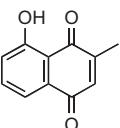
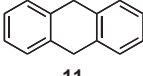
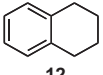
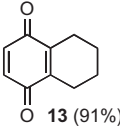
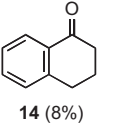
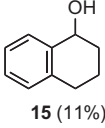
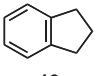
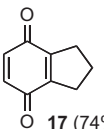
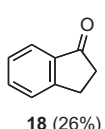
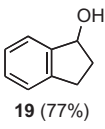
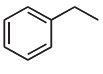
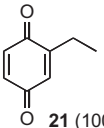

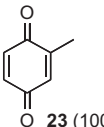

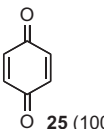

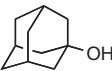



Entry	Catalyst (mol %)	Substrate	Time (min)	Conversion (%)	Products distribution (%)
1	None		2880	10	 <b>3</b> (100%)
2	<b>1</b> (5)	<b>2</b>	5	100	<b>3</b> (100%)
3	Fe(III)TPFPp <sup>b</sup> (5)	<b>2</b>	30	45	<b>3</b> (100%)
4	<b>1</b> (5)		10	100	 <b>5</b> (97%) <sup>c</sup>
5	None	<b>4</b>	30	0	None
6	<b>1</b> (5)		5	100	 <b>7</b> (47%)  <b>8</b> (47%)  <b>9</b> (4%)  <b>10</b> (2%)
7	None	<b>6</b>	1440	0	None
8 <sup>d</sup>	<b>1</b> (5)		10	100	<b>3</b> (100%)
9	None	<b>11</b>	60	14	<b>2</b> (93%), <b>3</b> (4%)
10	<b>1</b> (5)		10	100	 <b>13</b> (91%)  <b>14</b> (8%)
11	None	<b>12</b>	60	5	<b>14</b> (89%) +  <b>15</b> (11%)
12	<b>1</b> (5)		10	100	 <b>17</b> (74%)  <b>18</b> (26%)
13	None	<b>16</b>	60	14	<b>18</b> (23%) +  <b>19</b> (77%)
14	<b>1</b> (5)		30 <sup>e</sup>	90	 <b>21</b> (100%)
15	None	<b>20</b>	1440	0	None
16	<b>1</b> (5)		5 <sup>e</sup>	43 <sup>f</sup>	 <b>23</b> (100%)
17	None	<b>22</b>	1440	0	None
18	<b>1</b> (5)		5 <sup>e</sup>	38 <sup>f</sup>	 <b>25</b> (100%)
19	None	<b>24</b>	1440	0	None

Table 1 (continued)

Entry	Catalyst (mol %)	Substrate	Time (min)	Conversion (%)	Products distribution (%)
20	<b>1</b> (5)	 <b>26</b>	10 <sup>e</sup>	71	 <b>27</b> (57)  <b>28</b> (23)  <b>29</b> (12)  <b>30</b> (8)
21	None	<b>26</b>	1440	0	None

<sup>a</sup> Reactions were performed in dichloromethane at room temperature using 5 mol % of catalyst **1** and tetrabutylammonium oxone (6 equiv of active O) unless otherwise noted.

<sup>b</sup> Fe(III)TPFPF = 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III) chloride.

<sup>c</sup> According to GC–MS data the reaction mixture also contains 3% of products of hydroxylation of the anthracene core.

<sup>d</sup> 4 mol equiv of tetrabutylammonium oxone (8 equiv of active O) used.

<sup>e</sup> Longer reaction times lead to oxidative degradation of catalyst **1** and do not improve the conversion.

<sup>f</sup> Conversion measured by NMR.

(100  $\mu$ L) were collected every 1 min, the catalyst and tetrabutylammonium salts were removed by filtration through silica gel and the obtained solution was analyzed by GC–MS to determine the conversion of the hydrocarbon. 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 products. All reaction products were identified by comparison with commercially available samples and using EI-MS databases. Blank experiments in the absence of catalyst **1** were performed similarly using 3 mol equiv of tetrabutylammonium oxone in dichloromethane at room temperature.

The oxidation of anthracene **2** with tetrabutylammonium oxone in the absence of catalyst **1** at room temperature in dichloromethane proceeds extremely slow showing only 10% conversion to anthraquinone **3** after 48 h (entry 1). The addition of 0.05 mol equiv of Fe(III) phthalocyanine( $\mu$ -oxodimer) **1** leads to a dramatic increase in the reaction rate with a 100% conversion reached just in 5 min (entry 2). This is a much higher reactivity, compared to the previously reported metalloporphyrin (or phthalocyanine)-catalyzed oxidations of anthracene **2** using other terminal oxidants. For example, the oxidation of **2** to **3** in the presence of catalyst **1** using oligomeric iodosylbenzene sulfate (PhIO)<sub>3</sub>SO<sub>3</sub> requires 2 h for completion.<sup>4b,4c</sup> A common porphyrin catalyst, 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III) chloride, shows a significantly lower catalytic activity in this oxidation (entry 3). The reactions of less-reactive aromatic substrates **4** and **6** are extremely slow in the absence of catalyst **1** (entries 5 and 7) but occur almost instantaneously under catalytic conditions to afford products **5**, **7–10**, same as previously reported for other oxidants,<sup>4c</sup> but much faster. The oxidation of 9,10-dihydroanthracene **11** in the absence of catalyst **1** is very slow and affords mainly anthracene **2** as the product of oxidative aromatization (entry 9); under catalytic conditions this reaction affords exclusively anthraquinone **3** with a 100% conversion in 10 min (entry 8).

The molecules of substrates **12** and **16** have two competing reacting sites, C–H bonds in the aromatic ring and the benzylic C–H bonds. The oxidation of these substrates in the absence of catalyst **1** is very slow and occurs exclusively in the benzylic position (products **14** and **15**, entry 11 and products **18** and **19**, entry 13). In the presence of catalyst **1**, these oxidations are complete in 10 min to afford *p*-quinones **13** and **17** as major products.

Selective oxidation of benzene **24** and alkylbenzenes **20**, **22** to the respective *p*-quinones **25**, **21**, and **23** provides an impressive proof of the exceptional reactivity of the iron(III) phthalocyanine( $\mu$ -oxodimer)/tetrabutylammonium oxone catalytic system (entries 14, 16, and 18) taking into account that benzene and toluene previously have been commonly used as nonreactive organic solvents for similar metalloporphyrin (or phthalocyanine)-catalyzed oxidations.<sup>1,4</sup> In particular, the oxidation of benzene **24** to *p*-benzoquinone **25** selectively proceeds at room temperature with

35% conversion after 5 min at room temperature. Previously, the oxidation of benzene to phenol and traces of *p*-benzoquinone was performed at 60 °C using  $\mu$ -nitrido bridged diiron phthalocyanine in combination with hydrogen peroxide by Sorokin and co-workers.<sup>2e,2f</sup> In the absence of catalyst **1**, ethylbenzene **20**, toluene **22**, and benzene **24** cannot be oxidized with tetrabutylammonium oxone (entries 15, 17, and 19).

Furthermore, the iron(III) phthalocyanine( $\mu$ -oxodimer)/tetrabutylammonium oxone catalytic system is capable of efficient oxidation of adamantane **26** in 71% conversion after 10 min affording a mixture of 1-adamantanol **27**, 2-adamantanone **28**, 1-hydroxy-2-adamantanone **28**, and 4-protoadamantanone **29** (entry 20). The latter compound is a product of oxidative rearrangement of 1-adamantanol.<sup>7</sup>

Since tetrabutylammonium oxone is a well-known two-electron oxidant, based on the preliminary UV–vis, APCI, and MCD data, we speculate that the catalytically active species should include Pc<sup>2-</sup>Fe<sup>IV</sup>–O–Pc<sup>2-</sup>–Fe<sup>IV</sup> = O or Pc<sup>2-</sup>–Fe<sup>III</sup>–O–Pc<sup>1-</sup>–Fe<sup>IV</sup> = O species, detailed characterization of which will be presented later.

Typical experimental procedure for the catalytic oxidation of substrates: A solution of anthracene **2** (89 mg, 0.5 mmol) in dichloromethane (5 mL) was mixed with iron  $\mu$ -oxo dimer phthalocyanine **1**<sup>6</sup> (40 mg, 0.025 mmol, 5 mol %), and tetrabutylammonium oxone (containing about 37% of Bu<sub>4</sub>NHSO<sub>5</sub>)<sup>5a</sup> (2.9 g, 3 mmol, 6 equiv of active O), with stirring, at room temperature. Samples of the reaction mixture (100  $\mu$ L) were collected every 1 min, 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 then 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 100 mg (96%) of analytically pure anthraquinone **3**. All reaction products were identified by comparison with commercially available samples.

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