

## Reactive intermediates in iron(III) porphyrin-catalyzed oxidation reactions

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**Abstract.** In iron(III) porphyrin-catalyzed oxidation of organic substrates by various monooxo transfer agents, oxoiron(IV) porphyrin cation radical(oxene) has been thought to be the most probable reactive intermediate. Our work, as reported here, indicates that oxo transfer to suitable substrates is possible by a distinctly different route. In case of MCPBA, the oxo transfer is very strongly solvent dependent. For example, in pure toluene solvent, intermediacy of oxene is not at all important, whereas in dichloromethane–methanol mixed solvent, the role of oxene is very significant. We also note that solvent molecules are susceptible to self oxidation by various oxidizing systems.

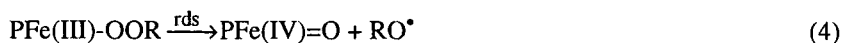
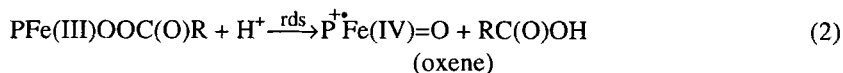
**Keywords.** Iron(III) porphyrin; oxidation; peracid; catalysis.

### 1. Introduction

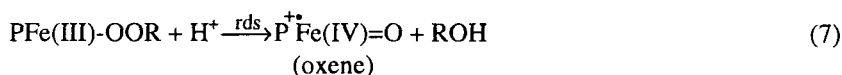
Iron(III) porphyrin is the active site of many metalloenzymes. Among many interesting reactions of cytochrome P-450, alkane hydroxylation and olefin epoxidation reactions have been thoroughly investigated and have been successfully mimicked by many simple iron(III) porphyrins<sup>1,2</sup>. Oxoiron(IV) porphyrin cation radical(oxene), oxoiron(IV) porphyrin, and ROO• radical are the three major reactive intermediates thought to play a vital role in these oxidation reactions<sup>3–11</sup>. Oxoiron(IV) porphyrin does not epoxidize olefins, thus oxene versus ROO• radical became the subject of intensive debate for epoxidation reactions<sup>6,13,14</sup>. MCPBA and iodosylbenzenes react with TMPFe(III)Cl at –78°C to give oxene which has been spectroscopically characterized<sup>15–17</sup>. Oxene generated from electronegative and sterically hindered iron(III) porphyrins are reported stable at relatively higher temperature (8°C)<sup>18</sup>. Detailed product analysis from hydrocarbon oxidation (under various reaction conditions) by iodosylbenzenes catalyzed by iron(III) porphyrins including TMPFe(III)Cl has unanimously concluded that iron(III) porphyrins react with iodosylbenzenes to give oxene as primary reactive species that finally oxidizes hydrocarbons<sup>19–23</sup>. In contrast the ROO• radical has been proposed as the major reactive species where hydroperoxides are terminal oxidants<sup>7,10–12</sup>. Thus reactions (1)–(2) for peracids (or iodosylbenzenes) and (3)–(6) for hydroperoxides have been proposed as below.



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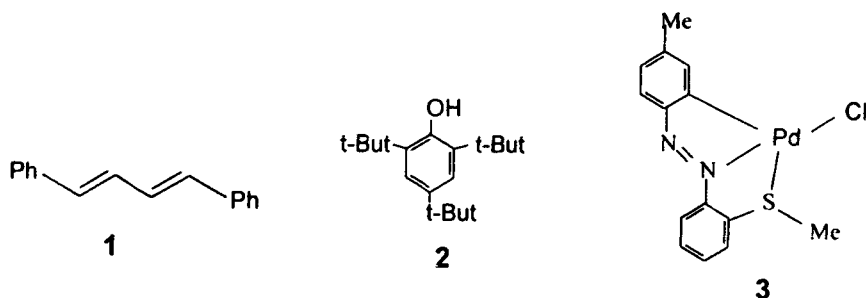
The radical path for hydroperoxides has however been questioned and the formation of oxene by the heterolytic cleavage of the peroxy bond of the hydroperoxide adduct has been recently suggested<sup>5,2</sup> as below.



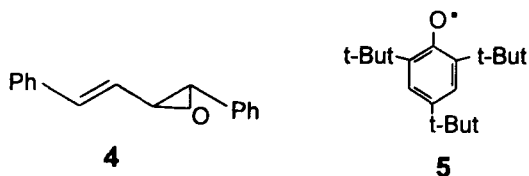
Herein we report our results that indicate that oxidation of substrates by various oxidizing systems does not always need to invoke these intermediates. Oxo transfer might take place by a distinctly different alternate path.

## 2. Results and discussion

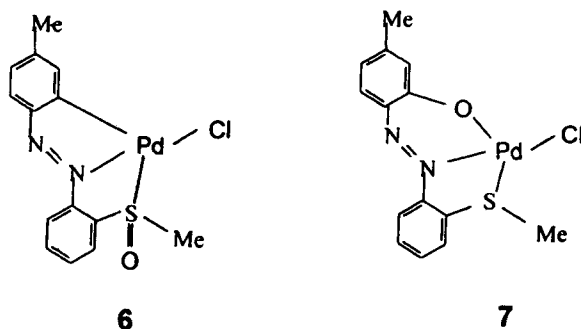
We have chosen compounds **1–3** as substrates and  $\text{F}_{20}\text{TPPFe(III)Cl}$  as a catalyst in the present study. An unequivocal oxene sample was first prepared by reacting



$\text{F}_{20}\text{TPPFe(III)Cl}$  and  $\text{C}_6\text{F}_5\text{IO}$  which epoxidizes compound **1** to give **4** in 90% yields in dichloromethane solvent. Yields of epoxidation go down substantially when the reaction is carried out in methanol. We have similar observations for the oxidation of compounds **2** and **3** in these two solvent systems.



In dichloromethane oxene oxidizes compound **2** smoothly to the phenoxy radical (**5**) in 94% yield. In methanol, however, the yield drops substantially (less than 40%) even under identical reaction conditions. Compound **3** has been found to show incredible selectivity towards nucleophilic and electrophilic oxidants. Thus electrophilic oxene converts compound **3** to compound **6** exclusively, whereas nucleophilic oxidant(s) like MCPBA and  $\text{ROO}^\bullet$  radical give Pd-C bond oxidized product **7**<sup>25</sup>. In this oxidation of **3** by MCPBA, the solvent plays a very important role. In pure toluene and dichloromethane solvents, **7** is the exclusive product whereas in dichloromethane-methanol mixed solvent system a considerable amount of **6** is also formed.



Lower yields of epoxidation and phenol in alcoholic solvents are possibly due to methanol oxidation to formaldehyde and formic acid. The change of selectivity in case of oxidizing compound **3** by MCPBA in toluene versus dichloromethane-methanol solvent system is rather interesting. We believe that the adduct formed by the reaction of  $\text{F}_{20}\text{TPPFe(III)Cl} + \text{MCPBA}$  before the formation of any oxene or other reactive intermediate transfers oxygen to the substrate. Expectedly this intermediate is stable in nonpolar solvents. Oxygenation of organic substrates by such adducts have been proposed from theoretical studies and also by biochemists<sup>26-28</sup>. Polar solvents like dichloromethane-methanol mixture help heterolytic cleavage of the peroxo bond of the peracid, thus giving oxene in solution. The presence of oxene has been detected by the selective oxidation of compound **3** at the sulphur centre to give **6** in appreciable yields.

### 3. Concluding remarks

Oxidation of organopalladium compound by MCPBA in alcoholic solvents gives two selective oxidation products. This has been demonstrated by the involvement of two distinctly different kinds of intermediates in iron(III) porphyrin-catalyzed oxidation of substrates by this oxidant. The lowering in the yields of oxidation in alcoholic solvents for three kinds of substrates indicate possible side reactions of the oxidant with solvent molecules. This needs detailed investigation.

### Acknowledgment

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