Chlorinated Phthalocyanine Iron(II) Complex Catalyzed Oxidation of Alkanes and Alkenes with Molecular Oxygen in the Presence of Acetaldehyde

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Abstract: Chlorinated phthalocyanine iron(II) complex is an excellent catalyst for the oxidation of alkanes and alkenes with molecular oxygen in the presence of acetaldehyde under O_2 (1 atm) at room temperature. The catalyst can be easily separated and reused for the next reaction.

Key words: oxidations, molecular oxygen, alkanes, iron phthalocyanine catalyst

The catalytic oxidation of alkanes using molecular oxygen is of importance in synthetic, industrial, and biological points of view.^{1,2} Development of new strategies for selective and efficient aerobic oxidation of alkanes under mild conditions still continues to be an important goal. Previously, we disclosed that the ruthenium-catalyzed oxidation of alkanes with peracetic acid and tert-butylhydroperoxide proceeds highly efficiently.3 Further, we developed catalytic oxidation of hydrocarbons with molecular oxygen in the presence of ruthenium, iron, and copper salt catalysts via in situ formation of peracetic acid from acetaldehyde and molecular oxygen.^{4,5} Furthermore, to get high turnover numbers, we developed an effective ruthenium porphyrin complex catalyst Ru(TPFPP)(CO), and found that the aerobic oxidation of alkanes with molecular oxygen can be carried out with high turnover number (TON) (~10000).^{6,7} We wish to report here that chlorinated phthalocyanine iron(II) is a highly efficient catalyst for aerobic oxidation of alkanes and alkenes in the presence of acetaldehyde under under O_2 (1 atm) at room temperature. (Scheme 1).

Metal phthalocyanine complexes have been much less studied as a catalyst for the catalytic oxidation of alkanes, comparing to metalloporphyrins.⁸ Phthlocyanines have extremely high stability and can be readily prepared; therefore metal phthalocyanines can be used for the catalytic oxidation of alkanes with molecular oxygen. The oxidations with phthalocyanine catalysts are limited to the reactions with peroxides in the presence of heterogeneous, immobilized metal phthalocyanine catalysts. *tert*-Butyl-hydroperoxide and iodosylbenzene have been used for the oxidation of alkanes in the presence of zeolite-encapsulat-

Synlett 2003, No. 3, Print: 19 02 2003. Art Id.1437-2096,E;2003,0,02,0321,0324,ftx,en;U12502ST.pdf. © Georg Thieme Verlag Stuttgart · New York ISSN 0936-5214





ed metal phthalocyanines,^{9,10} zeolite-engaged iron complex embedded in a polymer membrane,¹¹ MCM-41 supported metalphthalocyanines,¹² and activated carbon black supported metalphthalocyanines.¹³ The homogeneous catalytic oxidation of alkanes with KHSO₅ was recently reported in the presence of water soluble metal phthalocyanines.¹⁴

We examined the catalytic activity of 21 phthalocyanine complexes including five different Pc ligands $1-5^{15}$ for the aerobic oxidation of cyclohexane. The catalytic activity of Pc complexes is strongly dependent upon both central metal and ligand (Table 1). In general, the Fe, Co, Mn, and Ni complexes with substituted Pc ligands show better catalytic activity. The corresponding Mg(II), Zn(II), Sn(II), and Al(III)Cl complexes show no catalytic activity. The complex 3-Fe(II) (16Cl-Pc-Fe(II)) was found to be the most effective catalyst. Haloganated Pc ligands benefited the reaction due to enhancement of robustness of the ligands during reaction. The catalytic activity is in the order of 3-Fe(II) > 2-Fe(II) > 1-Fe(II).

Low temperature decreases the reaction rate, while yields remain almost the same, when the temperature increases from 20 °C to 40 °C or higher. The catalytic activity is affected by a solvent. Aprotic solvents such as dichloromethane are superior to others, and no product was obtained in ethanol. It is noteworthy that the reaction in benzotrifluoride (BTF), which is an alternative solvent to dichloromethane, gives moderate and comparable yields.

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Catalyst	Yield (%) (-ol:-one) ^b	TON	
1-Fe(II)	15 (53:47)	59	
1-Fe(III)Cl	11 (45:55)	45	
2-Fe(II)	16 (50:50)	62	
3-Fe(II)	22 (50:50)	88	
5-Fe(II)	16 (50:50)	62	
1-Co(II)	13 (54:46)	53	
2 -Co(II)	16 (44:56)	64	
4-Co(II)	15 (47:53)	58	
1-Mn(II)	16 (50:50)	62	
1-Ni(II)	16 (56:44)	64	
1-Cu(II)	14 (50:50)	55	
1-Ru(III)(DCB) ₂ Cl ^c	11 (18:82)	46	

^a In a typical experiment, a mixture of cyclohexane (40 mmol), a catalyst (0.010 mmol), acetaldehyde (4.0 mmol), and dry dichloromethane (10 mL) was vigorously stirred at room temperature under oxygen atmosphere (1 atm). After the usual work up, the reaction mixture was analyzed by GC and GC-MS. Yields were determined by GC analyses based on acetaldehyde used.

^b Cyclohexanol:cyclohexanone.

^c With an axial ligand of 1,2-dicyanobenzene.

Addition of pyridine or imidazole as an axial ligand showed little effect.

Induction period (IP) was observed in these reactions. The IPs range from several minutes to 3 hours, and the reactions were almost completed within the following 3 hours. A notable effect on the IP is dependent on either ligands or valency of central metals. For example, for the oxidation with 1-Fe(II) 2 hours of IP was needed, while very short IP was required for those with 1-Fe(III)Cl and 3-Fe(II). Because of the robustness of 3-Fe(II), the catalytic activity remained even after 15 hours, and the yields of the products are increasing gradually. On the other hand, the oxidation with 1-Fe(II) stopped after 6 hours because of the decomposition of the catalyst.

The catalyst **3**-Fe(II) is effective for the oxidation of both alkanes and alkenes. Representative results for the oxidation of hydrocarbons are shown in Table 2. Excess amount of substrate is used to retard the over-oxidation.^{3a,16} Tertiary C-H bonds can be oxidized easier than those of secondary or primary C-H bonds. In case of the oxidation of adamantane, the tertiary C-H bond was oxidized predominantly, and the 1-substituted products were obtained 15 times more than that of 2- position. From the oxidation of indan, 1-indanone and 1-indanol were obtained in 95% yield (44:56) based on acetaldehyde. The catalytic oxidation of indan without a solvent gave high TON 8500 with low catalyst loading (0.01% mmol). Fur-

thermore, the TON 11000 was obtained under 10% oxygen in nitrogen (1 atm $O_2 + 9$ atm N_2), which is a practical condition fallen outside the explosion limits. The catalyst **3**-Fe(II) could be reused after simple recovery,¹⁷ giving the similar result. The oxidation of cyclohexene with **3**-Fe(II) catalyst gave allylic oxidation products predominantly along with cyclohexene oxide.¹⁸

To clarify the reaction mechanism, we carried out competition experiments for the oxidation of para-substituted ethylbenzenes (p-X-C₆H₄CH₂CH₃, X = MeO, Me, H, Br) in the presence of 3-Fe(II) catalyst and acetaldehyde. The rate data correlate well ($r^2 = 0.995$) with Hammett linear free-energy relationship with use of σ^+ values. The observed ρ value (-1.34) is close to that reported for oxoiron porphyrin species (-1.69),¹⁹ and quite different from those for alkoxyl radical (-0.4).²⁰ To get further evidence, the competitive oxidations of cyclohexane/cyclohexane d_{12} and ethylbenzene/ethylbenzene- d_{10} were carried out, and the deuterium isotope effects $(k_{\rm H}/k_{\rm D} \text{ values})$ were determined to be 6.2 and 6.7, respectively, which are consistent with those of hydrogen abstraction process of oxometalloporphyrin species.^{6,21} The mechanistic study suggests that oxo-iron species would be generated from the iron phthalocyanine complex under the present reaction conditions. The present reaction can be rationalized by assuming cytochrome P-450 type mechanism. Oxo-metal species (3-Fe(IV) = O) would be formed from the reaction of 3-Fe(II) and peracetic acid, which is formed from the reaction of acetaldehyde with molecular oxygen in the presence of **3**-Fe(II) catalyst (Scheme 2).²² The reaction of alkane with oxo-metal species would give alcohol and 3-Fe(II) complex to complete the catalytic cycle. Alcohols can be further converted to the corresponding ketones under the reaction conditions. In the oxidation of alkenes, the product yields were dependent on the steric hindrance of the substrates. For example, the reaction of styrene gave styrene oxide in 37% yield, while the oxidation of more bulky cis-stilbene gave 9% of the trans-epoxide, and no epoxide was obtained from trans-stilbene.

 $CH_{3}CHO + O_{2} \xrightarrow{Pc-Fe(II) (cat.)} CH_{3}CO_{3}H$ $Pc-Fe(II) + CH_{3}CO_{3}H \longrightarrow Pc-Fe(IV)=O + CH_{3}CO_{2}H$ $Pc-Fe(IV)=O + R-H \longrightarrow Pc-Fe(II) + R-OH$

Scheme 2

In summary, aerobic oxidation of alkanes and alkenes with chlorinated phthalocyanine iron(II) catalyst in the presence of acetaldehyde occurs under O_2 (1 atm) at room temperature with high TON (up to 11000). Because of easy preparation of the catalyst and its stability, commercially available chlorinated phthalocyanine iron(II) catalyst is more attractive than Ru(TPFPP)(CO), which gives similar high TON. The mechanism was disclosed for the first time, to involve oxo-iron species likewise cytochrome P-450.

Substrates	Yield (%) ^b	Product (Selectivity /%)	TON
\bigcirc	22 21°	$\bigcirc -\text{OH} (50) (50)^c \bigcirc = 0 (50) (50)^c$	88 80 ^c
	47	OH (83) OH (8) (8) (8)	188
~~~	6	$\begin{array}{c c} & & & & & & & \\ & & & & & & \\ & & & & $	22
	95	OH O (44) (56)	377
	76	────────────────────────────────────	320
		(30)	

#### Table 2 Oxidation of Hydrocarbons with O2 with 3-Fe(II) Catalysta

^a In a typical experiment, a mixture of substrate (40 mmol), **3**-Fe(II) (0.010 mmol), acetaldehyde (4.0 mmol), and dry dichloromethane (10 mL) was vigorously stirred at room temperature under oxygen atmosphere (1 atm). After the usual work up, the reaction mixture was analyzed by GC and GC-MS.

^b Yields were determined by GC analyses based on acetaldehyde used.

^c The values were obtained by the reaction using the recycled catalyst.

## Acknowledgment

This work was supported by the Research for the Future Program, the Japan Society for the Promotion of Science.

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Synlett 2003, No. 3, 321-324 ISSN 0936-5214 © Thieme Stuttgart · New York

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