

## A New Iron (III) Porphyrin System for Olefin Epoxidation Catalysts

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The iron (III) porphyrin-hypochlorite systems have been developed into the efficient catalysts. Successful epoxidation of olefins (styrene,  $\alpha$ -methylstyrene, cyclohexene, and cyclooctene) using these catalytic systems have been demonstrated.

So far much efforts have been spent for exploitation of P-450 models which include the metalloporphyrin-iodosylbenzene,<sup>1)</sup> the metalloporphyrin-O<sub>2</sub>-reducing agent,<sup>2)</sup> or the manganese (III) porphyrin-hypochlorite systems.<sup>3)</sup> Although manganese (III) porphyrin has been well established for the olefin epoxidation in the whole three systems, iron (III) porphyrin has never shown the comparable catalytic activity in the hypochlorite system except one example.<sup>4)</sup>

The porphyrins 1,<sup>5)</sup> 2a, and 2b<sup>6)</sup> were used for our oxygenation experiment, and it was found that the olefin epoxidation capabilities of the manganese (III) complexes of these protected porphyrins (1, 2a, and 2b) were superior to those of the non-protected Mn porphyrins, such as MnTPP, in the stability of the catalyst.<sup>7)</sup> Judging from these results, it was supposed that the iron (III) complexes of 1, 2a, and 2b might show the sufficient activities as the oxygenation catalysts.

We report here the practical example of the successful epoxidation of olefins by iron (III) porphyrin-hypochlorite systems in the absence of the axial base-ligand.<sup>8)</sup>

The reaction rates and the yields by use of the iron complexes (1, 2a, and 2b) were measured for comparison with those of the authentic catalyst, MnTPP.<sup>9)</sup> All kinetic experiments were controlled as follows. The porphyrin (0.0082 mmol), olefin (7.8 mmol,

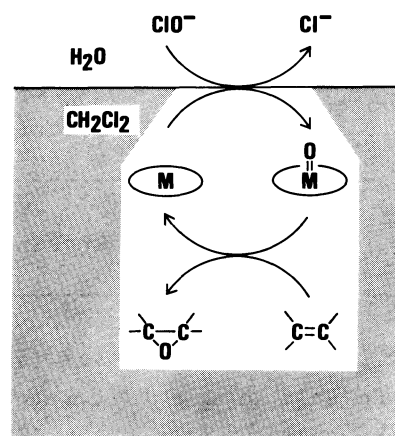


Fig. 1. Olefin epoxidation.

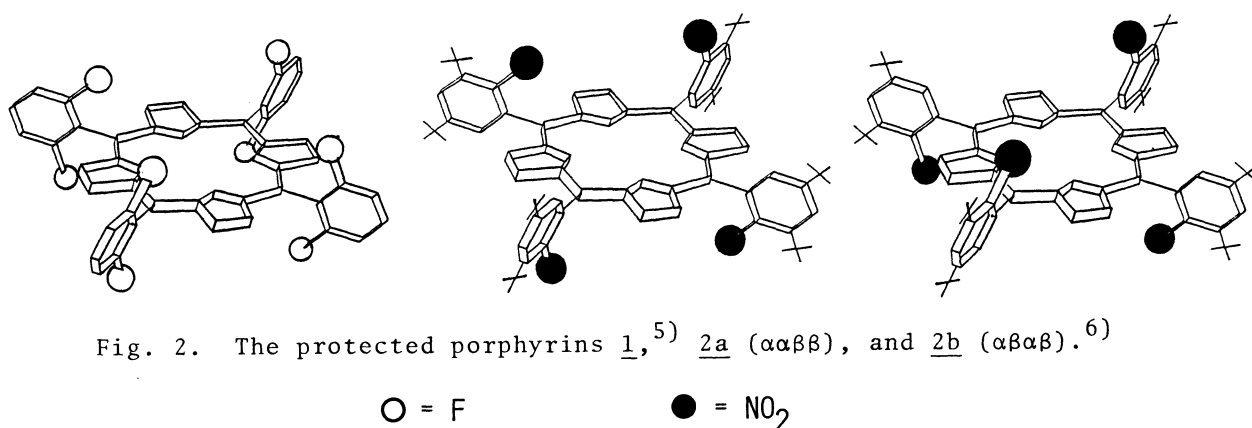


Fig. 2. The protected porphyrins 1,<sup>5)</sup> 2a ( $\alpha\alpha\beta\beta$ ), and 2b ( $\alpha\beta\alpha\beta$ ).<sup>6)</sup>

styrene,  $\alpha$ -methylstyrene, cyclohexene, or cyclooctene), internal standard reagent (p-dichlorobenzene or 1,3,5-trichlorobenzene), and phase transfer reagent (benzyltrimethyltetradecylammonium chloride) were dissolved in 20 cm<sup>3</sup> of dichloromethane. Then, 15 cm<sup>3</sup> of the sodium hypochlorite solution (8.7 mmol) was layered over the organic phase.<sup>10)</sup> The epoxidation reaction was initiated by stirring vigorously, and the reaction temperature was maintained at 22 °C. The products were periodically monitored by gas chromatography. The results (the reaction rates and the yields) are listed in Table 1. The reaction rates are represented by turnovers/sec, and the yields are represented by turnover numbers. The kinetic results of the epoxidation using MnTPP are also listed in Table 1.<sup>9)</sup>

For the purpose of measuring the oxygenation capabilities of the porphyrin catalysts, the reaction was continued until the porphyrins were decomposed by bleaching.<sup>11)</sup> The yields in these experiments are represented as "maximum turnover number" in Table 2.

The maximum turnover numbers of iron (III) complexes of 1, 2a, and 2b were comparable to those of MnTPP (See Table 2). In styrene and  $\alpha$ -methylstyrene epoxidation, both the reaction rates and the yields were similar to those of MnTPP.<sup>12)</sup> In cyclohexene and cyclooctene epoxidation, however, the reaction rates, as well as the yields, of these protected iron (III) porphyrins (1, 2a, and

Table 1. The reaction rates and the yields

	Styrene	$\alpha$ -Methylstyrene	Cyclohexene	Cyclooctene
MnTPP	3.7 (690)	1.6 (820)	0.037 ( 50)	0.14 (120)
Fe salt of <u>1</u>	1.1 (nd <sup>a</sup> )	2.5 ( nd)	1.2 ( nd)	2.1 ( nd)
Fe salt of <u>2a</u>	4.6 (890)	3.7 (870)	0.48 (570)	0.37 (760)
Fe salt of <u>2b</u>	1.8 (490)	2.5 (850)	0.40 (600)	1.1 (850)

a) Not determined.

Table 2. Maximum turnover numbers<sup>11)</sup>

	Styrene	$\alpha$ -Methylstyrene
MnTPP	5000	2900
Mn salt of <u>1</u>	38000	200000
Mn salt of <u>2a</u>	7300	31000
Mn salt of <u>2b</u>	21000	15000
FeTPP	300	400
FeTF <sub>5</sub> PPa)	33000	not determined
Fe salt of <u>1</u>	18000	18000
Fe salt of <u>2b</u>	1600	3500
Fe salt of <u>2b</u>	4300	1800

a) FeTF<sub>5</sub>PP = tetrakis (pentafluorophenyl) porphyrin.

2b) were considerably higher than those of MnTPP and manganese complexes of the respective porphyrins.<sup>13)</sup> These results clearly show that the iron (III) complexes of the protected porphyrins 1, 2a, and 2b are practical catalysts for the epoxidation.

Taken together, our protected porphyrins give the first example of the effective iron porphyrin catalysts for the olefin epoxidation without using pyridine or imidazole ligands in the hypochlorite system.

#### References

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- By using of the iron (III) "picket fence" porphyrin catalyst with bulky axial ligand, 1-hexene has been epoxidized. However, the catalytic oxygenation has been quite slow and the catalyst has not been as stable as the manganese system.

FeTPP has hardly shown a catalytic activity for the olefin epoxidation in our hands (See Table 2).

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- 7) The maximum turnover numbers of the manganese (III) complexes of the protected porphyrins 1, 2a, and 2b were considerably larger than those of MnTPP. (See Table 2) In  $\alpha$ -methylstyrene epoxidation, the maximum turnover number of Mn salt of 1 was seventy times as large as that of MnTPP.
- 8) In the presence of 1-triphenylmethyl imidazole, the iron complexes of our protected porphyrins have shown rather low catalytic activity compared with using no axial base-ligand.
- 9) When MnTPP was used, 1-triphenylmethylimidazole (0.46 mmol) was added to the  $\text{CH}_2\text{Cl}_2$  solution.
- 10) In kinetic experiment using the iron (III) complex of porphyrin 1, the reaction conditions were as follows. The porphyrin 1 (0.007 mmol), olefin (4.0 mmol), internal standard reagent, and phase-transfer reagent were dissolved in 10  $\text{cm}^3$  of  $\text{CH}_2\text{Cl}_2$ . Then, 20  $\text{cm}^3$  of the sodium hypochlorite solution (7 mmol) was added to the  $\text{CH}_2\text{Cl}_2$  solution.
- 11) To the experiments by use of Mn complexes of porphyrin 1, 2a, 2b, or TPP, 1-triphenylmethylimidazole or 4'-(imidazol-1-yl)acetophenone was employed. In a typical experiment, Mn porphyrin 1 (0.0041 mmol), 4'-(imidazol-1-yl)acetophenone (0.68 mmol), phase-transfer reagent, and internal standard reagent (p-dichlorobenzene) were dissolved in 40  $\text{cm}^3$  of  $\text{CH}_2\text{Cl}_2$ . Then, 160  $\text{cm}^3$  of  $\alpha$ -methylstyrene (1240 mmol) and 240  $\text{cm}^3$  of the sodium hypochlorite solution (1980 mmol) were added. The resulting two-phase mixture was stirred vigorously for 1 d at room temperature. The products were analyzed by GC. The total yield of the products based on porphyrin catalyst is represented as "the maximum turnover number".  
In each reaction, the main product is epoxide except for FeTPP. If FeTPP is employed, benzaldehyde or  $\alpha$ -phenylpropionaldehyde is mainly produced.
- 12) In styrene epoxidation using the iron (III) complexes of 1, 2a, and 2b, phenylacetaldehyde was not produced. By use of MnTPP, however, phenylacetaldehyde was produced (11%). These results show that the iron (III) porphyrin-hypochlorite systems have high selectivity for the epoxide production.
- 13) The reaction rates of cyclohexene and cyclooctene epoxidation using manganese complexes of 1 and 2b are follows: cyclohexene, 0.025(1), 0.007(2b); cyclooctene, 0.15(1), 0.05(2b). In cyclooctene epoxidation, the maximum turnover of iron complex of 1 (19000) is considerably larger than that of manganese complex of 1 (2000).

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