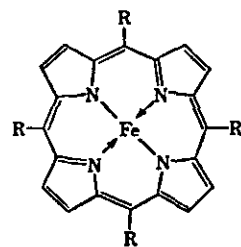


NOVEL FUNCTIONS OF PORPHYRIN-IRON COMPLEX AS A MODEL OF CYTOCHROME P-450:
DEOXYGENATION AND REDUCTIVE DIOXYGEN ACTIVATION

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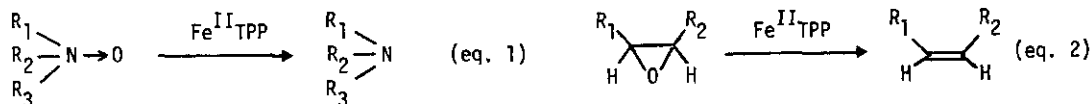
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As part of our program of chemical reconstitution of several catalytic functions of cytochrome P-450, we have already revealed that porphinatoiron (III)-oxene complex (TPPFe^V=O), generated by Groves system, has an ability of oxidative dealkylation of tertiary amines.¹⁾ Now we wish to report two catalytic properties of porphrin-iron complex. One is reductive deoxygenation from several oxides and the other is reductive activation of molecular oxygen, which are fundamentally important functions of cytochrome P-450.

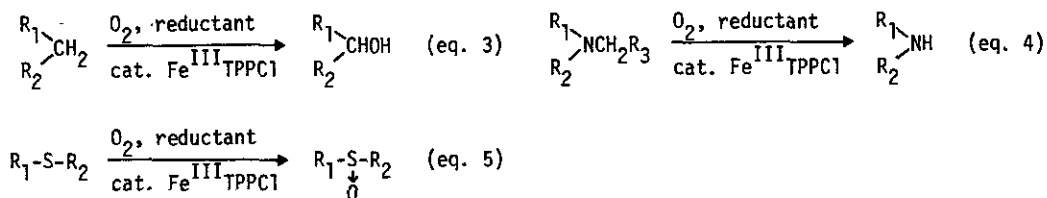


R = -C₆H₅
tetraphenylporphinatoiron

In a strictly anaerobic condition, tertiary amine N-oxides such as N,N-dimethylaniline N-oxide and quinoline N-oxide were smoothly deoxygenated by Fe^{II}TPP (eq. 1). Arene oxides including benzo-[a]pyrene-4,5-oxide were also deoxygenated (eq. 2). Intermediary formation of ferryl oxide (TPPFe^{IV}=O) has been proved by using triphenylphosphine as oxene acceptor from ferryl oxide.



Reductive activation of molecular oxygen was achieved by Fe^{III}TPPCl-reductant system in protic media using Zn/CH₃COOH, NaBH₄ or Na₂S₂O₄ as reductant and the active species formed by this system oxidized hydrocarbons (eq. 3), tertiary amines (eq. 4) and sulfides (eq. 5). These reactions proceeded with no induction period and Fe^{III}TPPCl acted as an effective catalyst in this system. Detailed studies on the real active species will also be discussed.



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Abbreviation: TPP, tetraphenylporphinato dianion

1) N. Miyata, H. Kiuchi and M. Hirobe, *Chem. Pharm. Bull.*, **29**, 1489(1981).