

# Intermediate species detected in oxidation reactions of FeTM(4)PyP<sup>5+</sup> with iodosylbenzene by EPR and UV–Vis spectroscopies

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## Abstract

The iron porphyrin, tetrakis (4-*N*-methylpyridyl) porphyrinato iron(III) perchlorate (FeTM(4)PyP<sup>5+</sup>) was studied as a catalyst for the oxidation reaction of an organic substrate by iodosylbenzene in organic solvents. The reaction system was studied by UV–Vis and EPR spectroscopic techniques at low temperature. The following intermediate species were detected: (i) iron(III)porphyrin rhombic species in the initial step of the reaction, (ii) oxo iron(IV)porphyrin (ferryl species) detected at 540 nm in the UV–Vis spectra and (iii) iron(III) N-oxides species (Fe–O–N) by EPR with *g* value 4.30. The species oxo iron(IV) porphyrin  $\pi$ -cation radical supposed to be present in the oxidation reaction was not detected in our experimental conditions. However, there is evidence for the existence of this species due to the reaction yields observed.

## Introduction

Molecular oxygen activation by cytochrome P-450 yields a species called 'oxenoid' (FeO<sup>3+</sup>) [1], an intermediate that is generally accepted but is still poorly understood in chemical terms. It seems that this intermediate is the key for hydroxylation catalysis for alkanes [2]. Iodosylbenzene, an oxygen atom donor, has been shown to be capable of replacing NADH and molecular oxygen in P-450 catalyzed reactions [3]. The oxenoid intermediate formation by iodosylbenzene ( $\phi$ IO) is referred to as the 'peroxide shunt mechanism' [4]. The oxo iron(IV) porphyrin  $\pi$ -cation radical (ferryl porphyrin  $\pi$ -cation radical) similar to the compound I of horseradish peroxidase (HRP) is accepted by most as the oxenoid intermediate observed in model systems [5].

FeTM(4)PyP<sup>5+</sup> is a synthetic polar iron porphyrin that has an unusual property: a low tendency to dimerize in organic solvent. Recent studies describe the bifacially hindered porphyrinato iron complex as a model that does not form  $\mu$ -oxo dimers that favors catalytic activity [6].

With this iron porphyrin system the advantage is that significant changes in catalytic activity are ob-

served just by changing solvents. Using  $\phi$ IO as an oxygen donor and cyclohexane as a substrate in methanol a yield of only 1% of cyclohexanol [7] was observed. When we performed this hydroxylation in methanol–dichloromethane the yield improved to 5% cyclohexanol and to 20% in acetonitrile [8]. The methanol–dichloromethane system presents a multiplicity of species. In this report, experiments were followed by EPR and UV–Vis techniques. The results provide information about intermediates species involved in the reaction pathways.

## Materials and methods

### UV–Vis optical absorption spectra

These were recorded with a Perkin-Elmer Coleman 575 spectrophotometer at 200 K, using the low temperature dewar adapted with a quartz cell with 0.6 mm optical length.

### EPR spectra

These were recorded at low temperature (110 K) on a Varian E-109 century line spectrometer operating at the X band. The *g* values were found by taking the frequency indicated on the dial of the microwave bridge and the field measured at the

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spectral features which were recorded with increased gain and expanded field. Routine calibrations of the field setting and scan were made with DPPH and  $\text{Cr}^{3+}$  reference signals. The frequency on the dial was checked with an HP 5340A frequency meter.

### Materials

Iron porphyrin (5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrinato)iron(III) pentaperchlorate (FePo) was purchased from MidCentury. Iodosylbenzene  $\phi\text{IO}$  was prepared by the hydrolysis of iodobenzene diacetate by the method of Sharefkin and Saltzman [9]. The purity was determined by titration with sodium thiosulphate (90%). Since iodosylbenzene will slowly disproportionate, care was taken to store the compound in the cold (273 K).

### Reaction conditions

Typical conditions for oxidation reaction for EPR and UV-Vis analysis were as follows. A solution of FePo in different solvents was added to a test tube and immediately frozen at 200 K. The FePo solutions were prepared with different solvents as follows: solution 1,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  in 11:10 ratio; solution 2,  $\text{CDCl}_3:\text{CH}_3\text{OH}$  in 11:10 ratio; solution 3, pure methanol; solution 4;  $\text{CH}_2\text{Cl}_2$ . Freshly prepared solutions of  $\phi\text{IO}$  (partially insoluble in solutions 1 and 3) were added in appropriate amounts to the solution of iron porphyrin at low temperature. The contents of the test tube were shaken at low temperature and if necessary the reaction was stirred at room temperature using an ultrasound laboratory cleaner (Minison Thornton) and quickly frozen again. The reaction mixture was then transferred to the EPR tube or UV-Vis cell for spectrum recording. This procedure was repeated to record spectra at different times.

## Results

### EPR spectra

The reactions were performed at room temperature for controlled times and inhibited at low temperature (200 K). The EPR spectra were registered at 80–120 K. The frozen condition is favorable for the EPR study of the very unstable iron porphyrin intermediate species.

The reactions of FePo with  $\phi\text{IO}$  took place in solution 1. Table 1 shows EPR data for specific reaction conditions. The  $g$  values are presented for different reaction times at room temperature with ultrasound stirring. For reaction series 3 solution number 2 was employed. The iron(III) porphyrin complex in this solvent mixture remains in the high-

spin state as is evident from the EPR spectra with a strong  $g_{\perp} = 5.30$  feature (Fig. 1, A).

Monitoring reaction 1 with EPR spectroscopy has shown the following evidence. (a) High-spin signals that exhibit rhombic distortion of 9.19% (see Table 2) that increases for the conditions that yield Fig. 1, B–D. (b) Comparing spectra B and C in Fig. 1 we observe that the total area in B for 15 s reaction time is smaller than that in C indicating a silent species. (c) The  $g = 4.30$  signal is already present at 15 s and increases with time until 30 s (Fig. 1, C). (d) The most intriguing signal appears at  $g = 2.37$ . It may be related to a short half-life species because it first appears in 30 s (Fig. 1, C), disappears in 40 s and reappears intensified in 90 s (Fig. 1, E), accompanied by a decrease of the  $g = 6.0$  and  $g = 4.3$  signals.

For reaction 2 (Table 1) the system is more diluted and the iodosylbenzene/iron porphyrin ratio is higher than that for reaction 1. The reaction time was 30 s at room temperature, unlike reaction 1 with less time. After 30 s reaction, the Fe(III) high-spin rhombic signal does not exist (see Fig. 2, A and Table 1). Only the intense  $g = 4.30$  signal is present. Its fading with time (Fig. 2, C), indicates that a process that turns the species diamagnetic is occurring. However, Fe(IV)-ferrylporphyrin, an intermediate species that is EPR silent, may simultaneously be present.

When the reaction was carried out in solution 2 and the system was frozen before any room temperature reaction (Table 1, 3A) the EPR spectrum showed a intense sharp line with  $g = 2.01$  and line width 9.0 gauss. After 15 s this signal disappears with the simultaneous appearance of evidence for a Fe(III)-porphyrin rhombic signal and a Fe–O–N species with signal at  $g = 4.30$  (Fig. 3). Evidently the reaction is occurring in a cyclic way.

### UV-Vis spectra

The reactions were performed at room temperature for controlled times and quenched at low temperature (200 K). The spectra were registered at 210–203 K. For these conditions it is not possible to replicate the species composition at each definite time because the quenching is not fast enough. The original iron porphyrin spectrum in this condition showed a Soret band at 398 nm (envelope band) with molar absorptivity of  $1.4 \times 10^5 \text{ l cm}^{-1} \text{ mol}^{-1}$ , at 210 K (Fig. 5, A). The spectra of reactions of FeTM(4)PyP( $\text{ClO}_4$ )<sub>5</sub> with iodosylbenzene in solution 1 are shown in Figs. 4–6. After 10 s at room temperature and cooling the sample to 203 K the Soret band is sharp, intense (molar absorptivity  $2.0 \times 10^5 \text{ l cm}^{-1} \text{ mol}^{-1}$ ) and a shift for 420 nm. A  $\beta$ -band at 540 nm characteristic

TABLE 1. Changes in  $g$  values observed in the reactions of FeTM(4)PyP<sup>5</sup> (FePo) with iodossylbenzene ( $\phi$ IO) in the solvent mixture CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH at the ratio 11:10 (solution 1)

Reaction	FePo	$\phi$ IO(M)	$\phi$ IO:FePo	$t$ (s)	$g$ values
1A	$9.4 \times 10^{-4}$				5.3; 2.17
1B	$1.3 \times 10^{-3}$	$1.5 \times 10^{-2}$	12:1	15	6.65; 5.18; 4.26
1C				30	6.94; 5.18; 4.30
1D				40	6.94; 5.18; 4.30
1E				90	7.00; 5.35; 4.30; 2.36
2A	$6.1 \times 10^{-3}$	$1.2 \times 10^{-2}$	19:1	30	4.26
2B				60	4.26
2C				90	4.26
3A	$1.5 \times 10^{-3}$	$1.4 \times 10^{-2}$	9:1	0	6.86; 5.26; 2.01
3B				15	7.01; 5.22; 4.30; 2.31

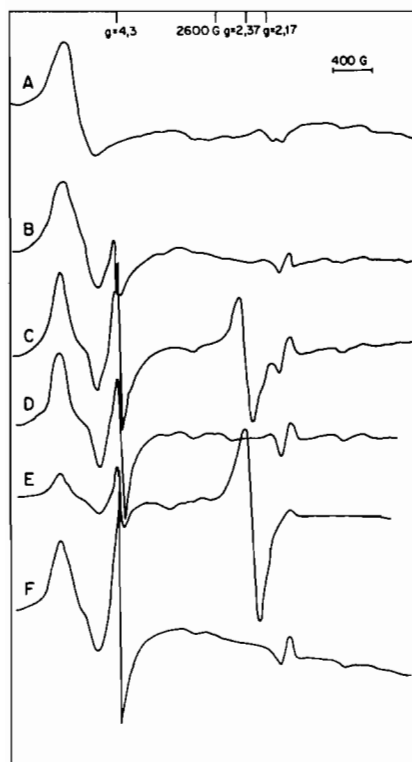


Fig. 1. EPR spectra for different times of reaction 1 of FePo and  $\phi$ IO in solution 1. A, original solution of FeTMPyP<sup>5+</sup>; B, reaction A after  $\phi$ IO addition and 15 s at room temperature with ultrasonic stirring; C, reaction B after 30 s; D, after 40 s; E, after 90 s. All spectra were recorded in the same conditions of gain  $2.5 \times 10^4$ , 10 gauss of modulation, 10 mW of microwave power, frequency of 9.14 GHz and temperature 110 K.

of oxo-Fe(IV)-ferryl porphyrin (oxo iron(IV) porphyrin) like compound II of the HRP analogue (Fig. 4B) is also present. When the system was warmed to room temperature, the spectrum indicated a partial recovery of the original species (Fig. 4, C).

TABLE 2. Effect of solvent on the iron symmetry in the reaction with iodossylbenzene

Solvent	FePo	$g_x$	$g_y$	Rhombicity (%)
Solution 1	FeTM(4)PyP <sup>5+</sup>	6.65	5.18	9.19
Solution 3	FeTM(4)PyP <sup>5+</sup>	6.94	5.53	8.81
Solution 4	FeTM(4)PyP <sup>5+</sup>	7.82	5.72	13.13
Solution 1	FeTPP <sup>+</sup>	6.32	5.83	3.06

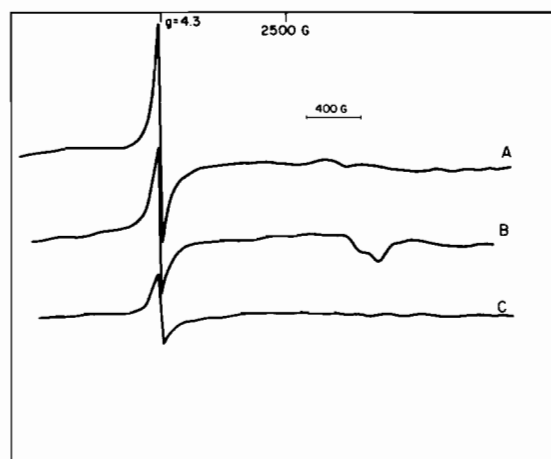


Fig. 2. EPR spectra of reaction 2 of FePo and  $\phi$ IO in solution 2 for different reaction times at room temperature function. A, after 30 s; B, after 60 s; C, after 90 s. Spectra were recorded at 110 K.

When the reaction time was 5 min at low temperature (200 K) and with more concentrated reagents (Fig. 5), the spectra initially show the same pattern as displayed in Fig. 4. In the interval from 1–5 min at room temperature, one observes that the Soret peak decreases and a large band appears at 460 nm (Fig. 5, C). This band is characteristic of Fe–O–N species that appears in the EPR spectra as a weak feature with  $g=4.30$  [10], indicating that



Fig. 3. EPR spectra of reaction 3 of FePo and  $\phi$ IO in solution 2, reaction at room temperature. A, reaction at 200 K; B, after 15 s of reaction at room temperature and ultrasonic stirring.

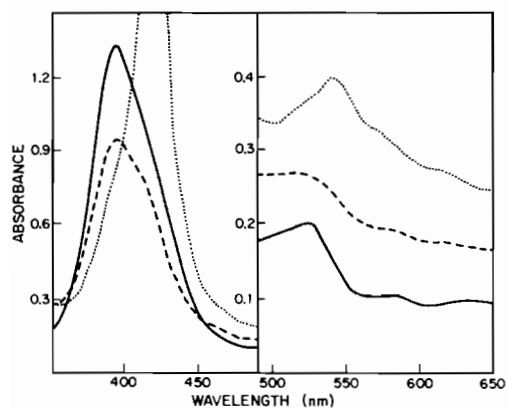


Fig. 4. UV-Vis spectra of: A (—), FePo in solution 1 ( $1.6 \times 10^{-4}$  M); B (·····) and C (---), time dependence of the spectra obtained from the oxidation in solution 1 of FePo ( $1.5 \times 10^{-4}$  M) by  $\phi$ IO ( $2.3 \times 10^{-3}$  M); B after 10 s of reaction at room temperature and ultrasonic stirring; C, after about 5 min at room temperature.

an oxidation process is occurring under these conditions. The band at 540 nm indicates that the species ferrylporphyrin coexists at this point in the reaction.

If the reagents in the system are about ten times more concentrated than in the former reactions (Figs. 4 and 5), and the reaction time was 100 min at 203 K, there appeared a Soret envelope with peak at 416 nm and shoulder at 395 nm and absorption features between 500 to 650 nm that are assigned to the ferryl porphyrin  $\pi$ -cation radical (Fig. 6). In Fig. 6 B, C and D indicate a partial recuperation of the original iron porphyrin.

## Discussion

Based on the results of EPR and UV-Vis measurements at low temperature we can suggest Scheme

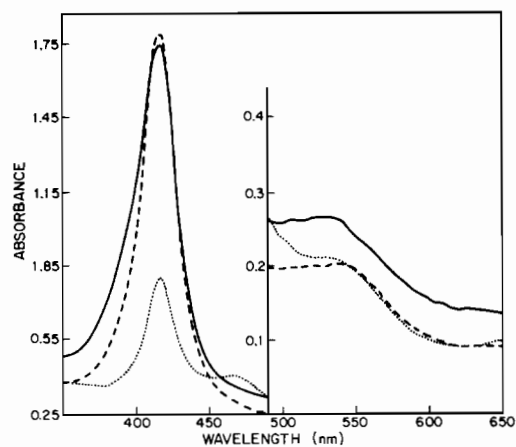


Fig. 5. Time dependence of the UV-Vis spectra obtained on oxidation reaction in solution 1 of FePo ( $4.6 \times 10^{-4}$  M) by  $\phi$ IO ( $5.4 \times 10^{-3}$  M). A (—), beginning of the reaction at room temperature; B (---), after 15 s of reaction; C (·····), after 60 s. Spectra were recorded at 210 K.

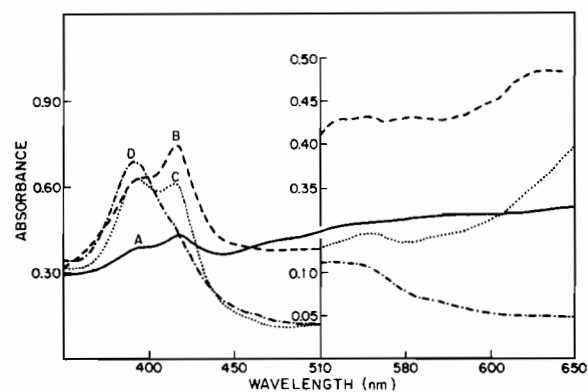
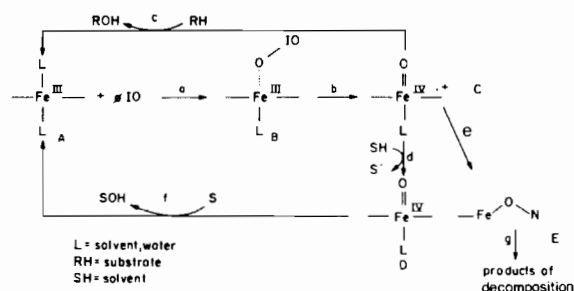


Fig. 6. UV-Vis spectra (210 K) of oxidation from FePo ( $4.5 \times 10^{-3}$  M) by  $\phi$ IO ( $4.1 \times 10^{-2}$  M). A, beginning of the reaction; B and C, registered after A without contact with reaction solution at ambient temperature; D, registered after 130 s of reaction at room temperature and ultrasonic stirring.

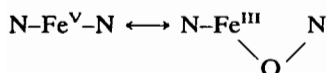


Scheme 1.

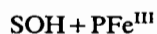
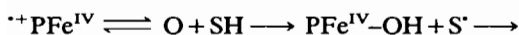
1 for the intermediates involved in the formation of the oxo-iron active species for oxidation in the methanol-dichloromethane system.

The iron porphyrin FeTM(4)PyP(ClO<sub>4</sub>)<sub>5</sub> (step a in Scheme 1) is initially in the monomer form. There is no evidence for dimerization in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH as is observed in water [8]. Probably the solvents in this case do not stabilize the four porphyrin periphery positive charges preventing the approximation of the two planes due to electrostatic repulsion [11]. The initial step give a high-spin ion porphyrin with rhombic symmetry as an intermediate species that is the B species (Scheme 1 a, Fig. 1, B-D). There is a tetragonal and rhombic distortion [12], that can be ascribed to the iron-iodosylbenzene interaction. The iron porphyrin charges and solvent may be responsible for the rhombic distortion. In the less polar solvent the iron porphyrin charges on the plane are not neutralized leading to an increase in the rhombic distortion with a decrease in the solvent polarity (Table 2).

With uncharged Fe(III)-porphyrin, like FeTPP<sup>+</sup> for example, a rhombic distortion was not detected in the initial step of the reaction, indicating the formation of ferryl species that are EPR silent. Traylor and co-workers reported a rhombic EPR spectra for metallacycle Fe(III)-porphyrin coordinated to pentafluoriodosylbenzene as intermediate in epoxidation reactions [13], similar to species B shown in Scheme 1. There is evidence that after 15 s of reaction that part of the rhombic species, is converted to a ferryl porphyrin  $\pi$  cation radical (species C in Scheme 1) complex in a heterolytic way in concentrated conditions (Fig. 6). There is an interconversion between the species C (PFe<sup>5+</sup>=O or <sup>++</sup>PFe<sup>4+</sup>=O) and the species E (Fe<sup>3+</sup>-O-N) structure (Scheme 1, step e) explained by the following isomerization [14]:



It seems that this polar system favors this isomerization. The mechanism of charge influence in these isomerizations is under investigation. In almost all reactions a ferryl porphyrin species is observed (Scheme 1, species E; Fig. 4). This is explained by an initial two-electron oxidation to the ferryl porphyrin  $\pi$ -cation radical followed by a one-electron reduction via hydrogen atom abstraction from the solvent [15, 16].



When the reaction was carried out in solution 2 a sharp EPR signal was observed at  $g=2.01$  and linewidth 9.0 gauss, Fig. 3, assigned to a solvent radical S<sup>·</sup> that can be quenched by 'oxygen rebound'

to the SOH product [17] recovering the initial Fe<sup>3+</sup>-porphyrin species (Scheme 1, step f). The study of the charge and solvent influence in the active species C leading, via isomerization, to the species E or to the reduction of the species D is important to better understand the catalytic mechanisms involved in this synthetic polar iron porphyrin.

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### References

- 1 G. A. Hamilton, in O. Hayashi (ed.), *Molecular Mechanisms of Oxygen Activation*, Academic Press, New York, 1974, p. 405.
- 2 J. T. Dawson and K. S. Eble, in A. G. Sykes (ed.), *Advances in Inorganic and Bioinorganic Mechanisms*, Vol. 4, Academic Press, Orlando, 1986, p. 1.
- 3 R. E. White and M. J. Coon, *Ann. Rev. Biochem.*, (1980) 49.
- 4 J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 110 (1988) 8443.
- 5 J. T. Groves, R. Quinn, T. J. McMurray, M. Nakamura, G. Lang and B. Bose, *J. Am. Chem. Soc.*, 107 (1985) 354.
- 6 T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 26 (1987) 1338.
- 7 J. R. Lindsay-Smith and S. Martimes, *J. Chem. Soc., Chem. Commun.*, (1985) 410.
- 8 S. Nakagaki and Y. Iamamoto, manuscript in preparation.
- 9 J. G. Sharefkin and H. Saltzman, *Org. Synth.*, 43 (1963) 62.
- 10 R. F. Pasternack, H. Lee, D. Malek and S. C. S. Spencer, *Inorg. Nucl. Chem.*, 39 (1978) 1865.
- 11 R. F. Pasternack, L. R. Francesconi and E. Spiro, *Inorg. Chem.*, 12 (1973) 11.
- 12 G. Feher, in *Electron Paramagnetic Resonance with Applications to Selected Problems in Biology*, Gordon and Breach, New York, 1970, p. 31.
- 13 T. Mashiko, D. Dolphin, T. Nakano and T. G. Traylor, *J. Am. Chem. Soc.*, 107 (1985) 3735.
- 14 J. P. Mahy, P. Battioni, G. Bedi, D. Mansuy, J. Fischer, R. Weiss and I. Morgenstern-Badarau, *Inorg. Chem.*, 27 (1988) 353.
- 15 A. Gold, K. Jayaraz, P. Doppelt, R. Weiss, G. Chatalard, E. Bill, X. Ding and A. X. Trautwein, *J. Am. Chem. Soc.*, 110 (1988) 5756.
- 16 T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, 109 (1987) 6201.
- 17 P. O. Montellano and R. A. Stearns, *J. Am. Chem. Soc.*, 109 (1977) 3415.