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Biomimetic oxidation of indole-3-acetic acid and related substrates with hydrogen peroxide catalysed by 5,10,15,20-tetrakis 2′,6′-dichloro-3′-sulfonatophenyl) porphyrinatoiron(III) hydrate in aqueous solution and AOT reverse micelles

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Abstract

The reaction of indole-3-acetic acid (IAA) with hydrogen peroxide catalysed by 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrinatoiron(III)hydrate [$Cl_8TPPS_4Fe(III)(OH_2)_2$] gives indole-3-carbinol (IC) and indole-3-carboxaldehyde (IA) in aqueous buffer solution. The oxidation of IAA with H_2O_2 in the presence of $Cl_8TPPS_4Fe(III)(OH_2)_2$ in AOT reverse micelles gives higher yields of IA than in aqueous solution at the same pH. The yields of different oxidation products in AOT reverse micelles depend on the pH, the water to surfactant ratio (Wo) and concentration of $Cl_8TPPS_4Fe(III)(OH_2)_2$ in AOT reverse micelles. The oxidation of IC with H_2O_2 in the presence of $Cl_8TPPS_4Fe(III)(OH_2)_2$ gives IA, indole-3-carboxylic acid (ICA), 2-oxo-indole-3-carbinol and 3-methylene oxindole. The oxidation of indole-3-propionic acid and indole-3-butyric acid with H_2O_2 in the presence of $Cl_8TPPS_4Fe(III)(OH_2)_2$ in aqueous buffer solution as well as AOT reverse micelles do not give the oxidative decarboxylation products. The formation of IC may be explained by the hydrogen abstraction from IAA by high valent oxo-iron(IV) radical cations followed by decarboxylation and subsequent recombination of either free hydroxy radical or hydroxyiron(III)porphyrin. The same abstraction and recombination mechanism has been proposed for oxidation of IC to IA and IA to ICA.

Keywords: Indole-3-acetic acid; Sulfonatophenyl-substituted porphyrin; Porphyrins; Iron; AOT reverse micelles; Micelles; Oxidation; Decarboxylation

1. Introduction

Horseradish peroxidase (HRP) catalyses the conversion of hydrogen peroxide to water by two successive electron abstractions from the substrates [1,2]. The reaction of HRP with hydrogen peroxide forms a high valent oxo-iron(IV) radical cation (compound I) which is reduced to the high valent oxo-iron(IV) intermediate (compound II) by accepting electrons from substrate to form the substrate radical. Compound II of HRP is reduced, by accepting an electron from the substrate molecule, to the

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resting Fe(III) state of the enzyme. The coupling, disproportionation and other reactions of substrate radicals are responsible for the formation of final products [3,4]. The anionic water-soluble iron(III)porphyrins [5–8] react with hydrogen peroxide and form the transient oxo-iron(IV) porphyrin radical cations as well as oxo-iron(IV)porphyrins in aqueous solution similar to compound I and compound II of HRP. Thus the anionic water-soluble iron(III)-porphyrins with hydrogen peroxide and oxone mimick selected reactions of HRP [9–12] and ligninases [13–15], respectively, in different reaction conditions.

Sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) forms thermodynamically stable water droplets surrounded by surfactant monolayers in oil or iso-octane [16,17]. The reverse micelles are variable reaction media [18,19] and they act as functional modulators [20–22] and accelerate the reactivity of heme peroxidases and other enzymes [22,23].

The oxidation of plant growth hormone indole-3-acetic acid (IAA) by heme peroxidase (HRP) is implicated in the regulation of different physiological functions of the plants [24–27]. The oxidation of IAA with hydrogen peroxide catalysed by HRP gives indole-3-carbinol, indole-3-carboxaldehyde, 3-methylene oxindole and 2-oxo-indole-3-carbinol in aqueous solution at different pH [28]. We report here the oxidation of IAA with hydrogen peroxide catalysed by 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrinatoiron(III)hydrate [**1a**, $Cl_8TPPS_4Fe(III)\ (OH_2)_2$] to elucidate the molecular mechanism of heme peroxidase and related enzymes in AOT reverse micelles in different reaction conditions.

2. Experimental

2.1. Materials and methods

Sodium bis-(2-ethylhexyl)sulfosuccinate (Aerosol-OT) was purified by a published procedure [29] before use. Indole-3-acetic acid (**6**), indole-3-propionic acid, indole-3-butyric acid and indole-3-carboxylic acid (**11**) were obtained from Fluka. Indole-3-carbinol (**9**), indole-3-carboxaldehyde (**10**), 2-oxo-indole-3-carbinol (**12**) and 3-methylene oxindole (**13**) were prepared by following literature procedures [28,30–32]. The oxidation products of indole-3-acetic acid were identified and quantified by using Waters HPLC equipped with a photodiode array detector (Model 991) on a μ-Bondapak C_{18} column (3.9 × 300 mm) using methanol: water (50:50) as eluent at a flow rate of 0.5 ml/min monitored at 235 nm and comparison of both UV–Visible spectra and retention time with that of authentic samples.

2.2. Preparation of 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrinatoiron(III) hydrate 1a

5,10,15,20-Tetrakis(2′,6′-dichlorophenyl)porphyrin (Cl_8TPP) was prepared by condensation of 2,6-dichlorobenzaldehyde (Aldrich) with freshly distilled pyrrole (Aldrich) by a published procedure [33]. The 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl) porphyrin (Cl_8TPPS_4) was prepared by sulfonation of Cl_8TPP with oleum at 130°C by following the literature procedure [34]. Reversed phase TLC of water-soluble Cl_8TPPS_4 indicates the presence of three spots, i.e. R_f (KC_{18}, ethanol): 0.97, 0.90 (less abundant than the other two) and 0.81. This may be either due to the presence of different atropisomers or the presence of minor amount of 4-isomer [5,6].

UV–Visible: λ_{max} nm (ε_{max} mM in methanol): 425.5 (0.74), 521.5 (0.03), 555 (0.01), 600 (0.01) and 658 (0.01). ^1H NMR: $\delta_H(D_2O)$ 8.77 (8H, s, pyrrolic protons), 8.62 (4H, m, aromatic) and 8.00 (4H, m, aromatic).

The 5,10,15,20-Tetrakis(2′,6′-dichloro-3′-sulfonatophenyl) porphyrinatoiron(III)hydrate **1a** [$Cl_8TPPS_4Fe(III)(OH_2)_2$] was prepared by refluxing the water-soluble free base porphyrin with a 40-fold excess of ferrous chloride in

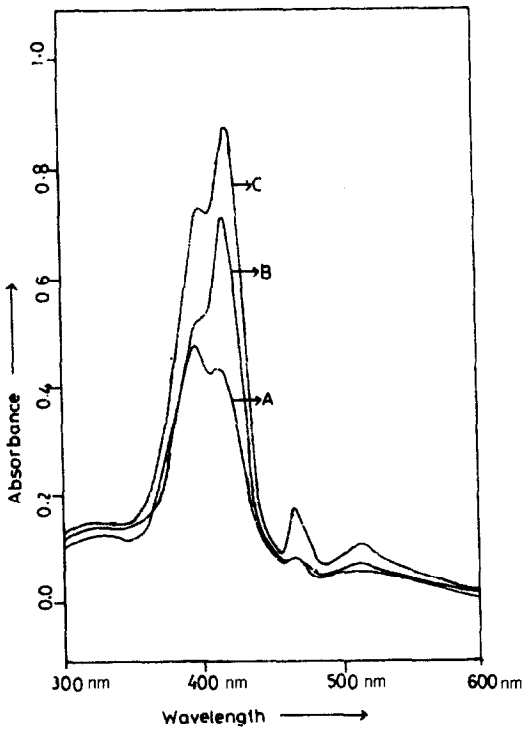


Fig. 1. UV visible spectra of **1** in phosphate buffer at different pH (A = 4.0, B = 7.0 and C = 9.3).

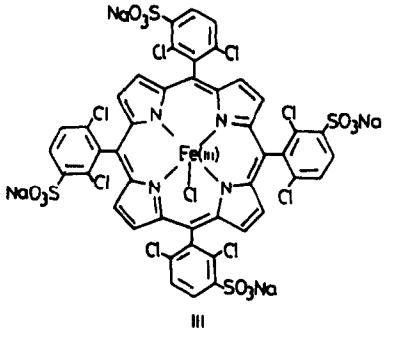
water (10 ml) following the literature procedure [5,6,12].

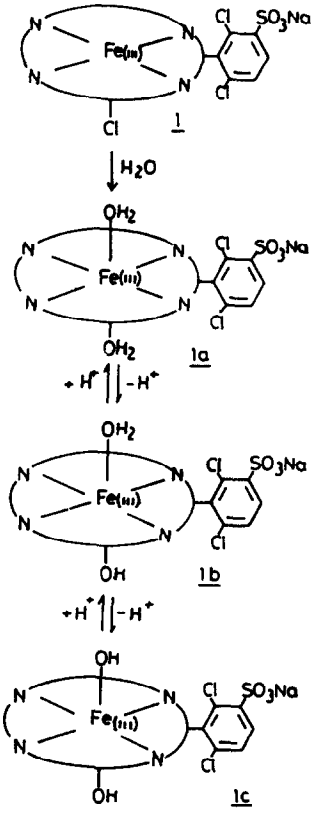
UV–Visible: λ_{max} nm (ε_{max} mM in water): 400 (0.34), 416.5 (0.72), 466 (0.08) and 512.5 (0.06).

The appearance of a split Soret band may be attributed to a difference in the electronic absorption spectra of different atropisomers or presence of **1a** versus **1b** [6] (Fig. 1, Scheme 1). Reversed phase TLC reveals two spots, R_f (KC_{18}, ethanol): 0.96, 0.89. Further HPLC analysis on a reversed phase column with methanol as eluent and monitored at 420 nm **1a** resolved two peaks having relative areas of 96% and 4%, respectively. This again indicates the presence of more than one atropisomer [5].

*2.3. UV–Visible spectroscopic study of **1a** in aqueous solution at different pH*

UV–Visible spectroscopy is an important and efficient technique for the observation of different species and in the study of environmental effects on metalloporphyrins. The aqueous solution of **1a** in acetate buffer (pH 4.0) shows the Soret peaks at 397 and 415 nm. The Soret of **1a** splits at 397 and 416.5 nm in phosphate buffer (pH 7.0), while it splits at 400 and 418 nm in phosphate buffer (pH 9.3) (Fig. 1). The presence of $Cl_8TPPS_4Fe(III)(OH_2)_2$ (**1a**) and $Cl_8TPPS_4Fe(III)(OH_2)(OH)$ (**1b**) species may





Scheme 1.

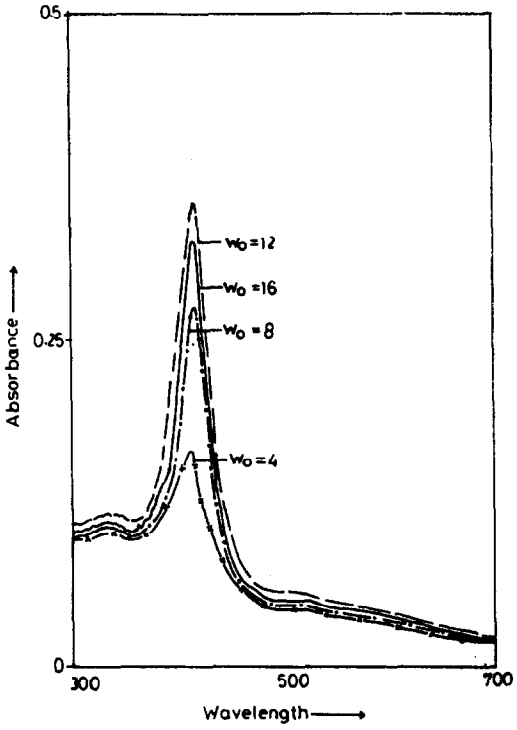


Fig. 2. Change in the UV visible spectrum of **1** at different water/AOT rations (Wo) in AOT reverse micelles.

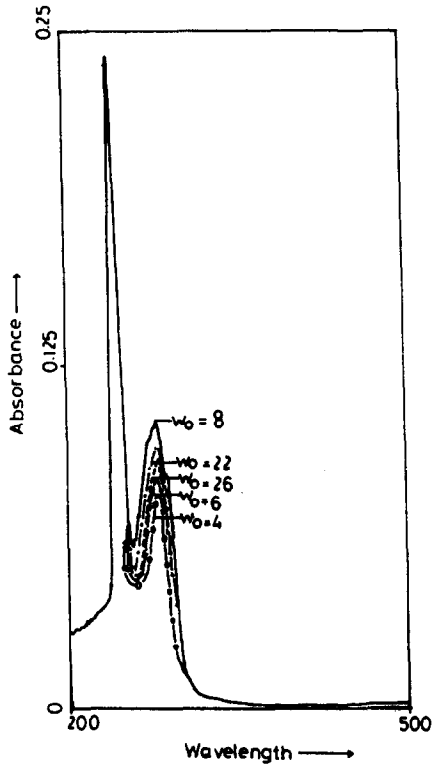


Fig. 3. Change in the UV spectrum of IAA (**6**) at different water/AOT ratios (Wo) in AOT reverse micelles.

Table 1
Oxidation of indole-3-acetic acid (**6**) with hydrogen peroxide catalysed by 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrinatoiron(III) chloride ($Cl_8TPPS_4Fe(III)Cl$, **1**) in water in iso-octane at different H_2O/AOT ratios (Wo)

Exp. no.	Reaction conditions [a]	Reaction time	Yield of products [b,c] (%)				
		(h)	**9**	**10**	**11**	**12**	**13**
1	acetate buffer (pH 4.0)	1.8	1.0	19.0			
2	H_2O/AOT (Wo = 10) (pH 4.0)	1.0		22.0			
3	H_2O/AOT (Wo = 12) (pH 4.0)	1.0		49.0			
4	H_2O/AOT (Wo = 14) (pH 4.0)	1.0		52.0 (45.0) [d]			
5	H_2O/AOT (Wo = 16) (pH 4.0)	1.0		21.0			
6	phosphate buffer (pH 7.0)	0.5	28.0	1.0			
7	H_2O/AOT (Wo = 14) (pH 7.0)	0.5	6.0	29.0			
8	H_2O/AOT (Wo = 14) (pH 8.0)	6.6		20.0	45.0		10.0
9	phosphate buffer (pH 9.3)	0.5	48.0				
10	H_2O/AOT (Wo = 14) (pH 9.3)	1.6	11.0	4.0	7.0		
11	H_2O/AOT (Wo = 14) (pH 9.3)	8.2	5.0	26.0	41.0	1.0	7.0

[a] All the reactions were performed at room temperature in acetate buffer (pH 4.0) and phosphate buffer (pH 7.0 and 9.3) and AOT reverse micelles; $Cl_8TPPS_4Fe(III)Cl$, **1**:H_2O_2:IOWA, **6** = 1:10:100.

[b] Products were characterised by TLC on silica gel (1-butanol:ethanol:25%ammonia = 8:2:2) by the use of Salkowski and DNP reagents, R_f: **11** 0.19, **6** 0.22, **9** 0.84, **10** 0.85 and **13** 0.86.

[c] HPLC retention time in min: **11** 3.0, **6** 3.9, **9** 8.7, **10** 10.7, **12** 12.8 and **13** 13.4.

[d] Isolated yield by preparative TLC.

be responsible for the appearance of peaks at 397–400 nm and 415–418 nm (Scheme 1). This kind of change in the UV–Visible spectra of **1a** in aqueous solutions at different pH has been reported [6,35].

2.4. The incorporation and UV–Visible spectroscopic study of *1a* in AOT reverse micelles

The anionic surfactant Aerosol-OT (4.4 g, 0.1 M) reverse micelle was prepared by a published procedure [36]. The incorporation of **1a** in Aerosol-OT (AOT) water in oil microemulsions was carried out by a published procedure [36,37]. A solution of **1a** (2 mg, 1.6 mM, 5.4 μl) in phosphate buffer (pH 7.0) was injected into 3 ml of 0.1 M AOT in iso-octane in a UV cell. The solution was shaken and UV–Visible spectra of transparent solution was recorded. Additional 5.4 μl of buffer was injected into the cell for each increment of the water to surfactant ratio (Wo). After each addition the solution was shaken thoroughly and the UV–Visible spectra of transparent solution was recorded between 300–700 nm (Fig. 2). The comparison of the UV–Visible spectra in phosphate buffer and methanol of **1a** indicates that **1a** resides in the interphase of AOT reverse micelles. The absorbance of the Soret peak of **1a** incorporated into reverse micelles increase with increment of water to surfactant ratio (Wo), reaches its maximum (Wo = 12) and then decreases at higher Wo.

2.5. Incorporation and UV spectroscopic study of IAA in AOT reverse micelles

The incorporation of IAA was achieved by injection of 5.4 μl solution of IAA prepared by dissolving 5 mg of IAA in 2 ml phosphate buffer (pH 7.0) into 3 ml of 0.1 M AOT in iso-octane and monitoring the UV spectra of the transparent solution between 200–400 nm. The incorporation of IAA at different water to surfactant (Wo) values was examined by UV spectroscopy (Fig. 3). Indole-3-acetic acid resides in the interphase of AOT reverse micelles, as inferred by the comparison of its UV spectra in reverse micelles with those in phosphate buffer (pH 7.0), methanol and chloroform. The maximum absorbance of IAA was obtained at water to surfactant ratio Wo = 8 of AOT reverse micelles.

2.6. Reaction of hydrogen peroxide with *1a* in aqueous solution and AOT reverse micelles

The detailed kinetics of the reaction of hydrogen peroxide with **1a** in aqueous solutions have been reported [32,33,38]. The reaction of hydrogen peroxide with iron(III) salts in AOT reverse micelles has also been studied [39,40] but kinetic reactions of hydrogen peroxide with **1a** in reverse micelles have not been reported yet [12].

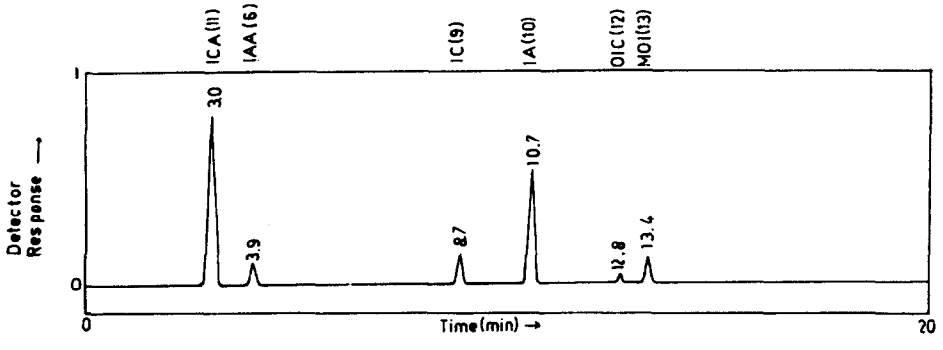


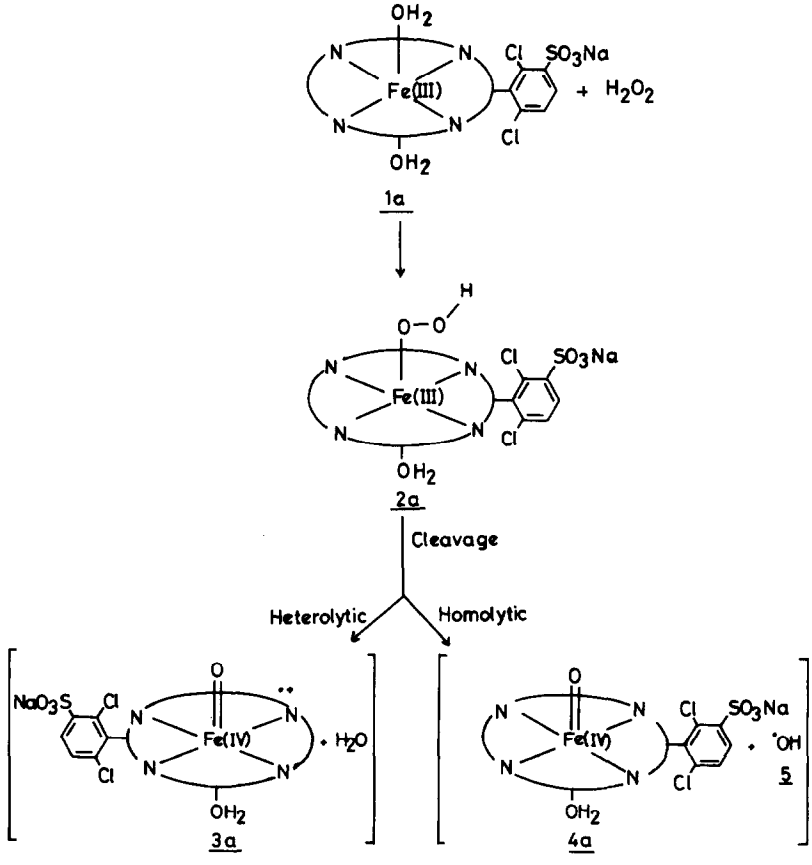
Fig. 4. HPLC profile for **1** + **6** + H_2O_2 in AOT reverse micelles (Wo = 14) at pH 9.3 phosphate buffer.

2.7. Oxidation of IAA with H_2O_2 catalysed by **1a** in AOT reverse micelles

The oxidation of IAA in AOT reverse micelles was studied by minor modifications of the known methods [12,34,40]. IAA (0.15 mole, 21.6 l) was added to a solution of AOT in iso-octane (3 ml, Wo = 14) containing 21.6 μl of $Cl_8TPPS_4Fe(III)(OH_2)_2$ (1.6 mmol). Hydrogen peroxide (30%, 0.1 mol, 5.4 μl) was added to above solution and shaken for 10 min at room temperature. The products were extracted with methanol (3 ml) at particular time intervals and then subjected to HPLC analysis (Fig. 4). The above procedure was followed for reactions at different water to surfactant ratio (Wo) and at different pH. The results are listed in Table 1.

3. Results and discussion

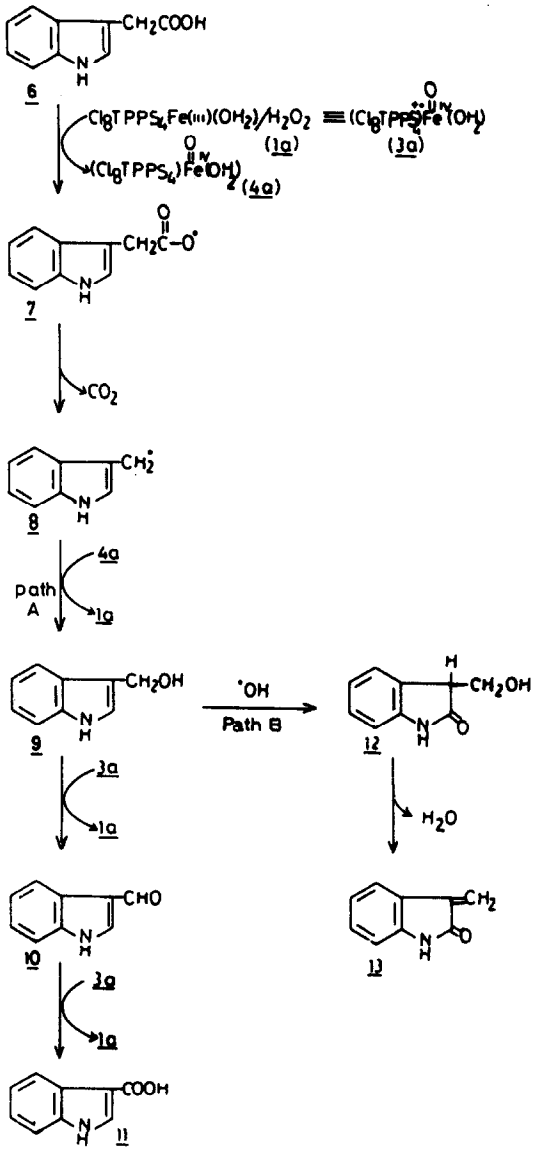
The reaction of $(Cl_8TPPS_4)Fe(III)Cl$ (**1**) with acidic aqueous buffer solution (pH 4.0) exchanges the axial chloride ligand and forms the $(Cl_8TPPS_4)Fe(III)(OH_2)_2$ (**1a**) whereas in neutral and basic buffer solutions it forms $(Cl_8TPPS_4)Fe(III)(OH_2)(OH)$ (**1b**) and $(Cl_8TPPS_4)Fe(III)(OH)_2$ (**1c**) respectively (Scheme 1). The reaction of hydrogen peroxide with $(Cl_8TPPS_4)Fe(III)(OH_2)_2$ (**1a**) at acidic pH forms $(Cl_8TPPS_4)Fe(III)(OH_2)(O_2H)$ (**2a**) which on heterolytic cleavage forms transient $(Cl_8TPPS_4)^{\cdot+}Fe^{IV}=O(OH_2)$ radical cations (**3a**) while the homolytic cleavage leads to the formation of $(Cl_8TPPS_4)Fe^{IV}=O(OH_2)$ (**4a**) as well as reactive free hydroxy radical (**5**) (Scheme



Scheme 2.

2). The formation of reactive species (**3a** and **4a**) has been proposed in the reaction of hydrogen peroxide and non μ-oxo dimer forming iron(III)porphyrin $(Cl_8TPPS_4)Fe(III)(OH_2)_2$ at acidic aqueous solution [32,33]. The reaction of indole-3-acetic acid (**6**) with hydrogen peroxide in presence of $(Cl_8TPPS_4)Fe(III)(OH_2)$ forms indole-3-carbinol (**9**) and indole-3-aldehyde (**10**) in 1% and 19% yields, respectively (Table 1, Scheme 2), in acetate buffer at pH 4.0. The percentage yield of indole-3-carbinol (**9**) increases while that of indole-3-aldehyde (**10**) decreases with increase in pH of aqueous buffer solution (Table 1). The formation of the products **9** and **10** from **6** may be explained by abstraction of hydrogen radicals by high valent oxo-iron(IV)porphyrins (**3a**) from **6** and the subsequent decarboxylation from **7** form indole-3-methyl radical (**8**). The recombination of **8** with chelated hydroxyl equivalent **4a** or free hydroxyl **5** gave indole-3-carbinol (**9**). This kind of oxidative decarboxylation of carboxylic acid with iodosylbenzene catalysed by 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinatoiron(III) chloride in organic solvent has been reported [41]. Further the reaction of high valent radical cation **3a** with carbinol **9** form the indole-3-carboxaldehyde (**10**) by abstraction and recombination mechanism. The same reaction sequence may form the corresponding indole-3-carboxylic acid (**11**) in very poor yield. This kind of abstraction and recombination mechanism has been proposed for the oxidation of primary alcohols to aldehydes and oxidation of aldehydes to corresponding acids with monooxygen donors catalysed by metalloporphyrins in organic [42,43] and aqueous solutions [44].

AOT reverse micelles form suitable and variable reaction media depending on water to surfactant ratio for the study of different types of organic and enzymatic reactions. Water-soluble and water-insoluble compounds are dissolved simultaneously in reverse micelles. The reaction of **6** with hydrogen peroxide catalysed by **1a** in AOT reverse micelles at pH 4.0 acetate buffer and water to surfactant ratio (Wo = 10) form **10** in 22% yield. The yield of **10** increases to 52% at pH 4.0 and water to surfactant ratio (Wo = 14) in AOT reverse micelles (Table 1). The percentage yield of **10** decreases at Wo = 14 with the increase in pH of aqueous buffer solution in AOT reverse micelles. The yield of **9** decreases slowly while the yield of **10** increases at pH 9.3 phosphate buffer in AOT reverse micelles (Wo = 14) with time indicating that the formation of



Scheme 3.

10 may be taking place from **9**. The aqueous core of AOT reverse micelles (Wo = 14) has suitable diameter for the incorporation of indole-3-acetic acid and $Cl_8TPPS_4Fe(III)(OH_2)_2$ such that they have maximum interaction and give high yield of different oxidation products. The reaction of reactive hydroxy radical (**5**) with indole-3-carbinol (**9**) may be responsible for the formation of 2-oxo-indole-3-carbinol (**12**) (Path B, Scheme 3) which on the elimination of water gives the 3-methylene oxindole (**13**). These products are not formed initially but they are formed later on with the reactive oxygen species including $HO_2^{\cdot}$, $O_2^{-\cdot}$ and $^{\cdot}OH$ radical during the reaction of hydrogen peroxide and oxo-iron(IV) species [45].

Similar reaction products have been observed at higher pH and different water to surfactant ratios (Wo) in different reaction conditions. The yield of **10** first increases and then decreases with time (Table 1). These products are reported to be formed by the reaction of indole-3-acetic acid with hydrogen peroxide in the presence of horseradish peroxidase (HRP) at different pH and reaction conditions. The oxidative decarboxylation and subsequent oxidative products of indole-3-acetic acid with hydrogen peroxide catalysed by HRP have been mimicked by hydrogen peroxide and $(Cl_8TPPS_4)Fe(III)(OH_2)_2$ in AOT reverse micelles. The AOT reverse micelles are more efficient reaction media than aqueous phosphate buffer in above oxidative decarboxylation and subsequent formation of oxidative products of indole-3-acetic acid. The higher yield of aldehyde **10** may be explained by preference of path A over path B in AOT reverse micelles (Table 1).

The reaction of indole-3-propionic acid and indole-3-butyric acid with hydrogen peroxide catalysed by **1a** either in aqueous phosphate buffer or AOT reverse micelles does not result in oxidative decarboxylation and subsequent oxidation products. Thus the substitution of an indole group at the α-position to carboxylic acid favours the oxidative decarboxylation and subsequent oxidation products in aqueous homogeneous medium as well as AOT reverse micelles at different pH and water to surfactant ratio (Wo). The oxidation of indole-3-acetic acid with hydrogen peroxide in cationic reverse micelles gives unusual products, the characterisation of these products is in progress and the results will be published in the near future.

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