

## Research Article

# Kinetics and Mechanism of *meso*-Tetraphenylporphyrin Iron(III) Chloride Catalysed Oxidation of Indole-3-Acetic Acid by Peroxomonosulphate

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Mechanistic study on *meso*-tetraphenylporphyrin iron(III) chloride (TPP) catalysed oxidation of indole-3-acetic acid by peroxomonosulphate (oxone) in aqueous acetonitrile medium has been carried out. The reaction follows a first order with respect to both substrate and oxidant. The order with respect to catalyst was found to be fractional. The order of reaction with respect to catalyst varies with a concentration of catalyst. Increase in percentage of acetonitrile decreased the rate. The reaction fails to initiate polymerization, and a radical mechanism is ruled out. Activation and thermodynamic parameters have been computed. A suitable kinetic scheme based on these observations is proposed. Significant catalytic activity is observed for the reaction system in the presence of TPP.

## 1. Introduction

Oxidation of indole-3-acetic acid (IAA) has received much attention because of the involvement of the indole derivatives in significant biological processes. They have anti-inflammatory [1, 2], tumor growth inhibitor [1, 2], antiviral, antitubercular, antibacterial, antiallergic, and psychotropic activities [3]. Oxidation of indole-3-acetic acid by dioxygen [4], Ce(IV) [4], 1,4-phenanthroline-manganese(II) complexes [5], hydrogen peroxide, persulphate, N-chlorosuccinimide, and sodium hypochlorite was reported [6]. Chlorophyll-sensitized photooxidation [7], peanut peroxidase [8], horseradish and tobacco peroxidase [9–11] catalysed oxidation of IAA have been studied.

The catalytic properties of the transition metal porphyrins are due to the fact that an oxotransition metal porphyrin intermediate is formed, which can transfer the oxygen atom to a substrate or can accept an electron from the substrate [12]. In the field of oxidation catalysed by transition metal porphyrins, the oxygen transfer step is the crucial step, and from an experimental point of view a lot of attention has been devoted to the nature of the oxotransition metal

bond [13]. Groves and coworkers [14] described the use of *meso*-tetraphenylporphyrin iron(III) chloride (TPP) in combination with the lipophilic iodosylbenzene, first used *in vivo* by Ullrich and Staudinger [15], for the epoxidation of olefins, and the hydroxylation of alkanes.

Although the oxidation of certain substituted indoles such as 2,3-dialkyl indoles by peroxodisulphate, peroxomonosulphate, peroxomonophosphoric, and peroxodiphosphoric acids has been already reported in the literature [16–18], the lack of kinetic and mechanistic investigation on TPP catalysed oxidation of IAA by peroxomonosulphate (oxone) instigated us to carry out this work.

## 2. Experimental

**2.1. Materials.** Indole-3-acetic acid, oxone, and TPP (Sigma Aldrich) were used as such. All the other chemicals and solvents used were of analytical grade (Merck, India). All the solutions used in the study were made by using doubly distilled water. All the reagents were prepared freshly and

used in the reaction. All the reactions were carried out in a thermostat and the temperature was controlled to  $\pm 0.1^\circ\text{C}$ .

**2.2. Kinetic Measurements.** The kinetic studies were carried out in aqueous acetonitrile medium under pseudo-first-order conditions. The reactions were performed by maintaining a large excess of [IAA] over [oxone] in the temperature range of 293–333 K. The reaction mixture was homogeneous throughout the course of the reaction. The reaction's progress was monitored for at least two half-lives by iodometric estimation of unchanged oxidant at regular time intervals. The rate constants ( $k_{\text{obs}}$ ) were evaluated from the slopes of linear plots of  $\log[\text{titre}]$  versus time.

**2.3. Stoichiometry.** Solutions of IAA containing an excess of oxone were kept overnight at room temperature. By titrimetric estimation of the concentration of oxone consumed and assuming that all the IAA taken had reacted, the stoichiometry of IAA : oxone was found to be 1 : 2.

**2.4. Product Analysis.** A reaction mixture containing slight excess of oxone, IAA, TPP, and acetonitrile-water mixture was kept aside at room temperature for a day, so that the substrate was completely converted into product. The mixture was extracted with ether. A resinous mass was obtained in the ether layer which is treated with acetone and then with methanol. The final product was obtained from the alcoholic solution and identified by UV-Visible absorption spectra ( $\lambda_{\text{max}}$ ) at 437 nm (Figure 6). The above product was also reported in the oxidation IAA by peroxomonosulphate [19].

**2.5. Data Analysis.** Correlation studies were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient,  $r$ , in the case of simple linear regression and  $R$  in the case of multiple linear regressions.

### 3. Results and Discussion

Factors influencing the rate of TPP catalysed oxidation of IAA by oxone such as [IAA], [oxone], [TPP],  $[\text{H}^+]$  and dielectric constant have been studied. Rate and activation parameters were evaluated.

**3.1. Effect of [IAA].** A constants [oxone], [TPP],  $[\text{H}^+]$  and fixed percentage of acetonitrile, kinetic runs were carried out with various initial concentrations of indole-3-acetic acid, which yielded rate constants whose values depended on [IAA]. The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) thus obtained were found to increase with [IAA] over a range of [IAA] used  $0.6\text{--}1.4 \times 10^{-2} \text{ mol dm}^{-3}$  (Table 1).

The plot (Figure 1) of  $\log k_{\text{obs}}$  versus  $\log[\text{IAA}]$  is linear with a slope of 0.91 showing that the reaction is first order in [IAA]. The plot (Figure 2) of  $1/[\text{IAA}]$  versus  $1/k_{\text{obs}}$  is linear with negligible intercept on the rate ordinate, giving the proof that the mechanism for the oxidation process is not of Michaelis-Menten type.

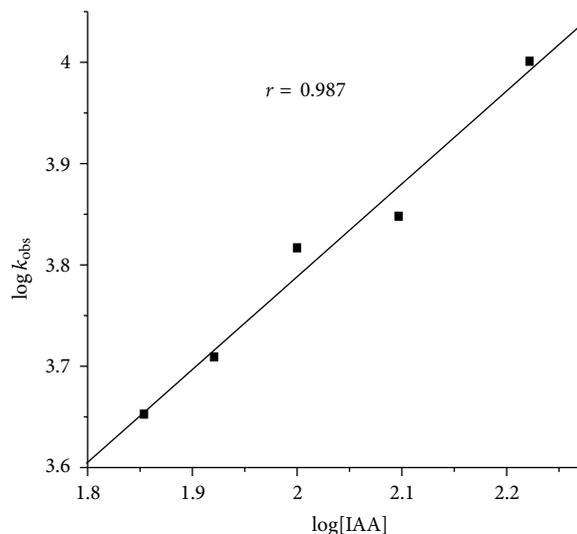


FIGURE 1: Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{IAA}]$  for TPP catalysed oxidation of IAA by peroxomonosulphate in acetonitrile medium.

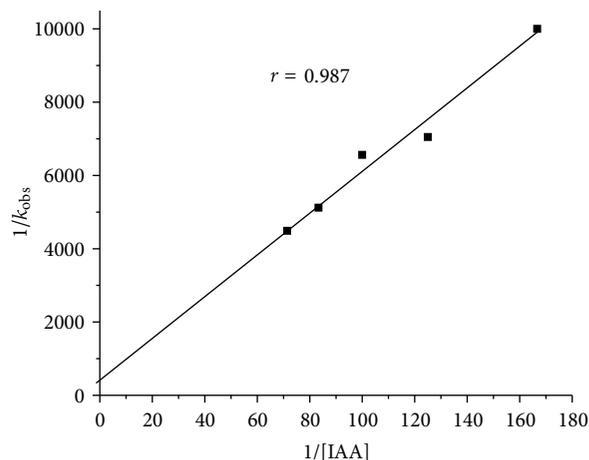


FIGURE 2: Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{IAA}]$  for TPP catalysed oxidation of IAA by peroxomonosulphate in acetonitrile medium.

**3.2. Effect of [Oxone].** The kinetics of TPP catalysed oxidation of indole-3-acetic acid has been studied at various initial concentrations of the oxidant, [oxone] ( $3 \times 10^{-4}$  to  $7 \times 10^{-4} \text{ mol dm}^{-3}$ ) and at fixed concentrations of other reactants. The plot of  $\log[\text{oxone}]$  versus time yields a straight line. The pseudo-first-order rate constants,  $k_{\text{obs}}$ , are calculated at various initial concentrations of the oxidant and are constant indicating a first order dependence of rate on oxone (Table 1).

**3.3. Effect of [TPP].** A constants [IAA], [oxone],  $[\text{H}^+]$ , and fixed percentage of acetonitrile, kinetic runs were carried out with various initial concentrations of [TPP], which yielded rate constants whose values depended on [TPP]. The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) thus obtained were found to increase with [TPP] (Table 2) over a range of [TPP] used ( $2.0\text{--}40.0 \times 10^{-8} \text{ mol dm}^{-3}$ ). A linear plot was obtained between  $\log k_{\text{obs}}$  and  $\log[\text{TPP}]$  (Figure 3(a)) with a slope of

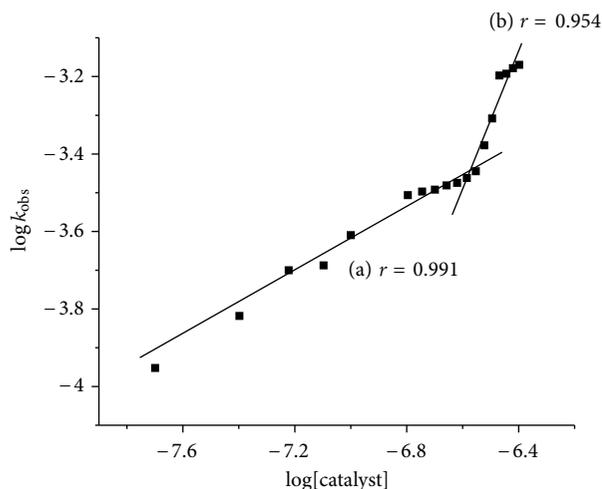


FIGURE 3: Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{catalyst}]$  showing the effect of catalyst concentration (a)  $2\text{--}20 \times 10^{-8} \text{ mol dm}^{-3}$ ; (b)  $22\text{--}40 \times 10^{-8} \text{ mol dm}^{-3}$  on reaction rate.

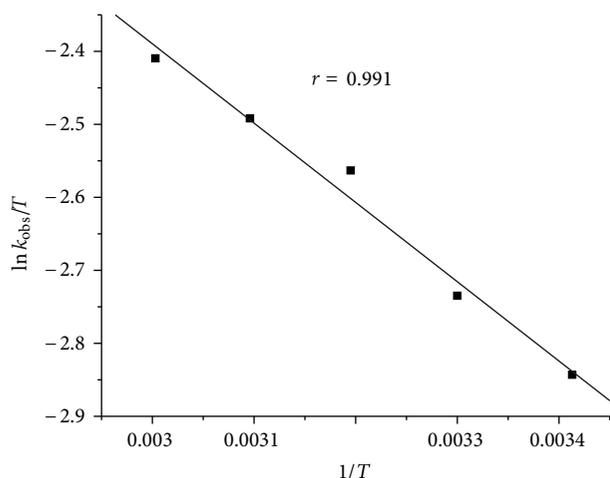


FIGURE 4: Plot of  $\ln k_{\text{obs}}/T$  versus  $1/T$  showing the effect of temperature on reaction rate.

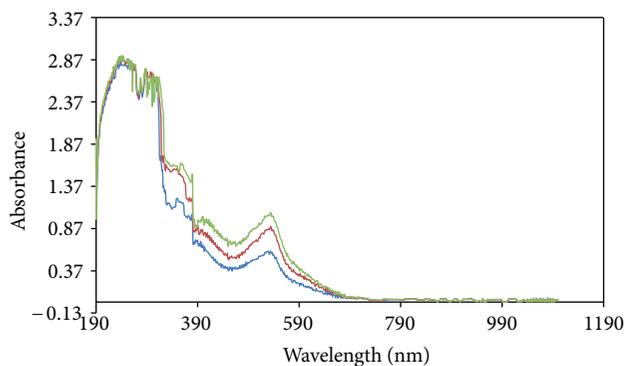


FIGURE 5: UV spectrum showing formation of intermediate complex at 534 nm between IAA and  $\text{PorFe}^{\text{V}}=\text{O}$ .

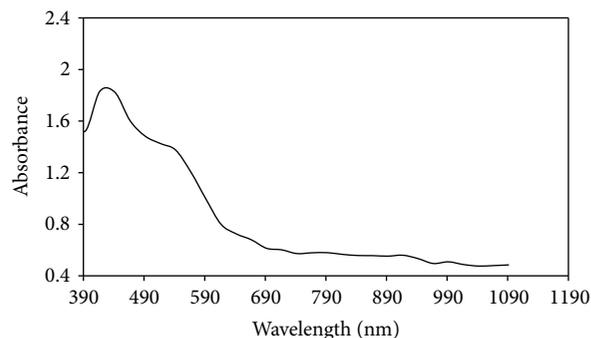


FIGURE 6: UV spectrum showing the formation of product at 437 nm in low catalyst concentration after the decomposition of intermediate complex at 534 nm.

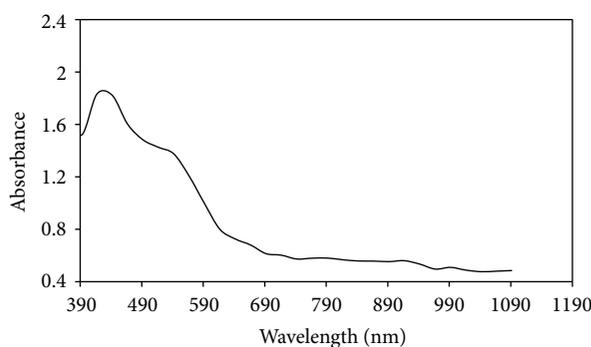


FIGURE 7: UV spectrum showing the formation of product at 432 nm in high catalyst concentration after the decomposition of intermediate complex at 534 nm.

0.48, indicating that the order of the reaction with respect to catalyst (a)  $[2\text{--}20 \times 10^{-8} \text{ mol dm}^{-3}]$  was fractional. Another linear plot was obtained between  $\log k_{\text{obs}}$  and  $\log [\text{TPP}]$  (Figure 3(b)) with a slope of 1.47, indicating that the order of the reaction with respect to catalyst (b)  $[22\text{--}40 \times 10^{-8} \text{ mol dm}^{-3}]$  was also fractional. The order of reaction with respect to catalyst varies with a concentration of catalyst. It clearly reveals that the reaction follows different mechanism at low (Scheme 1) and high concentrations of catalyst (Scheme 2). It is also noticed that higher concentration of catalyst exhibits an activation towards the reaction progress reaching a maximum value of  $k_{\text{obs}}$  6.76 at catalyst concentration of  $40 \times 10^{-8} \text{ mol dm}^{-3}$ . Also the catalytic activity of catalyst substantially exceeds in higher concentration due to more active centres which interact mutually with one another leading to the formation of bimetallic and multimetallic active centers which has more catalytic activity than monometallic ones of catalyst in lower concentration [20].

**3.4. Effect of  $[\text{H}^+]$ .** The reaction rates measured with various  $[\text{H}^+]$  ( $8.0\text{--}40.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) were found to be the same (Table 3). Such kinetic behavior indicates the nonexistence of any protonation equilibrium with respect to both oxone and IAA in the experiment.

TABLE 1: Pseudo-first-order rate constants for the TPP catalysed oxidation of IAA by peroxomonosulphate.

[IAA] $\times 10^2$ (mol dm <sup>-3</sup> )	[oxone] $\times 10^4$ (mol dm <sup>-3</sup> )	[TPP] $\times 10^8$ (mol dm <sup>-3</sup> )	CH <sub>3</sub> CN% (V/V)	$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )
0.6	5.0	4.0	50	0.99
0.8	5.0	4.0	50	1.42
1.0	5.0	4.0	50	1.52
1.2	5.0	4.0	50	1.95
1.4	5.0	4.0	50	2.22
1.0	3.0	4.0	50	1.97
1.0	4.0	4.0	50	1.53
1.0	6.0	4.0	50	1.46
1.0	7.0	4.0	50	1.44

TABLE 2: Effect of catalyst concentration on the reaction rate at 303 K.

[IAA] $\times 10^2$ (mol dm <sup>-3</sup> )	[oxone] $\times 10^4$ (mol dm <sup>-3</sup> )	[TPP] $\times 10^8$ (mol dm <sup>-3</sup> )	CH <sub>3</sub> CN% (V/V)	$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )
1.0	5.0	2.0	50	1.12
1.0	5.0	4.0	50	1.52
1.0	5.0	6.0	50	1.99
1.0	5.0	8.0	50	2.05
1.0	5.0	10.0	50	2.46
1.0	5.0	12.0	50	2.69
1.0	5.0	14.0	50	2.88
1.0	5.0	16.0	50	3.12
1.0	5.0	18.0	50	3.18
1.0	5.0	20.0	50	3.22
1.0	5.0	22.0	50	3.30
1.0	5.0	24.0	50	3.35
1.0	5.0	26.0	50	3.45
1.0	5.0	28.0	50	3.59
1.0	5.0	30.0	50	4.19
1.0	5.0	32.0	50	4.92
1.0	5.0	34.0	50	6.35
1.0	5.0	36.0	50	6.41
1.0	5.0	38.0	50	6.63
1.0	5.0	40.0	50	6.76

[oxone] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [IAA] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>] =  $40.0 \times 10^{-2}$  mol dm<sup>-3</sup>, acetonitrile : water = 50 : 50.

TABLE 3: Effect of [H<sup>+</sup>] concentration on the reaction rate at 303 K.

[H <sup>+</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )
8.0	1.22
16.0	1.24
24.0	1.18
32.0	1.29
40.0	1.52

[oxone] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [IAA] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [TPP] =  $4.0 \times 10^{-8}$  mol dm<sup>-3</sup>, acetonitrile : water = 50 : 50, temperature = 303 K.

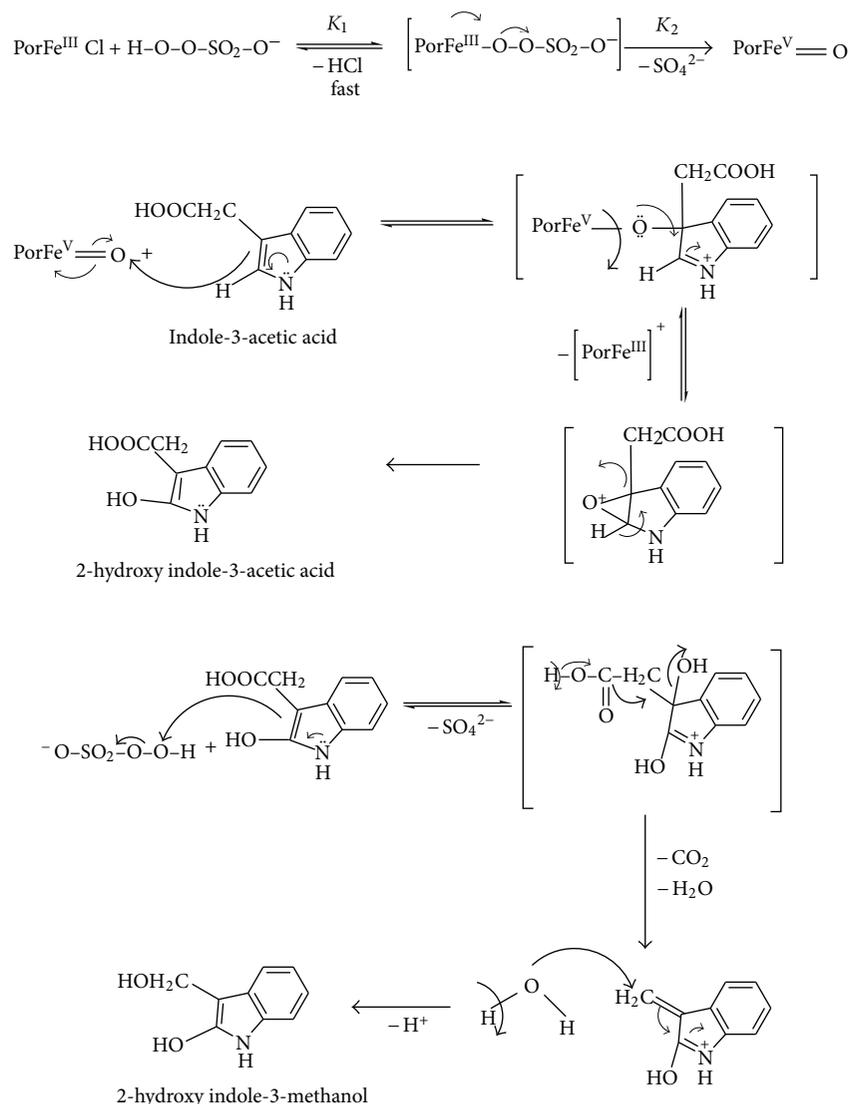
TABLE 4: Effect of dielectric constant on the reaction rate at 303 K.

CH <sub>3</sub> CN:H <sub>2</sub> O	$D^a$	$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )
70:30	49.71	0.68
60:40	53.83	0.96
50:50	57.95	1.52
40:60	62.06	2.89
30:70	66.18	5.47

[oxone] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [IAA] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [TPP] =  $4.0 \times 10^{-8}$  mol dm<sup>-3</sup>;  $D^a$ : values are calculated from the values of pure solvent.

**3.5. Effect of Dielectric Constant.** In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of IAA by peroxomonosulphate was studied in aqueous acetonitrile mixtures of various compositions (Table 4). The data clearly reveal that the rate increases with decrease in the percentage of acetonitrile, that is, with

increasing dielectric constant or polarity of the medium and leads to the influence that there is a charge development in the transition state involving a more polar activated complex than the reactants [21–24], a neutral molecule [IAA], and a mononegative ion (HSO<sub>5</sub><sup>-</sup>) suggesting a polar (ionic) mechanism.



SCHEME 1: Probable mechanism for the low concentration of *meso*-tetraphenylporphyrin iron(III) chloride catalysed oxidation of indole by peroxomonosulphate.

TABLE 5: Effect of temperature on the reaction rate.

Temp (K)	293	303	313	323	333
$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$	0.83	1.52	3.91	5.89	9.40

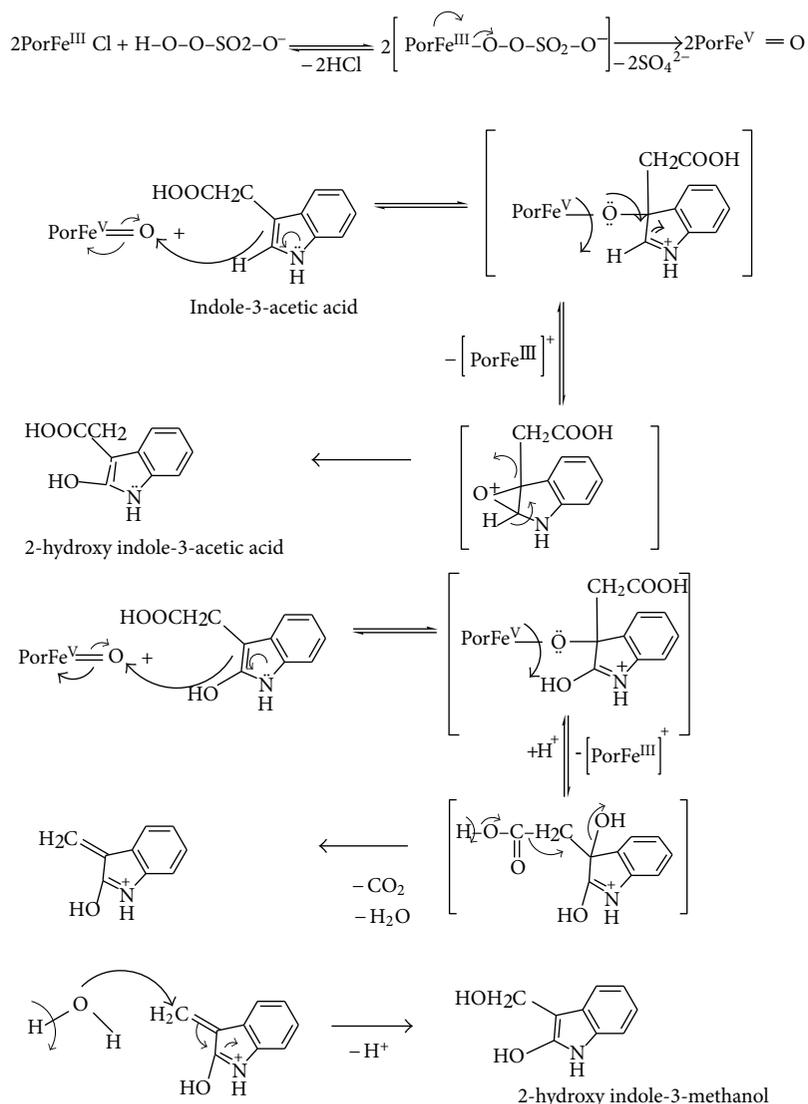
[oxone] =  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ; [IAA] =  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; [TPP] =  $4.0 \times 10^{-8} \text{ mol dm}^{-3}$ , acetonitrile : water = 50 : 50.

3.6. *Test for Free Radical Intermediates.* No polymer formation was observed when a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

3.7. *Rate and Activation Parameters.* The effect of temperature was studied in the range of 293 K–333 K and the results were shown in (Table 5). The Arrhenius plot of  $\ln k_{\text{obs}}/T$  versus  $1/T$  (Figure 4) was found to be linear. The value of energy of activation ( $E_a$ ) was found to be  $11.56 \text{ kJ mol}^{-1} \text{ K}^{-1}$

and  $\Delta H^\ddagger = 9.04 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -204.88 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^\ddagger = 71.11 \text{ kJ mol}^{-1}$ . The large negative value of entropy of activation ( $\Delta S^\ddagger$ ) obtained is attributed to the severe restriction of solvent molecules around the transition state.

3.8. *Mechanism.* Peroxomonosulphate exists [25] as  $\text{HSO}_5^-$  in solution. Although many peroxy anions are effective nucleophiles.  $\text{HSO}_5^-$  is very weak nucleophiles [26, 27]. In spite of the fact that free radicals can arise from the facile homolysis of the oxygen-oxygen bond [28], an ionic mechanism is favoured in certain reactions involving oxidations by peroxides. In the present investigation no observed polymerization in the presence of acrylonitrile rules out a free radical process. Generally, the enhancement of the electrophilic activity of peroxide will minimize the importance of undesirable free radical pathways, resulting in a mixture of products [29].



SCHEME 2: Probable mechanism for the high concentration of *meso*-tetraphenylporphyrin iron(III) chloride catalysed oxidation of indole by peroxomonosulphate.

The first step is the formation of a complex between oxone and TPP. This complex immediately decomposed and showed that  $\text{Por-Fe}^{\text{V}}=\text{O}$  is in agreement with the literature study [30]. This  $\text{Por-Fe}^{\text{V}}=\text{O}$  may further react with the IAA to form a complex (Figure 5) at 534 nm, which would give the product in the next step (Figure 6). This type of product was already reported [19]. The oxygen transfer step is associated with large negative value of entropies of activation and significant enthalpies of activation. The catalytic activity of TPP is significant, and this conversion exhibits fractional order. The order of the reaction varies with the concentration of catalyst [20]. It has value 0.48 for the catalyst concentration of  $2-20 \times 10^{-8} \text{ mol dm}^{-3}$  and has value 1.47 for the catalyst concentration of  $22-40 \times 10^{-8} \text{ mol dm}^{-3}$  (Table 2). It clearly reveals that the reaction follows different mechanism at low (Scheme 1) and high concentrations of catalyst (Scheme 2). Though the reaction mechanism is different in low and

high catalyst concentrations, the final product obtained is similar in low and high catalyst concentrations. This was confirmed by UV-Vis spectra shown in (Figures 6 and 7). In accordance with the above observations and stoichiometry of the reaction, the following reactions are involved to constitute the most probable mechanism of the reaction at low and high concentrations of catalyst (Schemes 1 and 2).

#### 4. Conclusion

In conclusion, *meso*-tetraphenylporphyrin iron(III) chloride has been proven to be an excellent catalyst for the oxidation of IAA by oxone. The kinetic and thermodynamic parameters for the TPP catalysed oxidation of IAA by oxone were determined, and the reaction scheme was proposed. The thermodynamic data obtained supported the proposed mechanism.

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