

# Kinetics and mechanism of *meso*-tetraphenylporphyriniron(III) chloride (TPP) catalysed oxidation of indole by sodium perborate

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Developing catalyst is very significant for biologically important reactions which yield products, used as drugs. Mechanistic study on *meso*-tetraphenylporphyriniron(III) chloride (TPP) catalysed oxidation of indole by sodium perborate in aqueous acetic acid medium have been carried out. The reaction follows a fractional order with respect to substrate and catalyst. The order with respect to oxidant was found to be one. Increase in the percentage of acetic acid and increase in the concentration of  $[H^+]$  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 has been proposed. Significant catalytic activity is observed for the reaction system in the presence of TPP.

**Keywords:** indole, sodium perborate, *meso*-tetraphenylporphyriniron(III) chloride, oxidation.

## INTRODUCTION

Indole, an electron-rich heteroaromatic nitrogenous compound, is found in many naturally occurring compounds such as various plant alkaloids and fungal metabolites<sup>1,2</sup> usually as metabolites of tryptophan. Indole is biologically active<sup>3-5</sup>. The catalyst plays a major role to speed up the above mentioned biologically important reaction. Lawson and Witkop have shown that N-bromosuccinimide can be used to convert indoles to oxindoles<sup>6,7</sup>. Rangappa et al<sup>8</sup> have examined the kinetics of oxidation of indole by chloramines-T in the presence of Os(VIII) in alkaline medium. Peroxomonosulphate can also be used to convert indoles to oxindoles<sup>9</sup>.

Sodium perborate, a peroxy salt of anionic formula:  $B_2(O_2)_2(OH)_4^{2-}$ , is a cheap, non-toxic, stable, easily handled, large scale industrial chemical, mostly used in detergents as a bleaching agent. Perborate in aqueous solution yields hydrogen peroxide and the kinetic studies in aqueous and partly aqueous acidic media confirm perborate oxidation as hydrogen peroxide oxidation<sup>10-13</sup>.

Oxidation of organic compounds catalysed by synthetic metalloporphyrin complexes has been one of the hot areas in chemistry during the last two decades<sup>14</sup>. The metalloporphyrins can catalyse the oxidation of a variety of organic substrates with many different terminal oxidants<sup>14,15</sup>. The catalytic properties of the transition metal porphyrins are due to the fact that an oxo-transition metal porphyrin intermediate is formed, which can transfer the oxygen atom to a substrate or can accept an electron from the substrate<sup>14</sup>. Many stable oxo-transition metal complexes are known and have been characterized, but several of these complexes are inert and non-reactive as oxygen transfer reagents. Groves and coworkers<sup>16</sup> described the use of *meso*-tetraphenylporphyriniron(III) chloride (TPP) in combination with the lipophilic iodosylbenzene, first used in vivo by Ullrich, for the epoxidation of olefins, and the hydroxylation of alkanes.

Literature survey reveals that no report was available on the kinetics of oxidation of *meso*-tetraphenylporphyriniron(III) chloride catalysed oxidation of indole. Oxindole is an oxidation product of indole with potential of biological activity<sup>3</sup>. So developing a catalyst for this oxidation of indole is very significant. In this aspect we

have taken *meso*-tetraphenylporphyriniron(III) chloride catalyst for the oxidation of indole by sodium perborate which promotes the reaction rate and gave the product which is used in medicinal field.

## EXPERIMENTAL

### Material

All the chemicals and solvents used were of analytical grade (Merck, India). Indole, sodium perborate and TPP (Sigma Aldrich) were used as such. The concentration of  $[indole] = 0.1$  m,  $[sodium\ perborate] = 0.01$  m,  $[TPP] = 10^{-8}$  m were maintained in this study. 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  $\pm 0.1^\circ C$ . Aqueous solution of sodium perborate was prepared fresh using double distilled water and standardized iodometrically. The analysis of the product was performed using Elico UV-VIS spectrophotometer-159.

### Kinetic measurements

The kinetic studies were carried out in 30% (v/v) aqueous acetic acid medium under pseudofirst-order conditions with a large excess of  $[indole]$  over sodium perborate (10 : 1). The reaction mixture was homogeneous throughout the course of the reaction. The reaction was followed by estimating the unreacted sodium perborate as a function of time by using the iodometric method. The liberated iodine was titrated against standard sodium thio sulphate solution by using starch as indicator. The pseudo first order rate constants ( $k_{obs}$ ) were evaluated from the slopes of linear plots of  $\log[sodium\ perborate]$  versus time. Replicate runs showed that the rate constants of oxidation reactions were reproducible within  $\pm 3\%$ .

### Stoichiometry

Solutions of indole containing an excess of sodium perborate were kept overnight at room temperature. Titrimetric estimation of the concentration of sodium perborate consumed and assuming that all the indole

taken had reacted, the stoichiometry of indole : sodium perborate was found to be 1 : 1.

### Product analysis

A reaction mixture containing excess of sodium perborate (0.2 m), indole (0.1 m), TPP ( $10^{-8}$  m), and acetic acid-water mixture was kept aside at room temperature for a day, so that the substrate was completely converted into a product. The reaction mixture was extracted with chloroform, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then evaporated. The residual brown solid obtained was subjected to column chromatography using silica gel and eluted with benzene and then evaporated. The melting point of the compound was found to be 116–118°C, which confirmed oxindole (literature value is 118–120°C) as the main product of the reaction. The product was also confirmed by UV-Visible absorption spectra at  $\lambda_{\text{max}}$  of 407 nm (Fig. 6) which is in agreement with literature values<sup>9</sup>.

### Data analysis

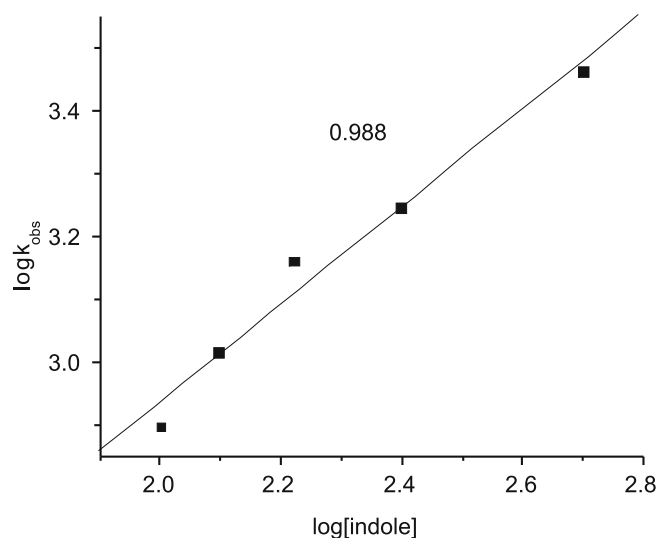
Correlation studies were carried out using Microcal origin (version 6) computer software. The appropriateness of the fit was discussed using the correlation coefficient,  $r$ , in the case of simple linear regression and  $R$  in the case of multiple linear regressions.

## RESULTS AND DISCUSSION

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

### Effect of [indole]

At a constant sodium perborate, [TPP],  $[\text{H}^+]$ , and fixed percentage of acetic acid, kinetic runs were carried out with various initial concentrations of indole, which yielded rate constants whose values depended on [indole]. The pseudo-first order rate constants ( $k_{\text{obs}}$ ) thus obtained were found to increase with [indole] (Table 1) over a range of [indole] used ( $2.0 - 10.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ). The plot (Fig. 1) of  $\log k_{\text{obs}}$  versus  $\log[\text{indole}]$  is linear with a slope of 0.77 showing that the reaction is fractional order in [indole]. The plot (Fig. 2) of  $1/k_{\text{obs}}$  versus  $1/[\text{indole}]$  is linear with definite intercept on the rate ordinate, which indicates the operation of Michalis-Menton mechanism,



**Figure 1.** Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{Indole}]$  for TPP catalysed oxidation of indole by sodium perborate in acetic acid medium

where  $K_3$  is the equilibrium constant for the formation of Michalis-Menton complex, and  $k_4$  the rate constant for the decomposition of Michalis-Menton complex. Usually the first step is a fast pre-equilibrium and the electron transfer step is rate determining<sup>17</sup>.

### Effect of sodium perborate

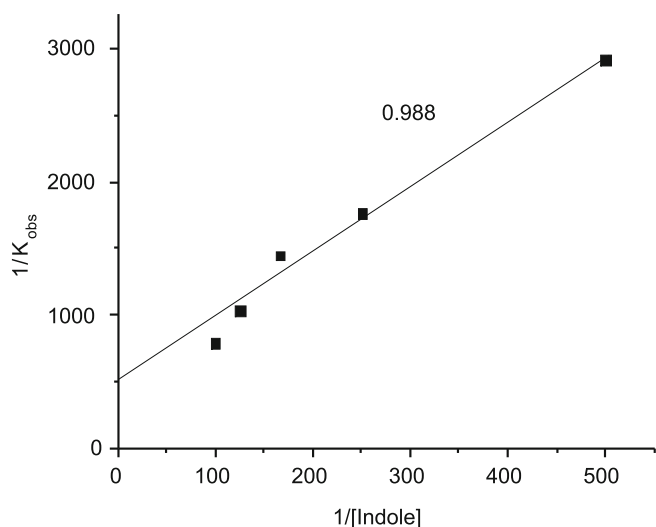
The kinetics of TPP catalysed oxidation of indole has been studied at various initial concentrations of the oxidant, [sodium perborate] ( $4.0 - 12.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) and at fixed concentrations of other reactants. The plot of  $\log$  [sodium perborate] versus time yields a straight line. The pseudo-first-order rate constants,  $k_{\text{obs}}$  are calculated at various initial concentrations of the oxidant, are constant indicating a first order dependence of rate on sodium perborate (Table 1).

### Effect of [TPP]

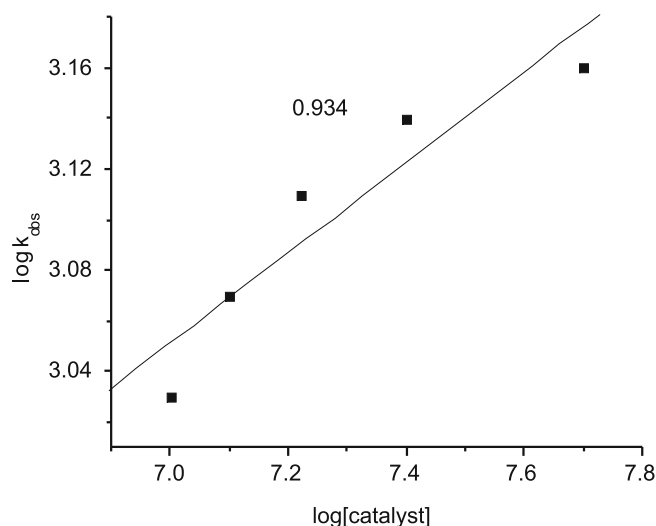
At a constant [indole], [sodium perborate],  $[\text{H}^+]$  and fixed percentage of acetic acid, kinetic runs were carried out with various initial concentrations of [TPP], which yielded rate constants whose values depended on [TPP]. The pseudo-first order rate constants ( $k_{\text{obs}}$ ) thus obtained were found to increase considerably from ( $6.11 - 9.38 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) with [TPP] (Table 1) over a range of [TPP] used ( $2.0 - 10.0 \times 10^{-8}$  mol  $\text{dm}^{-3}$ ). A linear plot was obtained between  $\log k_{\text{obs}}$  and  $\log[\text{TPP}]$  (Fig. 3) with

**Table 1.** Pseudo-first order rate constants for the TPP catalysed oxidation of indole by sodium perborate at 303K

| [indole] $\times 10^3$<br>(mol $\text{dm}^{-3}$ ) | [sodium perborate]<br>$\times 10^4$ (mol $\text{dm}^{-3}$ ) | [TPP] $\times 10^6$<br>(mol $\text{dm}^{-3}$ ) | $\text{CH}_3\text{COOH}$<br>% (V/V) | $k_{\text{obs}} \times 10^4$<br>( $\text{s}^{-1}$ ) |
|---|---|--|-------------------------------------|---|
| 2.0   | 6.0   | 2.0  | 30                                  | 3.43  |
| 4.0   | 6.0   | 2.0  | 30                                  | 5.67  |
| 6.0   | 6.0   | 2.0  | 30                                  | 6.88  |
| 8.0   | 6.0   | 2.0  | 30                                  | 9.62  |
| 10.0  | 6.0   | 2.0  | 30                                  | 12.6  |
| 6.0   | 4.0   | 2.0  | 30                                  | 6.99  |
| 6.0   | 8.0   | 2.0  | 30                                  | 6.55  |
| 6.0   | 10.0  | 2.0  | 30                                  | 6.32  |
| 6.0   | 12.0  | 2.0  | 30                                  | 6.11  |
| 6.0   | 6.0   | 4.0  | 30                                  | 7.25  |
| 6.0   | 6.0   | 6.0  | 30                                  | 7.71  |
| 6.0   | 6.0   | 8.0  | 30                                  | 8.53  |
| 6.0   | 6.0   | 10.0   | 30                                  | 9.38  |



**Figure 2.** Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{indole}]$  for TPP catalysed oxidation of indole by sodium perborate in acetic acid medium



**Figure 3.** Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{catalyst}]$  showing the effect of catalyst concentration on reaction rate

a slope of 0.17, indicating that the order of the reaction with respect to catalyst was fractional.

#### Effect of $[\text{H}^+]$

The required concentrations of  $[\text{H}^+]$  solutions were prepared from the stock solution of 4m concentration. The reaction rate constants measured with various  $[\text{H}^+]$  ( $2.4 - 8.8 \times 10^{-1} \text{ mol dm}^{-3}$ ) and were found to decrease with increase of  $[\text{H}^+]$  ion concentration (Table 2). This shows that added  $[\text{H}^+]$  retards the rate of reaction.

#### Effect of dielectric constant

In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of indole by sodium perborate was studied in aqueous acetic acid mixtures of various compositions (Table 3). The data clearly reveals that the rate increases with decrease in the percentage of acetic acid, i.e. 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<sup>18-20</sup>, a neutral molecule [indole], and a mono negative ion ( $\text{HSO}_5^-$ ) suggesting a polar (ionic) mechanism.

**Table 2.** Effect of  $[\text{H}^+]$  on the reaction rate

| $[\text{H}^+] \times 10^1$<br>( $\text{mol dm}^{-3}$ ) | $k_{\text{obs}} \times 10^4$<br>( $\text{s}^{-1}$ ) |
|--|---|
| 2.4  | 7.08  |
| 4.0  | 6.88  |
| 5.6  | 6.40  |
| 7.2  | 6.03  |
| 8.8  | 5.49  |

[sodium perborate] =  $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ , [indole] =  $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [TPP] =  $2.0 \times 10^{-8} \text{ mol dm}^{-3}$ , Acetic acid : water = 15:35, Temperature = 303K

**Table 3.** Effect of dielectric constant on the reaction rate at 303K

| $\text{CH}_3\text{COOH}:\text{H}_2\text{O}$ | $D^a$ | $k_{\text{obs}} \times 10^4$<br>( $\text{s}^{-1}$ ) |
|---|-------|---|
| 60:40                                       | 35.13 | 3.02  |
| 50:50                                       | 42.37 | 4.50  |
| 40:60                                       | 49.60 | 5.67  |
| 30:70                                       | 56.83 | 6.88  |
| 20:80                                       | 62.83 | 9.64  |

[sodium perborate] =  $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ , [indole] =  $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [TPP] =  $2.0 \times 10^{-8} \text{ mol dm}^{-3}$ , <sup>a</sup> values are calculated from the values of pure solvent.

#### Test for free radical intermediates

No turbidity was observed when a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

#### Rate and activation parameters

The effect of temperature was studied in the range of 283–323 K and the results were shown in Table 4. The Arrhenius plot of  $\ln k_{\text{obs}}/T$  versus  $1/T$  was found to be linear (Figure 4). The value of energy of activation ( $E_a$ ) was found to be  $12.37 \text{ kJ mol}^{-1} \text{ K}^{-1}$  and  $\Delta H^\ddagger = 9.85 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -210.21 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^\ddagger = 73.55 \text{ kJ mol}^{-1}$ . 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<sup>21</sup>.

#### Rate law

$$\begin{aligned} \frac{-d[\text{H}_2\text{O}_2]}{dt} &= k_4[\text{C}_3] \\ &= \frac{k_4 K_3 [\text{sub}] [\text{C}_2]}{1 + K_3 [\text{sub}]} \\ \frac{-d[\text{H}_2\text{O}_2]}{dt} &= \frac{K_2 K_3 k_4 [\text{sub}] [\text{oxi}] [\text{C}_1]}{\{1 + K_3 [\text{sub}]\}} \\ \frac{-d[\text{H}_2\text{O}_2]}{dt} &= \frac{K_1 K_2 K_3 k_4 [\text{sub}] [\text{oxi}] [\text{cat}]}{\{1 + K_3 [\text{sub}]\} \{1 + K_1 [\text{cat}]\}} \end{aligned}$$

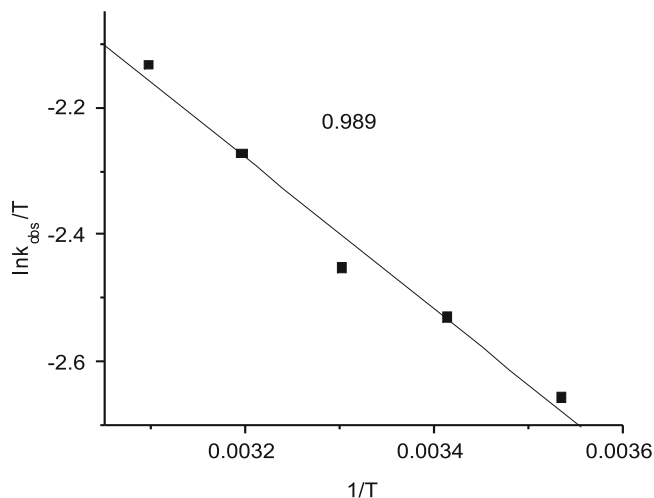
#### MECHANISM

Perborate in aqueous solution yields hydrogen peroxide and the kinetic studies in aqueous and partly aqueous acidic media confirm perborate oxidation as hydrogen peroxide oxidation<sup>10-13</sup>. In the present investigation no observed polymerization in the presence of acrylonitrile rules out a free radical process. Hence ionic mechanism was favoured in this study. Increase of  $[\text{H}^+]$  ion concentration decreased the rate. This showed that liberation of  $[\text{H}^+]$  during the reaction. The Michaelis-Menton dependence of the oxidation rate on [indole] confirms

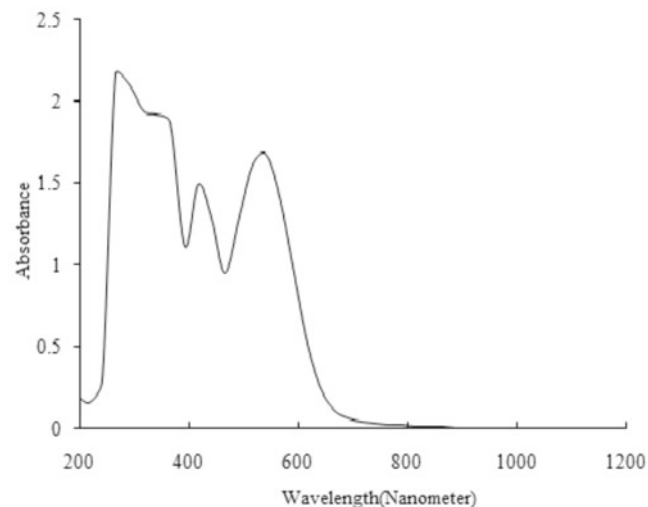
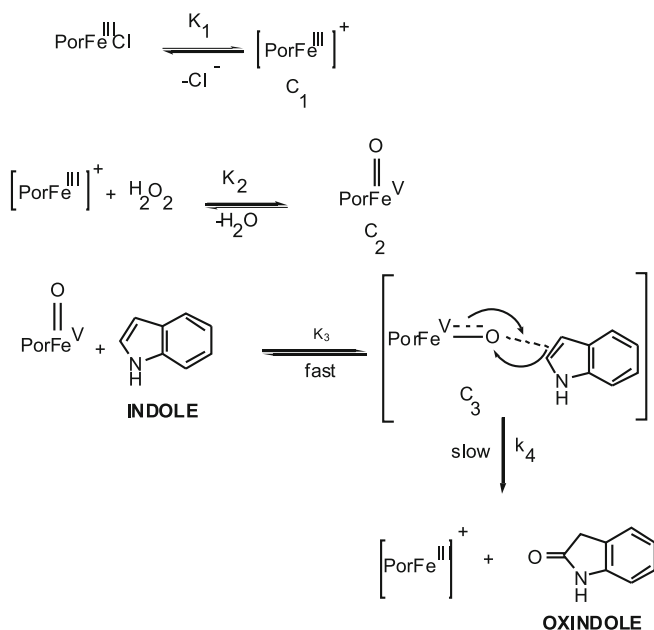
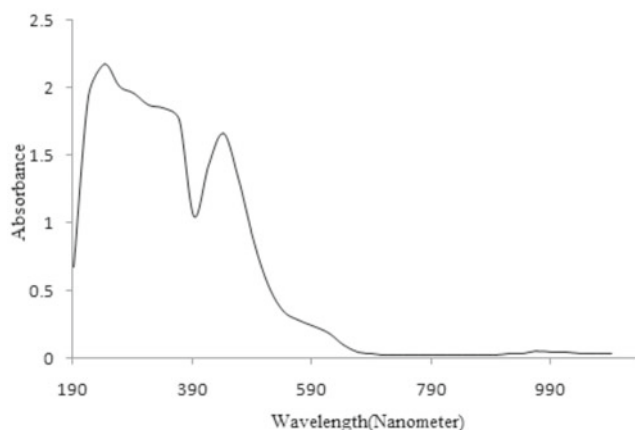
**Table 4.** Effect of temperature on reaction rate

| Temperature (K)                                     | 283  | 293  | 303  | 313  | 323  |
|---|------|------|------|------|------|
| $K_{\text{obs}} \times 104 \text{ (s}^{-1}\text{)}$ | 2.18 | 4.41 | 6.88 | 18.5 | 39.6 |

[sodium perborate] =  $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ , [indole] =  $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [TPP] =  $2.0 \times 10^{-8} \text{ mol dm}^{-3}$ , Acetic acid : water = 15:35.

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

the formation of complex in a rapid pre-equilibrium. The first step is the formation of a complex between sodium perborate and TPP. This complex immediately decomposed and give  $\text{Por-Fe}^{\text{V}} = \text{O}$  is in agreement with the literature study<sup>22</sup>. This  $\text{Por-Fe}^{\text{V}} = \text{O}$  may further react with the indole to form a complex (Fig. 5) at 602 nm, which would give the product in the next step (Fig. 6). This type of product was already reported<sup>9</sup>. 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 plot of  $\log [\text{catalyst}]$  versus  $\log k_{\text{obs}}$  is found to be linear. 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 (scheme 1).

**Figure 5.** UV spectrum showing the formation of the intermediate complex at 532 nm between indole and  $\text{PorFe}^{\text{V}} = \text{O}$ **Figure 6.** UV spectrum showing the formation of a product at 407 nm after the decomposition of intermediate complex at 532 nm

## CONCLUSIONS

In conclusion, *meso*-tetraphenylporphyriniron(III) chloride has been proven to be an excellent catalyst for the oxidation of indole by sodium perborate. The catalyst developed for this particular reaction has shown significant activity in yielding the biologically important product. The kinetic and thermodynamic parameters for the TPP catalysed oxidation of indole by sodium perborate were determined and the reaction scheme was proposed. The thermodynamic data obtained, supported the proposed mechanism.

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