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. Usually as metabolites of tryptophan. Indole is biologically active. 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. Rangappa et al 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.

Sodium perborate, a peroxo salt of anionic formula: B2(O2)2(OH)4, 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.

Oxidation of organic compounds catalysed by synthetic metalloporphyrin complexes has been one of the hot areas in chemistry during the last two decades. The metalloporphyrins can catalyse the oxidation of a variety of organic substrates with many different terminal oxidants. 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. 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 described the use of meso-tetraphenylporphyriniron(III) chloride (TPP) in combination with the lipophilic iodosylbenzenes, 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. 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^-4 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 ± 0.1°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.

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 thiosulphate solution by using starch as indicator. The pseudo first order rate constants (kobs) 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 ± 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^{-4} 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 Na_{2}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.

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], [H^{+}] and dielectric constant have been studied. The rate and activation parameters were evaluated.

Effect of [indole]

At a constant sodium perborate, [TPP], [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 x 10^{-3} mol dm^{-3}). The plot (Fig. 1) of log\( k_{\text{obs}} \) versus log[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/[indole] is linear with definite intercept on the rate ordinate, which indicates the operation of Michaelis-Menten mechanism,

where \( K_{3} \) is the equilibrium constant for the formation of Michaelis-Menten complex, and \( k_{4} \) the rate constant for the decomposition of Michaelis-Menten complex. Usually the first step is a fast pre-equilibrium and the electron transfer step is rate determining.

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 x 10^{-4} mol 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], [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 x 10^{-4} mol dm^{-3}) with [TPP] (Table 1) over a range of [TPP] used (2.0 – 10.0 x 10^{-8} mol dm^{-3}). A linear plot was obtained between log\( k_{\text{obs}} \) and log[TPP] (Fig. 3) with

<table>
<thead>
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<th>[indole] x 10^{-3} (mol dm^{-3})</th>
<th>[sodium perborate] x 10^{-4} (mol dm^{-3})</th>
<th>[TPP] x 10^{-4} (mol dm^{-3})</th>
<th>CH\text{COOH} % (V/V)</th>
<th>( k_{\text{obs}} \times 10^{4} ) (s^{-1})</th>
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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 kJ mol\(^{-1}\) K\(^{-1}\) and \( \Delta H^\# = 9.85 \) kJ mol\(^{-1}\), \( \Delta S^\# = -210.21 \) J K\(^{-1}\) mol\(^{-1}\), \( \Delta G^\# = 73.55 \) kJ mol\(^{-1}\). The large negative value of entropy of activation \( (\Delta S^\#) \) obtained is attributed to the severe restriction of solvent molecules around the transition state \(^{21}\).

Rate law

\[
\frac{-d[H_2O_2]}{dt} = k_4[C_3] = k_4K_3 \text{ [sub] [C}_2_\text{]} \frac{1 + K_5 \text{ [sub]}}{1 + K_5 \text{ [sub]}}
\]

\[
\frac{-d[H_2O_2]}{dt} = K_2 K_3 k_4 \text{ [sub] [o]x[i] [C}_3_\text{]}} \frac{1 + K_4 \text{ [sub]}}{1 + K_4 \text{ [sub]}}
\]

\[
\frac{-d[H_2O_2]}{dt} = K_1 K_2 K_3 k_4 \text{ [sub] [o]x[i] [c]a[t]}} \frac{1 + K_4 \text{ [sub]}}{1 + K_4 \text{ [sub]}} (1 + K_4 \text{ [c]a[t]})
\]

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\(^{10-13}\). In the present investigation no observed polymerization in the presence of acrylonitrile monomer rules out a free radical process. Hence ionic mechanism was favoured in this study. Increase of \([H^+]\) ion concentration decreased the rate. This showed that liberation of \([H^+]\) during the reaction. The Michaelis-Menton dependence of the oxidation rate on \([\text{indole}]\) confirms
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 Por-Fe\(^{3+}\) = O is in agreement with the literature study\(^2\). This Por-Fe\(^{3+}\) = 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\(^9\). 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 [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).

\[
\text{Por-Fe}^{3+} + \text{Cl}^- \rightarrow \text{Por-Fe}^{3+} + \text{Cl}^-
\]

\[
\text{Por-Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Por-Fe}^{3+} + \text{H}_2\text{O}
\]

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.

**CONCLUSIONS**


