meso-TETRAPHENYLIRONPORPHYRIN(III) CHLORIDE CATALYZED OXIDATION OF ANILINE AND ITS SUBSTITUENTS BY *m*-CHLOROPERBENZOIC ACID

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ABSTRACT

The most fascinating feature of heme-enzymes such as cytochromes P450 is their ability to carry out oxidations with high selectivity. Metalloporphyrin complexes are used as replicate compounds for cytochrome P450. A kinetic analysis has been carried out with the aim of understanding the mechanistic studies on oxidation of anilines by *m*-chloroperbenzoic acid catalyzed *by meso*-tetraphenylironporphyrin(III) chloride in aqueous acetic acid medium. The order of the reaction is found to be second order with respect to the substrate and first order with respect to the catalyst and oxidant. Product analysis proves that azobenzene is the sole product in the catalytic oxidation. The increase of $[H^+]$ in this oxidation retards the rate of the reaction. The effects of substituents on the oxidation rate are studied with 19 *ortho-, meta- and para-* substituted anilines at five different temperatures. The thermodynamic parameters for the oxidation have been determined and discussed. The catalysed *m*-chloroperbenzoic acid oxidation with substituted anilines fulfills the isokinetic relationship and Exner correlation but not to any of the linear free energy relationships. The solvent interaction also plays a major role in leading the reactivity. Based on the kinetic results and product analysis a probable mechanism is proposed.

Key words: Aniline, oxidation, m-chloroperbenzoic acid, meso-tetraphenylporphyriniron(III) chloride.

INTRODUCTION

Metalloporphyrin complexes are extensively used as mimetic compounds for the catalytic activity of cytochrome P450 enzymes in life process¹. Metalloporphyrins have been the subjects of a number of findings as they act as a selective catalyst. The relations between the oxygen donor and the metal centre of the catalyst form a high valent metal oxospecies which can act as a useful oxidising agent and is capable of transferring the oxygen atom to the substrate². Many mechanistic studies³⁻¹¹ have revealed that halogenated metalloporphyrin complexes are excellent catalysts for difficult oxidations with high selectivity. The potential of the heme group is to merge with tiny ligands (including molecular oxygen) in enzymatic oxidations. The contribution of heme in these oxidation processes has motivated chemists to proceed from these naturally occurring catalysts and to use them into industrial processes. In order to learn the core of the heme group, the porphyrin ring with the central metal iron atom has been selected. The iron complexes with meso-tetraphenyl groups are broadly considered as replicate of the natural ironporphyrins due to their useful properties such as catalytic and semi-conducting properties. Iron complexes of tetraphenylporphyrins can be regarded as macrocyclic ligands that has an intermediate structure sandwiched between common natural iron porphyrins with cytochrome P450. To complement the studies in the field of the catalytic oxidation of aniline, the oxidation of aniline by m-chloroperbenzoic acid catalysed by first generation porphyrin catalyst meso-tetraphenylporphyriniron(III) chloride (5,10,15,20-tetraphenyl-21h,23hporphineiron(III) chloride) has been selected for the research. A literature survey 12 reveals that the oxidation of anilines by a range of oxidants has been reported and only some of them authenticate Hammet equation. This is due to the fact that aniline in acid medium exists in dual forms, that is as free bases and as conjugate acids.

EXPERIMENTAL

The catalyst meso-tetraphenylporphyriniron(III) chloride (Sigma Aldrich) has been used as received. All chemicals and solvents used are of analytical grade (Merck, India). Aniline is redistilled before use. Acetic acid is purified by redistillation. All the reagents has been prepared fresh just before the reactions are carried out. A solution of m-chloroperbenzoic acid in acetic acid was prepared fresh and standardized iodometrically. The kinetic studies have been carried out under pseudo-first-order conditions with the [substrate] >> [*m*-chloroperbenzoic acid]. Kinetic studies are done with aniline by varying the concentration of aniline, m-chloroperbenzoic acid, meso-tetraphenylporphyriniron(III) chloride, acetic acid, H⁺ and by varying temperature. All the reactions have been carried out in a thermostat and the temperature is controlled to ± 0.1 °C. The progress of the oxidation reaction is followed by determining the amount of unconsumed *m*-chloroperbenzoic acid iodometrically up to 80% of completion of the reaction at different reaction time. The rate constants (k_{obs}) have been found out by the least square slopes of the linear plots of log[m-chloroperbenzoic acid] and time. Repeated runs show that the rate constants for oxidation reactions are reproducible within \pm 3%. The reaction is also carried out using acrylonitrile to find the presence of free radical mechanism. *ortho-*, *meta-* and *para-* substituents of aniline are redistilled / recrystallized before use. The oxidation reactions of *meta-* and *para-* substituents of aniline were studied at different temperatures via 292, 296, 300, 305.5, and 312 K to assess various thermodynamic parameters.

From the Eyrings equation¹³, the thermodynamic parameters enthalpy of activation and entropy of activation are figured out from the expression

$$k_{obs} = (k_b T/h) exp^{-\Delta G \#/R}$$

Where k_b is Boltzmann's constant, T is the temperature in Kelvin, h is plank's constant, R is the gas constant , $\Delta G^{\#}$ is the activation of Gibbs free energy, $\Delta H^{\#}$ is the enthalpy of activation and $\Delta S^{\#}$ is the entropy of activation. $\Delta G^{\#}$ and energy of activation (E_a) can be calculated from the following expressions respectively.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$
 and $Ea = \Delta H^{\#} + RT$

DATA ANALYSIS

Correlation studies are carried out using Microcal Origin (version 6) and SPSS computer software. The goodness of the fit is discussed using the correlation coefficient, r in the case of simple linear regression and R in the case of multiple linear regressions.

STOICHIOMETRY AND PRODUCT ANALYSIS

The stoichiometry of the reaction is found out by doing several sets of experiments by varying [*m*-chloroperbenzoic acid] in the range of 0.1-1.5M ([substrate] = 0.1M, [catalyst] = 1.4×10^{-6} M, acetic acid:water = 60:40, [H⁺] = 0.2N, temperature = 300 K). The estimation of unconsumed *m*-chloroperbenzoic acid shows that the stoichiometry of the reaction is found to be in the ratio of 1:2 (*m*-chloroperbenzoic acid : aniline). The oxidation product is confirmed using TLC. Under the pseudo-first order condition [aniline]>>[*m*-chloroperbenzoic acid] in acetic acid medium, the product obtained is followed spectrophotometrically at 429 nm which is the λ_{max} of azobenzene. This is in agreement with the literature value¹⁴.

RESULTS AND DISCUSSION

EFFECT OF VARIATION OF SUBSTRATE CONCENTRATION

At fixed concentrations of *m*-chloroperbenzoic acid and $H_2SO_{4^{\gamma}}$ the increase in concentration of substrate (aniline) increases the rate of the reaction. The plot in the Fig. 1, that is log $k_{obs} vs \log[aniline]$ was found to be a straight line with slope two. This reveals that the reaction is second order with respect to the substrate.



Fig. 1. Plot of $logk_{obs}$ versus log[aniline] for the oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride. [oxidant] = 0.005M, [catalyst] = 1.4x10^{-6}M, acetic acid:water = 60:40, [H⁺]=0.2N, temperature = 292K

EFFECT OF VARIATION OF *m*-CHLOROPERBENZOIC ACID CONCENTRATION

When the concentration of the substrate is constant, the increase in concentration of *m*-chloroperbenzoic acid does not affect the apparent rate constant of the reaction (Table 1). The first order plot of log[*m*-chloroperbenzoic acid] *vs* time is found to be linear. The *pseudo*-first order rate constants found from the plots are unaltered by the change in [*m*-chloroperbenzoic acid] which confirmed the first order dependence of the reaction rate on *m*-chloroperbenzoic acid.

Table 1. Pseudo-firstorderrate constants for the oxidation of an iline by varying [*m*-chloroperbenzoic acid] catalysed by *meso*-tetraphenylporphyriniron(III) chloride.

[oxidant] (M)	$10^{5} k_{obs} (s^{-1})$			
0.006	3.57			
0.007	3.44			
0.008	3.52			
0.009	3.49			
0.010	3.48			

[substrate] = 0.1M, [catalyst] = $1.4x10^{-6}$ M, acetic acid:water = 60:40, [H⁺] = 0.2N, temperature = 300 K

EFFECT OF VARIATION OF H⁺ CONCENTRATION

The reaction rate on the variation of hydrogen ion concentration has been determined at different initial concentrations and keeping the concentrations of the other reactants constant. The proton concentration is equated to the sulfuric acid concentration. The rate of the reaction decreases with increase in H_2SO_4 concentration. The plot (Fig. 2) $\log k_{obs}$ vs $\log[H^+]$ gives a straight line with unit slope which is inversely proportional to the proton concentration. Aniline in acid medium exists in dual forms, the free bases and conjugate acids, that is protonated ($C_6H_5NH_3^+$) and nonprotonated aniline ($C_6H_5NH_2$). The literature study²³ reveals that the reaction of aniline proceeds through protonated and unprotonated form of aniline and the (increase in $[H^+]$ increases the reaction rate) protonated aniline is more reactive in 3-butyn-2-one. But in the present study increase in $[H^+]$ leads to the decrease in reaction rate. (Increase of protonated aniline inhibits the reaction rate) This reveals that the protonated aniline is less reactive in this oxidation reaction.

EFFECT OF VARIATION IN CATALYST CONCENTRATION

The oxidation of aniline by *m*-chloroperbenzoic acid in acetic acid is very slow but when catalysed by *meso*-tetraphenylironporphyrin(III) chloride the reaction rate increases. But the plot (Fig. 3) of $\log_{obs} vs \log[catalyst]$ is found to be linear with a unit slope which indicates a first order dependence with respect to catalyst.



Fig. 2.Plot of $logk_{obs}$ versus $log[H^+]$ for the oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride. [substrate] = 0.1M, [oxidant] = 0.005M, [catalyst] = 1.4x10^{-6}M, acetic acid:water = 60:40, temperature = 300 K



Fig. 3. Plot of logk versus log[*meso*-tetraphenylporphyriniron(III) chloride] for the oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride. [substrate] = 0.1M, [oxidant] = 0.005M, acetic acid:water = 60:40, [H⁺] = 0.2N, temperature = 300K.

EFFECT OF VARIATION IN TEMPERATURE

The oxidation of aniline is studied at different temperatures *via* 292, 296, 300, 305.5 and 312 K maintaining the concentration of substrate, oxidant, H^+ , solvent and catalyst constant. The plot of $lnk_{obs}/T vs 1/T$ (Fig. 4) is found to be linear.



Fig. 4. Plot of $\ln k_{obs}/T$ versus 1/T for the oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride. [substrate] = 0.1M, [oxidant] = 0.005M, [catalyst] = 1.4×10^{-6} M, acetic acid:water = 60:40, [H⁺] = 0.2N

The values of thermodynamic parameters have been found as $\Delta H^{\#} = 15.07$ kJ mol⁻¹. $\Delta S^{\#} = -279.02$ J K⁻¹ mol⁻¹, $\Delta G^{\#} = 99.34$ kJ mol⁻¹ and $E_a = 17.59$ kJ mol⁻¹ K⁻¹. The high, negative, entropy of activation is compatible with the high (total) order of the reaction.

EFFECT OF DIELECTRIC CONSTANT

The effect of solvent on the reaction rate is studied by varying the composition of acetic acid from 40% to 80% (Table 2). The oxidations are carried out by maintaining the concentration of aniline, *m*-chloroperbenzoic acid, catalyst and temperature constant. The above observation clearly reveals that the rate decreases with increase in percentage of acetic acid, *i.e.* with decreasing dielectric constant (D) or polarity of the medium. This directs to the conclusion that there is a charge development in the intermediate state involving a more polar intermediate than reactants, suggesting a polar (ionic) mechanism.

Table 2. *Pseudo*-first order rate constants for the oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride in different acetic acid compositions.

% Acetic acid	D	$10^{5} k_{obs}(s^{-1})$
40	49.60	26.70
50	42.37	10.10
60	35.14	5.14
70	27.90	3.04
80	20.67	1.80

[substrate] = 0.1M, [oxidant] = 0.005M, [catalyst] = $1.4x10^{-6}M$, [H⁺] = 0.2N, temperature = 312K



Fig. 5. UV spectrum showing a probable formation of intermediate complex in oxidation of aniline by *m*-chloroperbenzoic acid catalysed by *meso*-tetraphenylporphyriniron(III) chloride.

Fig. 5 shows the UV spectrum at early stages and final stages of the oxidation reaction. At initial stages of the reaction a new peak at 717 nm appeares, slowly diminishes and vanishes at the final stages of the reaction. This may be due to the formation of an intermediate from which products are formed. Simultaneously, at 429 nm, a peak appears and is stable till the end of the reaction. The may be due to the formation of the product which is in agreement with literature value¹⁴ (429 nm is the λ_{max} of azobenzene in acetic acid medium).

SUBSTITUENTS EFFECT

The kinetics and oxidation of aniline and o-OCH₃, m-OCH₃, p-OCH₃, o-CH₃, m-CH₃, p-CH₃, o-Cl, m-Cl, p-Cl, o-Br, m-Br, p-Br, o-F, m-F, p-F, o-NO₂, m-NO₂, p-NO₂ anilines in the presence of catalyst are conducted under pseudo-first order conditions at various temperatures 292 K, 296 K, 300 K, 305.5 K and 312 K to determine various thermodynamic parameters. The various thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and E_a are found and tabulated (Table 3). The analysis of the data in the Table 3 indicates that the oxidation is neither isoenthalphic nor isoentropic but confirms with isokinetic relationship of compensation law. Since the reactions are of ion-polar, it is expected that the entropy of the activated complex for all the anilines should be nearly the same order of magnitude. But due to the variation in polarity of different anilines, $\Delta S^{\#}$ may be different for different anilines¹², as observed in the present findings. But the isokinetic relationship exists. The plot of

activation enthalpy *versus* activation entropy follows a straight line as shown in the Fig. 6. The function of isokinetic relationship^{15,16} reveals that a common mechanism is working in all the aniline oxidation reactions¹³. Isokinetic temperature is the temperature at which all the compounds react at same speed since this temperature variation of substituent has no influence on the free energy of activation. In an isoentropic oxidation, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalphic series and the reactivity is determined by the entropy of activation¹².

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\sharp}$$

 β is the isokinetic temperature which is found to be 329K and it is greater than the experimental temperature.



Fig. 6. Isokinetic plot for the *meso*-tetraphenylporphyriniron(III) chloride catalysed oxidation of anilines by *m*-chloroperbenzoic acid.

The values of free energy of activation of the reactions are found to be more or less similar. This is due to the fact that at isokinetic temperature the change of substituent has no influence on the free energy of activation. If the isokinetic temperature is infinite in isoentropic oxidation reactions, only the enthalpy of activation finalizes the reactivity and if the isokinetic temperature is zero in isoenthalpic oxidation reactions, only the entropy of activation finalizes the reactivity¹⁰.



Fig. 7. Exner plot for the *meso*-tetraphenylporphyriniron(III) chloride catalysed oxidation of anilines by *m*-chloroperbenzoic acid.

The Exner relationship (Fig. 7), the linear double logarithmic relationship between the rates at different temperatures, also confirms the common mechanism throughout the series.

STRUCTURE-REACTIVITY CORRELATION

The outcome in the Table 3 reveals that the ΔG^{μ} values differ with substrate. This may be due to the difference in polarity of various anilines. So the obtained rate constants show deviation with substituents. Negative entropy of activation also gives the information that the complex formed is an associate type with a greater degree of charge in transition state than initial state¹³.

Aniline substituents	$10^{5} k_{obs} (s^{-1})$				$\Delta H^{\#}$	- Δ S [#]	$\Delta G^{\#}$	Е		
	292 K	296 K	300 K	305.5 K	312K	kJ mol ⁻¹	J K ⁻¹ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹ K ⁻¹	r
o-OCH ₃	18.17	22.30	27.91	31.61	48.61	33.27	-203.00	94.58	35.78	0.987
<i>o</i> CH ₃	2.91	3.71	4.06	4.57	6.04	23.07	-252.72	99.39	25.58	0.981
oCl	15.90	23.61	37.94	59.13	130.57	76.67	-56.20	93.64	79.18	0.997
o–Br	74.00	87.43	93.35	128.62	176.84	30.69	-200.44	91.22	33.20	0.986
<i>о</i> –F	40.15	47.99	62.05	78.09	113.97	76.67	-56.20	93.64	79.18	0.998
o-NO ₂	54.05	66.50	76.73	105.60	fast	33.84	-192.05	91.84	36.35	0.994
<i>m</i> –OCH ₃	2.30	3.07	4.29	7.28	12.25	62.75	-120.03	98.99	65.26	0.997
<i>m</i> –CH ₃	1.24	1.50	1.91	2.81	4.12	44.13	-188.58	101.1	46.64	0.997
<i>m</i> –Cl	2.97	4.65	5.50	9.32	12.25	51.45	-15.54	98.39	53.95	0.988
<i>m</i> –Br	1.32	2.79	4.08	6.50	17.14	89.52	-32.11	99.21	92.03	0.991
<i>m</i> –F	6.39	9.40	12.84	20.34	40.45	66.55	-98.28	96.23	69.06	0.997
<i>m</i> –NO ₂	8.80	11.28	13.77	23.91	29.92	59.02	-119.2	95.02	61.53	0.987
<i>p</i> -OCH ₃	23.85	39.56	62.32	112.06	187.83	51.93	-151.15	97.57	54.44	0.997
р-СН ₃	0.60	0.95	1.25	1.70	2.80	53.59	-161.39	102.3	56.10	0.993
p-Cl	3.45	4.54	6.34	9.51	14.29	52.51	-151.17	98.17	55.03	0.999
<i>p</i> –Br	1.02	2.07	4.52	6.14	17.45	101.0	5.18	99.46	103.5	0.987
р-F	0.39	0.74	1.68	3.77	8.37	76.67	-56.20	93.64	79.18	0.997
p-NO ₂	77.16	102.37	109.67	183.03	fast	46.67	-163.47	96.02	49.18	0.998
Н	3.41	3.72	4.17	4.73	5.36	15.08	-279.02	99.34	17.59	0.998

Table 3. Pseudo-first order rate constants for *meso*-tetraphenylporphyriniron(III) chloride catalyzed *m*-chloroperbenzoic acid oxidation of *meta*- and *para*-substituted anilines at different temperatures, thermodynamic and activation parameters.

 $[substrate] = 0.1M, [oxidant] = 0.005M, [catalyst] = 1.4x10^{6}M, acetic acid:water = 60:40, [H⁺] = 0.2N$



Fig. 8. Hammet plot for the *meso*-tetraphenylporphyriniron(III) chloride catalysed oxidation of anilines by *m*-chloroperbenzoic acid.

The rate data obtained is also unsuccessful in proving that the typical Hammet equation $logk_{obs}$ vs σ is a dispersed gram and a sensitive plot (Fig. 8) at the temperatures studied. Substituents p-OCH₃, m-NO₂, p-CH₃, m-CH₃, m-Cl, p-Cl, p-Br, are found to be deviating largely. The correlation coefficient (r) of the dispersed gram is found to be 0.461 with standard deviation of 0.565. Literature study¹⁷ also reveals that correlation contre, where the problem arose with anilinium ions, where a lone pair of electrons on the NH₂ group can be delocalized into substituents such as p-NO₂.

The correlation of oxidation rates of *meta*- and *para*- substituted anilines are correlated separately with any of the unit parameters (meta: σ , σ_m^+ ; *para*: σ , σ_p^+ , σ_p^-) and is also found to be ineffective. The oxidation rates measured at 292, 296, 300, 305.5 and 312K are analysed in terms of dual substituent parameter equations (*meta*: σ_1 , σ_R ; σ_1 , σ_R^- ; σ_r , σ_R^+ ; F, R; *para*: σ_1 , σ_R ; σ_r , σ_R^- ; σ_1 , σ_R^+ ; F, R) and is also found to be unsuccesful. The pKa of anilines changes with substituents (1.59 for p-cyano to 6.08 for p-amino) so that the concentration of the substituted protonated aniline varies. This strongly affects the rate of the reaction. So the correlations are found to be unsuccessful. The possible reason for the lack of free energy relationship is the isokinetic temperature 329 K which is greater than the experimental temperature. The same type of results is also reported by Elango and Buvaneswari¹⁸. Operation of inductive and resonance effect opposing each other is known¹⁹ but the present study has no parallel. The less pronounced substituent can be explained only by the compensation effect. Aniline in basic and neutral media is present as free bases but in acid medium it exists in dual forms the free bases and conjugate acids¹⁹. The stoichiometry of the findings shows that two aniline molecules are involved in the reaction. This shows that the catalyst-aniline complex is likely to be the electrophile and free aniline may be the nucleophile. The influence of the substituents on the reactivity of the nucleophile is approximately compensated by the influence of the substituted aniline, exact compensation is doubtful and the result effect is experienced on the oxidation rate.

MECHANISM

The known fact is that the free radicals can be produced by the homolytic fission of peroxide bond. But the addition of acrylonitrile monomer shows no variation in the reaction rate and no formation of turbidity (no formation of

polymer) in the oxidation of aniline. This rules out the presence of free radical mechanism in this oxidation reaction. So the ionic reaction is preferred in this oxidation study. Generally, the enhancement of the electrophillic activity of peroxide will minimize the importance of undesirable free radical pathways, resulting in a mixture of products²⁰. In acetic acid medium, catalyst–oxidant adduct is formed first, which then decomposes to evolve oxoiron(V) species which is the major reactive intermediate. The proposed route of the formation of the reactive intermediate is represented in the first step of the mechanism (Scheme 1). Literature study²¹ also confirms the formation of the same catalyst–oxidant adduct. The investigation results illustrate a fascinating note that H⁺ retards the rate of the reaction. This gives the evidence that H⁺ ion is released in the rate determining step. No Hammet equation originates in the substituents effect. The results can be explained by the formation of intermediate complex. Usually peroxy ions act as strong nucleophiles.

Based on the stoichiometry of the reaction and above experimental outcomes, the following reactions (scheme 1) are considered to constitute the most probable mechanism of the reaction.



Scheme 1. Probable mechanism for the meso-tetraphenylironporphyrin(III) chloride catalysed oxidation of aniline by m-chloroperbenzoic acid.

The formation of the first intermediate and the formation of Por-Fe^v=O are in agreement with the literature study²² and the intermediate formed is experimentally confirmed at 717 nm. The third step is a slow reaction and is likely to be the rate determining step.

RATE LAW

The above suggested mechanism leads to the rate law which is in agreement with the experimental findings.

$\frac{-d[oxidizing agent]}{dt} = \frac{K_1 K_2 K_3 K_4 k_2 [PhNH_2]^2 [PorFe^{III}C1] [oxidizing agent]}{[H^+]^2}$

CONCLUSION

The oxidation of aniline by *meso*-tetraphenylporphyriniron(III) chloride is second order with respect to the substrate, first order with respect to the oxidant and first order with respect to the catalyst. The addition of H^+ ions retards the rate of the reaction. The rate data obtained is also unsuccessful in proving the Hammet equation. The correlations of oxidation rates substituted anilines are correlated separately with any of the unit parameters which is also found to be ineffective. The oxidation rates analysed in terms of dual substituent parameter equations is also found to be unsuccessful. Solvent interaction also plays an important role in leading the reactivity. Suitable mechanism is proposed for the catalysed oxidation reaction. The strength of isokinetic relationship and various free energy relationships have been related and discussed. With *m*-chloroperbenzoic acid as oxygen donor, the first generation ironporphyrin catalyst is proved to be a more effective catalyst in oxidising aniline.

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