Kinetics and mechanism of Iron (III) phthalocyanine chloride catalysed oxidation of Aniline and its substituents by meta-Chloroperbenzoic acid in aqueous acetic acid medium

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ABSTRACT

Phthalocyanins are macrocyclic compounds that are structurally related to porphyrin complexes and due to its remarkable stability they are used as catalyst in oxidation and reduction reactions. Iron (III) phthalocyanine chloride was utilized for the first time as a significant catalyst in the selective oxidation of aniline and its substituents with meta-chloroperbenzoicacid as oxidant in aqueous acetic acid medium. The oxidation reaction with respect to the catalyst indicates that there is no degradation of the catalyst. The reaction follows second order with respect to aniline and first order with respect to meta-chloroperbenzoicacid. Substituent effect has been studied by applying Hammett equation. Azobenzene was the product obtained as the result of oxidation which has been confirmed by UV spectroscopy. The activation parameters for the oxidation reaction have been evaluated and a suitable mechanism and rate law has been proposed.

KEY WORDS: Aniline, meta-chloroperbenzoicacid, iron (III) pthalocyanine chloride, kinetics, oxidation.

1. INTRODUCTION

Aniline is an organic compound comprising a phenyl group affixed to an amino group. It undergoes oxidation with many oxidants and the various oxidation products of aniline finds application in agriculture, antioxidants, herbicides, polymer formation, rubber industries and in drug and dye formation (Zvi Rappoport, 2007). Literature survey explains the formation of various products like nitro, nitroso and azocompounds (Sigeki Sakaue, 1993; Saeid Farhadi, 2007), as the oxidation product of aromatic amines. Among these products the formation of azobenzenes have gained much interest due to their characteristic colour and due to their application in various fields like chemosensors, photochemical properties and in liquid crystals (Mi-Jeong Kim, 2003). Literature studies also shows the kinetics and mechanistic study of aniline by various oxidizing agents (Zudin and James, 1995; Sheik Mansoor and Syed Shafi, 2014; Alhaji, 2013; Adalagere, 2016). Meanwhile the kinetics and mechanistic study of oxidation of aniline and substituted anilines by meta-chloroperbenzoicacid catalyzed by iron (III) phthalocyanine chloride has not yet been studied. Therefore the present work has been carried out to understand the mechanism of oxidation of aniline and its substituents catalyzed by iron (III) phthalocyanine chloride with meta-chloroperbenzoicacid.

Meta-chloroperbenzoicacid is a strong oxidising agent which is comparable with other peracids. It is one of the most familiar oxidizing reagent in organic synthesis, because of its outstanding reactivity, regio and stereo selectivity. It is inexpensively available with high purity and can be used readily. Literature study on meta-chloroperbenzoicacid comprises a huge area in the oxidation of various several organic and inorganic compounds (Samuel and Jennings, 1984; Raja and Karunakaran, 2012; Nasser Safari, 2005; Toshifumi Dohi, 2005).

Phthalocyanins are macrocyclic compounds which contains four pyrrole units and they are structurally similar to porphyrins. Generally pthalocyanines are highly coloured compounds which are stable to alkalies and less stable to acids. They readily form complex metallic compounds. The two hydrogen atoms attached to the two isoindole group can be replaced by metal atoms from every group of the periodic table to form metal phthalocyanines among which iron (III) phthalocyanine chloride is taken into consideration to carry out the present work. Generally iron phthalocyanines catalyse many organic compounds (Junlong Zhao, 2016; Mirela Filipan-Litvic, 2008; Alexander B Sorokin, 2013).

Literature study reveals that no report was available on kinetics and mechanistic study of oxidation of iron(III) phthalocyanine chloride catalysed oxidation of aniline and as a result the work was carried out with meta-chloroperbenzoicacid as oxidant.

2. EXPERIMENTAL

Material: All the chemicals and solvents used in the study were of analytical grade (Merck, India). Meta-chloroperbenzoicacid and iron(III) phthalocyanine chloride (Sigma Aldrich) were used as such. The derivatives of aniline used were m-Br, m-Cl, m-F, m-NO$_2$, m-CH$_3$, m-OCH$_3$, p-Br, p-Cl, p-NO$_2$, p-CH$_3$ and p-OCH$_3$. All the solutions used in the study were freshly prepared with double distilled water. The kinetic runs were carried out in a thermostat where the temperature was maintained constant with an accuracy of $\pm\, 0.2^{\circ}$C.

Kinetic measurements: The reactions were conducted by retaining pseudo first order conditions by keeping an excess of the concentration of aniline over meta-chloroperbenzoicacid in an aqueous acetic acid medium. The

reaction mixture was homogeneous throughout the course of the reaction. The progress of the reaction was followed by titrimetric procedure. The rate constants (k_{obs}) were evaluated by least square method from the slopes of linear plots of log [titre] versus time.

Stoichiometry: The stoichiometric studies for the oxidation of the reaction was carried out by doing several sets of experiments as per the standardised method followed by Raja and Karunakaran (2012), with slight modifications. The stoichiometry was calculated from the concentration of unconsumed meta-chloroperbenzoicacid and was found to be in the ratio of 1:2 (meta-chloroperbenzoicacid:aniline).

Product analysis: The product obtained in the oxidation reaction was identified to be azobenzene which has been confirmed by melting point determination and by comparing it with authentic samples (Karunakaran and Kamalam, 2002). The melting point of the product obtained was found to be $66^{\circ}C$ which also confirms that the product obtained was azobenzene. Under pseudo first order condition the product obtained was confirmed spectrophotometrically at 429nm.
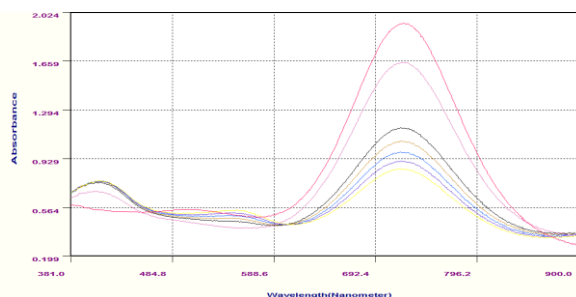

Figure.1. UV spectrum showing a probable formation of intermediate in oxidation of aniline by meta-chloroperbenzoic acid catalysed by iron(III) phthalocyanine chloride

The λ_{max} of azobenzene was confirmed by correlating with that of the authentic sample which was in agreement with the literature value (Raja and Karunakaran, 2012).

Data analysis: Correlation analysis was carried out using Microcal origin (version 6) computer software.

3. RESULTS AND DISCUSSION

By varying the concentration of aniline, meta-chloroperbenzoicacid, iron(III) phthalocyanine chloride, sulphuric acid, manganous sulphate, acrylonitrile, acetic acid and temperature, the various factors influencing the rate of the oxidation reaction of iron(III) phthalocyanine chloride catalysed oxidation of aniline have been studied. From the reaction rate the thermodynamic and activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and E_a have been tabulated, reviewed and discussed.

Variation of Rate Constant with respect to Aniline concentration: The kinetic analysis has been made at various concentration of substrate and at a fixed concentration of other reagents. By carrying out the titrimetric estimation the concentration of meta-chloroperbenzoicacid remains unconsumed and it was well-defined that when the concentration of the substrate increases the rate of the reaction increases. A linear plot was obtained with $\log k_{obs}$ versus log [aniline] (Fig.2) with a slope of two. The order of the reaction was found to be two with respect to the substrate (aniline).
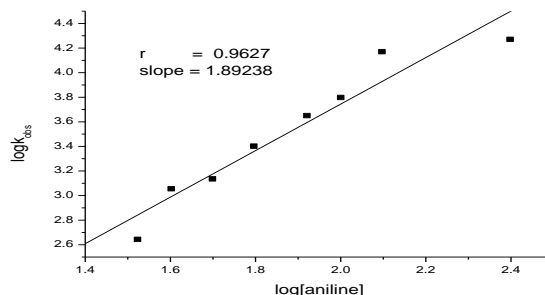

Figure.2. Plot of $\ln k_{obs}$ versus log[aniline] for the oxidation of aniline by meta-chloroperbenzoic acid catalyzed by iron(III) phthalocyanine chloride showing the effect of variation of substrate on reaction rate

Variation of Rate constant with respect to Iron(III) pthalocyanine chloride: At a fixed concentration of aniline, meta-chloroperbenzoicacid, H_2SO_4 and acetic acid, titrimetric estimation were carried out by changing the concentration of iron(III) phthalocyanine chloride, which yielded rate constants whose values depends with respect to the concentration of the catalyst. The rate of the reaction was found to increase with the increase in concentration of the catalyst. The plot (Fig.3) of $\log k_{obs}$ versus log [catalyst] is found to be linear with a unit slope depicting a first order dependence with respect to the catalyst. The linearity of the slope depicts that there is no degradation of the catalyst.
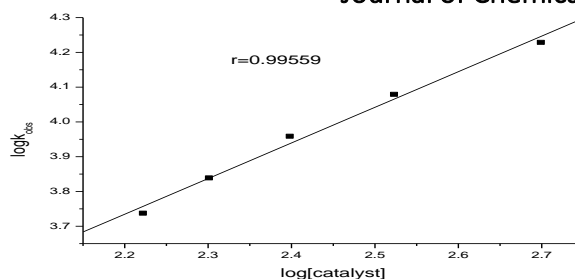
Figure.3. Plot of logk$_{obs}$ versus log[catalyst] showing the effect of catalyst concentration on reaction rate
Variation of Rate constant with respect to Meta-Chloroperbenzoic acid concentration: The kinetics of oxidation of aniline has been investigated at various concentration of meta-chloroperbenzoicacid by maintaining aniline, iron(III) phthalocyanine chloride and other reagents at fixed concentrations. It has been noted that a progressive increase in concentration of *meta*-chloroperbenzoicacid does not affect the rate constant of the reaction (Table.1).

Table.1. Pseudo-first order rate constants for the oxidation of aniline by varying meta-chloroperbenzoic acid concentration catalyzed by Iron (III) pthalocyanine chloride

[oxidant] (M)	10^5 k$_{obs}$ (s^{-1})
0.003	6.25
0.004	6.36
0.005	5.58
0.006	6.14
0.007	5.78

[substrate] = 0.1M, [catalyst] = 1x10^{-3}M, acetic acid:water = 50:50, [H$^+$] = 0.002N, temperature = 303K.
Variation of Rate constant with respect to acid concentration: The rate of the reaction by varying the hydrogen ion concentration in the oxidation of aniline has been determined by maintaining the concentration of other reagents constant. With the increase in concentration of acid the rate of the reaction decreases. The added acid will be favouring the formation of protonated (C$_6$H$_5$NH$_3^+$) and nonprotonated aniline (C$_6$H$_5$NH$_2$) aniline (Shrivastava and Ranveer Singh, 1995). Literature study (Ik-Hwan Um, 2001), reveals that increase in [H$^+$] increases the reaction rate. But in the present study the rate of the reaction decreases with the increase in [H$^+$] which confirms the fact that protonated aniline(C$_6$H$_5$NH$_3^+$) is found to be less reactive (C$_6$H$_5$NH$_3^+$)which inhibits the rate of the reaction.

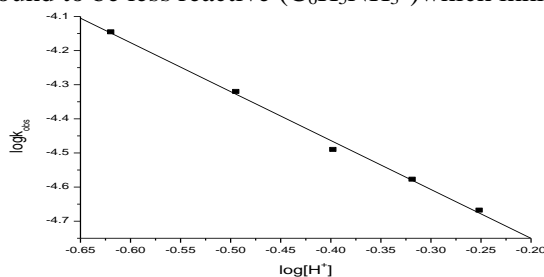**Figure.4. Plot of logk$_{obs}$ versus log[H$^+$] showing the effect of acid concentration on reaction rate**
Variation of Rate constant with respect to temperature: The study of oxidation of aniline and its substituents have been studied by subjecting it to different temperature range of 293K, 303K, 313K, 323K and 333K and by maintaining the concentration of other reagent as constant.
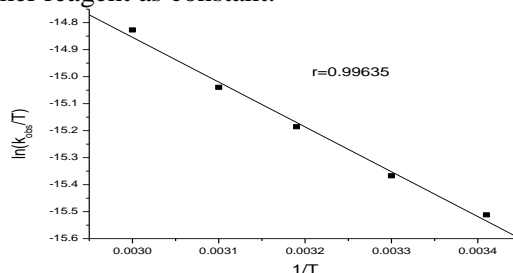

Fig.5. Plot of lnk$_{obs}$/T versus 1/T for oxidation of aniline by meta-chloroperbenzoic acid catalyzed by iron(III) phthalocyanine chloride showing the effect of temperature variation on reaction rate
The plot lnk$_{obs}$ /T versus 1/T (Fig.5), was found to be linear and the rate constant and the various activation parameters are presented in Table-3. The value of various activation parameters were found to be ΔH$^{\#}$ = 13.81 kJ mol^{-1}, ΔS$^{\#}$ = -279.76 kJ mol^{-1}, and ΔG$^{\#}$ = 98.3 kJ mol^{-1}, E$_a$ = 16.32 kJ mol^{-1} K^{-1}. The high negative value of entropy of activation reflects that the transition state is more rigid than the initial state. The nearly constant value of ΔG$^{\#}$ indicates a similar mechanism operating throughout the oxidation of anilines. Same results are verified in similar observations (Patwari, 2009).

Variation of Rate constant with respect to Solvent concentration [Acetic Acid]: The impact of solvent concentration on the rate of the reaction was observed by varying the concentration of acetic acid from 40% to 80% and by retaining the concentration of other reagents constant.

Table.2. Pseudo-first order rate constants for the oxidation of aniline by meta-chloroperbenzoic acid catalyzed by Iron (III) pthalocyanine chloride in different acetic acid compositions

% Acetic acid	D	$10^5 k_{obs}(s^{-1})$
40	49.604	22.64
50	42.37	10.18
60	35.136	5.05
70	27.902	2.95
80	20.668	1.95

The data portrayed in Table.2, clearly reveals that the rate of the oxidation reaction decreases with the increase in percentage of acetic acid. Literature study (Ugye, 2013), gives more information about the effect of dielectric constant on kinetic study and the present work leads to a finalisation that there is a charge development in the transition state than the reactants signifying a polar ionic mechanism.

Variation of Rate constant with respect to Acrylonitrile concentration: Addition of freshly prepared acrylonitrile monomer to the reaction mixture did not initiate polymerisation indicating the absence of free radical species.

Variation of Rate constant with respect to Manganous Sulphate concentration: At a constant concentration of aniline, meta-chloroperbenzoic acid, catalyst, H^+ and solvent the reaction was carried out by varying the concentration of $MnSO_4$. It was found that the rate of the reaction decreases with the increase in Mn (II) indicating a two electron process.

Variation of Rate constant with respect to Aniline and its Substituents: The oxidation reactions of aniline and its meta- and para- substituents were studied at different temperature range of 293K, 303K, 313K, 323K and 333K to evaluate the various thermodynamic parameters such as $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$ and E_a. The pseudo first order rate constant obtained for various substrates are given in Table.3.

Table.3. Pseudo-first order rate constants for Iron (III) pthalocyanine chloride catalysed meta-chloroperbenzoic acid oxidation of para- and meta- substituted anilines at different temperatures, thermodynamic and activation parameters

Aniline substituents	$10^4 k_{obs}(s^{-1})$					$\Delta H^\#$ kJ mol^{-1}	$-\Delta S^\#$ J K^{-1} mol^{-1}	$\Delta G^\#$ kJmol^{-1}	E_a kJ mol^{-1} K^{-1}
	293 K	303 K	313K	323K	333 K				
H	5.39	6.44	7.98	9.52	12.14	13.81	279.76	98.3	16.32
m–Br	6.56	11.8	33.98	111	214	72.02	80.77	96.42	74.54
m–Cl	6.01	8.93	20.18	52.58	110	58.95	126.54	97.16	61.46
m–F	7.21	11.91	30.25	57.19	113	55.01	137.52	96.54	57.52
m–NO$_2$	4.59	9.78	11.93	79.14	148	70.33	90.14	97.55	72.84
m–CH$_3$	3.71	7.56	13.91	21.93	50.32	48.6	164.11	98.16	51.11
m–OCH$_3$	3.52	4.08	5.01	7.32	8.76	16.91	273.06	99.38	19.42
p-Br	3.64	4.90	8.50	10.49	11.46	22.45	253.04	98.87	24.96
p-Cl	4.05	6.41	8.72	12.14	21.81	30.01	226.9	98.53	32.52
p-F	7.17	8.92	9.39	11.95	18.54	16.25	269.12	97.53	18.76
p-NO$_2$	3.59	4.51	5.92	7.28	7.36	13.24	284.62	99.20	15.75
p–CH$_3$	3.56	3.49	7.58	1.38	2.21	36.14	208.07	98.98	38.65
p–OCH$_3$	3.98	7.28	11.79	15.27	24.43	33.16	215.55	98.25	35.67

([substrate]=0.1M, [oxidant]=0.005M, [catalyst] = 1×10^{-3}M, acetic acid:water=50:50, [H$^+$]=0.002N)

The data represented in Table-3 validates the isokinetic relationship.

$$\Delta H^\# = \Delta H^o + \beta \Delta S^\#$$

Where, β is the isokinetic temperature, $\Delta H^\#$ is the activation enthalpy, $\Delta S^\#$ is the activation entropy and ΔH^o is the intercept term. The isokinetic temperature (β) is the temperature at which all the compounds of the series react equally fast. At this temperature the variation of the substituent has no influence on the free energy of activation (Bhuvaneshwari and Elango, 2006). The isokinetic temperature (β) was calculated from the slope of linear plot of $\Delta H^\#$ versus $\Delta S^\#$ (Fig.6) and was observed as 329K which lies within the experimental temperature range (293K-333K) used in the present study.
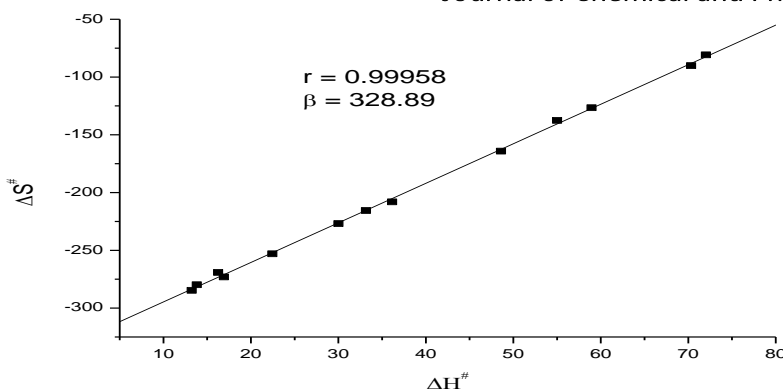
Figure.6. Isokinetic plot for reaction of Iron(III) phthalocyanine chloride catalysed oxidation of anilines by meta-chloroperbenzoic acid

This linear plot brings out a fact that all the substituted anilines are oxidised through a common mechanism. The value of $\Delta S^{\#}$ was found to be dissimilar for different anilines due to the variation in the polarity (Karunakaran and Palanisamy, 1997).
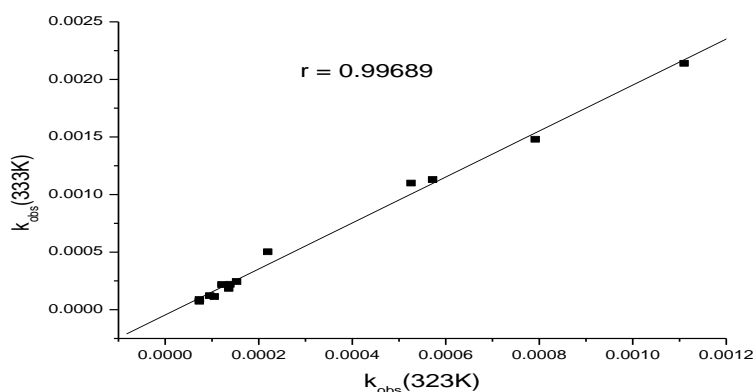

Figure.7. Exner plot for iron(III) phthalocyanine chloride catalysed oxidation of anilines by meta-chloroperbenzoic acid

The Exner plot (Figure.7), between the rates at different temperatures (323K and 333K), also confirms a common mechanism throughout the reaction.

Structure –Reactivity Correlation: The influence of structure on reactivity can be studied by subjecting the meta- and para- substituents of aniline at five different temperature range at 293K, 303K, 313K, 323K and 333K in acetic acid- water medium. The data obtained have been measured, discussed and tabulated in Table.3. The Hammet plot between σ *versus* $\log k_{obs}$ (293K) (Figure.8) shows a dispersed gram.
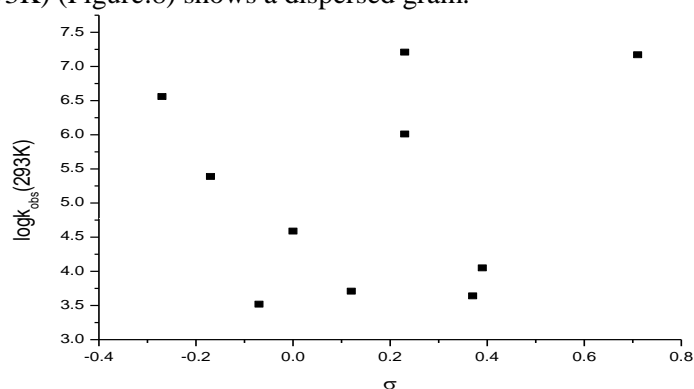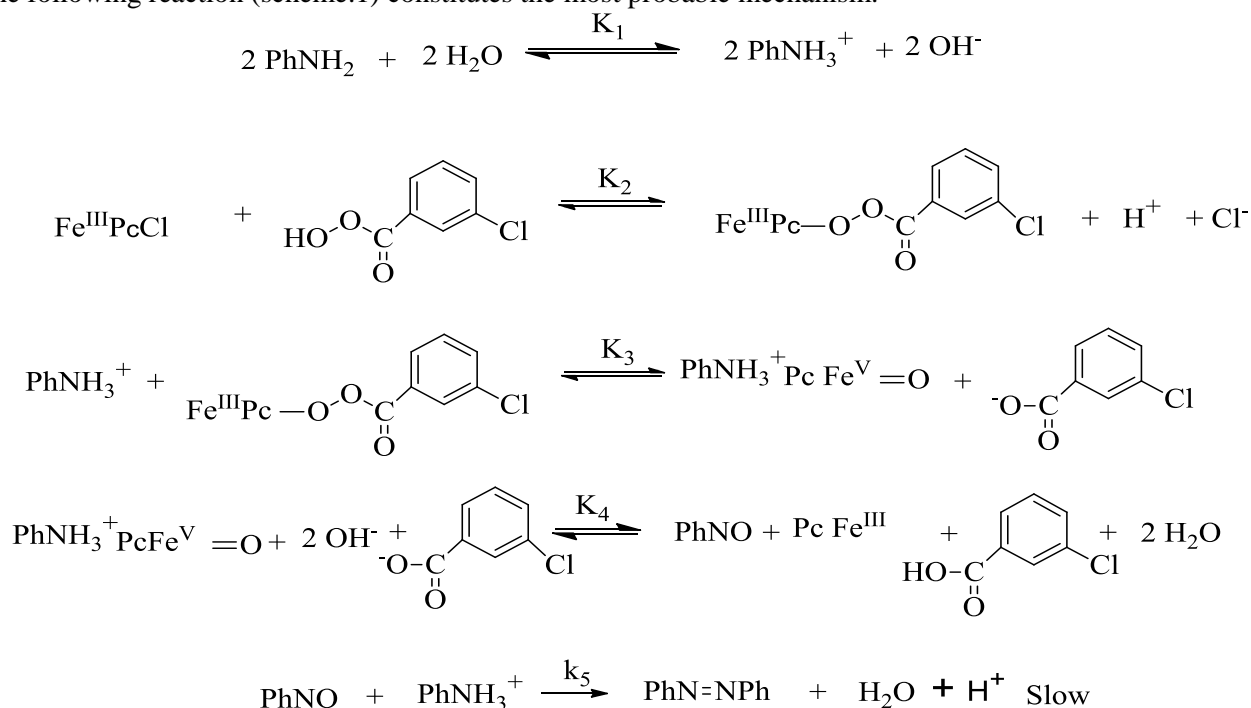

Figure.8. Hammet plot for the Iron(III) phthalocyanine chloride catalysed oxidation of anilines by meta-chloroperbenzoic acid

The results in table.4, depicts the correlation study of meta- and para- substituted anilines by correlating with any of the unit and dual substituted parameter equations (Hansch, 1991), and it was also found to be ineffective.

Table.4. Results of simple correlations of rate constants with substituent parameters for the Iron(III) phthalocyanine chloride catalysed oxidation of substituted anilines by meta- chloroperbenzoic acid

Explanatory variable	$100r^2$	N	
meta-substituents only			
σ	23 – 71	6	
$\sigma+$	55 – 89	6	
σ_1, σ_R	31 – 85		6
σ_1, σ_R^-	28 – 67		6
σ_1, σ_R^+	34 – 78		6
F, R	30 – 85		6
para-substituents only			
σ	13 – 48	6	
σ_R^+	16 – 72	6	
σ^-	13 – 47	6	
σ_1, σ_R	79 – 99	6	
σ_1, σ_R^-	80 – 95	6	
σ_1, σ_R^+	78 – 99	6	
F, R	76 – 99	6	
para- and meta-substituents			
σ	34 – 70	12	
$\sigma+$	49 – 71	12	

Mechanism: The present study on the rate of the reaction with respect to oxidant clearly reveals that two aniline molecules are involved in the reaction. Ionic reaction was preferred in this oxidation study due to the absence of free radical mechanism in this reaction. In the proposed mechanism the catalyst combines with the oxidant to form the adduct which then decomposes to evolve the reactive intermediate which is represented in the first step of the mechanism. Literature study (Agarwala, 2005), also confirms the formation of the same catalyst oxidant adduct. It was found that the H^+ released in the rate determining step retards the rate of the reaction. Based on the stoichiometry the following reaction (scheme.1) constitutes the most probable mechanism.

$$2\ PhNH_2 \ + \ 2\ H_2O \ \underset{K_1}{\rightleftharpoons} \ 2\ PhNH_3^+ \ + \ 2\ OH^-$$

Scheme.1. Probable mechanism for the Iron(III) phthalocyanine chloride catalysed oxidation of anilines by meta-chloroperbenzoic acid

The following rate law was deduced based on the above mechanism.

$$\frac{-d\ [oxidising\ agent]}{dt} = \frac{K_1\ K_2\ K_3\ K_4\ K_5\ [substrate]^2\ [oxidising\ agent]\ [catalyst]}{[H^+]^2}$$

4. CONCLUSION

The oxidation of aniline by meta-chloroperbenzoic acid is second order with respect to the aniline, first order with respect to meta-chloroperbenzoic acid. Literature study reveals that there is a degradation of catalyst in the oxidation study of metalloporphyrin (Raja and Karunakaran, 2013). In the present study the plot log[iron(III) phthalocyanine chloride] versus [log K_{obs}] shows a straight line indicating that there is no degradation of iron(III) phthalocyanine chloride even though it resembles the structure of metalloporphyrin. This is due to its higher reactivity and thermal stability of the catalyst. The addition of [H^+] affects the rate of the reaction which represents that the protonated aniline is less reactive in this kinetic study. The kinetic study with respect to solvent confirms that there is a charge development in the intermediate state signifying a polar or ionic mechanism. The validity of isokinetic relationship have been calculated and discussed. The negative value of entropy of activation suggests the formation of complex transition state in the rate determining step. The kinetic and activation parameters for iron(III) phthalocyanine chloride catalysed oxidation of aniline by meta-chloroperbenzoic acid were evaluated and a most probable scheme was presented for the oxidation reaction. The thermodynamic data obtained, supports the mechanism proposed for the oxidation.

REFERENCES

Adalagere Somashekar Manjunatha, Shankarlingaiah Dakshayani, Nirmala Vaz and Puttaswamy, Oxidative conversion of anilines to azobenzenes with alkaline chloramine-T, Korean J. Chem. Eng., 33 (2), 2016, 697-706.

Agarwala A, Bagchi V and Bandyopadhyay D, Iron (III) porphyrin-catalysed oxidation reactions by m-chloro-perbenzoic acid: Nature of reactive intermediates, J. Chem. Sci., 117 (2), 2005, 187-191.

Alexander B Sorokin, Phthalocyanin metal complexes in catalysis, Chem. Rev., 113 (10), 2013, 8152-8191.

Alhaji NMI, Ayyadurai GK and Shajahan A, Kinetics and mechanism of oxidation of aniline by N-bromophthalimide, Chem. Sci. Trans., 2 (2), 2013, 467-472.

Bhuvaneshwari DS and Elango KP, Preferential solvation effects on the kinetics and thermodynamics of oxidation of anilines by chromium(VI), Z. Phys. Chem., 220 (6), 2006, 697-721.

Chapman NB and Shorter J, Advances in linear free energy relationships, Springer, 2005.

Ik-Hwan Um, Eun-Ju Lee and Erwin Buncel, Solvent effect on the α-effect for the reactions of aryl acetates with butane-2, 3-dione monoximate and p-chlorophenoxide in MeCN-H_2O mixtures, J. Org. Chem., 66 (14), 2001, 4859-4864.

Junlong Zhao, Jun qiu, Xiaofeng Gou, Chengwen Hua and Bang Chen, Iron(III) phthalocyanine chloride-catalysed oxidation-aromatization of α, β-unsaturated ketones with hydrazine hydrate: Synthesis of 3,5-disubstituted 1H-pyrazoles, Chin. J. Cat., 37 (4), 2016, 571-578.

Karunakaran C and Kamalam PN, Mechanism and reactivity in perborate oxidation of anilines in acetic acid, J. Chem. Soc., Perkin Trans., 2 (12), 2002, 2011-2018.

Karunakaran C and Palanisamy PN, Kinetics of hexacyanoferrate(III) catalysed perborate oxidation of some para-, meta- and ortho- substituted anilines, Gazzetta Chimica Italina, 127 (10), 1997, 559-565.

Mi-Jeong Kim, Eun-Mi Seo, Doojin Vak and Dong-Yu Kim, Photodynamic properties of azobenzene molecular films with triphenylamines, Chem. Mater, 15 (21), 2003, 4021-4027.

Mirela Filipan-Litvic, Mladen Litvic and Vladimir Vinkovic, A highly efficient biomimetic aromatization of Hantzsch-1,4-dihydropyridines with t-butylhydroperoxide, catalysed by iron(III) phthalocyanine chloride, Bioorganic and Medicinal Chemistry, 16 (20), 2008, 9276-9282.

Nasser Safari and Farzad Bahadoran, Cytochrome P-450 model reactions: a kinetic study of epoxidation of alkenes by iron phthalocyanine, J. Mol. Cat A: Chemical, 171 (1), 2001, 115-121.

Nasser Safari, Shahab-al-din Naghavi S and Hamid Reza Khavasi, Homogeneous m-CPBA-oxidation of anthracene by electron withdrawing metalloporphyrins in different reaction conditions, Applied Catalysis A:General, 285 (1), 2005, 59-64.

Patwari SB, Khansole SV and Vibhute YB, Kinetics and mechanism of oxidation of aniline and substituted anilines by isoquinolinium bromochromate in aqueous acid, J. Iran. Chem. Soc., 6 (2), 2009, 399-404.

Raja M and Karunakaran K, Kinetics and mechanism of meso-Tetraphenyl-porphyriniron (III) chloride catalysed oxidation of aniline and its substituents by oxone in aqueous acetic acid medium, Int. J. Chem. Kin., 45 (9), 2013, 580-587.

Raja M and Karunakaran K, Meso-tetraphenyl ironporphyrin(III) chloride catalysed oxidation of aniline and its substituents by m-chloroperbenzoic acid, J. Chil. Chem. Soc., 57 (4), 2012, 1355-1360.

Raja Manickam and Karunakaran Kulandaivelu, Meso-tetraphenyl porphyriniron(III) chloride catalysed oxidation of aniline and its substituents by magnesium monoperoxyphthalate in aqueous acetic acid medium, Pol. J. Chem. Tech., 14 (4), 2012, 35-41.

Saeid Farhadi, Parisa Zaringhadama A, and Reza Zarei Sahamiehb, Photo-assisted oxidation of anilines and other primary aromatic to azocompounds using Mercury(II) oxide as a photo-oxidant, Acta Chim. Slov, 54 (3), 2007, 647-653.

Samuel B Gingerich and Jennings PW, Mechanism for the m-chloroperbenzoic acid oxidation of trialkyl-substituted furans, J. Org. Chem., 49 (7), 1984, 1284-1286.

Sheik Mansoor S and Syed Shafi S, Oxidation of aniline and some *para*-substituted anilines by benzimidazolium fluorochromate in aqueous acetic acid medium-A kinetic and mechanistic study, Arab. J. Chem, 7, 2014, 171-176.

Shrivastava KBL and Ranveer Singh, Kinetics of oxidation of aniline by chromic acid, Asian J. Chem., 7 (4), 1995, 767-774.

Sigeki Sakaue, Takashi Tsubakino, Yutaka Nishiyama, Yasutaka Ishii, Oxidation of aromatic amines with hydrogen peroxide catalysed by cetylpyridinium heterpolyoxometalates, J. Org. Chem, 58 (14), 1993, 3633-3638.

Toshifumi Dohi, Akinobu Maruyama, Misaki Yoshimura, Koji Morimoto, Hirofumi Tohma and Yasuyuki Kita, Versatile Hypervalent- Iodine(III)-catalysed oxidations with m- chloroperbenzoic acid as a cooxidant, Angewandte Chemie., 117 (38), 2005, 6349-6352.

Ugye TJ, Uzairu A, Idris SO, Kwanashie HO, The effect of dielectric constant on the kinetics of reaction between plasma and formaldehyde in ethanol-water mixtures, Chem. Mat. Res., 3 (9), 2013, 137-147.

Zudin Zhu and James H Espenson, Kinetics and mechanism of oxidation of anilines by hydrogen peroxide as catalysed by methylrhenium trioxide, J. Org. Chem, 60, 1995, 1326-1332.

Zvi Rappoport, The Chemistry of Anilines-Part 1, 1807, Wiley, 2007.