Kinetics and Mechanism of *meso*-Tetraphenylporphyriniron (III) Chloride Catalyzed Oxidation of Aniline and Its Substituents by Oxone in Aqueous Acetic Acid Medium

M. RAJA, K. KARUNAKARAN

Department of Chemistry, Sona College of Technology, Salem 636 005, India

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ABSTRACT: Metalloporphyrins are present naturally in cytochromes and hemoglobins. Perhaps the most interesting feature of heme-enzymes, such as cytochromes P450, is their ability to perform extremely difficult oxidations with high selectivity. The present work is undertaken with the aspiration of designing the mechanistic studies on *meso*-tetraphenylporphyriniron(III) chloride catalyzed oxidation of anilines by potassium peroxymonosulfate (oxone) in aqueous acetic acid medium. The study of oxidation with respect to the catalyst reveals that there is degradation of the catalyst. The concentration-protonated aniline (a less reactive species) increases due to the increase in $[H^+]$, which inhibits the rate of the reaction. The thermodynamic parameters for the oxidation have been determined and discussed. It confirms the Exner relationship and also the activation parameters to the isokinetic relationships. The oxone oxidation with 12 meta- and para-substituted anilines complies with the isokinetic relationship but not with any of the linear free energy relationships. The solvent interaction plays a major role in governing the reactivity. A suitable mechanism is proposed for this reaction. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 580–587, 2013

Correspondence to: M. Raja, e-mail: raja72slm@yahoo.co.in. © 2013 Wiley Periodicals, Inc.

INTRODUCTION

Chemists have paid a great deal of attention to modeling of cytochrome P450 monooxygenase using synthetic metalloporphyrins, as they have a striking resemblance to heme, in both structures and catalytic properties. The potential of the heme group is to combine with tiny ligands (including molecular oxygen) in enzymatic oxidations. The contribution of heme in these oxidation processes has led chemists to study these naturally occurring catalysts for use in industrial processes. To study the core of the heme group, the porphyrin ring with the central metal iron atom has been selected. Metalloporphyrin iron complexes have been the subject in a number of studies, as they can be added as catalysts in selective oxidation of aniline. Many mechanistic studies [1-9] have revealed that halogenated metalloporphyrin complexes are excellent catalysts for difficult oxidations with high selectivity. The iron complexes with *meso*-tetraphenyl groups are extensively considered as models of the natural ironporphyrins due to their constructive properties, such as, catalytic and semiconducting properties. Iron complexes of tetraphenylporphyrins, which can be regarded as macrocyclic ligands, have 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 oxone catalyzed by a first-generation catalyst mesotetraphenylporphyriniron(III) chloride (5,10,15,20tetraphenyl-21H,23H-porphineiron(III) chloride) was selected for the study. Kinetics of oxidation of anilines by a variety of oxidants has been reported [10-14], and a few of them authenticate the Hammett equation.

EXPERIMENTAL

The catalyst *meso*-tetraphenylporphyriniron(III) chloride (Sigma Aldrich, St. Louis, MO) was used as received. All chemicals and solvents used were of analytical grade (Merck, Bangalore, India). Aniline was redistilled before use. Acetic acid was purified by redistillation. All the reagents were prepared just before the reactions were carried out. The aqueous solution of oxone was prepared fresh and standardized iodometrically. Kinetic studies were made with aniline by varying the concentration of aniline, oxone, *meso*tetraphenylporphyriniron(III) chloride, acetic acid, and H⁺ and by varying temperature. All the reactions were carried out in a thermostat, and the temperature was controlled to $\pm 0.1^{\circ}$ C. The reaction rate was calculated by estimating the amount of unconsumed oxone iodometrically up to 80% of the completion of the reaction. The rate constants (k_{obs}) were determined by the least square slopes of the linear plots of log [oxone] and time. Replicate runs showed that the rate constants for oxidation reactions were reproducible within $\pm 3\%$. The reaction was also carried out using acrylonitrile to find the presence of a free radical mechanism. Meta- and parasubstituents of aniline were redistilled/recrystallized before use. The oxidation reactions of meta- and parasubstituents of aniline were studied at different temperatures at 293, 303, 313, and 323 K to evaluate various thermodynamic parameters.

From the Eyring equation [10], the thermodynamic parameters, enthalpy of activation, and entropy of activation were determined from the following expression:

$$k_{\rm obs} = (k_{\rm b}T/h) \exp^{-\Delta G^{\#}/RT}$$

where $k_{\rm b}$ 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 $E_a = \Delta H^{\#} + RT$

Various thermodynamic parameters were found and recorded.

Stoichiometry and Product Analysis

The stoichiometry of the reaction was found by doing several sets of experiments by varying [oxone] in the range of 0.1–1.5 M ([substrate] = 0.1 M, [catalyst] = 1.4×10^{-6} M, acetic acid:water = 50:50, [H⁺] = 0.2 N, and temperature = 303 K). The estimation of unconsumed oxone acid showed that the stoichiometry of the reaction was found to be in the ratio of 1:2 (oxone:aniline). The oxidation product was confirmed using thin layer chromatography. Under the pseudo–first-order condition [aniline] \gg [oxone] in acetic acid medium, the product obtained was followed spectrophotometrically at 429 nm, which is the λ_{max} of azobenzene. This was in agreement with the literature value [15].



Figure 1 Plot of log k_{obs} versus log [aniline] for the oxidation of aniline by oxone catalyzed by *meso*tetraphenylporphyriniron(III) chloride. [Oxidant] = 5 × 10^{-3} M, [catalyst] = 1 × 10^{-6} M, acetic acid:water = 50:50, [H⁺] = 0.2 N, temperature = 303 K.

RESULTS AND DISCUSSION

Effect of Variation of the Substrate Concentration

At the constant concentration of oxone and H_2SO_4 , an increase in the concentration of the substrate (aniline) increases the reaction rate. The plot of log k_{obs} versus log [aniline] (Fig. 1) was found to be linear with slope 2, representing the second-order dependence of the reaction rate on the substrate.

Effect of Variation of the Oxone Concentration

The first-order dependence of the reaction on oxone is obvious from the linearity of the plots of log [oxone] versus time. Furthermore, the pseudo-first-order-rate

Table IPseudo-First-Order Rate Constants for theOxidation of Aniline by Varying [Oxone] Catalyzed byMeso-Tetraphenylporphyriniron(III) Chloride

[Oxidant] (10 ³ M)	$k_{\rm obs} \; (\times 10^4 \; {\rm s}^{-1})$		
6	59		
7	58		
8	59		
9	57		
10	60		

[Substrate] = 0.1 M, [catalyst] = 1×10^{-6} M, acetic acid: water = 50:50, [H⁺] = 0.2 N, temperature = 303 K.



Figure 2 Plot of log k_{obs} versus log [H⁺] for the oxidation of aniline by oxone catalyzed by *meso*-tetraphenylporphyriniron(III) chloride. [Substrate] = 0.1 M, [oxidant] = 5 × 10⁻³ M, [catalyst] = 1 × 10⁻⁶ M, acetic acid:water = 50:50, temperature = 303 K.

constants, k_{obs} , do not depend on the initial concentration of oxone [11] (Table I).

Effect of Variation of the H⁺ Concentration

The increase in the hydrogen-ion concentration decreases the rate of the reaction. The plot of log k_{obs} versus log [H⁺] (Fig. 2) gave a straight line with a negative slope. Aniline, in acid medium, exists in dual forms: the free bases and conjugate acids [16] [protonated (C₆H₅NH₃⁺) and nonprotonated (C₆H₅NH₂) aniline]. The literature study [16] reveals that (an increase in [H⁺] increases the reaction rate) protonated aniline is more reactive in 3-butyn-2-one. But in the present study, an increase in [H⁺] leads to the increase in protonated aniline, which inhibits the reaction rate. This reveals that protonated aniline is less reactive in this oxidation reaction.

Effect of Variation in the Catalyst Concentration

The oxidation of aniline by oxone in acetic acid is very slow, but when catalyzed by *meso*-tetraphenylporphyriniron(III) chloride the reaction rate increases at a remarkable rate. The increase in the concentration of the catalyst enhances the rate of the reaction. But the plot of log k_{obs} versus log [catalyst] (Fig. 3) was not found to be linear. The slight curvature that was obtained shows that there is a hindrance in the catalytic activity. The literature study [17] revealed that the initial ironporphyrin chloride in the oxidation reaction subsequently decayed and a degree of bleaching



Figure 3 Plot of log k_{obs} versus log [*meso*-tetraphenylporphyriniron(III) chloride] for the oxidation of aniline by oxone catalyzed by *meso*-tetraphenylporphyriniron(III) chloride. [Substrate] = 0.1 M, [oxidant] = 5×10^{-3} M, acetic acid:water = 50:50, [H⁺] = 0.2 N, temperature = 303 K, [*meso*-tetraphenylporphyriniron(III) chloride] = (1-10) × 10^{-6} M.

(the degradation of the catalyst at 412 nm) takes place even with a highly halogenated metalloporphyrin. This shows that the variation in catalytic activity in this oxidation reaction may be due to the degradation of the catalyst. So the study was focused toward lower concentration of the catalyst. The plot of log k_{obs} versus log [catalyst] was found to be linear (Fig. 4).



Figure 4 Plot of log k_{obs} versus log [*meso*-tetraphenylporphyriniron(III) chloride] for the oxidation of aniline by oxone catalyzed by *meso*-tetraphenylporphyriniron(III) chloride. [Substrate] = 0.1 M, [oxidant] = 5×10^{-3} M, acetic acid:water = 50:50, [H⁺] = 0.2 N, temperature = 303 K, [*meso*-tetraphenylporphyriniron(III) chloride] = (1-10) × 10^{-7}) M.



Figure 5 Plot of ln k_{obs}/T versus 1/T for the oxidation of aniline by oxone catalyzed by *meso*-tetraphenylporphyriniron(III) chloride. [Substrate] = 0.1 M, [oxidant] = 5 × 10⁻³ M, [catalyst] = 1 × 10⁻⁶, acetic acid:water = 50:50, [H⁺] = 0.2 N.

Effect of Variation in Temperature

The oxidation of aniline was studied at different temperatures (293–343 K), maintaining the concentration of substrate, oxidant, H⁺, solvent, and catalyst constant. The plot of ln k_{obs}/T versus 1/T (Fig. 5) was found to be linear. The thermodynamic parameter $\Delta H^{\#}$ was found to be 49.54 kJ mol⁻¹, $\Delta S^{\#} = -165.66$ J K⁻¹ mol⁻¹, $\Delta G^{\#} = 99.24$ kJ mol⁻¹, and $E_a = 52.03$ kJ mol⁻¹ K⁻¹. The negative values of entropy of activation reveal that the intermediate state is more stable than the initial state.

Effect of the Dielectric Constant

To focus on the result of the dielectric constant (polarity) of the medium, the oxidation was carried out by maintaining the concentration of aniline, oxone, catalyst, and temperature as the constant and varying the aqueous acetic acid mixtures of various compositions (Table II).

The above results clearly reveal that the rate increases with a decrease in the percentage of acetic acid, that is, with increasing dielectric constant (*D*) or polarity of the medium. This directs us to the conclusion that there is a charge development in the intermediate state, involving a more polar activated complex than the reactants, a neutral molecule (aniline), and a more negative ion (HSO₅⁻), suggesting a polar (ionic) mechanism. Figure 6 shows the UV spectrum at early stages of the oxidation reaction. At a visible range (717 nm), a new peak appeared and then slowly disappeared at the later stages of the reaction. This may be due to the formation

Table IIPseudo-First-Order Rate Constants for theOxidation of Aniline by Oxone Catalyzed byMeso-Tetraphenylporphyriniron(III) Chloride in DifferentAcetic Acid Compositions

Acetic Acid (%)	D	$k_{obs} (\times 10^4 \text{ s}^{-1})$
70	27.90	30
60	35.14	33
50	42.37	43
40	49.60	51
30	56.83	78

 $[Substrate] = 0.1 \text{ M}, [oxidant] = 5 \times 10^{-3} \text{ M}, [catalyst] = 1 \times 10^{-6} \text{ M}, [H^+] = 0.2 \text{ N}, \text{temperature} = 303 \text{ K}.$

of a charged intermediate from which products were formed.

Substituents Effect

The kinetics and oxidation of aniline and *p*-OCH₃, *p*-CH₃, *p*-Cl, *p*-Br, *p*-NO₂, *p*-F, *m*-OCH₃, *m*-CH₃, *m*-Cl, *m*-Br, *m*-NO₂, *m*-F anilines in the presence of catalyst were conducted under pseudo–first-order conditions at various temperatures to determine various thermodynamic parameters. The various thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$, and E_a were determined and are presented in Table III. The analysis of the data given in the Table III indicates that the oxidation is neither isoenthalphic nor isoentropic, but it conforms with the isokinetic relationship of the 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 of nearly the same order of the magnitude. But owing to the variation in the polarity of different anilines, $\Delta S^{\#}$ may be different for different anilines [11], as observed in the present study; but the isokinetic relationship exists. The plot of activation enthalpy versus activation entropy follows a straight line as shown in Fig. 7.

The isokinetic temperature is the temperature at which all the compounds of the series react equally fast [11] and was determined from the following equation:

$$\Delta H^{\#} = \Delta H^{\rm o} + \beta \Delta S^{\#}$$

where β is the isokinetic temperature and it was found to be 346 K, which is greater than the experimental temperature. The function of the isokinetic relationship and Exner relationship (Fig. 8) reveals that a common mechanism is applicable in all the aniline oxidation reactions. The values of free energy of activation of the reactions were found to be more or less similar.

Structure–Reactivity Correlation

Table III reveals that the $\Delta G^{\#}$ values vary with the substrate. This may be due to the dissimilarity in the polarity of various anilines. The pKa of the anilines changes with the substituents (1.59 for the *p*-cyano to 6.08 for the *p*-amino). So the concentration of protonated and deprotonated species varies with respect to



Figure 6 UV spectrum showing a probable formation of intermediate in the oxidation of aniline by oxone catalyzed by *meso*-tetraphenylporphyriniron(III) chloride.

Aniline Substituent	$k_{\rm obs} \; (\times 10^4 \; {\rm s}^{-1})$							
	293 K	303 K	313 K	323 K	$\Delta H^{\#}$ (kJ mol ⁻¹)	$-\Delta S^{\#}$ (J K ⁻¹ mol ⁻¹)	$\Delta G^{\#}$ (kJ mol ⁻¹)	$ E_a (kJ mol^{-1}) K^{-1}) $
Н	23	35	76	153	50	166	100	31
<i>m</i> -Cl	40	64	100	125	29	233	99	47
<i>m</i> -Br	31	65	116	337	58	134	98	60
<i>m</i> -F	38	71	116	207	41	189	98	44
<i>m</i> -CH ₃	30	37	55	69	21	262	100	23
<i>m</i> -OCH ₃	45	85	153	191	37	203	98	39
<i>m</i> -NO ₂	120	243	491	1290	59	119	95	62
p-Cl	20	40	76	115	44	183	99	47
<i>p</i> -Br	42	94	206	401	57	135	98	59
<i>p</i> -F	24	37	55	85	31	228	99	33
p-CH ₃	15	43	76	153	56	144	100	59
p-OCH ₃	46	85	180	364	52	151	98	54
<i>p</i> -NO ₂	2100	Fast	Fast	Fast	-	-	-	_

 Table III
 Pseudo–First-Order Rate Constants for Meso-Tetraphenylporphyriniron(III) Chloride Catalyzed Oxone

 Oxidation of Para-and Meta- Substituted Anilines at Different Temperatures and Thermodynamic and Activation

 Parameters

 $[Substrate] = 0.1 \text{ M}, [oxidant] = 5 \times 10^{-3} \text{ M}, [catalyst] = 1 \times 10^{-6} \text{ M}, acetic acid:water = 50:50, [H^+] = 0.2 \text{ N}.$



Figure 7 Isokinetic plot for the *meso*-tetraphenylporphyriniron(III) chloride catalyzed oxidation of anilines by oxone.



Figure 8 Exner plot for the *meso*-tetraphenylporphyriniron(III) chloride catalyzed oxidation of anilines by oxone.

substituents. This strongly affects the reaction rate. So the obtained rate constants show deviation with substituents.

The rate data obtained were also unsuccessful in proving that the typical Hammett equation log k_{obs} versus σ is in a dispersed form; therefore a sensitive plot (Fig. 9) at the temperatures was studied. The literature study [18] reveals that the correlation obtained with it was poor as the substituents were conjugated with the reaction center, where the problem arose with anilinium ions, where a lone pair of electrons on the

 NH_2 group could be delocalized into substituents such as p-NO₂.

The correlation of oxidation rates of meta- and parasubstituted anilines with any of the unit parameters (para: σ , σ_p^+ , σ_p^- ; meta: σ , σ_m^+) was also found to be ineffective (Table IV).

The less pronounced substituents can be explained only by the compensation effect. Aniline in basic and neutral medium is present as free bases, but in acid medium it exists in dual forms, the free bases and conjugate acids [19]. The stoichiometry of the reaction



Figure 9 Hammett plot for the meso-tetraphenylporphyriniron(III) chloride catalyzed oxidation of anilines by oxone.

Table IV Results of Simple Correlations of Rate Constants with Substituent Parameters for the Meso-Tetraphenylporphyriniron(III) Chloride Catalyzed Oxidation of Substituted Anilines by Oxone

Explanatory Variable	$100r^{2}$	n			
Para- and meta-substituents					
σ	64-71	10			
σ^+	35-46	10			
$\sigma_{\rm p}^{-}$ and $\sigma_{\rm m}$	62-65	10			
Para-sub	stituents only				
σ	5-39	4			
σ^+	12-23	4			
σ^{-}	1-42	4			
Meta-sul	ostituents only				
σ	78-86	5			
σ^+	45-70	5			

shows that two aniline molecules were involved in the reaction. In the literature study [20], also the oxidation involves two aniline molecules in the rate-determining step. This shows that the catalyst-aniline complex is likely to be the electrophile and free aniline may be the nucleophile. In some of the substituted aniline, exact compensation is doubtful and the resultant effect is decided on the oxidation rate.

MECHANISM

The addition of the acrylonitrile monomer showed no variation in the reaction rate and no formation of turbidity (no formation of polymer) in the oxidation of aniline. This ruled out the presence of the free radical mechanism in this oxidation reaction. So the ionic reaction was preferred in this oxidation study. Generally, the enhancement of the electrophilic activity of peroxide will minimize the importance of undesirable free radical pathways, resulting in a mixture of products [21]. The literature study [21] reveals that at higher pH the peroxomonosulfate exists as a dianion (-O-O- O^{-}) and at lower pH the oxidant exists as HSO_5^{-} ions. In the present study, the reaction was carried out at lower pH and the oxidant existed as HSO₅⁻ ions. Usually peroxy ions act as strong nucleophiles, but HSO_5^{-} is a weak nucleophile. The absorption spectra show spectral changes, supporting the complex formation. The investigation illustrates a fascinating result that an increase in H⁺ retards the rate of the reaction. With the decrease in pH the molecule gains a proton, becomes less negatively charged, and hence the rate of the reaction decreases [22]:

$$\mathrm{HSO}_5^- \stackrel{\scriptscriptstyle\leftarrow}{\to} \mathrm{SO}_5^{2-} + \mathrm{H}^+$$

Por Fe^{III}Cl +
$$\overset{K}{\overset{OH}{O}}_{O} \overset{OH}{\overset{H}{\longrightarrow}}_{O} \overset{K_{1}}{\overset{H}{\longrightarrow}}$$
 Por Fe^{III} $\overset{OH}{\overset{O}{\longrightarrow}}_{O} \overset{OH}{\overset{H}{\longrightarrow}}$ + KCl

PhNH₂ + Por Fe^{III} O-O-S=O
$$\underbrace{K_2}_{O}$$
 PhNH₂PorFe^V=O + HSO₄⁻

$$PhNH_2 + HSO_4 + PhNH_2PorFe^{V} \longrightarrow PhNO + PhNH_2PorFe^{III} + H_2SO_4 + H^+$$
 Slow

$$PhNO + PhNH_2$$

 $PhN=NPh + H_2O$

Fast



The species HSO_5^- is more reactive than the SO_5^{2-} species. The high reactivity of HSO_5^- is consistent with both an electrostatic effect and the weakening of the peroxide bond by the proton [23].

Based on the stoichiometry of the reaction and above experimental results, the reactions presented in Scheme 1 are believed to constitute the most probable mechanism of the reaction.

The formation of Por-Fe^v=O is in agreement with the literature study [6,24], and the intermediate formed was experimentally confirmed at 717 nm. The third step (formation of aniline oxide) was a slow reaction and is likely to be the rate-determining step. Based on the above mechanism, the rate law was derived:

 $\frac{-d[\text{oxidizing agent}]}{dt}$ $= k_3 k_2 k_1 [\text{substrate}]^2 [\text{oxidizing agent}] [\text{catalyst}]$

CONCLUSIONS

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⁺ retards the rate of the reaction and reveals that protonated aniline is the less reactive species in this reaction. A correlation of the experimental data of the solvent reveals that the solvent interaction plays a major role in the reactivity. The formation of a charged intermediate compound was supported by the highly negative values of entropy of activation, and the most probable mechanism has been proposed for the mesotetraphenylporphyriniron(III) chloride catalyzed oxidation of anilines by potassium peroxymonosulfate. The validity of the isokinetic relationship and thermodynamic relationships has been tested and discussed. With oxone as the oxygen donor, the first-generation catalyst ironporphyrin is proved to be a more effective catalyst in oxidizing aniline.

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