OXIDATION OF AROMATIC ANIL BY PYRAZINIUM CHLOROCHROMATE

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Abstract:Oxidation of aromatic anil by pyrazinium chlorochromate [PzCC] in water and acetic acid medium has been studied under pseudo first order condition. The reaction shows unit order dependence each with respect to oxidant. The reaction with respect to substrate and hydrogen ion concentration are found to be fractional order. The reaction rate decreases with increasing the concentration of Mn^{2+} ions. The reaction does not induce the polymerization of acrylonitrile. A possible mechanism has been proposed in the formation of benzaldehyde and azobenzene.

Index terms- **Oxidation, aromatic anil , pyrazinium chlorochromate, Kinetics.**

1 INTRODUCTION

Among oxo derivatives of variable valence metals , Chromium compound play the most important role , in oxidative reaction .A number of Chromium reagents are readily available . Almost every oxidizable functional group may undergo Chromium oxidation. .Chromium (VI) containing reagents include Chromium acid , dichromate ion , Chromyl chloride , chromyl acetate , t – butyl Chromate , Chromyl nitrate and Co – ordination complexes of Chromium trioxide .Chromium (VI) oxidations are usually performed under acidic condition . Co – solvents like (Jone's reagent) benzene, methylenechloride (Two Phase system) are often added in order to deal with water insoluble organic complexes .These reagents offer the advantage of reducing the work of procedure to more filtration . Recently some neutral or almost neutral Chromium (VI) reagents have been developed to effect oxidation under mild condition.

1.1 CHEMICAL REACTIONS OF ANILS

The commonest type of reaction between a primary amine and an aldehydes[1] results in the formation of an azomethine. R-CHO + H_2 N-R' -------> R-CH=NR' + H_2O

It had been observed in the case of aniline and benzaldehyde as early as 1850 by Laurent and Gerhardt. Later, Schiff found that many aromatic and aliphatic aldehydes condensed with aniline in a similar way. The formation of Schiff s bases or azomethines succeeds best with aromatic aldehydes and primary aromatic amines for the products show comparatively little tendency to polymerise. As many of them are crystalline they are frequently used for the characterization of aldehydes and primary amines. The Schiff base form stable iminium salts with protic acids such as perchloric acid. Reduction of aliphatic aldimines by sodium and alcohol had been reported to yield the secondary amine.[2] With bromine the product of reactions of benzylidene aniline is formulated as N-bromoiminium bromide [Ph-CH=N (Br) Ph (Br)] in carbon tetrachloride.

By analogy with the carbonyl carbon-oxygen double bond, the carbon-nitrogen double bond may be considered as a resonance hybrid of the canonical forms,

-C=N- → -C-N- This dipolar nature of bond explains the attack of electrophile predominantly at the nitrogen atom in these compounds and the nucleophiles at the carbon atom.

Moreover, iminium salts in accordance with the resonance shown below exhibit enhanced reactivity towards nucleophilic attack.

-C=N- → - C-N-

Iminium salts are very quickly hydrolyzed by water. This salt hydrolysis has been used in a synthesis of secondary amines from primary amines, which involves the conversion into aldimine and then alkylation into the iminium salt followed by hydrolysis to give secondary amine.[3] In oxidation reactions, the carbon-nitrogen double bond in the Schiff base is attacked by a large number of oxidizing agents ranging in character from mono, diperoxy acids, and ozone to typical metal-based oxidants like mercuric oxide and lead tetra acetate. In synthetic organic chemistry Schiff bases oxidation is a very useful one in providing routes to inaccessible products. Schiff bases with a-alkyl substituents containing at least one free a-hydrogen atom exhibit special features in their reactivity towards organometallic and related reagents as a consequence of the opportunity for a-hydrogen abstraction.

1.2 OXIDATION KINETICS OF ANILS

Rindone and Scolastico[4] have been reported the oxidation of aromatic anils with lead tetraacetate (LTA) in benzene. The results of four substrates indicated a reaction mechanism occurring via the formation of a nitrene. They reported that the LTA oxidation of benzaldehyde anil yielded azobenzene, benzaldehyde and a small amount of aniline.[5] With p-methoxy benzaldehyde anil, it gave again the same products but the reaction was very fast whereas p-nitro benzaldehyde anil did not react under the same conditions. When anil compounds contain labile *ortho-suhstituenis* such as NH_2 or OH in the N-aryl ring, oxidative cyclisation to benzimidazole and benzoxazole occurred. [6] The kinetics of oxidation of aromatic anils by phenyliodosoacetate in methylene chloride has been studied by Venkatasubramanian *et al***.** [7] Oxidation of aromatic anils by acid bromated[8] in H_2SO_4 - AcOH mixture is enhanced by electron withdrawing substituent both in benzaldehyde as well as in aniline moieties. The q (which is known as the cross interaction constant) calculation showed that it is a constant for all the substituents studied indicating that IFER for MSE are applicable for the oxidation of aromatic anils by acid bromate also. Ru(III) catalyzed oxidation of benzaldehyde anils by chloramine-T in acid medium has been studied by Gopalakrishnan *et al.[9]* The kinetics of pemanganate (Mno_4) oxidation of some substituted aromatic anils, with substituent in the aniline moiety has been studied in melthylene chloride by Gopalakrishnan and Mohankumar.[10] Gurumurthy *et al [11]* has been studied the kinetics of oxidation of aromatic anil by pyridinium chlorochromate (PCC) in 70% aqueous acetic acid. The kinetics of oxidation of the Schiff bases, 2-hydroxy-l-naphthalidene anil by Ce(IV) in aqueous H_2SO_4 acid medium has been studied by Ramesh *et al[12]* Umesh *et al [13]* investigated the oxidation mechanism of kinetics of Schiff bases, 2-hydroxyl-l-

naphthalidene anils by potassium bromate in aqueous acetic acid. The kinetics of oxidation of a number of *meta*- and para-substituted aromatic anils with quinolinium chlorochromate, was studied by Karthikeyan *et al [14]* Karunakaran *et al [15]* reported interactive free energy relationship on the oxidation of aromatic anils by phenyliodosoacetate (PIA). The results were analysed in terms of an interactive free-energy relationship. Basheer Ahamed has investigated the oxidation of aromatic anils by N-Chlorobenzamide in aqueous methanol medium. [16]Ramalingam [17] studied the oxidation kinetics of anils by PFC in presence of oxalic acid in aqueous acetic acid medium. The kinetics and mechanism of oxidation of some substituted anils by quinolinium fluorochromate in 60% acetic acid in the presence of oxalic acid have been studied by Jayanthi *et al[18]*

V.Krishnasamy *et al [19] studied the* kinetic study of simple and substituted anils ware studied under various conditions viz., solvent ,oxidants , electrolyte , catalysts and mixture of catalysts and temperature; simple and substituted anils , pyridinium Chloro Chromate (PCC) ,Pyridinium Dichromate (PDC) were prepared in the laboratory and kinetic study were carried out.

The kinetics of oxidation of aromatic anil by pyrazinium chlorochromate has not been reported. We report here in the kinetics of the oxidation of aromatic anil by pyrazinium chlorochromate and he mechanistic aspects are also discussed.

2. EXPERIMENTAL METHODS

2.1 Preparation of Pyrazinium chlorochromate[20]

Pyrazinium chlorochromate was prepared by the addition of pyrazine (0.7g) in aqueous HCl (0.8ml MCI in 16ml H_2O) to a cooled solution of chromium trioxide (0.9g chromium trioxide in 0.8ml HCl of 8ml H_2O). The solution was stirred at 0°C with 20min. After stirring, a bright-orange crystal was formed and it's collected in a sintered crucible. Then, it was recrystallized with minimum amount of acidified water and dried for one hour in vacuum (yield 80%).The solid was not appreciably hygroscopic and can be stored for extended periods at room temperature without change. The pyrazinium chlorochromate formed was confirmed with its physical constant (m.p. 148-150°C) and further analyzed through IR and UV spectrum.

2.2 Preparation of aromatic anil

The aromatic anil was prepared[21,22] by refluxing-equimolar quantities of benzaldehyde and aniline in alcohol for about 2 to 3 h. The resulting solution was cooled and poured in to cold water. The precipitated anil was filtered, washed dried and recrystallized from alcohol. The purity of the anils was checked by determining their melting points.

2.3.Purification of Acetic acid

Acetic acid of AR grade was first refluxed with chromium trioxide (20g per litre) for 4hrs. and then distilled . It was refluxed again with Chromium trioxide again with chromium trioxide (2g per litre) for 2 hrs. Then it was fractionated through a Dufton column and the fraction at 117 – 118 0 was collected.[23]

2.4.Purification of water

De – ionized water was distilled over Potassium Permanganate in an all glass corning vassel . All the aqueous solutions were prepared using this double – distilled water .

2.5 Kinetic measurements

The reactions were carried out in 60% aqueous acetic acid-water (v/v). The following solutions of the desired concentrations were prepared and used.

1. Anil in acetic acid
2. PzCC in double distilled water
3. Other reagents in double distilled water

The reactions were carried out under pseudo-first order conditions at 313 *K* . All the solutions were thermostated atleast one hour before use .The progress of the reaction was monitored by withdrawing aliquots from the reaction mixture at regular intervals of time and estimating the unreacted PzCC by iodometric method.

2.6 Stoichiometry

A number of reaction mixtures containing excess of PzCC atleast twice the concentration of anil in the presence of perchloric acid were kept at room temperature for sufficient length of time. The estimation of unreacted PzCC showed that one mol of PzCC consumed three moles of substrate.

2.7 Product analysis

To the substrate (0.3 mol) in acetic acid, PzCC (0.1 mol) was added and the medium was maintained acidic using perchloric acid. After slight warming the reaction mixture was maintained at room temperature for two days. Then the reaction mixture was extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was separated and then evaporated on a hot water bath to get the solid product. The products of oxidation were identified as the corresponding benzaldehyde and azobenzene . benzaldehyde was characterized as the 2, 4 – dinitropheynyl hydrozone derivative . The remaining solution on evaporation yielded azobenzene , these products were identified by characteristics of IR, H^1, C^{13} and mass spectrum.

3. RESULTS AND DISCUSSIONS

Kinetics and mechanism of oxidation of anil by Pyrazinium chlorochromate

The kinetics of oxidation of anil by Pyrazinium chlorochromate (PzCC) in the presence of aqueous acetic acid was studied at 313K. The results are summarized in the following pages.

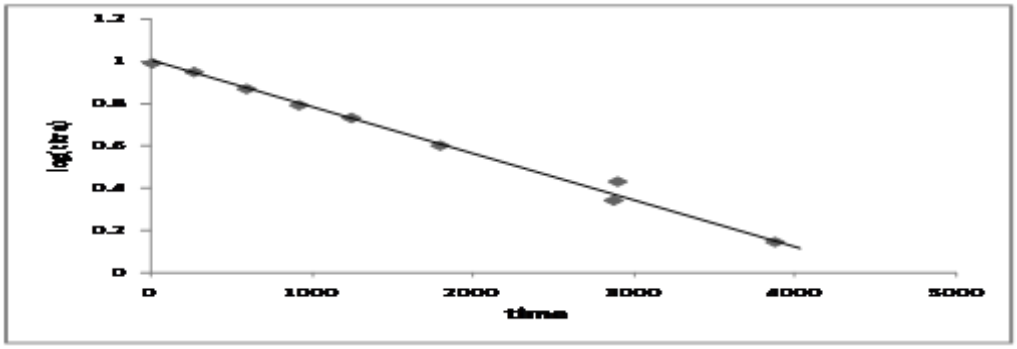
3.1. Effect of varying the [oxidant]

The reaction was investigated with varying concentration of PzCC, keeping the concentration of aniline always in excess and perchloric acid constant. The reaction was found to be first order with respect to the oxidant [PzCC] as evidence by the linear plot of log (titre) versus time (Figure. 1). This was further confirmed by the constancy of the pseudo-first order rate constants determined at various initial concentration of the oxidant (Table – 1).

Table - 1 : Effect of Varying oxidant concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Substrate] = 3.00 x 10^{-2} *mol dm* $^{-3}$ Solvent = 60 % acetic acid-water (v/v)
[H^+] =1.50 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*

[Oxidant] x 10^3 ***mol*** dm^{-3}	**k_1 x 10^4** s^{-1}
0.50	4.02
1.00	4.03
1.50	4.04
2.00	4.06
2.50	5.08



3.2. Effect of varying the [Substrate]

At constant concentration of oxidant and H^+, the reaction was carried out varying the concentration of the substrate. The pseudo-first order rate constants increase with increase in the concentration of substrate and the plot of logk_1 *versus* [substrate] gave a straight line with a slope of 0.25 (Figure. 2) showing a fractional order dependence on substrate (Table – 2). It was also verified by Michaelis- Menten plot[24,25] (Figure . 3).

Table - 2 Effect of substrate concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol* dm^{-3} Solvent = 60 % acetic acid-water (v/v)
[H^+] = 1.50 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*

[Substrate] x 10^2 ***mol*** dm^{-3}	**k_1 x 10^4** s^{-1}
1.50	3.45
2.25	3.70
3.00	4.04
3.75	4.28
4.50	4.54

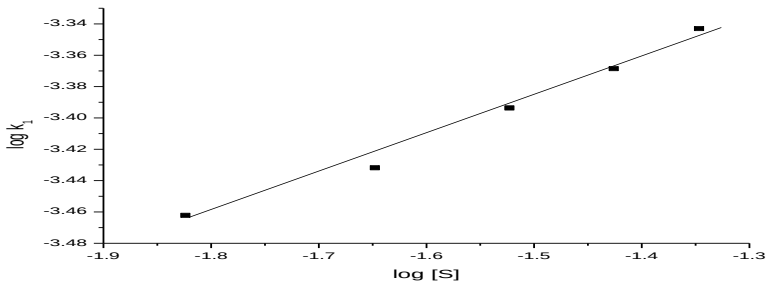


Figure .2 Plot of log k_1 *versus* log [S]

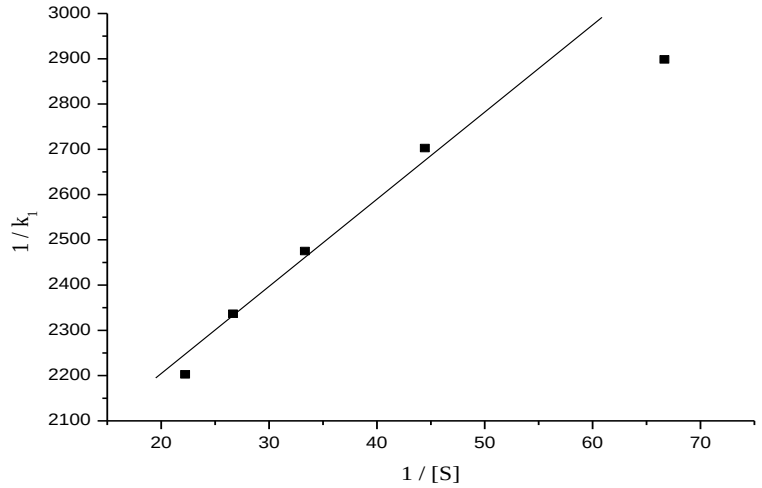


Figure.3 Plot of 1 / k_1 *versus* 1 / [S]

3. 3. Effect of varying the hydrogen ion concentration

To know the effect of change in acidity on the rate of the reaction the rates were measured at different perchloric acid concentration at constant [substrate], [oxidant] and temperature. The rate constants increase with increase in the concentration of perchloric acid (Table – 3). The plot of log k versus log [H^+] gave a straight line with a slope of 0.12 indicating fractional order dependence of [H^+] (Figure. 4).

Table - 3 Effect of Hydrogen ion concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol* dm^{-3} Solvent = 60 % acetic acid-water (v/v)

[Substrate] = 3.00 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*

[H^+] x 10^2 ***mol*** dm^{-3}	**k_1 x 10^4** s^{-1}
0.75	3.77
1.50	4.04
2.25	4.28
3.00	4.51
3.75	4.73

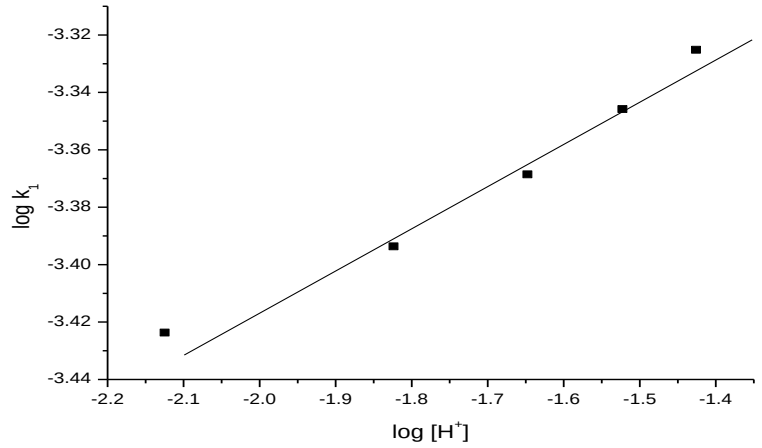


Figure.4 Plot of log k_1 *versus* log [H^+]

3.4. Effect of varying the ionic strength

The effect of ionic strength on the reaction rate was studied with varying concentrations of sodium perchlorate keeping all other factors constant. The results indicated that ionic strength has no appreciable effect on the reaction rate (Table – .4). It indicated the absence of ion- ion (or) ion- dipole interaction in the slow step [26] which confirmed by the participation of an ion and neutral molecule in the rate controlling step.

Table - 4 Effect of varying ionic strength of the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol* dm^{-3} Solvent = 60 % acetic acid-water (v/v)
[Substrate] = 3.00 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*
$[H^+]$ =1.50 x 10^{-2} *mol* dm^{-3}

$[NaClO_4]$ x 10^3 *mol* dm^{-3}	k_1 x 10^4 s^{-1}
0.00	4.04
0.50	4.07
1.00	4.18
1.50	4.09
2.00	4.07

3. 5. Effect of varying the solvent composition

The reactions were carried out at five different percentages of acetic acid- water mixtures and keeping the other factors constant (Table – 5). It was observed that an increase in the percentage of acetic acid considerably increased the rate of the reaction. This suggests the involvement of an ion-dipole interaction in the rate determining step[27].

Table - 5 Effect of varying solvent composition of the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol* dm^{-3} Solvent = 60 % acetic acid-water (v/v)
[Substrate] = 3.00 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*
$[H^+]$ = 1.50 x 10^{-2} *mol* dm^{-3}

% acetic acid-water (v/v)	k_1 x 10^4 s^{-1}
40	2.29
50	3.06
60	4.04
70	4.47
80	4.91

3.6. Effect of varying the [acrylonitrile]

The reaction was studied with varying concentration of acrylonitrile, keeping all the other factors constant. The addition of acrylonitrile shows no significant effect on the reaction rate indicating the non-involvement of free radical pathway in the rate-limiting step (Table – 6).

Table - 6 Effect of varying acrylonitrile concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol* dm^{-3} Solvent = 60 % acetic acid-water (v/v)
[Substrate] = 3.00 x 10^{-2} *mol* dm^{-3} Temperature = 313 *K*
$[H^+]$ = 1.50 x 10^{-2} *mol* dm^{-3}

[acrylonitrile] *mol* dm^{-3}	k_1x 10^4 s^{-1}
0.00	4.04
0.50	4.06
1.00	4.05
1.50	4.07
2.00	4.06

3.7 Effect of Manganous sulphate

The reaction was followed with varying concentrations of Mn^{2+} ions keeping all the other factors constant. The increase in the concentration of manganous sulphate slightly increases the rate of the reaction. It has been found that the added Mn^{2+} ion has a noticeable catalytic effect on the reaction rate[28,29] (Table - 7)

$[Mn^{2+}] \times 10^3$ *mol dm^{-3}*	$k_1 \times 10^4$ *s^{-1}*
0.00	4.04
0.50	4.27
1.00	4.58
1.50	4.89
2.00	5.37

Table - 7 Effect of varying manganous sulphate concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol dm^{-3}* Solvent = 60 % acetic acid-water (v/v)
[Substrate] = 3.00 x 10^{-2} *mol dm^{-3}* Temperature = 313 *K*
$[H^+]$ = 1.50 x 10^{-2} *mol dm^{-3}*

3.8 Effect of varying the $[Al^{3+}]$

The reaction was carried out with varying concentration of aluminium chloride, keeping all the other factors constant. There was an appreciable decrease in the rate with the increasing concentration of Al^{3+} ions suggesting the involvement of three electron transfer process in this reaction (Table – 8).

$[Al^{3+}] \times 10^3$ *mol dm^{-3}*	$k_1 \times 10^4$ *s^{-1}*
0.00	4.04
0.50	3.41
1.00	3.10
1.50	3.41
2.00	3.60

Table - 8 Effect of varying Al^{3+} ion concentration on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol dm^{-3}* Solvent = 60 % acetic acid-water (v/v)
[Substrate] = 3.00 x 10^{-2} *mol dm^{-3}* Temperature = 313 *K*
$[H^+]$ = 1.50 x 10^{-2} *mol dm^{-3}*

3.9 Effect of varying the temperature

The reaction has been studied at four different temperatures keeping other factors constant. The pseudo-first order rate constants are given (Table – 9). The activation parameters were calculated from the least square procedure of a linear plot of ln (k_1 / T) versus 1/T of Eyring's equation[30] (Figure. 5).

$\Delta H^{\ddagger}$ = 30.42 *kJ mol^{-1}*
$\Delta S^{\ddagger}$ = -213.61 *JK^{-1} mol^{-1}*
$\Delta G^{\ddagger}$ = 97.28 *kJ mol^{-1}*

Temperature *K*	$k_1 \times 10^4$ *s^{-1}*
303	2.44
313	4.04
323	5.82
333	8.12

Table - 9 Effect of varying temperature on the oxidation of aromatic anil by pyrazinium chlorochromate

[Oxidant] = 1.50 x10^{-3} *mol dm^{-3}* $[H^+]$ =1.50 x 10^{-2} *mol dm^{-3}*
[Substrate] = 3.00 x 10^{-2} *mol dm^{-3}* Solvent = 60 % acetic acid-water (v/v)

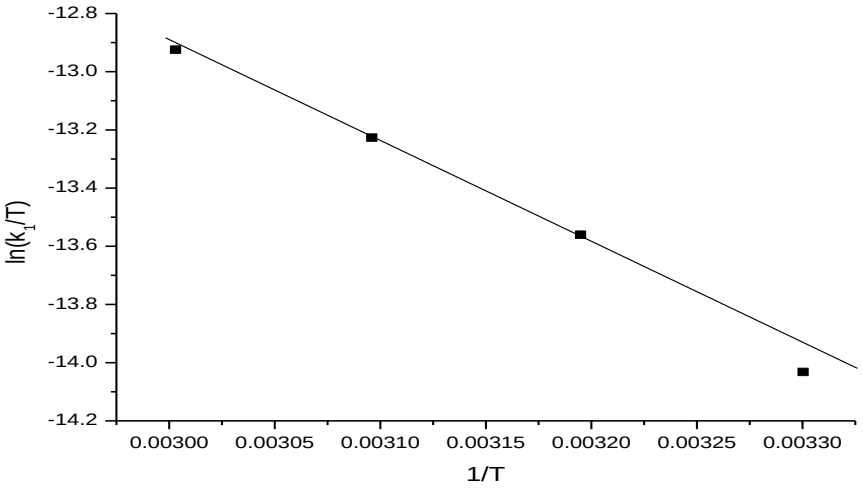


Figure. 5 Plot of ln (k_1/T) *versus* 1/T

3.10 Mechanism and the rate law

From the above observation it is clear that the reaction is showing first order dependence with respect to oxidant and fractional order with respect to substrate and [H^+] ion.

The oxidation by Cr(VI) will vary with nature of the Cr(VI) species used and the solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ions the following equilibria are existing[31].

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \quad K_1 = 1.21\ mol\ dm^{-3}$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{--} \quad K_2 = 3.0 \times 10^{-2}\ mol\ dm^{-3}$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^- + H_2O \quad K_3 = 35.5\ mol\ dm^{-3}$$

Here the dimerization equilibrium is of considerable importance. In water the dichromate ion will be predominating species only at the concentration of Cr(VI) is greater than about 0.05 mol dm^{-3}. In this case, as the concentration of Cr(VI) is less than 0.05 mol dm^{-3} monomeric form predominates and the active oxidizing species is $HCrO_4^-$. The reaction is acid catalysed one.

The rate increases with decrease in the dielectric constant of the medium and increase in ionic strength has negligible effect on the rate. The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The addition of Mn^{2+} ion has noticeable catalytic effect on the reaction rate. The addition of Al^{3+} ion decreases the oxidation rate due to the formation of complex between Al^{3+} ion and substrate. Based on the above observation a probable mechanism has been proposed and sustained with rate law (Scheme-1).

$$(C_6H_5O_2N^+H)_2Cr_2O_7 + H_2O \overset{K_1}{\rightleftharpoons} 2HCrO_4^- + 2C_6H_5O_2N^+H$$

$$C_6H_5CH=NC_6H_5 + HCrO_4^- \overset{K_2}{\rightleftharpoons} [Complex]$$

$$[Complex] \xrightarrow[slow]{k_3} C_6H_5CHO + C_6H_5{}^+NH + Cr^{++}$$

$$2C_6H_5{}^+NH \xrightarrow{Dimerises} C_6H_5N=NC_6H_5 + 2H^+$$

Scheme 1

3.11 Rate Law

Rate

$$= \frac{k_3 K_1 K_2 [S] [PzCC]}{1 + K_2 [S]}$$

Conclusion:

The rate of oxidation of aromatic anil with pyrazinium chlorochromate under pseudo-first order conditions ha been studied at 313 K.The reaction shows first order dependence with respect to oxidant and H^+. The reaction follows fractional order kinetics with respect to substrate. Increase in ionic strength has no effect on the reaction rate and decrease in the dielectric constant of the medium decreases the reaction rate. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of manganous sulphate retards the reaction rate which confirms the two electron transfer involved in the mechanism. Based on the experimental observations a suitable mechanism has been proposed and rate law has been derived. The products of the oxidation reaction are found to be corresponding benzaldehyde and azobenzene.

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