1, 10-PHENANTHROLINE PROMOTED OXIDATION OF PYRIDINE-3-CARBOXYLIC ACID BY IMIDAZOLIUM DICHROMATE: A KINETIC STUDY

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Abstract: Kinetic Investigations of oxidation of Pyridine-3-arboxylic acid by Imidazolium dichromate in aqueous acetic acid medium using 1,10-phenanthroline have been studied. In the absence of mineral acids, the oxidation kinetics of Pyridine-3-carboxylic acid by Imidazolium dichromate shows a first-order dependence on Imidazolium dichromate and fractional order on Pyridine-3-carboxylic acid. The variation of ionic strength, H^+ and reaction product have in significant effect on reaction rate. Activation parameters have been evaluated for the reaction from the Arrhenius plot by studying the reaction at different temperatures.

Keywords: Pyridine-3-carboxylic acid, Oxidation, Imidazolium dichromate, 1,10-phenanthroline

I. INTRODUCTION

Almost every oxidizable functional group is oxidized by a variety of compounds containing Cr(VI) as a versatile reagent[1-4]. Several new chromium (VI) containing compounds, with heterocyclic bases, like pyridinium chlorochromate (PCC), quinolinium fluorochromate (QFC), pyridinium bromochromate (PBC), quinoliium chlorochromate (QCC), imidazolium fluorochromate (IFC), pyridinium fluorochromate (PFC), imidazolium dichromate(IDC), quinolinium bromochromate (QBC) and quinolinium dichromate(QDC) shows selective oxidation in organic species [5-9]. The kinetics and mechanism of oxidation of aromatic aldehydes and acids by various oxidants have been reported.

The kinetics of oxidation of substituted Pyridine-3-carboxylic acid by halochromates such as quinolinium brom6ochromate, pyridinium bromochromate, benzyl triethylammonium chlorochromate, tetrabutylammonium tribromide, quinoxalinium bromochromate etc. have been studied earlier. Several reports on kinetic studies of oxidation of Pyridine-3-carboxylic acid with a variety of N-halo compounds such as N-bromosuccinimide, N-bromosaccharin, N-bromoacetamide and chloramine as oxidants have also been made [10-16]. Imidazolium dichromate is a good oxidizing agent and has some reported benefits over other N-halogeno oxidants, which have been regularly used in the estimation of organic substrates [17-22]. There is a lack of data on the kinetics of oxidation of Pyridine-3-carboxylic acid by Imidazolium dichromate using 1,10-phenanthroline as a catalyst [23-25]. The present work reports the kinetics and mechanism of oxidation of Pyridine-3-carboxylic acid by Imidazolium dichromate in 50% acetic acid with catalyst 1, 10-phenanthroline.

II. EXPERIMENTAL

2.1 Materials: Pyridine-3-carboxylic acid purchased from Sigma Aldrich. The Purity of the Pyridine-3-carboxylic acid was checked by thin-layer chromatography and melting point. The oxidant Imidazolium dichromate (Aldrich sample) was used as received. Acetic acid (A.R. grade) was purified in the laboratory. The standard solutions of Pyridine-3-carboxylic acid were prepared in acetic acid. Tripled deionized water was employed in all kinetic studies. The freshly prepared solution of Imidazolium dichromate was stored in an amber-coloured bottle to avoid the photochemical effect and its strength was checked iodometrically using a 1% solution of freshly prepared starch as an indicator.

2.2 Kinetic measurements: Kinetic experiments are studied under pseudo-first-order conditions by keeping a large excess of Pyridine-3-carboxylic acid over oxidant Imidazolium dichromate. A mixture containing the required amounts of solutions of Pyridine-3-carboxylic acid in 50% acetic acid was equilibrated at 303 K. To this mixture a measured amount of pre-equilibrated (303 K) standard solution of Imidazolium dichromate was added. To maintain the desired temperature (within ±0.1 °C) the reaction mixture was kept in a thermostat water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time intervals. The pseudo-first-order rate constants k' were computed from linear least squares plot -log [a - x] Vs time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±4%.

Here (a-x) is calculated by using the equation

$$(a-x) = \frac{B.R \times [Na_2S_2O_3]}{5}$$

The value of k’ is obtained from the slope of the plot of –log (a-x) against time by using the relation, k’= 2.303 x slope

2.3 Stoichiometry and product analysis: Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of Imidazolium dichromate over Pyridine-3-carboxylic acid and catalyst Imidazolium dichromate in 50% acetic acid for 24 h at 30 °C. By iodometrically the unreacted oxidant was determined. The estimated amount of unreacted Imidazolium dichromate showed that one mole of Pyridine-3-carboxylic reacts with one mole of

Imidazolium dichromate.Pyridine-3-carboxylic acid (0.2 mol) and Imidazolium dichromate (0.4 mol) was reacted together with 1,10-Phenanthroline (0.5 mol) in 50% aqueous acetic acid (total volume 100 ml). The reaction mixture was kept for about 24 hours to ensure completion of the reaction. It was then extracted with ether after evaporation. The layer was separated and dried. The residue was confined by melting point and thin-layer chromatography.

III. RESULTS AND DISCUSSION

The kinetics of oxidation of Pyridine-3-carboxylic acid by Imidazolium dichromate in 50% acetic acid was carried out at 303 K under pseudo-first-order conditions. The plot of log [Imidazolium dichromate] vs time was found to be linear indicating first-order kinetics of the reaction rate and from the slopes of such plots, the pseudo-first-order rate was evaluated. The rate constant (k') has been found to increase with the increase in the concentration of Pyridine-3-carboxylic acid and the plot of log k' vs log [Pyridine-3-carboxylic acid] was linear ($r^2 = 0.999$) with a slope less than unity for all the Pyridine-3-carboxylic acid indicating a fractional order dependence of rate. The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H_2SO_4 keeping the concentration of the other reactants constant. There was no drastic change in rate constant with variation of H^+ ion was observed. The influence of ionic strength on the reaction rate was studied. It was found that the ionic strength of the reaction medium has a negligible effect on the reaction rate. This is observed in the rate-determining step due to the attack of an ion on a neutral molecule. The oxidation reactions of Pyridine-3-carboxylic acid with Imidazolium dichromate at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals. The effect of variation in solvent composition on the reaction rate was studied by varying concentrations of acetic acid from 20-70%. From the rate constant it is observed that the decrease in the rate of reaction with increasing in the acetic acid concentration. In the absence of mineral acid, the probable oxidizing species is free Imidazolium dichromate under the present experimental condition.

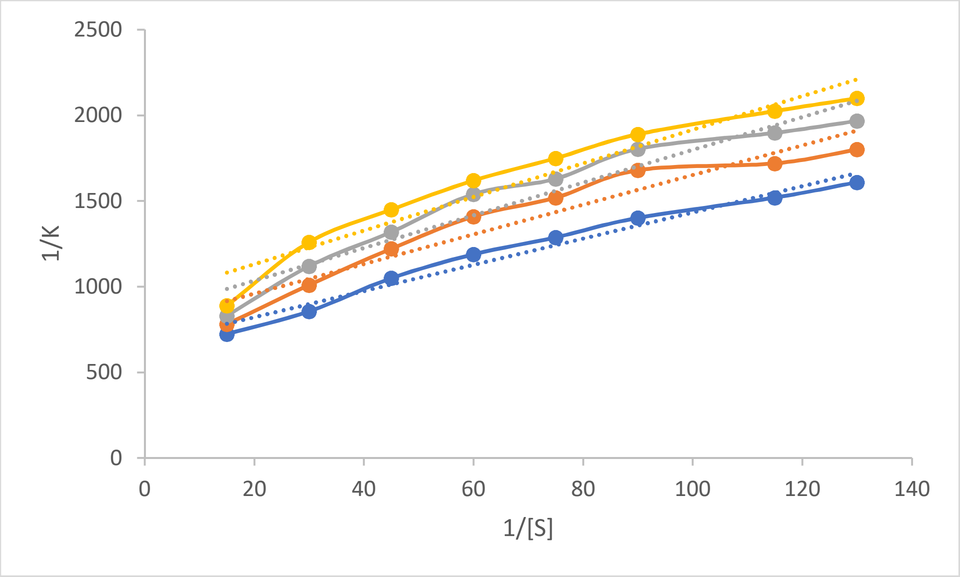
3.1 Effect of substituents: The oxidation of Pyridine-3-carboxylic acid by Imidazolium dichromate were carried out by varying the temperature in the range of 30-45 °C. The observed rate constants were found to increase with temperature for all the compounds. The rate of oxidation increases by the electron-donating groups and decreases by the electron-withdrawing groups. The order of reactivity of different Pyridine-3-carboxylic acid with Imidazolium dichromate is p-OCH_3> p-CH_3> H > p-Br > p-Cl > p-NO_2. Hammett's plot of log k' Vs σ is linear with a reaction constant $\rho = -0.21$ and a correlation coefficient of 0.885. The reaction constant ρ was found to be negative which indicates the formation of carbonium ion in the transition state and also supports the loss of secondary hydrogen atom as hydride in the slow step.

Table 1: Effect of substrate concentration on rate of reaction

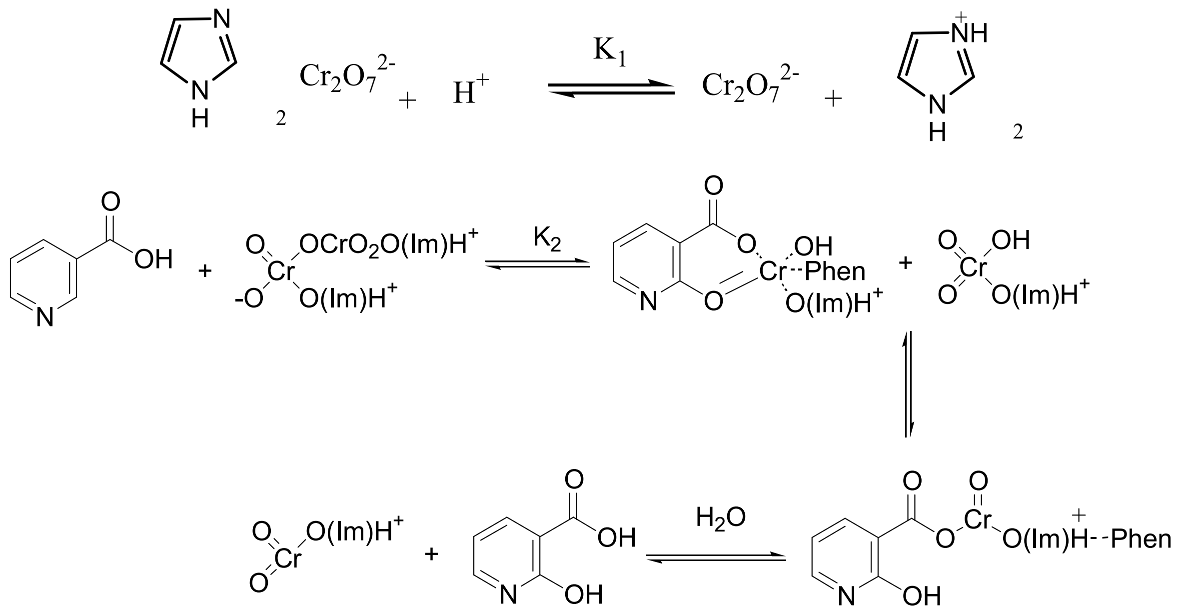
10^2[Aldehyde and Acid] (mol dm^{-3})	k'x10^4(s^{-1})
1.00	3.98
2.00	4.25
3.00	5.87
4.00	6.33
5.00	7.51
6.00	8.07

Effect of Pyridine-3-carboxylic acid on rate of reaction at different temperature

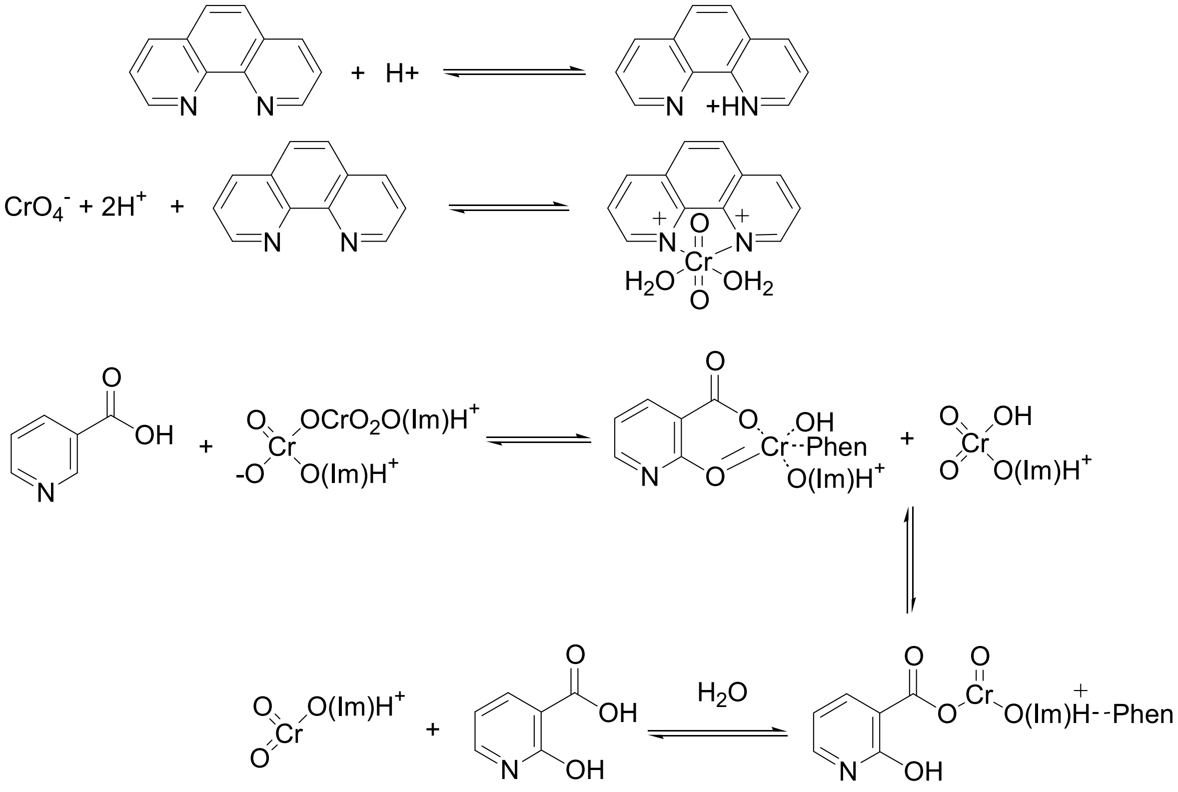
Time (min)	Vol.(ml) of $Na_2S_2O_3$ used	(a-x)	-Log(a-x)
0	24.5	0.000996	3.0020
5	22.2	0.000895	3.0480
10	20.3	0.000884	3.0535
15	16.9	0.000625	3.2040
20	14.0	0.000556	3.2550
25	11.6	0.000461	3.3360
30	10.2	0.000425	3.3716
35	7.7	0.000323	3.4910
40	6.0	0.000241	3.6180
45	5.2	0.000233	3.6330
50	4.5	0.000181	3.7420
55	3.7	0.000161	3.7930
60	3.2	0.000135	3.8700
70	2.1	0.000095	4.0220


2500
2000
1500
1000
500
0
1/K
0
20
40
60
80
100
120
140
1/[S]

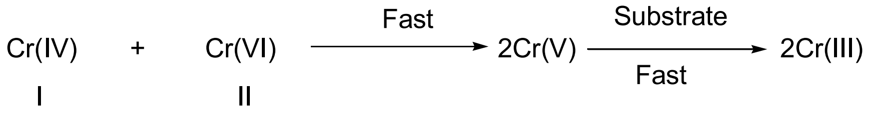
Double reciprocal plot of Pyridine-3-carboxylic acid [I]



Scheme 1: Mechanism of Oxidation of Pyridine-3-carboxylic acid in absence of 1,10-Phenanthroline [II]



Scheme 2: Mechanism of Oxidation 2-furaldehyde in presence of 1, 10-Phenanthroline



$$\underset{\text{I}}{\text{Cr(IV)}} + \underset{\text{II}}{\text{Cr(VI)}} \xrightarrow{\text{Fast}} 2\text{Cr(V)} \xrightarrow[\text{Fast}]{\text{Substrate}} 2\text{Cr(III)}$$

3.2 Mechanism and derivation of rate law: Depending upon the experimental studies it was observed that the most plausible mechanism and rate expression can be derived by applying steady-state approximation. The possibility of the formation of a binary complex involving oxidant and substrate is observed from the kinetic data which undergoes redox decomposition. This type of binary complex formation was also studied kinetically by the non-zero intercept of the double reciprocal plot of k' vs 1/ [S]. The decomposition rate constant k and formation constant K_1 were determined from a double reciprocal plot of 1/k' vs 1/ [S]. At different temperatures rate of oxidation was determined and the Arrhenius plots of log k versus l/T were linear. From these plots, the activation and thermodynamic parameters for equilibrium and rate-determining steps of the scheme were evaluated. The observed ΔS# values are large and negative. It may be interpreted that the fraction of collisions becomes more stringent and the decomposition of the activation complex is a quite slow process. ΔH# shows that the reactions are enthalpy-controlled. The validity of the isokinetic relation can be tested graphically by plotting log k (303) vs log k (313). The isokinetic temperature β evaluated from the Exner criterion was found to be 351.03 K (slope = 0. 857 and r^2 = 0.989), which is above the experimental temperature and implies that all the compounds are oxidized by the same mechanism. Further, the constancy in the calculated values of ΔG# for this oxidation reaction indicates that the same type of reaction mechanism could be operative for the reaction.

Decomposition rate constant (k), formation constant (k_1) and activation parameters of substituted Pyridine-3-carboxylic acidat 303 K

Substituent X	k X 10^4 S^{-1}	K_1 dm^3 mol^{-1}	Ea kj mol^{-1}	ΔH# kj mol^{-1}	ΔG# kj mol^{-1}	ΔS# JK^{-1} mol^{-1}
4-OCH_3	15.24	56.15	14.55	19.11	61.01	-408.10
4-CH_3	13.48	61.25	16.24	19.35	61.42	-408.18
-H	12.24	65.17	20.45	19.65	61.62	-408.28
4-Br	11.43	71.28	22.28	19.89	61.91	-408.39
4-Cl	8.22	76.75	24.71	20.09	62.06	-408.52
4-NO_2	7.46	79.34	26.21	20.18	62.23	-408.65

3.3 Rate law

The rate law has been derived as follows:

-d[Imidazolium dichromate$^+$] / dt = k_3 [E] = k_3 [Hy][Imidazolium dichromate$^+$]

where [Hy] = k_2 [A][H_2O]

substituting the values of [Imidazolium dichromate$^+$] and [Hy] in the above Equation (taking the activity of water to be unity), we obtain

-d[Imidazolium dichromate] / dt = $k_1k_2k_3$[A][Imidazolium dichromate][H+]

Indicating that reaction exhibited first-order dependence on the concentrations of each reactant (substrate, oxidant and acid)

[1,10-phenanthroline] = 5x10^4mol dm^{-3}

[Imidazolium dichromate]=1.00x10^3mol dm^{-3}

[$Hg(OAc)_2$]=2x10^3moldm^{-3}

Medium=50%AcOH-H_2O(v/v)

10^2 [Pyridine-3-carboxylic acid](moldm^{-3})	k'x10^4(s^{-1})			
	303K	308K	313K	318K
1.00	3.90	5.12	6.23	8.10
2.00	4.81	6.61	7.78	9.25
3.00	5.50	7.19	8.60	10.02
4.00	6.72	8.88	9.52	11.21
5.00	7.97	9.78	10.08	12.00

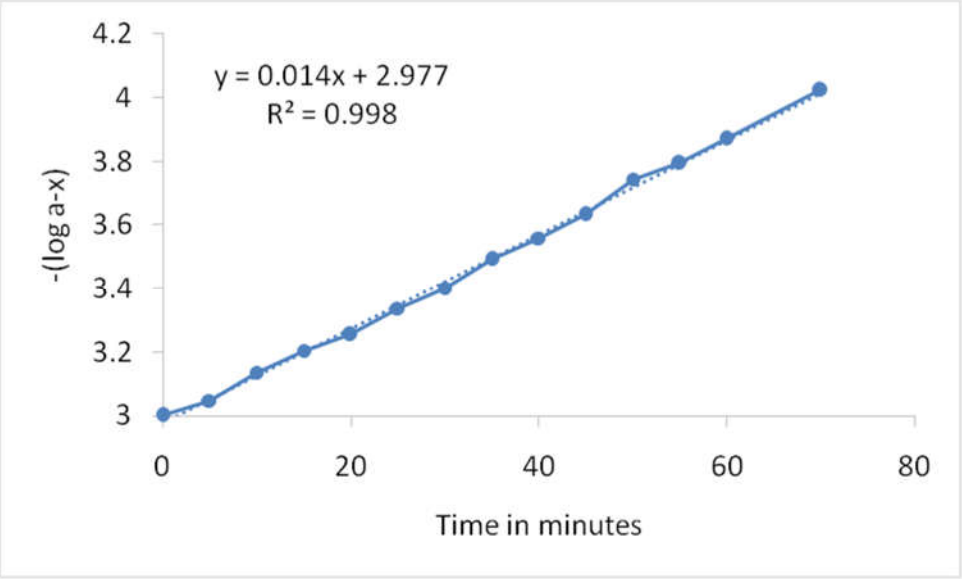


Fig. Plot of –log(a-x) Vs Time for Pyridine-3-carboxylic acid

6Temp.	10^3/T	kx10^4(s^{-1})	Log$k$
303 K	3.3003	7.25	-3.1452
308 K	3.2467	9.09	-3.0785
313 K	3.1948	10.31	-2.9562
318 K	3.1446	12.05	-2.9128

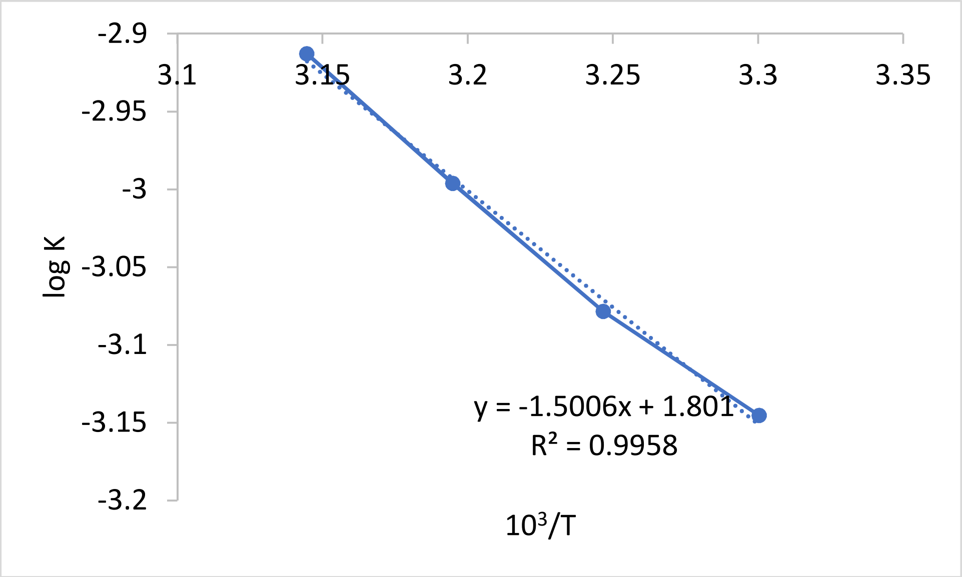
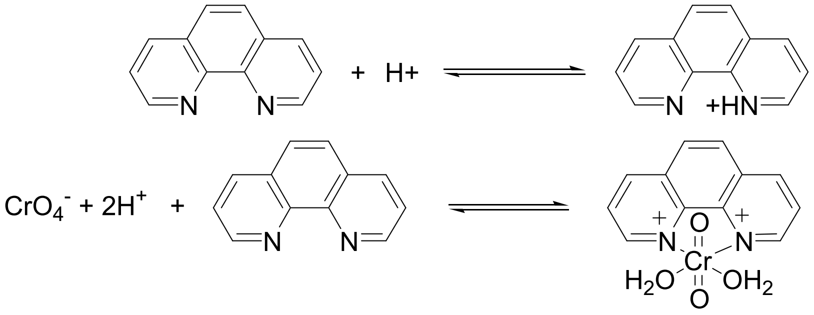


Fig. Arrhenius plot for oxidation of Pyridine-3-carboxylic acid

Scheme 1:



Scheme 2: Mechanism of Oxidation Pyridine-3-carboxylic acid in presence of 1, 10-Phenanthroline

IV. CONCLUSION

The kinetics of oxidation Pyridine-3-carboxylic acid with Imidazolium dichromate using 1,10-Phenanthroline as a catalyst has been investigated in aqueous acetic acid water medium. Concerning the Pyridine-3-carboxylic acid, Imidazolium dichromate and [H+] the oxidation of Pyridine-3-carboxylic acid by Imidazolium dichromate is first-order catalyzed by acetic acid. The reaction rate increases by lowering the dielectric constant. The absence of a free radical intermediate in the oxidation is indicated by the no-polymerization. Under pseudo-first-order conditions, the monomeric species of Cr(VI) was found to be kinetically active in the absence of 1,10-phenanthroline whereas, in the phenanthroline promoted path, the Cr(VI)-phen complex undergoes a nucleophilic attack by pyridine-3-carboxylic acid form a ternary complex which subsequently experiences a redox decomposition leading to hydroxy and Cr(III)-phen complex. A combination of Imidazolium dichromate and phenanthroline will be ideal for chromic acid oxidation of pyridine-3-carboxylic acid in aqueous media.

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