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Research Article

Amino acid oxidation

Catalytic Oxidation of 2-Amino-3-Sulfhydryl Propanoic Acid (ASPA) by 2,6-Dicarboxypyridinium Fluorochromate (DCPFC) : A Kinetic and Mechanistic Study

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Abstract: 2-(Pyridin-2-yl) pyridine catalyzed oxidation of 2-amino-3-sulfhydryl propanoic acid (ASPA) by 2,6-DicarboxyPyridinium Fluoro Chromate (DCPFC) has been carried out at 308 K. This amino acid oxidation leads to the formation of a product. Main objective of our present investigation is, Kinetic Oxidation reaction is carried out, from this, reaction rate law, rate equation, mechanisms and rate constant values were measured. Various factors such as Oxidant, Substrate, Acid, Solvent, Catalyst, $MnSO_4$, Acrylonitrile, and $NaClO_4$ influence the reaction rate. This kind of systematic kinetic work explores the physical characterization of the reacting Species. This catalyzed reaction exhibits first order dependence, with respect to [DCPFC] and fractional order with respect to [ASPA], [H^+] and 2-(pyridin-2-yl)pyridine. The above reaction is carried out at methane carboxylic acid-water medium. Rate of the reaction has been influenced by varying the percentage of methane carboxylic acid. Addition of $NaClO_4$ appreciably decreases the rate of the reaction. Addition of acrylonitrile does not influence the rate of the reactions, which rules out the polymerization reaction indicating the lack of a free radical pathway. Slight increase in the rate values occur by the addition of $MnSO_4$, which implies that, slight catalytic behaviour of Mn^{2+} on Oxidation reaction. The reaction described above was carried out at four different temperatures to determine, thermodynamic parameters such as enthalpy and entropy of activation. The appropriate mechanism has been suggested based on the observed data. Our Aim is to find out the reaction mechanism pathway, Order of the reaction by means of various effects such as Oxidant effect, Solvent & Catalyst Effect, etc.,. The product analysis has been confirmed by IR spectral studies and derivative test.

Keywords: Amino acid, Oxidation, Catalyst, Kinetic studies, Mechanism, DCPFC, ASPA, 2-(Pyridin-2-yl) pyridine

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1. INTRODUCTION

1.1 Oxidation

A series of chemical reactions determines a life cycle, as we know that all of our fundamental needs are met by chemicals in different forms. Chemical reaction can have many aspects, one of which is oxidation. Oxidation reactions are no less common in general chemistry and their importance has resulted in the accumulation of a large number of empirical observations and conclusions. The Study of such oxidation through elucidation of their mechanisms and the investigation of kinetics in chemical reactions are considered as an important aspect in chemical and biological fields. [1-3]

1.2 Chromium (VI) – As Oxidizing agents

Chromium(VI) is employed for the oxidation of organic compounds and it is reduced to lower oxidation states. The Chemistry of Cr(V) and Cr(IV) as intermediate species which is formed during the reduction of Cr(VI) has been an attraction for many researchers. This created attraction because of their Involvement in the mechanism of Cr-Induced Cancers [4] Chromium (VI) is a versatile oxidant but is a rather drastic and non - selective oxidant. To improve the selectivity of Cr(VI), a number of organic halo chromates have been synthesized which are used as mild and selective oxidizing agents in synthetic organic chemistry [5-9]. Numerous reagents and methods have been developed to carry out this kind of oxidation reactions by using Cr(VI) agents [10-20]

1.3 2,6-DicarboxyPyridinium Fluoro chromate (DCPFC)

A variety of oxidants has been designed to improve the selectivity of organic oxidation reactions. 2,6 - Dicarboxypyridinium fluoro chromate is such a rapid, effective, mild & selective reagent used as a oxidant in the oxidation of various functional group [21-24] In our present investigations, 2-amino-3-sulfhydryl propanoic acid is converted in to corresponding product by DCPFC.

1.4 Oxidation of Amino Acids

Oxidation of amino acid is of great importance and interest both from a chemical point of view and from its bearing on the mechanism of amino acid metabolism. Amino acids undergo various types of reaction, depending on whether the particular amino acid contain non-polar groups, polar substituent,acidic or basic substituent[25].The study of amino acids is one of the most exciting fields in organic chemistry. Amino acids are the building blocks in protein synthesis. They play a significant role in a number of metabolic reactions like biosynthesis of polypeptide and nucleotides. To Understand some aspects of kinetics, it may be beneficial to investigate the mechanism of similar non-enzymatic chemical reactions in amino acid oxidation. The oxidation of amino acid is of interest as the oxidation products differ for various Oxidants [26]. Amino acids have been oxidized by a variety of reagents under different experimental condition[27-31].

1.5 2-amino-3-sulfhydryl propanoic acid (ASPA)

Amino acids find a number of applications in biochemical research, metabolism, microbiology, nutrition, pharmaceuticals and fertilization of foods and feeds. 2-amino-3-sulfhydryl propanoic acid is a non-essential amino acid. It contains sulphur in the form of thiol group (-SH) at the end of its side chain [32]. The –SH group is responsible for the high reactive capacity of amino acid and therefore it is responsible for many of its biological functions like folding and stabilization of the tertiary structure of proteins in human beings [33-36] (Fig. 1)

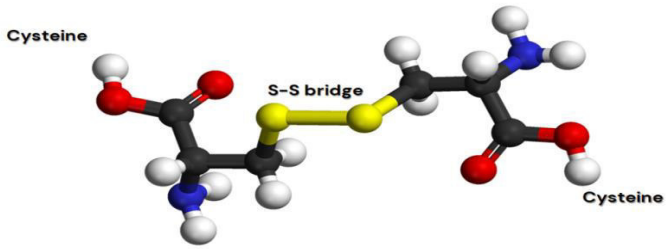

Fig. 1 – 3D Structure of Cysteine (S-S Bridge)

1.6. 2-(Pyridin -2-yl)Pyridine

2-(Pyridin-2-yl)Pyridine has found its application in various fields of chemistry such as macromolecular, supramolecular, material chemistry, photochemistry, electrochemistry due to their extraordinary co-ordination properties, as ligands in metal-catalysed reactions [37-43]. 2-(Pyridin-2-yl)Pyridine framework bears pendent chiral substituents, they have been studied as potential ligands in Metal – Catalysed Asymmetric reactions. The Synthesis of a new series of Pyridine derivations continue to attract great interest in biological as well as research field [44-50]. The reports of 2-(Pyridin-2-yl)Pyridine catalytic oxidation of ASPA by 2,6-DCPFC is lacking in the literature and hence the title is taken for our present Investigation.

2. EXPERIMENTAL METHODS AND MATERIALS

2.1 Materials

The reagents such as $NaClO_4$, Perchloric acid and $MnSO_4$, etc., used in this work are Analar grade. Deionized Water was distilled twice in "Corning" glass vessels, the second distillation being from alkaline Potassium Permanganate and it was used throughout the kinetic

measurements. All the Solutions were prepared by using the above said Deionized water. ASPA Solution was prepared by Methane Carboxylic acid medium[51-52.]

2.2 Methods

DCPFC was synthesized by the literature [53] and 2-(Pyridin-2-yl)Pyridine was described [54]. Methane Carboxylic acid was purified by the standard procedure and the fraction distilling at 118°C was collected[55] 2,6-DicarboxyPyridinium Fluoro chromate (DCPFC) is easily prepared by the reaction of pyridine-2,6-dicarboxylic acid with chromium trioxide in HF[53]

2.2.1 Kinetic Measurements

The essence of this experiment is to determine the order of the reaction and the rate constant with respect to Oxidation[56,62.] To achieve that, Pseudo – first order conditions have to be maintained by making the concentration of the substrate in large excess over DCPFC. The rate constants were evaluated from the linear plot of log(Absorbance) versus time by the least square method.

2.3 Stoichiometry and product analysis

2.3.1 Product Analysis

Equimolar (0.01 mol) mixture of ASPA and DCPFC were combined together with perchloric acid in 50% (V/V) of aqueous Methane Carboxylic acid. Catalyst used for the above reaction is 2-(Pyridin-2-yl)Pyridine. The reaction mixture was kept for 24h to ensure the completion of the reaction. The Solution was extracted with Chloroform and the organic layer was washed with water, dried over anhydrous Sodium Sulphate. The formed product was confirmed by IR spectral studies and a derivative test. However, in the oxidation of 2-amino-3-sulfhydryl propanoic acid (ASPA), its monomer by chromic acid in HClO4 medium, Mc Cann and Mc Auley [57,58] noticed the formation of a transient orange red 1:1 chromate ester, spectrophotometrically at 420 nm. Since the –SH groups of the two 2-amino-3-sulfhydryl propanoic acid molecules are involved in the formation of disulfide bridge (-S-S-) in cystine, there may not be spectrophotometric evidence for complexation between cystine and chromium(VI). But the carboxylic and amino groups may also coordinate to chromium(VI), which supports the kinetic evidence for complexation between L-cystine and chromium(VI).

2.3.2 Stoichiometry

Stoichiometry is a balanced chemical equation. The Stoichiometry of a reactions are carried out with relative amount of reactant and product in a balanced chemical equation. 1 mole of 2-amino-3-sulfhydryl propanoic acid (ASPA) was reacted completely with a known excess of 2,6-DicarboxyPyridinium FluoroChromate (DCPFC) (1 mole) at 35^{0}C in the presence of all other reactant in Pseudo first order condition and after 24 hrs the residual 2,6-DicarboxyPyridinium FluoroChromate in this case was determined Iodometrically [56]. The Stoichiometry of the reaction was found from the following equation,

$$\underset{(1\text{ mole})}{C_3H_7NO_2S} + \underset{(1\text{ mole})}{C_7H_6CrFNO_7} \longrightarrow \text{Product}$$

3. RESULTS AND DISCUSSION

3.1. Effect of varying Oxidant (DCPFC) Concentration

The Concentration of DCPFC was varied from 0.50 x 10^{-3} to 2.25 x 10^{-3} mol dm^{-3} and keeping all other reactant concentrations i.e. substrate, acid, catalyst and solvent as constant and the rate was measured (Table-1). The non-variation in the Pseudo-first order rate constants at various concentrations of DCPFC indicates that the order with respect to [DCPFC] is unity[59,60] This was confirmed from the linearity plot of log titre vs time. (r = 0.999) by least square method. (Fig.2)

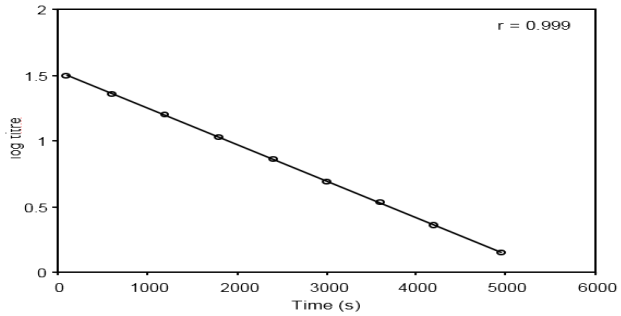

Fig. 2. Plot of log titre *versus* time (s)

3.2. Effect of varying ASPA concentration

The concentration of 2-amino-3-sulfhydryl propanoic acid (ASPA) is varied from 0.50 x 10^{-2} to 3.00 x 10^{-2} mol dm^{-3} at fixed concentration of the other reaction components i.e. Concentration of oxidant, acid, catalyst and solvent. The rate of the reaction increases with increasing the concentration of ASPA[61] (Table-1) A plot

of log k_{obs} versus log [ASPA] gives a straight line (Fig. 3) with a slope value (B = 0.4935), the correlation co-efficient being 0.99. The rate of the reaction is fractional order with respect to [ASPA][62]

Table 1 – Effect of Concentration of 2-amino-3-sulfhydryl propanoic acid (ASPA), 2,6-DicarboxyPyridinium Fluoro Chromate (DCPFC) on the pseudo first order rate constant

[ASPA] × 10^2 (mol dm^{-3})	[DCPFC] × 10^3 (mol dm^{-3})	k_{obs} × 10^4 (s^{-1})			
		298 K	303 K	308 K	313 K
0.50	1.25	0.30	1.80	3.38	4.17
1.00	1.25	1.20	3.25	5.12	7.20
1.50	1.25	4.28	5.85	6.40	8.32
2.00	1.25	4.50	6.10	7.57	9.30
2.50	1.25	4.90	6.80	8.50	10.40
3.00	1.25	5.50	7.60	9.53	11.60
1.50	0.50	-	-	6.11	-
1.50	1.00	-	-	6.24	-
1.50	1.25	4.28	5.85	6.40	8.32
1.50	1.50	-	-	7.17	-
1.50	1.75	-	-	7.27	-
1.50	2.00	-	-	7.33	-
1.50	2.25	-	-	7.63	-

[ASPA] = 1.50×10⁻² mol dm⁻³, [DCPFC] = 1.25×10⁻³ mol dm⁻³, [Bipy] = 1.25×10⁻³ mol dm⁻³, [H⁺] = 10.00×10⁻³ mol dm⁻³, Solvent = 50:50 (% v/v) AcOH-H₂O, Temperature =308 K.

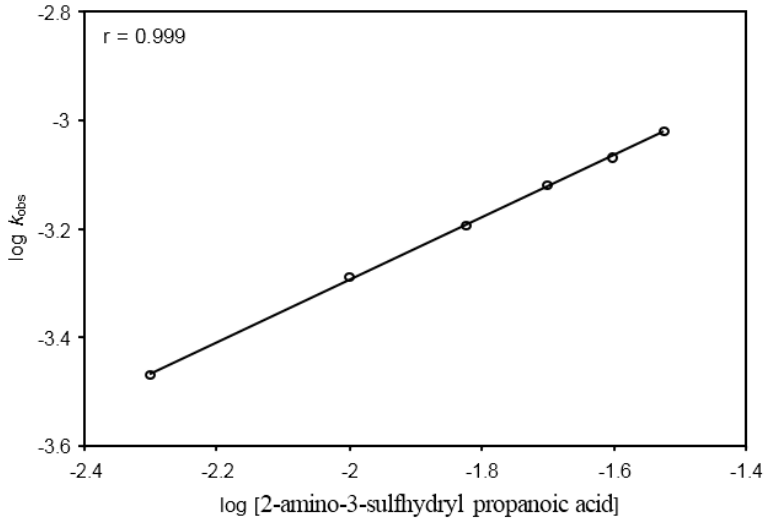

Fig. 3. Plot of log k_{obs} *versus* log [2-amino-3-sulfhydryl propanoic acid]

3.3. Effect of varying perchloric acid [$HClO_4$] concentration

Perchloric acid concentration was varied in the range of 5.00 x 10^{-3} to 15.00 x 10^{-3} mol dm^{-3} and keeping the concentrations of all other reactant concentrations i.e. oxidant, substrate, catalyst, solvent as constant and the rate was measured (Table-2). The rate of oxidation reaction increases with increase in perchloric acid concentration. Hydrogen Ions added have a very significant effect on the reaction rate showing that, H^+ ions provided by the solvent molecule were not adequate for the protonation of oxidant [63,64]. The plot of log k_{obs} versus log [H^+] gives a straight line with slope value of B=0.5009 and r = 0.9997, Implies that the reaction is fractional order dependence with respect to [H^+] ions.

Table 2– Effect of Concentration of H^+ on the pseudo first order rate constant *k*

$[H^+] \times 10^3$ (mol dm^{-3})	[ASPA] × 10^2 (mol dm^{-3})	[DCPFC] $\times 10^3$ (mol dm^{-3})	$[NaClO_4] \times 10^3$ (mol dm^{-3})	$[MnSO_4] \times 10^3$ (mol dm^{-3})	[Acrylonitrile] x 10^3 (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1}) at 308 K
10.00	1.50	0.50	-	-	-	6.11
10.00	1.50	1.00	-	-	-	6.24
10.00	1.50	1.25	-	-	-	6.40
10.00	1.50	1.50	-	-	-	7.17
10.00	1.50	1.75	-	-	-	7.27
10.00	1.50	2.00	-	-	-	7.33
10.00	1.50	2.25	-	-	-	7.63
10.00	0.50	1.25	-	-	-	3.38
10.00	1.00	1.25	-	-	-	5.12
10.00	1.50	1.25	-	-	-	6.40
10.00	2.00	1.25	-	-	-	7.57
10.00	2.50	1.25	-	-	-	8.50
10.00	3.00	1.25	-	-	-	9.53
5.00	1.50	1.25	-	-	-	4.56
7.50	1.50	1.25	-	-	-	5.62
10.00	1.50	1.25	-	-	-	6.40
12.50	1.50	1.25	-	-	-	7.24
15.00	1.50	1.25	-	-	-	7.89
10.00	1.50	1.25	0.00	-	-	6.40
10.00	1.50	1.25	5.00	-	-	6.14
10.00	1.50	1.25	10.00	-	-	6.02
10.00	1.50	1.25	15.00	-	-	6.00
10.00	1.50	1.25	20.00	-	-	6.00
10.00	1.50	1.25	-	0.00	-	6.40
10.00	1.50	1.25	-	5.00	-	6.54
10.00	1.50	1.25	-	10.00	-	6.66
10.00	1.50	1.25	-	15.00	-	6.83
10.00	1.50	1.25	-	20.00	-	6.94
10.00	1.50	1.25	-	-	0.00	6.40
10.00	1.50	1.25	-	-	5.00	6.45
10.00	1.50	1.25	-	-	10.00	6.46
10.00	1.50	1.25	-	-	15.00	6.49
10.00	1.50	1.25	-	-	20.00	6.51

[ASPA] = 1.50×10^{-2} mol dm^{-3}, [DCPFC] = 1.25×10^{-3} mol dm^{-3}, [Bipy] = 1.25×10^{-3} mol dm^{-3}, [H$^+$] = 10.00×10^{-3} mol dm^{-3}, Solvent = 50:50 (% v/v) AcOH-H_2O, Temperature = 308K.

3.4. Effect of Ionic strength by varying $NaClO_4$ Concentration

In order to know about the effect of Ionic strength on the reaction rate, the reaction was carried out with varying concentration (5.00 x 10^{-3} to 20.00 x 10^{-3} mol dm^{-3}) of added sodium perchlorate and keeping all other reactant concentration i.e., [ASPA] = 1.50×10^{-2} mol dm^{-3}, [DCPFC] = 1.25×10^{-3} mol dm^{-3}, [Bipy] = 1.25×10^{-3} mol dm^{-3}, [H^+] = 10.00×10^{-3} mol dm^{-3}, Temperature 308K , as constant.(Table-2). The rate value slightly decreases as $[NaClO_4]$ increases which implies that the reaction may be in between an Ion and a neutral molecule[65,66]and also the rate was not influenced by Ionic Strength.

3.5. Test for free radical intermediates

The reaction was studied, by varying the concentration (5 x 10^{-3} to 20 x 10^{-3} mol dm^{-3}) of Acrylonitrile and keeping all other reactant concentration constant (Table-2). Addition of acrylonitrile to the reaction mixture has no effect on the reaction rate as well as no white deposition was found, which shows the absence of free radical pathway mechanism[67,68].

3.6. Effect of Mn^{2+} on the reaction rate

Slight increase in the rate constant values occur by increasing the concentration of $[MnSO_4]$. (Table-2) Addition of Mn^{2+} shows, slight catalytic effect on the oxidation reaction [69,70]

3.7. Effect of dielectric constant

In order to determine the effect of dielectric constant (Polarity) of the medium on reaction rate, 2-(Pyridin-2-yl)pyridine catalyzed oxidation of 2-amino-3-sulfhydryl propanoic acid (ASPA) by 2,6-DicarboxyPyridinium Fluoro Chromate (DCPFC) has been carried out at 308 K in methane carboxylic acid and water medium of various compositions. When the acid content increases in the medium, the acidity

of the medium is increased whereas the dielectric constant of the medium is decreased. The data clearly reveals that the rate decreased with increase in the percentage of methane carboxylic acid (Table – 3) The plot of log k_{obs} versus 1/D gives a linear slope with 'r' value 0.99. This Indicates that there is a charge development in the transition state involving a more polar activated complex than reactant. This shows that the reaction is in between a neutral molecule (ASPA) and an Ion (Cr(VI)) and this might be probably due to ion-dipole interaction in the rate determining step[71,72] which is also supported by the negative entropy value was obtained in my work.

Table 3 - Effect of variation of solvent composition

AcOH-H_2O (% v/v)	1/D value x 10^4	$k_{obs} \times 10^4$ (s^{-1})
30:70	4.1981	25.10
40:60	3.1685	12.50
50:50	**2.5445**	**6.40**
60:40	2.1258	5.20
70:30	1.8254	3.98

[ASPA] = 1.50×10⁻² mol dm⁻³, [DCPFC] = 1.25×10⁻³ mol dm⁻³, [Bipy] = 1.25×10⁻³ mol dm⁻³ [H⁺] = 10.00×10⁻³ mol dm⁻³, Solvent = 50:50 (% v/v) AcOH-H₂O, Temperature = 308 K.

3.8. Rate and activation parameters

This Oxidation reaction was conducted at four different temperatures viz., 298, 303, 308 and 313k.(Table - 4 & 5). The rate of the reaction and activation parameters were calculated by using Eyring's Equation. Plot of ln k_{obs} /T versus 1/T is linear (Fig-4). Activation parameters like $\Delta H^{\#}$ = 35.18 kJ mol^{-1} and $\Delta S^{\#}$ = –188.56 J K^{-1} mol^{-1} were calculated from the slope and intercept of the plot. We will get the activation of entropy with large negative value, indicates the restriction of solvent molecule in the transition state and also reveals that the complex is rigid than the reactant[73,]

Table 4 - Effect of Temperature on Reaction Rate

Temperature(K)	k_{obs} x10^4 (S^{-1}) (Graphical)	k_{obs} x10^4 (S^{-1}) (Observed)	R Correlation Coefficient
298	4.28	4.20	0.996
303	5.85	5.75	0.993
308	6.52	6.40	0.999
313	8.32	8.05	0.994

[ASPA] = 1.50 x 10⁻² mol dm⁻³ , [Bipy] = 1.25 x 10⁻³ mol dm⁻³, [DCPFC] = 1.25 x 10⁻³ mol dm⁻³ , [H⁺] = 10.0 x10⁻³ mol dm⁻³ , Solvent = 50 : 50 (% V/V) ACOH - H₂O, Temperature = 308

Table 5 – Kinetics Data at Differernt Temperature

Temperature(K)	r	SD
298	0.996	0.003190
303	0.993	0.003180
308	0.999	0.003200
313	0.994	0.003183

[ASPA] = 1.50×10⁻² mol dm⁻³, [DCPFC] = 1.25×10⁻³ mol dm⁻³, [Bipy] = 1.25×10⁻³ mol dm⁻³, [H⁺] = 10.00×10⁻³ mol dm⁻³, Solvent = 50:50 (% v/v) AcOH-H₂O, T = 308 K

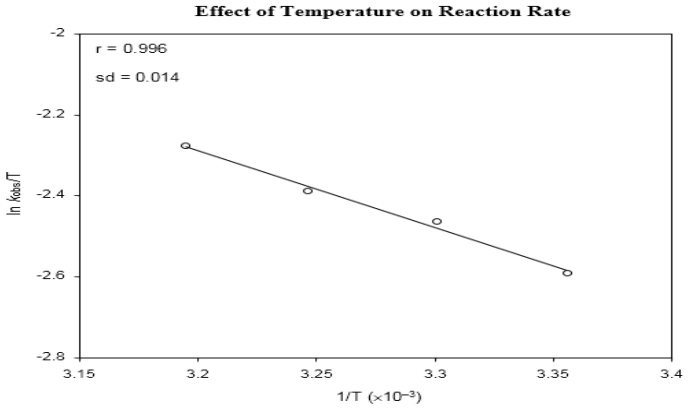

Fig. 4. Plot of ln k_{obs}/T *versus* 1/T

3.9. Effect of varying the Catalyst concentration

2-(Pyridin-2-yl)Pyridine concentration was altered in the range of 0.50 x 10^{-3} to 1.75 x 10^{-3} mol dm^{-3} while keeping all other reactant concentration constant.(Table-6). The rate of the reaction increases when we increase the catalyst concentration[75,76]. Plot of log k_{obs} versus log[2-(Pyridin-2-yl)] Pyridine gives a straight line with slope value of B=0.4920 and r =0.9922 shows that, the reaction is fractional order dependence with respect to 2-(Pyridin-2-yl) Pyridine.

Table 6 – Effect of variation of [2-(Pyridin-2-yl)Pyridine] on Reaction Rate

[2-(Pyridin-2-yl)Pyridine]x10^3 (mol dm^{-3})	k_{obs} x10^4 (S^{-1})
0.50	2.81
1.00	5.24
1.25	**6.40**
1.50	7.58
1.75	8.70

[ASPA] = 1.50×10⁻² mol dm⁻³, [DCPFC] = 1.25×10⁻³ mol dm⁻³, [Bipy] = 1.25×10⁻³ mol dm⁻³, [H⁺] = 10.00×10⁻³ mol dm⁻³, Solvent = 50:50 (% v/v) AcOH-H₂O, Temperature = 308 K

3.10. Reaction Mechanism and Rate law

From the observed kinetic results, the following possible mechanism has been proposed for our kinetic study. In the first step protonated oxidant [21] reacts with 2-(Pyridin-2-yl)Pyridine [39] and forms a complex C_1 in the Equilibrium step. After that complex C_1 reacts with 2-amino-3-sulfhydryl propanoic acid [34] to form complex C_2. In the next step C_2 dissociates to give product which is the slow step as well as rate determining step.

$$\text{DCPFC} + H^+ + \text{Bipy} \overset{K_1}{\rightleftharpoons} \text{Complex } (C_1)$$

$$\text{Complex } (C_1) + \text{ASPA} \overset{K_2}{\rightleftharpoons} \text{Complex } (C_2)$$

$$\text{Complex } (C_2) \xrightarrow[\text{slow}]{k_3} \text{Product} + \text{Cr (IV)}$$

Rate law for the above reaction is,

$$\text{Rate law} = \frac{-d[\text{Cr(VI)}]}{dt} = \frac{K_1K_2k_3[\text{ASPA}][\text{Bipy}][\text{DCPFC}][H^+]}{\{1+K_1[H^+]\}\{1+K_1[\text{Bipy}]\}\{1+K_2[\text{ASPA}]\}}$$

4. CONCLUSION

In this study, 2-(Pyridin-2-yl)Pyridine Catalysed oxidation of ASPA by DCPFC was reported and the following conclusions are given: The reaction was first order with respect to [DCPFC], and Fractional order with respect to [ASPA],[H^+] and 2-(Pyridin-2-yl)Pyridine. The rate constant value Increases linearly with H^+ concentration and Indicates the role of H^+ Ion in oxidant protonation. Changing the percentage of Methane carboxylic acid and water Influence the reaction rate , Suggests that the Mechanistic pathway may be Ion - dipole Interaction. Addition of Acrylonitrile has no significant effect on reaction rate , which rules out the free radical formation. $MnSO_4$ Addition shows , the slight catalytic behaviour due to Mn^{2+} Ions in the oxidation reaction. Eyring's plot gives Thermodynamic Parameters such as $\Delta H^{\neq}$ & $\Delta S^{\neq}$ low activation Enthalpy and a negative value of Entropy provide a support for the formation of a rigid activated complex in oxidation reaction The Obtained product is required for proper utilization of vitamin B_6 and also helpful in healing of wounds and burns.

5. APPLICATIONS

Oxidation reaction is a fundamental chemical reaction, it is found very useful in our day to day life cycle and chemical industries for the production of various commercial products. Cystine is a covalently linked dimeric non essential amino acid formed by the oxidation of cysteine. Formed molecule contains a disulphide bond which is important in the formation of active structural domains in a large number of proteins. The cysteine sulfhydryl group is nucleophilic and easily oxidized. The reactivity is enhanced when the thiol is oxidized, because of its high reactivity, the sulfhydryl group of cysteine has numerous biological applications, like precursor to the antioxidant glutathione & Iron-sulfur cluster as well as used as a metal ion binder.

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7. AUTHORS CONTRIBUTION STATEMENT

Both Authors Conceptualized and gathered the data with regard to this work. Data Analysis and necessary inputs were given by all authors and also discussed the methodology, results and equal contribution given to the final manuscript.

8. CONFLICT OF INTEREST

Conflict of Interest declared none.

9. REFERENCE

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