Pd (II) Catalytic Oxidation of L-Histidine by Cerium (IV) in Acidic Medium by Spectrophotometry Method

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Abstract

The rate of reaction of L-histidne with Ce (IV) acidic medium has been kinetically studied in the presence of Pd (II) as catalyst using a spectrometric method. The reactions have been performed at temperatures range from 298 K to 318 K in interval of 10 minutes. In the case of Ce (IV), this reaction would be a first order reaction. The results exhibits first order each in Ce (IV) and metal ion Pd(II) and positive fractional order with respect to [L-Histidine]. This would have a first order reaction between the Ce (IV) and L- histidine in the presence and absence SDS, CTAB and KCl. The rate constant decreases with increasing the concentration of $[HSO_4^-]$ and $[H^+]$ ion. The thermodynamical parameter values such as $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ are increases with increaseing temperature.

$$k_{obs} = \frac{kK[L-pro][Pd(II)]}{1+K[H^+][L-pro]}$$

Keywords: Kinetics, Oxidation, L- Histidine, Cerium (IV), Pd(II), Sulphuric acid, KCl, Mechanism.

1.1 INTRODUCTION

Amino acid is an organic compound which contains an amino group ($-NH_2$) and a carboxylic group (-COOH). The amino acid is formation nucleotides to the polypeptides and protein synthesis. Amino acid has biological importance and metabolic role [1-2]. The importance function of L- histidine in the human body has to be oxidation of neurotransmission, gastric secretion and immune system. L- histidine is essential in the human body from which external sources [3-7].

Cerium (IV) is strong oxidant reagent and redox potential of the Ce^{4+} /Ce^{3+} couple under carefully controlled condition in sulphuric acid. The redox potential is +1.28V in 1M HCl ,+1.44V in 1M H_2SO_4, +1.61V in 1M HNO_3, +1.70 V in 1M $HClO_4$ and + 1.87 V in 8M $HClO_4$ acid. [8-10] L- histidine is oxidation reaction of organic compound by cerium (IV) usually proceeds via an intermediate complex. The oxidation has reported by the formaldehyde, carbon dioxide, and ammonia and with $K_2S_2O_8$, $KMnO_4$, potassium bromated and aquomanganese (III), while the products obtained with ferricyanide are keto acid and ammonia [11-13].

Transition metal ion is used extensively as catalysts to effect much reaction. Transition metal Pd (II) is studied as a catalyst to trace the mechanism of reactions of Ce (IV). Which accelerates the reactions between the Ce (IV) and L-histidine and the product gets variation in short time.The oxidation of the transition metal as a catalyst for amino acids is important. The kinetic probes in their biological systems are used in the field of chemistry. From this study we found that this type of Pd (II) of L- histidine has been investigated by Ce (IV) in performance to explain the deposition of activator species in sulphuric acid medium by oxidant [14-17].

1.2 EXPERIMENTAL

1.2.1 Materials

Throughout the experiment double distilled water is used. A stock solution L- histidine (A.R. E. Merck) was prepared by dissolving in water [14-16]. The solution of cerium (IV) ammonium sulphate (A.R. E. Merck) was prepared by dissolving ceric ammonium sulphate in 1.0 mol dm^{-3} of solution to obtain a clear and stable colour. Other chemicals and reagent such as CTAB, SDS, KCl and Pd (II) used were of analytical grade (A.R. E. Merck). The standardized stock solutions were diluted before used in kinetic reaction.
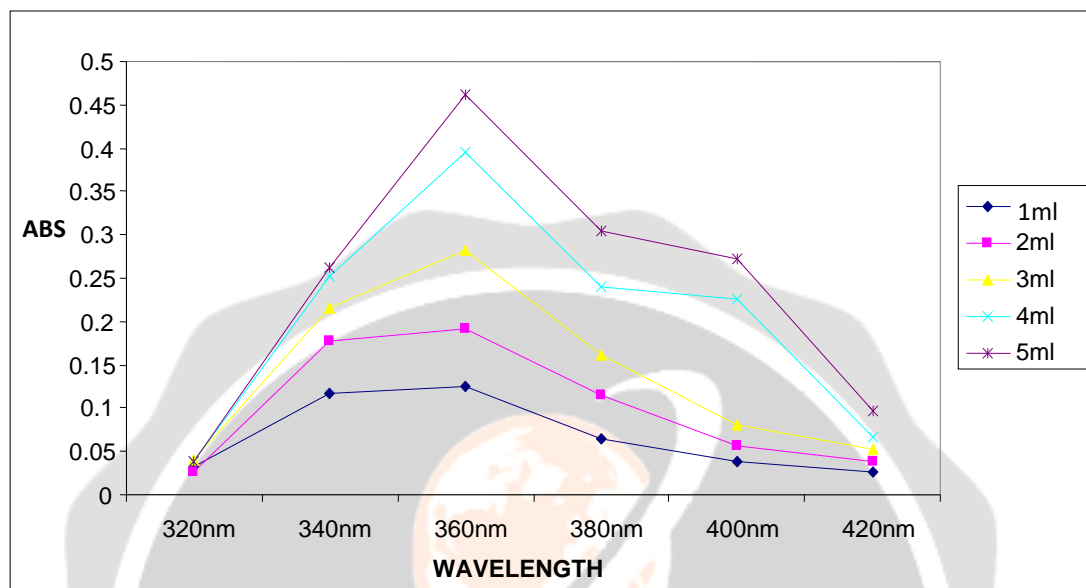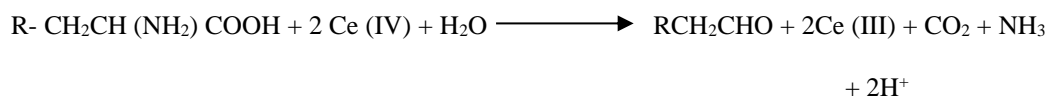

Fig 1.1 Plots between absorbance and concentration (λ_{max}) of cerium (IV)

1.2.2 Kinetic measurements and product Analysis

The solution was first placed in glass vessel at raining temperature from 298 K to 318 K in thermostat water both for 30 minutes. The UV- visible spectrophotometer error checks the blank sample through the cuvette [18-20]. The reaction was followed by measuring the absorption of cerium (IV) at 360nm with Systronics (105) UV- Visible Spectrophotometer [21-24]. The kinetic reaction was performed under pseudo first order conditions with L-histidine at concentration 1.0 x 10^{-2} mol dm^{-3} and cerium (IV) at concentration 5.0 x 10^{-4} mol dm^{-3} .It was observed that cerium ammonium sulfate on excess concentration of more than 5.0 x 10^{-3} mol dm^{-3} and on addition of L-histidne amino acid first order reaction. The UV–Visible spectrophotometer Beer's law use verified sample it becomes and calibrated between 5 x 10^{-4} to 5 x 10^{-3} mol dm^{-3} at 360 nm under the reaction condition with the molar extinction coefficient ε =2622 dm^{-3} mol^{-1} cm^{-1} .The pseudo first order rate constants (k_{obs}) were obtained from the slope by plotting log absorbance versus time. The aldehyde group was confirmed with qualitative test such as Schiff's reagent and 2, 4 DNP test [25]. The oxidation products were identified as Ce (III), 3-imidazolepropanal, ammonia and carbon dioxide. The ammonia was detected by Nesseler's regent test and the qualitative detected by CO_2 was passing the liberated gas through a tube containing lime water.
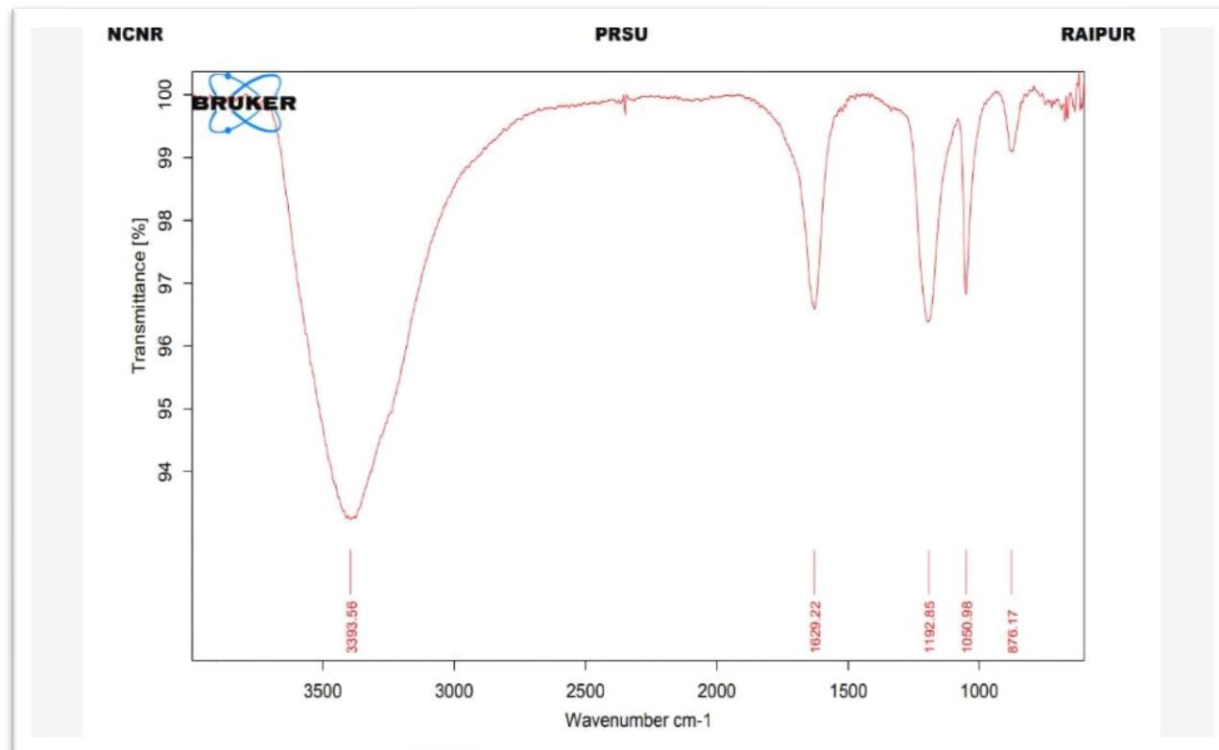
$$\text{R- } CH_2CH(NH_2)COOH + 2\,Ce\,(IV) + H_2O \longrightarrow RCH_2CHO + 2Ce\,(III) + CO_2 + NH_3$$

$$+\ 2H^+$$

R = $C_3H_3N_2$ (imidazole)   **Scheme -1.1**

Fig 1.2 FTIR plot between Transmittance [%] and Wavenumber cm^{-1}

1.3 RESULTS AND DISCUSSION

1.3.1 Effect of Concentration of Cerium (IV) [Cerium (IV)]

To study the rate of reaction, the concentration of the reactant in which various concentrations of cerium (IV) are added from 1.0×10^{-4} to 5.0×10^{-3} mol dm^{-3} and 1.0 mol dm^{-3} increases the acidity property. And other chemicals are taken in a fixed concentration of L- histidine 1.0×10^{-2} mol dm^{-3} and [Pd (II)] = 2.0×10^{-4} mol dm^{-3} at temperature range 298 K to 318 K at interval of 10 K. When Pd (II) catalyst is added to it, the rate of their reaction is more than the rate uncatalysis. The absorbance is directly proportional to the concentration of cerium (IV) and temperature but inversely proportional with time. The pseudo first order plots suggested that the rate constant (k) is decrease while increasing concentration of cerium (IV) for the oxidation of L-histidine. The pseudo first order of cerium (IV) respectively. The rate vs concentration of cerium (IV) is found to be linear with negative intercept.

Table 1.1: Variation of Cerium ammonium sulphate

[Ce(IV)] = 1.0×10^{-2} to 5.0×10^{-4} mol dm^{-3},   [L- His] = 1.0×10^{-2} mol dm^{-3},

 [H$^+$]   =   1.0 mol dm^{-3} Temp.   =   298 K

[Pd (II)] = 2.0×10^{-4} mol dm^{-3}

10^{-4} [Ce (IV)]$^{-1}$ mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.134	0.292	0.437	0.643	0.874
10	0.092	0.211	0.332	0.512	0.721
20	0.072	0.172	0.296	0.453	0.678
30	0.058	0.146	0.247	0.402	0.623

40	0.046	0.123	0.218	0.367	0.587
50	0.037	0.108	0.189	0.328	0.539
60	0.031	0.089	0.165	0.311	0.521
70	0.028	0.076	0.144	0.287	0.512
80	0.023	0.064	0.136	0.275	0.487
10^{-4} (k_{obs}), s^{-1}	**3.95**	**3.78**	**3.05**	**2.45**	**1.80**

Table 1.2: Variation of Cerium ammonium sulphate

$[Ce(IV)]$ = 5.0×10^{-4} mol dm^{-3}, $[L\text{-His}]$ = 1.0×10^{-2}

$[H^+]$ = 1.0 mol dm^{-3} Temp. = 308 K

$[Pd(II)]$ = 2.0×10^{-4} mol dm^{-3}

10^{-4} $[Ce(IV)]^{-1}$ mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.105	0.221	0.408	0.543	0.675
10	0.071	0.157	0.307	0.419	0.532
20	0.056	0.123	0.267	0.365	0.488
30	0.043	0.103	0.228	0.332	0.445
40	0.034	0.083	0.202	0.301	0.421
50	0.028	0.072	0.171	0.276	0.389
60	0.025	0.065	0.151	0.246	0.355
70	0.023	0.055	0.133	0.219	0.332
80	0.019	0.048	0.123	0.208	0.321
10^{-4} (k_{obs}), s^{-1}	**4.62**	**4.06**	**3.29**	**2.68**	**2.22**

Table 1.3: Variation of Cerium ammonium sulphate

$[Ce(IV)]$ = 5.0×10^{-4} mol dm-3, $[L\text{-His}]$ = 1.0×10^{-2}

$[H^+]$ = 1.0 mol dm-3   Temp. = 318 K

$[Pd(II)]$ = 2.0×10^{-4} mol dm^{-3}

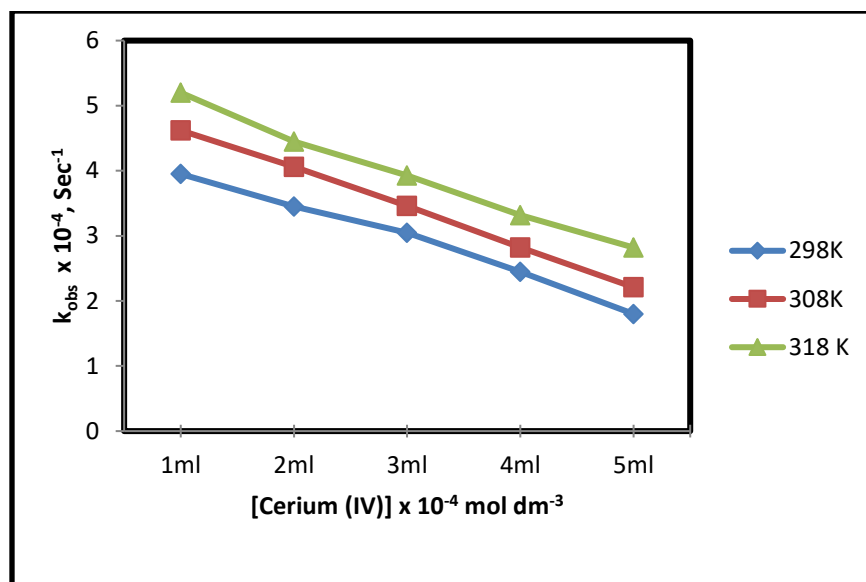| 10^{-4} $[Ce(IV)]^{-1}$ mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.091	0.181	0.378	0.504	0.611
10	0.061	0.127	0.276	0.386	0.467
20	0.047	0.1	0.244	0.323	0.423
30	0.036	0.083	0.206	0.287	0.383
40	0.029	0.067	0.186	0.246	0.356
50	0.024	0.057	0.157	0.221	0.332
60	0.021	0.052	0.136	0.208	0.318
70	0.018	0.044	0.121	0.189	0.297
80	0.016	0.038	0.108	0.168	0.282
10^{-4} (k_{obs}), s^{-1}	**1.67**	**1.71**	**1.81**	**1.87**	**1.94**

Fig. 1.3 Plots of [Cerium(IV)] vs k_{obs} sec^{-1}

1.3.2 Effect of Concentration of L-Histidine [L-Histidine]

The rate of reaction of L- histidine at different concentrations like = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3} and at a certain concentration of cerium (IV) = 5.0×10^{-4} mol dm^{-3}, $[H^+] = 1.0$ mol dm^{-3} and [Pd (II)] = 2.0×10^{-4} mol dm^{-3} at temperature range 298 K to 318 K at interval of 10 K has been chemical kinetic studied. In which if the reaction with the concentration of increases; the rate of reaction starts increasing rapidly with increase in temperature. Absorbance decreases with increasing concentration of L-histidine. The plot of k_{obs} versus [L- histidine] exhibits linearly with positive intercept and slope.

Table 1.4: Variation of L- Histidine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3},   [L- His]   = 5.0×10^{-2} to 1.0×10^{-2}

$[H^+]$ =   1.0 mol dm^{-3} Temp.   =   298 K

[Pd (II)] = 2.0×10^{-4} mol dm^{-3}

10^{-2} [L-His] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	1.011	0.921	0.833	0.765	0.628
10	0.876	0.794	0.707	0.641	0.521
20	0.787	0.712	0.636	0.581	0.467
30	0.725	0.656	0.590	0.539	0.432
40	0.687	0.612	0.529	0.487	0.408
50	0.643	0.584	0.517	0.464	0.381
60	0.615	0.559	0.498	0.443	0.364
70	0.578	0.527	0.467	0.421	0.334
80	0.556	0.501	0.434	0.406	0.326
10^{-4} (k_{obs}), s^{-1}	1.67	1.71	1.81	1.87	1.94

Table 1.5: Variation of L- Histidine

$[Ce(IV)]$ = 5.0 x 10^{-4} mol dm^{-3}, $[L\text{- His}]$ = 5.0 x 10^{-2} to 1.0 x 10^{-2}

$[H^+]$ = 1.0 mol dm^{-3} Temp. = 308 K

$[Pd (II)]$ = 2.0 x 10^{-4} mol dm^{-3}

10^{-2} [L-His] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.984	0.867	0.785	0.624	0.576
10	0.821	0.712	0.639	0.521	0.452
20	0.756	0.665	0.597	0.487	0.421
30	0.701	0.611	0.532	0.428	0.372
40	0.643	0.567	0.496	0.411	0.346
50	0.611	0.523	0.476	0.387	0.321
60	0.578	0.479	0.443	0.356	0.301
70	0.534	0.454	0.421	0.334	0.285
80	0.523	0.436	0.401	0.311	0.271
10^{-4} (k_{obs}), s^{-1}	1.84	1.94	1.99	2.14	2.27

Table 1.6: Variation of L- Histidine

$[Ce(IV)]$ = 5.0 x 10^{-4} mol dm^{-3}, $[L\text{- His}]$ = 5.0 x 10^{-2} to 1.0 x 10^{-2}

$[H^+]$ = 1.0 mol dm^{-3} Temp. = 318 K

$[Pd (II)]$ = 2.0 x 10^{-4} mol dm^{-3}

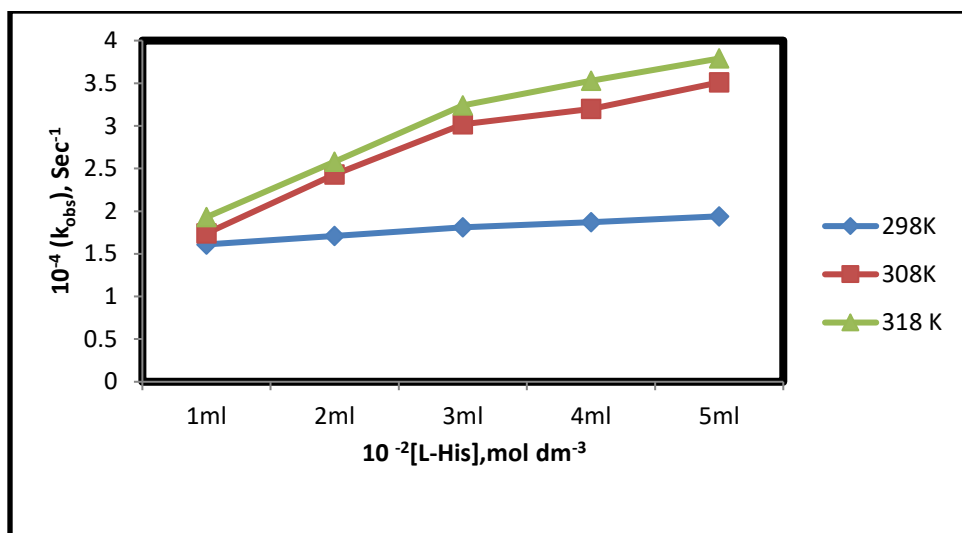| 10^{-2} [L-His] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.932	0.813	0.723	0.611	0.497
10	0.765	0.662	0.581	0.487	0.387
20	0.712	0.618	0.543	0.432	0.348
30	0.656	0.567	0.503	0.411	0.323
40	0.605	0.523	0.461	0.387	0.289
50	0.571	0.481	0.421	0.354	0.276
60	0.532	0.434	0.381	0.319	0.254
70	0.501	0.415	0.367	0.309	0.246
80	0.489	0.403	0.345	0.285	0.226
10^{-4} (k_{obs}), s^{-1}	1.91	2.01	2.10	2.20	2.36

Fig. 1.4 Plots of [L –His] vs (k_{obs}), sec^{-1}

1.3.3 Effect of Concentration of Palladium [Pd (II)]

To accelerate the rate of kinetic energy, a catalyst [Pd (II)] is added to it. It is found that the rate become reaction become faster. The effect of [Pd (II)] catalyst concentration from 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} and constant concentration of [cerium (IV)] = 5.0×10^{-4} mol dm^{-3}, [L- histidine] = 2.0×10^{-2} mol dm^{-3} and [H$^+$] = 1.0 mol dm^{-3} on the reaction from temperature 298 K to 318 K has been studied. In which there is an increase in the rate due to the catalyst of [Pd (II)] as fast as the L- histidine is converted into product. It we found out here that is the first order of [Pd (II)] reaction. k_{obs} versus [Pd (II)] yielded good linear plots (Fig.4.2.2) passing through the intercept.

Table 1.7: Variation of Palladium

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3},   [L- His] = 2.0×10^{-2} mol dm^{-3}

[H$^+$] = 1.0 mol dm^{-3} Temp. = 298 K

[Pd (II)] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}

10^{-4} [Pd (II)] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	1.081	0.896	0.789	0.641	0.521
10	0.914	0.723	0.615	0.478	0.381
20	0.842	0.623	0.523	0.412	0.331
30	0.784	0.579	0.465	0.356	0.271
40	0.751	0.523	0.412	0.321	0.245
50	0.723	0.497	0.376	0.298	0.221
60	0.676	0.478	0.334	0.263	0.197
70	0.643	0.456	0.295	0.231	0.172
80	0.614	0.432	0.278	0.218	0.154
10^{-4} (k_{obs}), s^{-1}	1.65	2.26	2.82	3.05	3.31

Table 1.8: Variation of Palladium

$[Ce(IV)]$ = 5.0×10^{-4} mol dm^{-3}, $[L\text{- His.}]$ = 2.0×10^{-2} mol dm^{-3}

$[H^+]$ = 1.0 mol dm^{-3} Temp. = 308 K

$[Pd(II)]$ = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}

10^{-4} [Pd (II)] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.993	0.845	0.714	0.563	0.489
10	0.829	0.668	0.545	0.418	0.345
20	0.768	0.581	0.456	0.345	0.307
30	0.708	0.523	0.414	0.301	0.245
40	0.661	0.489	0.345	0.278	0.223
50	0.645	0.456	0.306	0.245	0.201
60	0.614	0.423	0.287	0.219	0.173
70	0.587	0.398	0.268	0.201	0.154
80	0.556	0.376	0.245	0.182	0.134
10^{-4} (k_{obs}), s^{-1}	1.74	2.43	3.02	3.20	3.51

Table 1.9: Variation of Palladium

$[Ce(IV)]$ = 5.0×10^{-4} mol dm^{-3}, $[L\text{- His.}]$ = 2.0×10^{-2} mol dm^{-3}

$[H^+]$ = 1.0 mol dm^{-3} Temp. = 318 K

$[Pd(II)]$ = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}

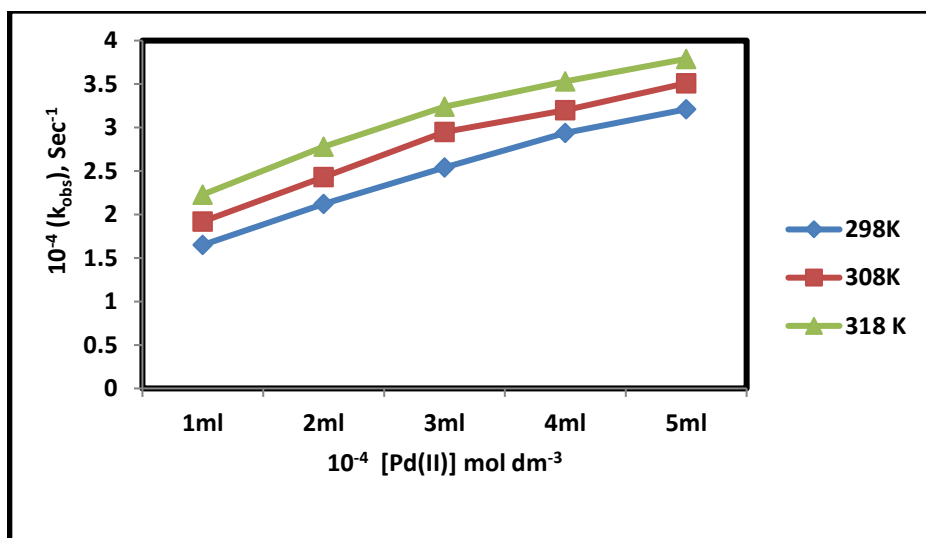| 10^{-4} [Pd (II)] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.888	0.767	0.678	0.532	0.434
10	0.721	0.594	0.512	0.389	0.303
20	0.651	0.523	0.432	0.323	0.267
30	0.615	0.456	0.362	0.268	0.214
40	0.576	0.432	0.321	0.227	0.178
50	0.562	0.383	0.278	0.201	0.151
60	0.531	0.367	0.245	0.189	0.132
70	0.508	0.356	0.223	0.167	0.121
80	0.481	0.332	0.211	0.148	0.111
10^{-4} (k_{obs}), s^{-1}	1.93	2.58	3.24	3.53	3.79

Fig. 1.5 Plots of [Pd(II)] vs (k_{obs}) , sec^{-1}

1.3.4 Effect of SDS Surfactant

SDS are anionic surfactants which increase the rate of reaction and these [SDS] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} at different concentrations are added at a certain concentration [cerium (IV)] = 2.0×10^{-4} mol dm^{-3}, [L-histidine] = 1.0×10^{-2} mol dm^{-3}, [H$^+$] = 1.0 mol dm^{-3} and [Pd (II)] = 2.0×10^{-4} mol dm^{-3} at temperature 298 K to form the first order of the reaction. The absorbance decreases as their concentration increases.

Table 1.10: Variation of SDS

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3},   [L- His] = 2.0×10^{-2} mol dm^{-3}

[H$^+$] = 1.0 mol dm^{-3} Temp. = 298 K

[Pd (II)] = 2.0×10^{-4} mol dm^{-3} [SDS] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}

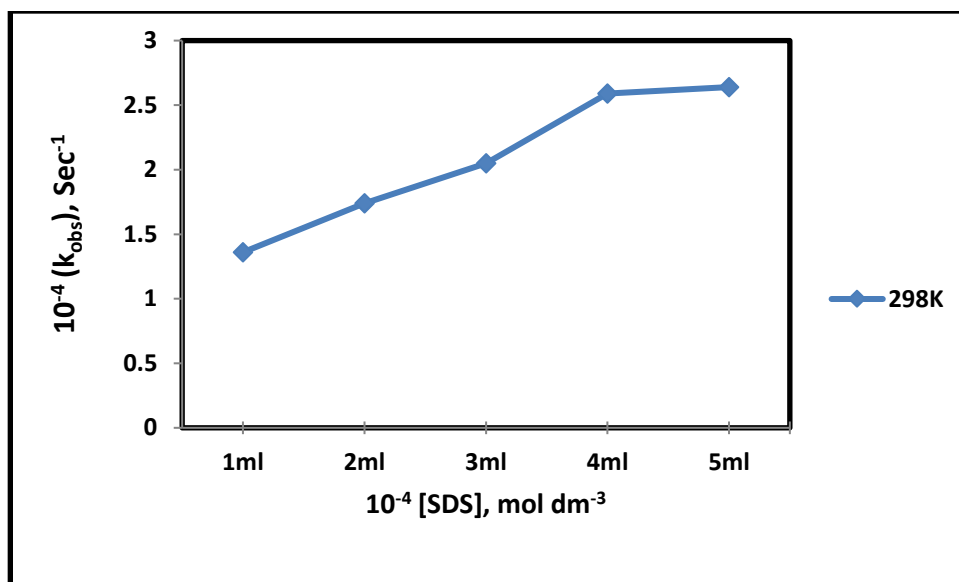| 10^{-4} [SDS] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.753	0.687	0.543	0.456	0.335
10	0.674	0.598	0.467	0.378	0.271
20	0.618	0.523	0.406	0.328	0.237
30	0.571	0.477	0.354	0.285	0.203
40	0.532	0.456	0.321	0.245	0.179
50	0.518	0.428	0.312	0.213	0.155
60	0.506	0.408	0.286	0.187	0.142
70	0.487	0.387	0.267	0.167	0.129
80	0.454	0.374	0.254	0.156	0.118
10^{-4} (k_{obs}), s^{-1}	1.36	1.74	2.05	2.59	2.64

Fig 1.6 Plot for the variation of SDS at 298 K

1.3.5 Effect of CTAB

These are cationic surfactants at different concentrations of [CTAB] 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} to which a certain concentration [Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [L- histidine] = 1.0×10^{-2} mol dm^{-3}, [H$^+$] = 1.0 mol dm^{-3} and [Pd (II)] = 2.0×10^{-4} mol dm^{-3} is added. These reactions increase the reaction rate at 298 K. Due to which the absorbance is reduced. Thus the rate of reaction is of the first order. The rate of reaction is increase with increase in the concentration of surfactant [CTAB].

Table 1.11: Variation of SDS

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3},   [L- His] = 2.0×10^{-2} mol dm^{-3}

[H$^+$] = 1.0 mol dm^{-3} Temp. = 298 K

[Pd (II)] = 2.0×10^{-4} mol dm^{-3} [CTAB] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}

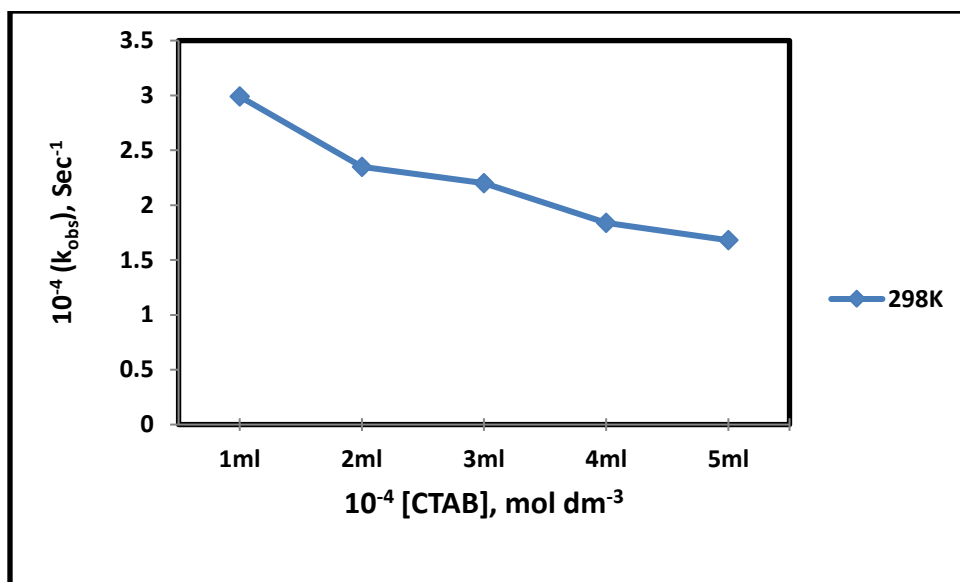| 10^{-4} [CTAB] mol dm^{-3}	1.0	2.0	3.0	4.0	5.0
Time in minutes	Absorbance				
0	0.774	0.632	0.523	0.412	0.321
10	0.621	0.521	0.432	0.346	0.278
20	0.523	0.444	0.383	0.317	0.245
30	0.434	0.402	0.345	0.291	0.231
40	0.367	0.368	0.313	0.277	0.223
50	0.319	0.328	0.284	0.253	0.204
60	0.297	0.308	0.267	0.238	0.197
70	0.256	0.287	0.249	0.221	0.184
80	0.237	0.264	0.229	0.204	0.176
10^{-4} (k_{obs}), s^{-1}	2.99	2.35	2.20	1.84	1.68

Fig 1.7 Plot for the variation of CTAB at 298 K

1.4 Mechanism

The catalyses oxidation of L-histidine by cerium (IV) acidic medium under the present experiment condition. The oxidation state of cerium (IV) was reduces to cerium (III) by L-histidine. The order with H^+ ion concentration was less than unity and negative. As the sulphuric acid concentration increases, the H^+ concentration increases, but there is also a corresponding increase in HSO_4^- ion concentration. Since the rate is inversely proportional to the HSO_4^- concentration, the overall effect of adding sulphuric acid would be to lower the rate [26-27]. L- histidine dependence from first order can be ascribed to complexation with cerium (IV). The reaction of cerium (IV) in acid medium proceeds much faster than the reaction in sulphate medium cerium (IV) is known in several complexes of sulfuric acid sulfate media such as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$, and $H_3Ce(SO_4)_4^-$ etc [28-29]. Since the rate is inversely dependent on the HSO_4^- concentration the overall effect of rate of reaction. Considering all these facts along with experimental results a reaction mechanism consisting of step, as follows,
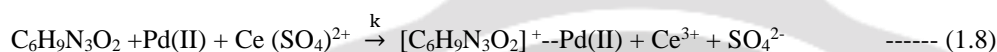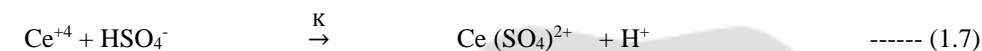
$$Ce^{4+} + H_2O \rightleftharpoons Ce(OH)^{3+}, + H^+ \qquad\qquad K_{OH} \qquad ------------ (1.1)$$

$$Ce^{4+} + SO_4^{2-} \rightleftharpoons Ce(SO_4)^{2+} \qquad\qquad K_1 \qquad ------------ (1.2)$$

$$Ce(SO_4)^{2+} + SO_4^{2-} \rightleftharpoons Ce(SO_4)_2 \qquad\qquad K_2 \qquad ------------ (1.3)$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons Ce(SO_4)_2 HSO_4^- \qquad\qquad K_3 \qquad ------------- (1.4)$$

$$Ce(SO_4)_2 HSO_4^- + HSO_4^- + H^+ \rightleftharpoons H_3Ce(SO_4)_4^- \qquad K_4 \qquad ------------ (1.5)$$

The Ce (OH) $^{3+}$ in the solution may be present and their concentration varied acidity. The cumulative equilibrium constants K_{OH}, β_1, β_2, β_3, and β_4, as shown in eq. (1.6)

$$[Ce^{4+}]_T = [Ce^{4+}]_F \{1 + K_{OH}/[H^+] + \beta_1[SO_4^{2-}] + \beta_2[SO_4^{2-}]^2 +, \beta_3[SO_4^{2-}]^2[HSO_4^-] +$$

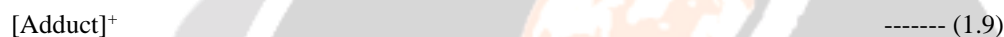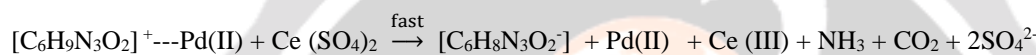$$\beta_4[SO_4^{2-}]^2[HSO_4^-] + [H+]\} \qquad\qquad ------------(1.6)$$

It is observed that SO_4^{2-} ions retards the rate of oxidation coupled with the observation that in $[H^+]$ decrease the rate, pointing to the fact that the neutral covalently bound $Ce(SO_4)_2$ is the active species of oxidant. The slight effect of

ionic strength indicate that a neutral molecule is involved in rate determining step, which further confirms the $Ce(SO_4)_2$ as the kinetically active species in the present study.

(Ce (IV) when reacted with L-histidine in the absence of catalysis in an aqueous acidic medium. So the rate of reaction is slow. But when it is added to the transition element Pd (II) catalysis of the d-block. So the rate of reaction increases. Firstly the rate of reaction is slow. They then form Pd complex with L-histidine; when Ce (IV) is added to it. So the change in Ce (III) takes place and builds [Adduct] $^+$ into the product. In this [Adduct] $^+$ the rate of reaction is fast. The free radical changes when this free radical is again treated with Ce $(SO_4)_2$. The result suggest that L-histidine combines with cerium (IV) to form of complex, when the slow step with one mole of $Ce(SO_4)_2$ to give the product cerium(IV), complex- L-histidine and SO_4^{2-}. It reacts with another mole of Ce $(SO_4)_2$ in a further fast step to give cerium (III), 3-imidazolepropanal, ammonia and carbon dioxide. The results are accommodated in scheme-1.2

$$Ce^{+4} + HSO_4^- \quad \xrightarrow{K} \quad Ce\ (SO_4)^{2+}\ + H^+ \qquad \text{------ (1.7)}$$

$$C_6H_9N_3O_2 + Pd(II) + Ce\ (SO_4)^{2+} \xrightarrow{k} [C_6H_9N_3O_2]^+\text{--}Pd(II) + Ce^{3+} + SO_4^{2-} \qquad \text{------ (1.8)}$$

[adduct]

$$[C_6H_9N_3O_2]^+\text{---}Pd(II) + Ce\ (SO_4)_2 \xrightarrow{fast} [C_6H_8N_3O_2^-]\ + Pd(II)\ + Ce\ (III) + NH_3 + CO_2 + 2SO_4^{2-}$$

[Adduct]$^+$ ------- (1.9)

Scheme -1.2

The proposed mechanism leads to the rate law (4.2.10)

$$\frac{-d[Ce(IV)]}{dt} = \frac{kK[Ce(IV)][L-His][Pd(II)]}{1+K[H^+][L-His]} \qquad \text{----- (1.10)}$$

$$\frac{-d[Ce(IV)]/dt}{[Ce(IV)]} = k_{obs} = \frac{kK[L-His][Pd(II)]}{1+K[H^+][L-His]} \qquad \text{------ (1.11)}$$

Where k_{obs} is pseudo first order rate constant.

The thermodynamic parameter for catalysed reaction of the rate determining energy of activation (Ea) is calculated. The table-1.12 shows the k increase with increase of temperature, indicating the reaction is endothermic, which is consistent with $\Delta H^\# > 0$. The moderate value of the $\Delta H^\#$ and $\Delta S^\#$ were favorable for electron transfer processes [29-31].

Table 1.12:- Kinetic and thermodynamic activation parameters for catalysed reaction

at 298 K temperature

Parameter	L-histidine
Ea$^\#$ (kJ mol^{-1})	52.12
$\Delta H^\#$ (kJ mol^{-1})	76.23
$\Delta S^\#$ (J mol^{-1})	-17.81
$\Delta G^\#$ (kJ mol^{-1})	82.21
log A	7.87

1.5 Conclusion

The reaction between L-histidine amino acid and cerium (IV) is slow reaction at room temperature. The reaction occurs in measurable quantities at different temperature 298 k to 318 k and 1 M H_2SO_4 concentration in catalyst. The

first order with respect to oxidant substrate and catalyst are found. The main active species of cerium (IV) is considered as $Ce(SO_4)_2$, although other species might be active to much lesser extent. The overall mechanistic descried here is consistent with product, kinetic and mechanistic study. The transition state theory of reaction rate other physical parameter value $\Delta H^{\#}$ (76.23 x $10^3 JK^{-1}$ mol^{-1}) $\Delta S^{\#}$ (-17.81 JK^{-1} mol^{-1}) ΔG (82.21 x $10^3 JK^{-1}$ mol^{-1}) were determined.

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