Kinetic And Mechanism of Pd (II) Catalytic Oxidation of Dl-Threonine by Cerium (IV) In Acidic Medium by Spectrophotometery Method

GAJANAND SAHU[1], SANJAY GHOSH[2]
[1, 2] Department of Chemistry, Govt. N.P.G. College of Science, Raipur 492010 (C.G) India

Abstract— In this reaction, the kinetic which is catalysesd in the presence of Pd (II) on the oxidation of DL-threonine through the acidic medium of Ce (IV) has been studied. In which the study has been done at three different temperature from 298 K to 318 K at temperature difference 10 K in which the factors affecting the rate of the reaction such as SDS, CTAB, KCl and the rate of the reaction in acidic medium have been determined. This is the rate of reaction is of first order in the presence of Pd (II). The proposed mechanism and results is discussed in the kinetic studies. This is shown by the following equation.

$$k_{obs} = \frac{kK[DL-thr]}{1+K[H+][DL-thr]}$$

Indexed Terms-- Kinetics, Oxidation, DL- threonine, catalysis Pd (II), Cerium (IV) acidic medium, mechanism,

I. INTRODUCTION

Oxidative deamination and decarboxylation convert CO_2 and H_2O into carbohydrates by oxidation by amino acids providing energy for all[1-3]. Oxidation amino acids Ce(IV) rapidly in the presence of a catalyst. There are mainly four types of element present in amino acid such as carbon, hydrogen, oxygen and nitrogen which is necessary for all living beings[4-5]. Amino acids contain amine group and organic groups and side chain. The biological importance of the amino acid was proved by its role in the synthesis of polypeptide proteins and nucleotides. Threonine present in central nervous system present is helpful for treating different type's depression. Metabolism of fat in the liver is caused by amino acids. Some amino acids are helpful in digestion process in human body for amino acids are used in genetic coding. DL- Threonine cannot be syntheses by your body but by outer fulfilled sources are like beef, cottage chesses, fish, bleak and sesame seeds[6-10].

The Ce (IV) as a powerful oxidizing agent in acidic medium. Here the Ce (IV) in H_2SO_4 medium has been acts as oxidizing agent. Ce (III) is reduced by the transfer of one electron from Ce (IV) via the acidic medium. The intermediate complex is located at a higher concentration in the acid of Ce (IV). Many reports are available for the kinetics of oxidation of N-bromonanisamide, tributylammoium chlorochromate, tripropylammonium fluorochromate, iron (III) -1, 10-phenathroline complex, chloromine –T, vanadium (V), manganese (III), n-bromosuccinimide, pyridiniumdichromate. The reaction of Ce (IV) with DL- threonine in aqueous acidic medium in gives up many species like Ce $(OH)^{3+}$, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ HSO_4^- and $H_3Ce(SO_4)$[11-17], but their rule has not attention so far.

The role of metals in biological system is important due to which the kinetic investigation on the oxidation of amino acids catalyses by various metals is considered an important filed of chemistry. Pd (II) catalysis reactions in many fields have also found widespread use in organic chemistry, pharmaceutical chemistry and chemical preparation. Their usefulness as a non- toxic and homogenous catalyst has been described in the several workers. Due to the formation of different oxidation states of Pd (II), the ecosystem becomes quit complex with various intermediate complexes[18-23].

We have obtained the reactive species in the acidic medium of the Ce (IV) by the present investigation. There was no information on the kinetics and mechanism of the oxidation of DL-threonine in sulphuric acid medium with Ce (IV) in the presence Pd (II) as catalyst. Therefore the oxidation Ce (IV) of

DL- threonine in a medium containing sulphuric acidic in the presence of a Pd (II) catalyst has been carefully studied.

II. EXPERIMENT

Ce (IV), DL-threonine and Pd (II) chemicals G.E. (Merck) brand was used. Other chemicals such as CTAB, SDS and sulphuric acid LOBA brand were used. The solution was prepared by dissolving in double distilled water to analysis all the chemicals. A stock solution was prepared by mixing ceric ammonium sulphate with 1.0 M sulphuric acid. The stock solution was encapsulated in aluminum foil bottles to prevent photochemical decomposition of Pd (II) chloride and their strength was checked from time to time in the of spectrophotometrically. The prepared stock solution is used for studying the reaction in kinetic[24-25].

- Kinetic measurement

All stock solution are kept in a thermostat for 30 minutes at a temperature of 298 K to 318 K. in this experiment, the temperature difference is 10 K and the time difference is also 10 minutes. These solutions are then absorbances by the 105 systronic spectrophotometer at 360 nm form these solution. The kinetic reaction was performed under pseudo first order condition with DL-threonine at concentration $1.0x10^{-2}$ to $5.0x10^{-2}$ mol dm^{-3} and Ce(IV) at concentration $1.0x10^{-4}$ to $5.0x10^{-4}$ mol dm^{-3}. The UV-visible spectrophotometer is calibration between $1.0x10^{-2}$ to $5.0x10^{-4}$ mol dm^{-3} at 360 nm under the reaction condition with the molar extinction coefficient $\varepsilon = 2622$ dm^{-3} mol^{-1} cm^{-1} by using Beer's law[26]. The pseudo first order rate constant rate constants (k_{obs}) were obtained from the slope of the plot of absorbance versus time[27].

- Stoichiometry and product analysis

The concentration of the reactant at 318 K for 24 hour in different reaction mixtures in different sets where Ce(IV) had constant ionic strength acidity and the concentration of the catalyst Pd in it was higher than the DL- threonine concentration. In which Ce(IV) was estimated in different sets after the reaction was completed. According to this equation two moles of Ce (IV) were consumed for one mole DL-threonine which is as follows.

$$R – CH (NH)_2 COOH + 2 Ce (IV) + H_2O \xrightarrow{Pd\ (II)} RCHO + 2Ce (III) + CO_2 + NH_3 + 2H^+$$

$$R\text{-} CH_3CH_2OH\text{--------------------} (1)$$

Scheme -1

The oxidation products were identified as Ce (III), 2 – hydroxyl propanal, ammonia and carbon dioxide. 2-Hydroxide propanal was confirmed by the IR spectrum of the corresponding species. The reaction mixture was treated with acidified with acidified 2, 4-dinitrophenyl hydrazine solution, which yielded a hydrazone, which indicater the presence of 2 – hydroxy propanal. The other product ammonia was detected by Nesselen's reagent test and CO_2 was qualitatively detected by passing the liberated gas through a tube containing lime water.

III. RESULTS

- Cerium (IV) Dependence

To study the rate of reaction, the concentration of the reactant in which various concentrations of Ce (IV) are added from $1.0x10^{-4}$ to $5.0x10^{-3}$ mol dm^{-3} and 1.0 mol dm^{-3} increases the acidity property. And other chemicals are taken in a fixed concentration of DL-threonine $1.0x10^{-2}$ mol dm^{-3} and [Pd (II)] = $5.0x10^{-4}$ mol dm^{-3} at temperature range 298 K to 318 K at interval of 10 K.

Table 1- Effect of variation of [Ce (IV)] on the reaction rate, at 298 K
[Ce (IV)] = $1.0x10^{-4}$ to $5.0x10^{-4}$ mol dm^{-3}, [DL- threonine] = $1.0x10^{-2}$ mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [Pd (II)] = 2.0 x 10^{-3} mol dm^{-3}

Time in minutes	Absorbance				
10^{-4} [Ce(IV)]	1.0	2.0	3.0	4.0	5.0
0	0.281	0.403	0.581	0.841	1.143
10	0.205	0.312	0.527	0.748	1.080

20	0.181	0.256	0.474	0.718	0.966
30	0.131	0.225	0.417	0.662	0.906
40	0.112	0.203	0.390	0.627	0.880
50	0.098	0.187	0.352	0.598	0.795
60	0.078	0.161	0.294	0.532	0.757
70	0.061	0.142	0.263	0.486	0.684
80	0.031	0.137	0.231	0.432	0.621
10^{-4} (k_{obs}), S^{-1}	4.03	2.99	1.77	1.36	1.19

Table 2- Effect of variation of [Ce (IV)] on the reaction rate, at 308 K
[Ce (IV)] = 1.0x10^{-4} to 5.0x10^{-4} mol dm^{-3}, [DL-threonine] = 1.0x10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [Pd (II)] = 2.0 x 10^{-3} mol dm^{-3}

Time in minutes	Absorbance				
10^{-4} [Ce(IV)]	1.0	2.0	3.0	4.0	5.0
0	0.312	0.477	0.656	0.888	1.023
10	0.218	0.348	0.562	0.767	0.918
20	0.173	0.311	0.482	0.719	0.863
30	0.141	0.267	0.448	0.689	0.821
40	0.113	0.233	0.417	0.653	0.782
50	0.081	0.208	0.397	0.633	0.733
60	0.064	0.187	0.354	0.582	0.693
70	0.032	0.163	0.335	0.521	0.665
80	0.024	0.139	0.302	0.489	0.617
10^{-4} (k_{obs}), S^{-1}	4.89	3.19	1.94	1.46	1.23

Table 3- Effect of variation of [Ce (IV)] on the reaction rate, at 318 K

[Ce (IV)] = 1.0x10^{-4} to 5.0x10^{-4} mol dm^{-3}, [DL- threonine] = 1.0x10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [Pd(II)] = 2.0 x 10^{-3} mol dm^{-3}

Time in minutes	Absorbance				
10^{-4} [Ce(IV)]	1.0	2.0	3.0	4.0	5.0
0	0.345	0.455	0.672	0.902	0.998
10	0.232	0.332	0.576	0.767	0.876
20	0.184	0.264	0.504	0.721	0.804
30	0.153	0.247	0.432	0.656	0.756
40	0.127	0.218	0.412	0.629	0.724
50	0.091	0.193	0.387	0.589	0.684
60	0.064	0.169	0.345	0.557	0.635
70	0.037	0.151	0.327	0.518	0.618

80	0.028	0.139	0.310	0.502	0.612
10^{-4} (k_{obs}), S^{-1}	5.02	3.37	2.06	1.64	1.44

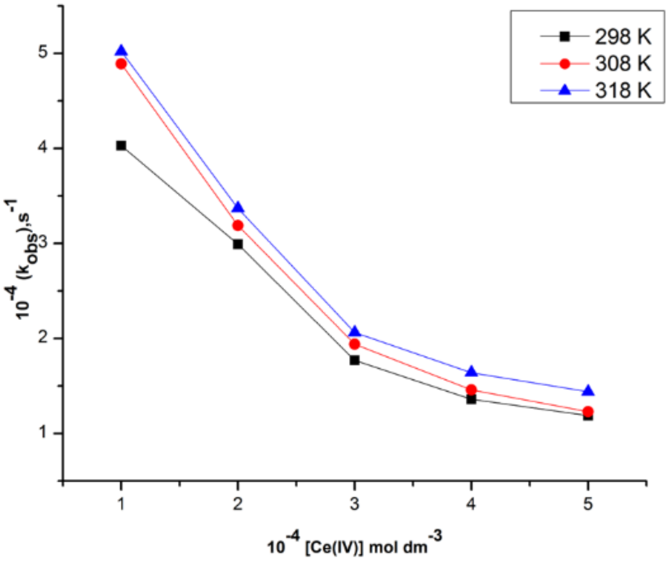


Fig: - 1 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-4} Ce (IV) mol dm^{-3}

Table 4- Effect of variation of [DL- threonine] on the reaction rate, at 298 K
[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL-threonine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

- DL- threonine Dependence

The rate of reaction of DL- threonine at different concentrations like = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3} and at a certain concentration of Ce (IV) = 5.0×10^{-4} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and [Pd (II)] = 5.0×10^{-2} 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 DL-threonine increases; the rate of reaction starts increasing rapidly with increase in temperature. Results are given Table 4, 5 and 6. Absorbance decreases with increasing concentration of DL-threonine. The plot of k_{obs} versus [DL- threonine] exhibits linearly with positive intercept and slope.

Time in minutes	Absorbance				
10^{-2} [DL-threonine]	1.0	2.0	3.0	4.0	5.0
0	1.023	0.932	0.827	0.745	0.639
10	1.001	0.898	0.791	0.711	0.607
20	0.985	0.876	0.768	0.687	0.582
30	0.973	0.847	0.743	0.665	0.564
40	0.940	0.823	0.732	0.637	0.545
50	0.917	0.817	0.718	0.618	0.528
60	0.896	0.809	0.707	0.601	0.518

70	0.845	0.801	0.694	0.586	0.509
80	0.821	0.793	0.683	0.571	0.496
10^{-4} (k_{obs}), S^{-1}	0.37	0.46	0.52	0.63	0.66

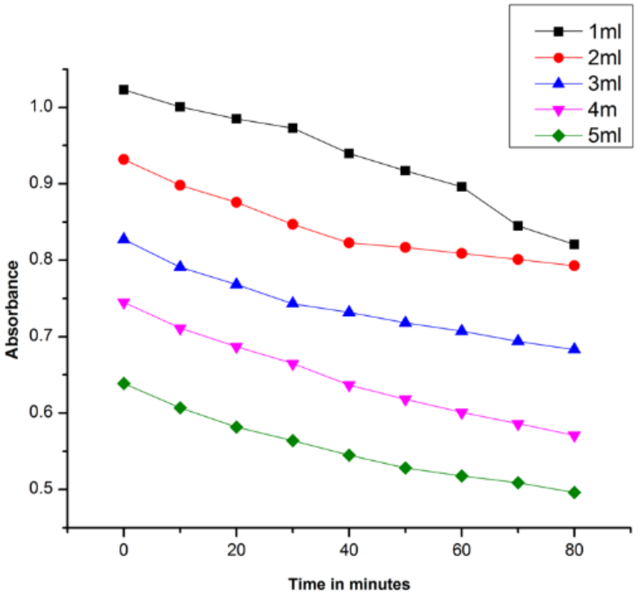


Fig: - 2 First order plots for the variation of Ce (IV) at temperature 298 K

Table 5- Effect of variation of [DL-threonine] on the reaction rate, at 308 K
[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL-threonine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

Time in minutes	Absorbance				
10^{-2} [DL-threonine]	1.0	2.0	3.0	4.0	5.0
0	1.143	0.987	0.879	0.767	0.659
10	0.976	0.848	0.749	0.648	0.547
20	0.923	0.786	0.686	0.576	0.492
30	0.887	0.734	0.633	0.538	0.438
40	0.849	0.712	0.604	0.513	0.416
50	0.828	0.694	0.569	0.489	0.372
60	0.811	0.632	0.543	0.456	0.354
70	0.793	0.614	0.532	0.421	0.321
80	0.789	0.577	0.516	0.404	0.301
10^{-4} (k_{obs}), S^{-1}	1.34	1.51	1.65	1.82	2.09

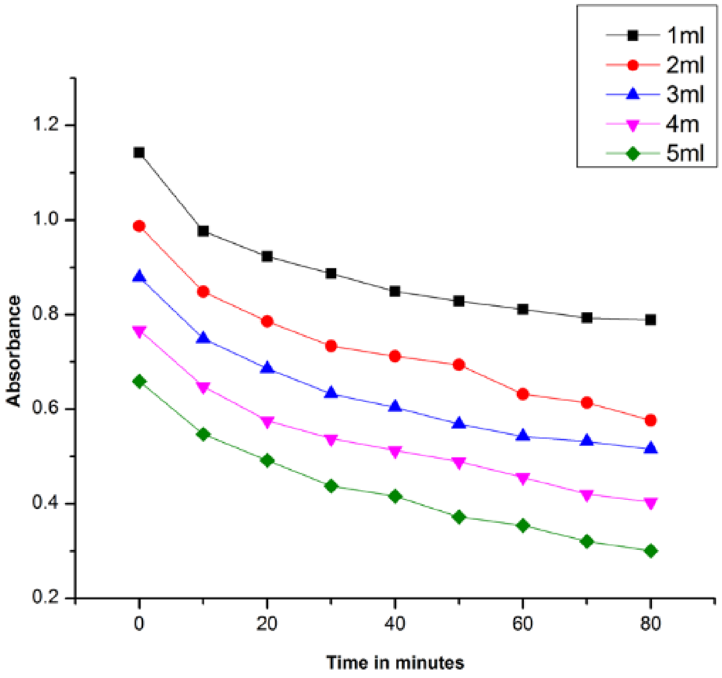


Fig: - 3 First order plots for the variation of Ce (IV) at temperature 308 K

Table 6- Effect of variation of [DL-threonine] on the reaction rate, at 318 K
[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL-threonine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

Time in minutes	Absorbance				
10^{-2} [DL-threonine]	1.0	2.0	3.0	4.0	5.0
0	0.996	0.897	0.833	0.698	0.623
10	0.843	0.761	0.702	0.579	0.513
20	0.769	0.703	0.634	0.521	0.457
30	0.752	0.662	0.593	0.487	0.415
40	0.712	0.636	0.538	0.439	0.378
50	0.667	0.613	0.513	0.414	0.343
60	0.621	0.579	0.487	0.395	0.318
70	0.602	0.521	0.429	0.378	0.286
80	0.589	0.467	0.403	0.352	0.238
10^{-4} (k_{obs}), S^{-1}	1.57	1.62	1.88	1.96	2.23

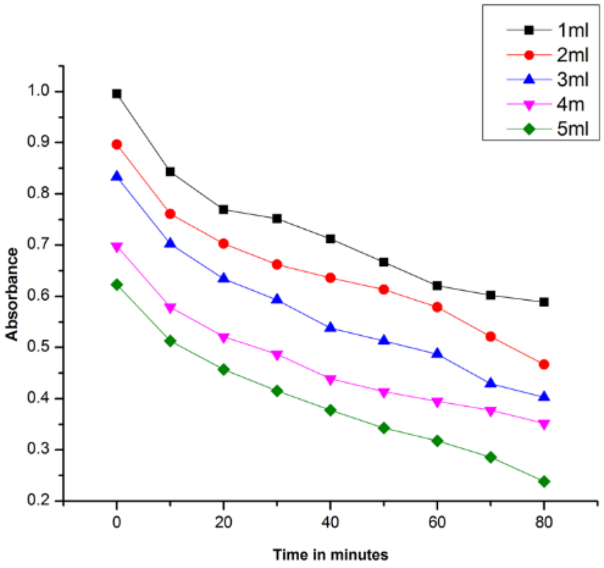


Fig: - 4 First order plots for the variation of Ce (IV) at temperature 318 K

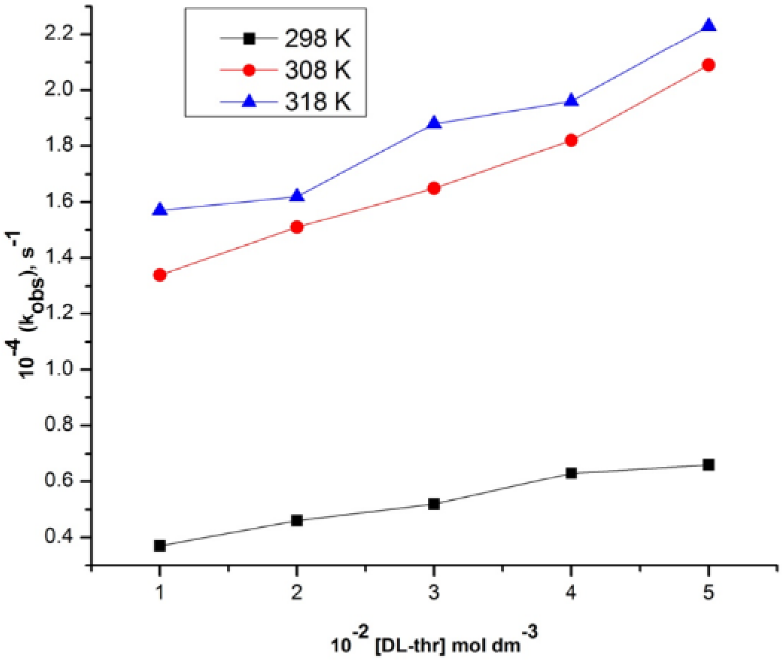


Fig: - 5 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-2} [DL- thre] mol dm^{-3}

Table 7- Effect of variation of palladium chloride on the reaction rate, at 298 K

[Ce (IV)] = 5.0x10^{-4} mol dm^{-3}, [DL- threonine] = 2.0x10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 1.0x10^{-3} to 5.0x10^{-3} mol dm^{-3}

- Palladium (II) Dependence

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 1.0x10^{-3} to 5.0x 10^{-3} mol $dm^{-3}$and constant concentration of [Ce (IV)] = 5.0x10^{-4} mol dm^{-3}, [DL- threonine] = 2.0x10^{-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 DL- threonine 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.6) passing through the origin. The result are given in Table 7,8,9

Time in minutes	Absorbance				
10^{-3} [Pd(II)]	1.0	2.0	3.0	4.0	5.0
0	0.738	0.623	0.521	0.428	0.316
10	0.630	0.516	0.414	0.329	0.263
20	0.586	0.476	0.378	0.302	0.210
30	0.505	0.432	0.341	0.278	0.141
40	0.460	0.407	0.319	0.243	0.107
50	0.433	0.384	0.286	0.211	0.085
60	0.422	0.353	0.267	0.184	0.080
70	0.395	0.334	0.247	0.134	0.048
80	0.365	0.311	0.224	0.121	0.033
10^{-4} (k_{obs}), S^{-1}	1.86	1.91	2.28	2.77	4.10

Table 8- Effect of variation of palladium chloride on the reaction rate, at 308 K

[Ce (IV)] = 5.0x10^{-4} mol dm^{-3}, [DL- threonine] = 2.0x10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 1.0x10^{-3} to 5.0x10^{-3} mol dm^{-3}

Time in minutes	Absorbance				
10^{-3} [Pd(II)]	1.0	2.0	3.0	4.0	5.0
0	0.833	0.754	0.637	0.521	0.472
10	0.714	0.619	0.508	0.417	0.394
20	0.634	0.567	0.456	0.354	0.289
30	0.578	0.524	0.413	0.303	0.213
40	0.517	0.486	0.376	0.264	0.176
50	0.476	0.439	0.337	0.223	0.142
60	0.453	0.407	0.316	0.184	0.094
70	0.435	0.378	0.289	0.156	0.068
80	0.419	0.359	0.264	0.138	0.027
10^{-4} (k_{obs}), S^{-1}	1.92	2.02	2.37	3.01	4.33

Table 9- Effect of variation of palladium chloride on the reaction rate, at 318 K

[Ce (IV)] = 5.0x10^{-4} mol dm^{-3}, [DL- threonine] = 2.0x10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 1.0x10^{-3} to 5.0x10^{-3} mol dm^{-3}

Time in minutes	Absorbance				
10^{-3} [Pd(II)]	1.0	2.0	3.0	4.0	5.0
0	0.996	0.897	0.673	0.902	0.998
10	0.843	0.761	0.576	0.767	0.876
20	0.789	0.703	0.504	0.721	0.804
30	0.752	0.662	0.432	0.656	0.756
40	0.712	0.636	0.412	0.629	0.724
50	0.667	0.613	0.387	0.589	0.684
60	0.621	0.579	0.345	0.557	0.635
70	0.602	0.521	0.327	0.518	0.618
80	0.589	0.467	0.310	0.502	0.612
10^{-4} (k_{obs}), S^{-1}	1.57	1.62	2.06	1.64	1.44

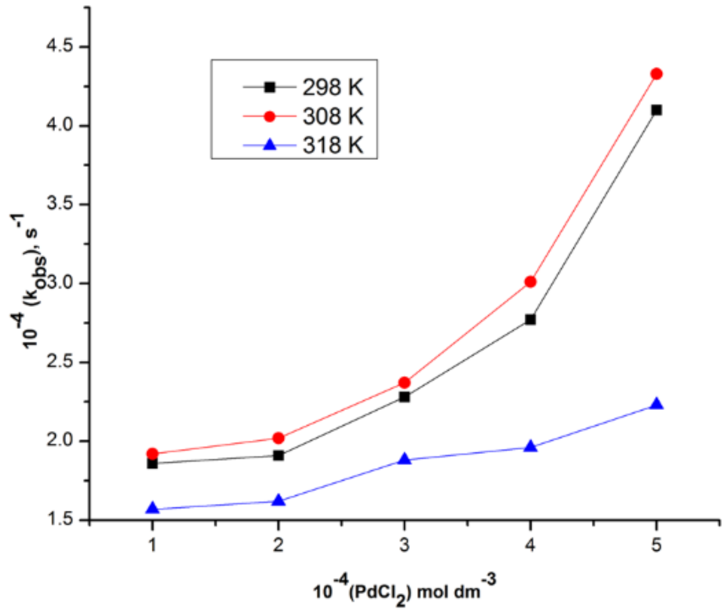


Fig: - 6 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-3} [Pd (II)] mol dm^{-3}

Effect of SDS Surfactant

SDS are anionic surfactants which increase the rate of reaction and these [SDS] = 1.0 X 10^{-4} to 5.0 X 10^{-4} mol dm^{-3} at different concentrations are added at a certain concentration [Ce (IV)] = 2.0x10^{-4} mol dm^{-3}, [DL - threonine] = 2.0x10^{-2} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and [Pd (II)] = 2.0x10^{-3} mol dm^{-3} at temperature 298 K to form the first order of the reaction. The absorbance decreases as their concentration increases. Result is given in Table 11. The plot of rate versus [SDS] has been straight line passing through the origin Fig.7

Table 10- Effect of variation of SDS on the reaction rate, at 298 K
[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL- threonine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

Time in minutes	Absorbance				
10^{-3} [SDS]	1.0	2.0	3.0	4.0	5.0
0	0.495	0.413	0.351	0.329	0.278
10	0.476	0.373	0.318	0.273	0.221
20	0.454	0.357	0.288	0.252	0.196
30	0.435	0.341	0.264	0.239	0.183
40	0.420	0.317	0.211	0.214	0.176
50	0.329	0.298	0.195	0.197	0.155
60	0.279	0.234	0.186	0.178	0.142
70	0.223	0.221	0.178	0.163	0.129
80	0.201	0.213	0.171	0.153	0.117
10^{-4} (k_{obs}), S^{-1}	1.18	1.32	1.73	1.94	2.30

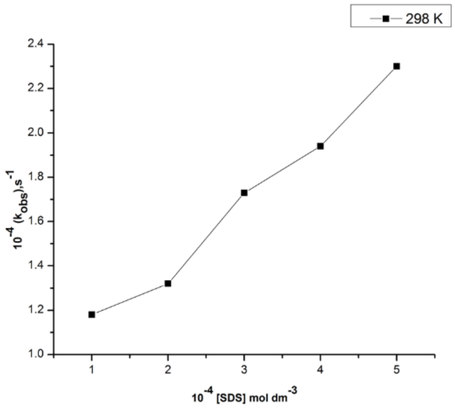


Fig: - 7 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-4} [SDS] mol dm^{-3}

- Effect of CTAB

These are cationic surfactants at different concentrations of [CTAB] 1.0 x 10^{-4} to 5.0 x 10^{-4} mol dm^{-3} to which a certain concentration [Ce (IV)] = 2.0×10^{-4} mol dm^{-3}, [DL-threonine] = 2.0×10^{-2} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and Pd (II) = 2.0×10^{-3} 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 11. Plots of kobs versus [CTAB] gives a straight line with positive slope and intercept Fig.8

Table 11- Effect of variation of CTAB on the reaction rate, at 298 K

[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL- threonine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

Time in minutes	Absorbance				
10^{-4} [CTAB]	1.0	2.0	3.0	4.0	5.0
0	0.324	0.245	0.195	0.183	0.161
10	0.284	0.189	0.161	0.149	0.131

20	0.272	0.163	0.149	0.135	0.117
30	0.226	0.152	0.123	0.117	0.104
40	0.218	0.139	0.111	0.103	0.092
50	0.182	0.130	0.103	0.091	0.083
60	0.163	0.118	0.091	0.084	0.071
70	0.152	0.114	0.083	0.077	0.062
80	0.141	0.111	0.074	0.071	0.0.52
10^{-4} (k_{obs}), S^{-1}	1.83	2.01	2.33	2.42	2.49

Fig: - 7 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-4} [CTAB] mol dm^{-3}

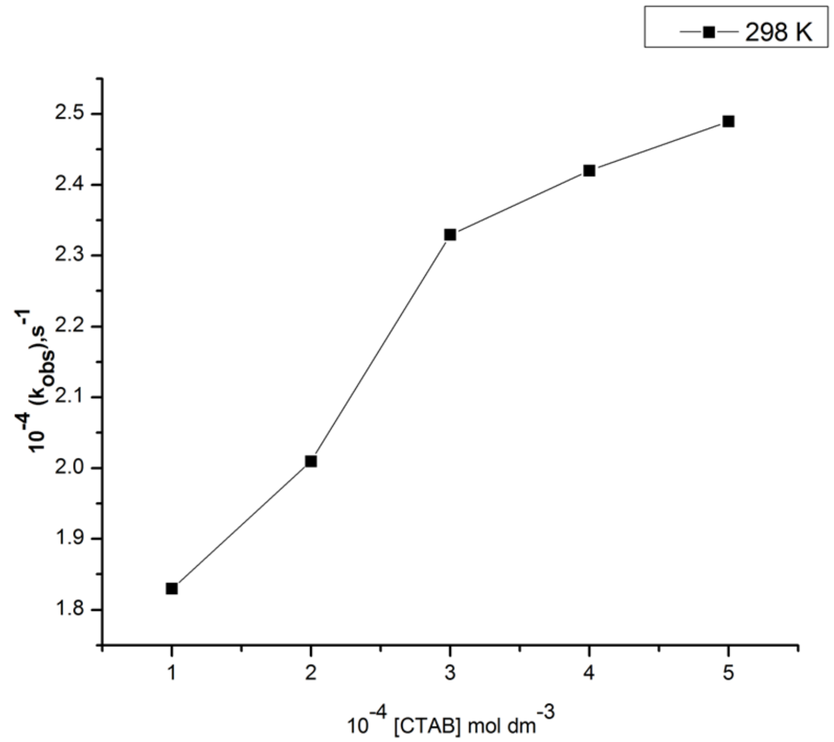


Fig: - 8 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-4} [CTAB] mol dm^{-3}

- Effect of Salt KCl

KCl is the univalent ionic strength that increases the rate of a reaction. Various concentrations of [KCl] = 1.0 X 10^{-3} to 5.0 X 10^{-3} mixed with a certain concentration of [Ce (IV)] = 3.0×10^{-4} mol dm^{-3}, [L-Proline] = 4.0×10^{-2} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and [Mn (II)] = 2.0×10^{-3} mol dm^{-3} have been studied to rate the reaction at a temperature of 298 K. As the concentration of KCl increases, thus it is a first order reaction.

Table 12- Effect of variation of KCl on the reaction rate, at 298 K
[Ce (IV)] = 5.0×10^{-4} mol dm^{-3}, [DL-thronine] = 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3} [Pd (II)] = 2.0×10^{-3}mol dm^{-3}

Time in minutes	Absorbance				
10^{-3} [KCl]	1.0	2.0	3.0	4.0	5.0

0	0.967	0.785	0.687	0.623	0.504
10	0.894	0.689	0.588	0.529	0.399
20	0.827	0.609	0.527	0.467	0.342
30	0.779	0.559	0.467	0.414	0.291
40	0.748	0.536	0.438	0.387	0.223
50	0.716	0.513	0.403	0.361	0.167
60	0.683	0.472	0.386	0.342	0.163
70	0.668	0.458	0.357	0.311	0.145
80	0.652	0.425	0.343	0.264	0.123
10^{-4} (k_{obs}), S^{-1}	1.05	1.64	1.90	2.03	3.24

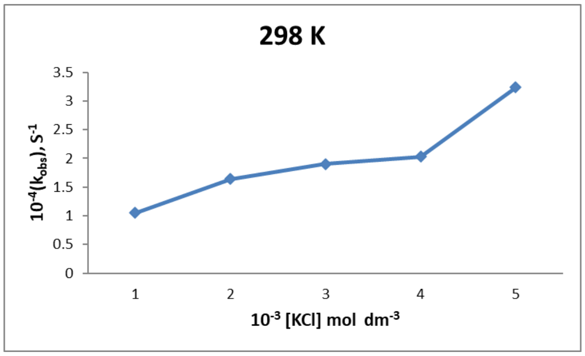


Fig: - 9 Plot of 10^{-4} (k_{obs}), Sec^{-1} versus 10^{-3} [KCl] mol dm^{-3}

IV. DISCUSSION

Their ionic strength is increased by adding 1.0 M H_2SO_4 to Ce (IV). And Ce is a good oxidant reactant in its species which accepts electrons. Their reaction rate of reaction decreases with increasing acidic medium with amino acids. For this reason, several complexes have been formed and studied at a temperature of 298 K to 318 K Ce after an interval of 10 minutes by adding Ce (IV) as an oxidant to a solution of sulphuric acid. This is given below.

$$Ce^{4+} + HSO_4^- \overset{a}{\Longleftrightarrow} Ce(SO_4)^{2+} + H^+ \quad \text{---} (2)$$

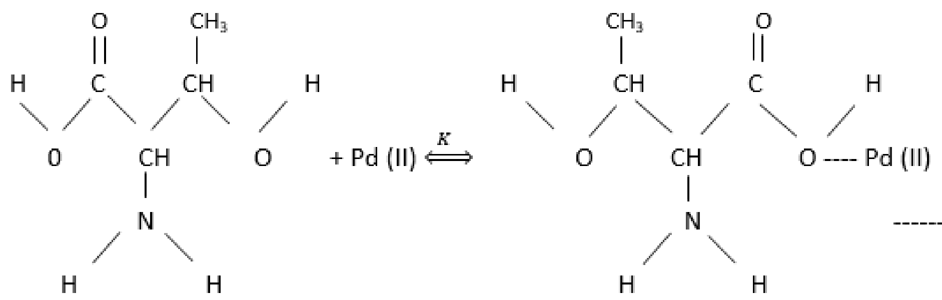
$$Ce(SO_4)^{2+} + HSO_4^- \overset{b}{\Longleftrightarrow} Ce(SO_4)_2 + H^+ \quad \text{----------------------------------} (3)$$

$$Ce(SO_4)_2 + HSO_4^- \overset{c}{\Longleftrightarrow} HCe(SO_4)_3^- \quad \text{-------------------------------------} (4)$$

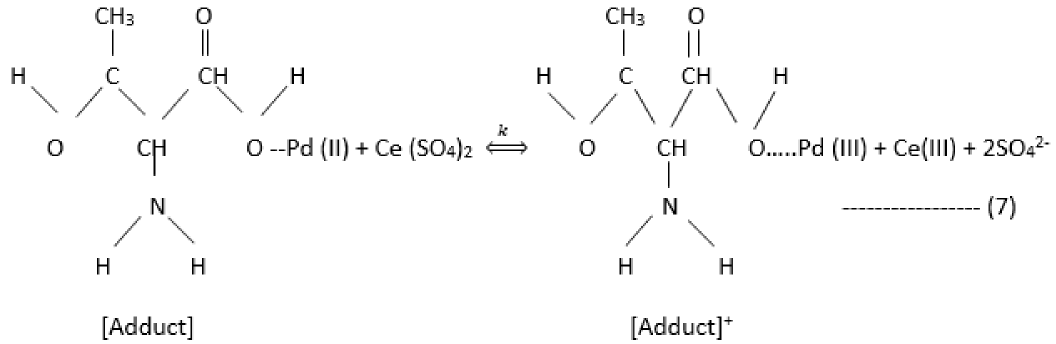
$$HCe(SO_4)_3^- + HSO_4^- \overset{d}{\Longleftrightarrow} H_2Ce(SO_4)_4^{2-} \quad \text{--------------------------------------} (5)$$

Where the equilibrium constants for the above phases at equilibrium i.e. a,b,c and d are reported to be 3500, 3000 and 20 at temperatures from 298 K to to be 3500, 3000 and 20 at temperatures from 298 K to 318 K respectively. Thus redox reaction takes place in it. In which $HCe(So_4)^-_3$ is ruled out from the reactive form of Ce (IV) with DL- threonine in a more acidic medium.

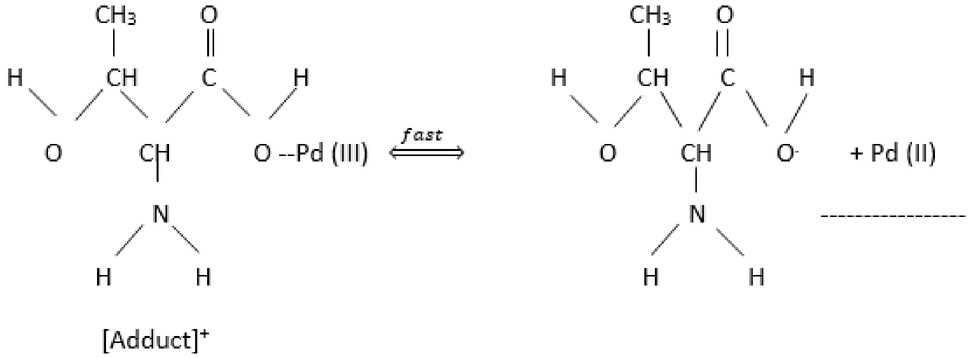
Ce (IV) when reacted with DL- threonine in the absence of catalysis in an aqueous acidic medium. So the rate rate of reaction is slow. But when it is added to the transition element Pd (II) catalysis of the d-block. So the rate of reaction increases. Firstly the rate of reaction is slow. They then form Pd complex with DL-threonine; 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 $(SO_4)_2$. So the product forms as propanal, carbandioxide, ammonia, sulphate and Ce (III) gets changed. This reaction below.


+ Pd (II)
K
O ---- Pd (II)

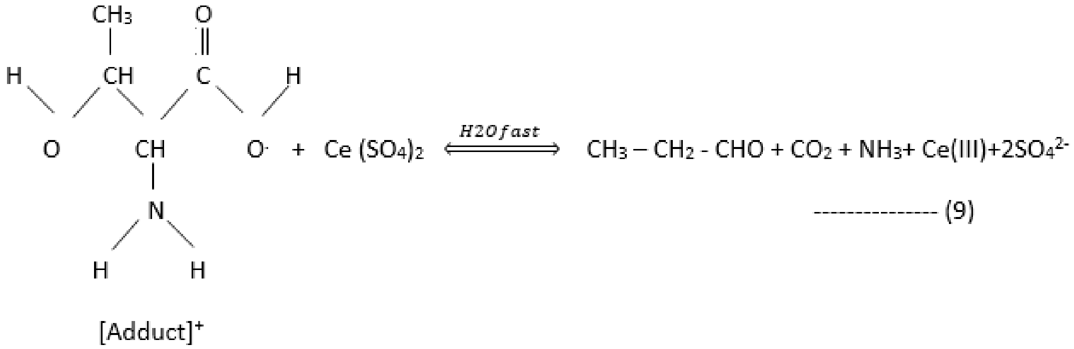
-------------- (6)


O --Pd (II) + Ce (SO4)2
k
O.....Pd (III) + Ce(III) + 2SO4 2-
[Adduct]
[Adduct]+

----------------- (7)


O --Pd (III)
fast
O-
+ Pd (II)
[Adduct]+

----------------- (8)


O- + Ce (SO4)2
H2O fast
CH3 – CH2 - CHO + CO2 + NH3+ Ce(III)+2SO4 2-
[Adduct]+

--------------- (9)

The proposed mechanism leads to the rate law (10)

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{kK[\mathrm{Ce(IV)}][\mathrm{DL-thr}][\mathrm{Pd(II)}]}{1+K[\mathrm{H+}][\mathrm{DL-thr}]} \quad -$$

-------------------- (10)

$$\frac{-d[\mathrm{Ce(IV)}]/dt}{[\mathrm{Ce(IV)}]} = k_{obs} = \frac{kK[\mathrm{DL-thr}][\mathrm{Pd(II)}]}{1+K[\mathrm{H+}][\mathrm{DL-thr}]} \quad -$$

------------------- (11)

Where k_{obs} is pseudo first order rate constant. Since the order with respect to Pd (II) rate law further change to (12)

$$k_{obs} = \frac{kK[\mathrm{DL-thr}]}{1+K[\mathrm{H+}][\mathrm{DL-thr}]} \quad -$$

----------------(12)

After rearranging equation (12)

$$k_{obs} = \frac{kK[\mathrm{DL-thr}]}{1} + \frac{k}{[\mathrm{H+}]} \quad -$$

-----------------(13)

Similarly it is clear from equation (13) that with increase in the rate of reaction concentration $[H^+]$, there is a decrease in k_{obs} and forms a straight line between k_{obs} and DL-threonine and the intercept intercept is zero. It is clear from table-2 that the thermodynamics parameters have evaluated the parameters of kinetic energy in which the process of the reaction is the endothermic process. Because the value of entropy is negative. This is clear from Fig -4 that activation energy has been calculated from the Arrhenius equation. In which the rate of reaction increases with increase in temperature due to which there is an increase in the value of ΔG, ΔH and a decrease in the activation energy; the values are as follows $\Delta G^{\#} = 31.58$ kJ mol^{-1}, $\Delta H^{\#} = 26.12$ kJ mol^{-1}, $\Delta S^{\#} = -17.29$ J mol^{-1} and log A = 2.44 .

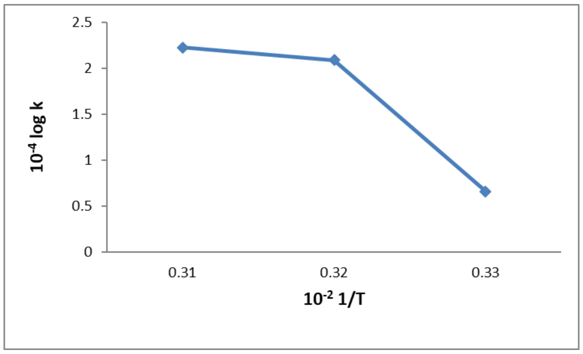


Fig: - 10 Plot of 10^{-4} log k versus 10^{-2} x 1/T that the reaction is Arrhenius plots show the linear

Table 13:- Kinetic and thermodynamic activation parameter for catalyses reaction

Parameter	DL-threonine
$Ea^{\#}$ (kJ mol^{-1})	0.66
$\Delta H^{\#}$ (kJ mol^{-1})	26.12
$\Delta S^{\#}$ (J mol^{-1})	-17.29
$\Delta G^{\#}$ (kJ mol^{-1})	31.58
logA	2.44

CONCLUSION

Oxidation of DL- threonine takes place by Ce (IV). But the rate of reaction is slow in the absence of catalysed. It occurs in acidic medium and on adding the catalyst Pd (II) the rate of the the reaction increases. This is the first order of the rate of the reaction. It was found that reactant species for the oxidation of Ce (IV) in acidic medium $CuSO_4$ although is much less active than other species. Therefore, the DL- threonine reacted with $CuSO_4$, and the catalyst Pd (II) easily oxidizes amino acids in acidic medium.

REFERENCES

[1] S.Huo, C. Song, J. Shan, S.Shen and H. Sun, J.Iran. Chem. Soc., 6,243, 2009. D.Bilehal, R.Kulkarni and S.T. Nadibewoor, J.Mol.Catal. A: Chemical, 232,21,2005.

[2] Y.R. Katre, A.K. Singh, G.K. Joshi and S.Patil, Oxid. Commun., 29, 137, 2006.

[3] R. V. Nadh and M. Sireesha, Bul. Chem. Commun. 47, 13, 2015.

[4] S.Mathur, M.B. Yadav and V.Devra, Int. J. Chem. Sci., 13, 641, 2015.

[5] Martha H, Marie A. Biochemical, Physiological, and Molecular Aspects of Human Nutrition - E-Book. Elsevier Health Sciences 2013.

[6] Jastrzab, Renata. Studies of new phosphothreonine complexes formed in binary and ternary systems including biogenic amines and copper (II). J. Coord. Chem. 2013; 66:98-113.

[7] AS, Food and Nutrition Board, Institute of Medicine; Dietary Reference Intakes for Energy,

Carbohydrate, Fiber, Fat, Fatty Acids, Cholesterol, Protein, and Amino Acids (Macronutrients). National Academy Press, Washington, D.C., pg. 730, 2009. Available from, as of March 10, 2010: http://www.nap.edu/catalog/10490.html

[8] L-Threonine is a large neutral amino acid that is indispensable. ... L-threonine does not take part in transamination reactions.

[9] NAS, Food and Nutrition Board, Institute of Medicine; Dietary Reference Intakes for Energy, Carbohydrate, Fiber, Fat, Fatty Acids, Cholesterol, Protein, and Amino Acids (Macronutrients). National Academy Press, Washington, D.C., pg. 606, 2009. Available from, as of March 10, 2010:

[10] Malviya LN, Siriah VK, Badole MK. Kinetics and mechanism of oxidation of glycine by N-bromoanisamide. Int. J. Inn. Sci. Eng. Tech. 2015; 2: 565 – 570.

[11] Prabhakar K, Hussain K. Kinetics of oxidation and mechanism of glycine by tributylammonium chlorochromate in acid medium. Int .J. Phar. Phceu. Rea. 2017; 10:224-234.

[12] Kishore KK, Vani P. Kinetic and mechanism of oxidation of glycine by iron (III) Phenantroline complex in perchloric acid medium. J. Chem. Sci. 2005; 117:329 -332.

[13] Kishore KK, Vani P. Kinetic and mechanism of oxidation of glycine by iron (III) Phenantroline complex in perchloric acid medium. J. Chem. Sci. 2005; 117:329 -332.

[14] Grover N, kambo N, Upadhayay SK. Kinetics and mechanism of palladium (II) catalysed oxidation of some α - amino acids by chloromine-T in perchloric acid Indian. J. Chem. 2002; 41: 2482 -2488.

[15] Joshi SK, Kandpal ND. Kinetics of Ruthenium (III) catalysed oxidation of amino acids by vanadium (V) in aqueous perchloric acid. Phy. Chem .Indian. J. 2006; 1:106 – 111.

[16] Chimatadar SA, Basavaraj T, Nandibewoor ST. Mechanistic Study of Oxidation of Palladium (II) by Cerium (IV) in Aqueous Acid. Trans. Met. Chem. 2006; 31:186–193.

[17] A. Canty, Handbook of Organopalladium Chemistry of Organic Synthesis, E.I. Negishi, Eds. John Wily& Sons, New York 189, 2002.

[18] Rodic P, Milosev I. The influence of additional salts on corrosion inhibition by cerium (III) acetate in the protection of AA7075-T6 in chloride solution. Corros. Sci. 2019; 149:108-122.

[19] K. Muniz, Angew Chem. Int. Ed. Engl,. 48, 9412, 2009.

[20] E. I. Negishi, Handbook of Organopalladium Chemistry of Organic Synthesis, E.I. Negishi, Eds. John Wiely & Sons, New York, 17, 2002.

[21] S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, Trans. Mel. Chem., 26, 662, 2001.

[22] S. Srivastava and P. Singh, Bull. Catal. Soc. Ind., 7, 12, 2008.

[23] A. Kinetic and Mechanistic Aspects of Oxidation of Aminotriazole Formamidine by Cerium (IV) in Aqueous Perchloric and Sulfuric Acid Solutions: A Comparative Study. J. Soln. Chem. 2016; 45:246-264.

[24] . Jarange, A.B., Patil, S.V., Malkhede, D.D., Deodhar, S.M., Nandre, V.S., Athare, S.V., Kodam, K.M., Gejji, S.P. p-Sulfonatocalixarene versus p-thiasulfonatocalixarene: encapsulation of tenofovir disoproxil fumarate and implications to ESI-MS, HPLC, NMR, DFT and anti-MRSA activities. J. Incl. Phenom. Macrocycl. Chem. 2021; 99: 43-59.

[25] Hosahalli RV, savanur AP, Nandibewoor ST, Chimatadar SA, Int. J. Chem. Kinetic., 42 (2010) 440

[26] Savanur AP, Nandibewoor ST, Chimatadar SA, Manganese (II) catalysed oxidation of glycerol by cerium (IV) in aqueous sulphuric acid medium: a kinetic and mechanistic study. Trans. Met. Chem. 2009; 34:711-718.