Asian Journal of Chemistry; Vol. 34, No. 6 (2022), 1361-1365

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23540

Kinetic and Mechanism of Mn(II) Catalytic Oxidation of L-Proline by Cerium(IV) in Acidic Medium by Spectrophotometry Method

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Received: 18 September 2021; *Accepted*: 18 November 2021; *Published online*: 18 May 2022; AJC-20793

The rate of reaction of L-proline with Ce(IV) acidic medium has been kinetically studied in presence of Mn(II) as catalyst using a spectrophotometric method. The reactions have been performed at temperatures range from 298 K to 318 K in interval of 10 min. 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 Mn(II) and positive fractional order with respect to [L-proline]. This would have a first order reaction between the Ce(IV) and L-proline 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 $\Delta S^\#$ increased with increasing temperature so that the rate equation derived for this mechanism could explain all observed results.

Keywords: Kinetics, Oxidation, L-Proline, Cerium(IV), Sulphuric acid, Mn(II), Mechanism.

INTRODUCTION

Proline is an essential element for the human body and used to manufacture proteins in human body as well as they are used to repair skin, repair joints and make collagen. Proline is classified as a proteinogenic amino acid. It secondary amine protonated NH^+_3 as in other condition, while the carboxy group is in the form of deprotonatd –COO [1-4]. The side chain from α-carbon to nitrogen creates a pyrrolidine loop. L-proline is the building block for amino acid and proteins. Occasionally biochemical reaction is most common oxidation reactions of amino acids because this reaction serves as a model for the oxidation of protein [5-7].

Cerium(IV) accepts an electron in the acidic medium and work like a powerful oxidant. The ability of redox reaction of Ce(IV) to Ce(III) is depending on the concentration of the acid. For example, the redox potential is +1.28 V in 1 M HCl; +1.44 V in 1 M H_2SO_4; +1.61 V in 1 M HNO_3; +1.70 V in 1 M $HClO_4$ and it are high as + 1.87 V in 8 M $HClO_4$. The report is available on the chemical dynamics of oxidation of L-proline by many oxidants namely acetaminophen tyrosinase, Mn(VII), *bis*(hydrogen periodato)argentate(III), pyridine-*N*-oxide, ruthenium(III), alkaline diperiodatoargentate(III) and hexacyanoferrate(III). The oxidation of L-proline by Ce(IV) usually proceeds *via* an intermediate complex [8-16]. The more powerful oxidant in Ce(IV) acidic medium. The Ce(IV) oxidation potential in the presence of sulphuric acid has been established and oxidant has been reported to exist as a sulphato species. The solution is stable for a long time in Ce(IV) acidic medium and not established in the light and rising temperature for short time. Among useful synthetic studies are the mechanical studies of oxidation of organic compound.

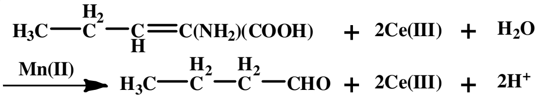
Transition metal ion is used extensively as catalysts to effect much reaction. Manganese(II) is studied as a catalyst to trace the mechanism of reactions of Ce(IV), which accelerates the reactions between the Ce(IV) and L-proline and the product gets variation in short time.The oxidation of the transition 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 Mn(II) of L-proline has been investigated by Ce(IV) in performance to explain the deposition of activator species in sulphuric acid medium by oxidant [17].

EXPERIMENTAL

All solutions used for the analysis were prepared with double distilled water. The chemicals used were G.E. (Merck) branded Ce(IV), L-proline and Mn(II). While SDS, CTAB and KCl belonged to the LOBA brand. Ce(IV) stock solution was prepared by dissolving ceric ammonium sulphate in 1.0 M sulphuric acid. Stock solution of Mn(II) was prepared in double distilled water. Then prepared stock solution is used for studying the reaction in kinetic [18].

Kinetic measurements: All stock solutions were heated in a thermostat for 30 min from 298 K to 318 K. These solutions were then absorbances by the 105 systronic spectrophotometer at 360 nm form these solution. Further absorbance by this solution was taken in an interval of 10 min. The kinetic reaction was performed under pseudo first-order condition with L-proline at concentration 1.0×10^{-2} to 5.0×10^{-3} mol dm^{-3} and Ce(IV) at concentration 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}. The UV-visible spectrophotometer is calibration between 1.0×10^{-2} to 5.0×10^{-3} 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 [19]. The pseudeo first-order rate constant rate constants (k_{obs}) were obtained from the slope of the plot of absorbance *versus* time.

Stoichiometry and product analysis: The reactions were studies when an excess of Ce(IV) with L-proline and at constant concentration of catalyst were kept for 24 h at 318 K. The aldehyde groups was confirmed with qualitative test such as Schiff's reagent and 2,4-DNP test and ammonia was detected by passing the liberating gas through a tube containing lime water. The identified group was promoted by putting these samples in FTIR instrument [20,21]. The IR peaks at 2827.45, 1078.32 and 1429.57 cm^{-1} were attributed to –CHO, -NH and $–CH_2$ stretching, respectively. The oxidation products were identified as Ce(III), 1-butanal, ammonia and carbon dioxide. The results indicated that two moles of Ce(IV) were consumed by one mole of L-proline as shown in **Scheme-I**.



$$H_3C{-}\overset{H_2}{C}{-}\underset{H}{C}{=}C(NH_2)(COOH) + 2Ce(III) + H_2O \xrightarrow{Mn(II)} H_3C{-}\overset{H_2}{C}{-}\overset{H_2}{C}{-}CHO + 2Ce(III) + 2H^+$$

Scheme-I

RESULTS AND DISCUSSION

Cerium(IV) dependence: To study the rate of reaction, Ce(IV) was taken at different concentration of value 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} other chemical were at fixed concentration that is Mn(II) = 2.0×10^{-4} mol dm^{-3}, L-proline = 5.0×10^{-4} mol dm^{-3} and $[H^+]$ = 1.0 mol dm^{-3} 1.0 mol dm^{-3} at the temperature range 298K to 318 K at interval of 10 K. The first order suggested that the rate constant (k_{obs}) decreases on increasing concentration of cerium for the oxidation of L-proline. The reaction was observed first order as shown in Table-1 and the (k_{obs}), s^{-1} *versus* concentration of Ce(IV) is found to be linear with negative intercept.

The reaction occurs through the species of an electron using the Ce(IV) ion as the oxidant. A good result is obtained when the cerium in acidic medium. For this reason, Ce(IV) acts as an oxidant. The formation of several complexes by adding Ce(IV) as in solution with sulphuric acid and they have been studies after 10 min interval at a temperature of 298 K to 318 K. The following chain of reactions occured in 1.0 M sulphuric acid.

$$Ce^{4+} + HSO_4^- \xrightleftharpoons{a} Ce(SO_4)^{2+} + H^+ \qquad (3)$$

$$Ce(SO_4)^{2+} + HSO_4^- \xrightleftharpoons{b} Ce(SO_4)_2 + H^+ \qquad (4)$$

$$Ce(SO_4)_2 + HSO_4^- \xrightleftharpoons{c} HCe(SO_4)_3^- \qquad (5)$$

$$HCe(SO_4)_3^- + HSO_4^- \xrightleftharpoons{d} H_2Ce(SO_4)_4^{2-} \qquad (6)$$

where the equilibrium constants such as a, b, c and d for above steps are reported to be 3500, 200 and 20 at temperature 298 K to 318 K, respectively. Thus the species $H_2Ce(SO_4)_4^{2-}$ is ruled out to be reactive form of Ce(IV) under experimental conditions.

Effect of L-proline: In this reaction, the concentration of L-proline is varied to know 1.0×10^{-2} to 5.0×10^{-2} mol dm^{-3} the rate of the reaction at fixed concentration of $[H^+]$ = 1.0 mol dm^{-1}, Ce(IV) = 5.0×10^{-4} mol dm^{-1} and Mn = 2.0×10^{-3} mol dm^{-3} at 298 K to 318 K. An increase in the concentration of L-proline and a decrease in the absorbance value were accompanied by an increase in the rate of the reaction (Table-2). The addition of Mn(II) catalysis to L-proline and Ce(IV) fast of rate of reaction. The order of reaction was obtained from the linear regression of k_{obs} *versus* concentration of L-proline and the order found was first order.

TABLE-1
EFFECT OF VARIATION OF [Ce(IV)] ON THE REACTION RATE AT 298 K, 308 K AND 318 K
[Ce(IV)] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}, [L-proline] = 1.0×10^{-2} mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, [Mn(II)] = 2.0×10^{-3} mol dm^{-3}

Time (min)	298 K					308 K					318 K				
	10^{-4} [Ce(IV)]														
	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0
	Absorbance														
0	0.051	0.275	0.325	0.467	0.574	0.123	0.365	0.521	0.643	0.771	0.178	0.421	0.634	0.732	0.843
10	0.032	0.176	0.195	0.311	0.378	0.71	0.231	0.323	0.421	0.534	0.101	0.261	0.389	0.467	0.566
20	0.025	0.131	0.151	0.238	0.309	0.57	0.0164	0.251	0.329	0.442	0.081	0.187	0.303	0.371	0.478
30	0.021	0.108	0.126	0.209	0.293	0.041	0.121	0.201	0.265	0.343	0.056	0.132	0.241	0.298	0.366
40	0.017	0.096	0.112	0.187	0.272	0.032	0.089	0.183	0.221	0.313	0.045	0.113	0.211	0.251	0.321
50	0.013	0.081	0.103	0.143	0.256	0.024	0.076	0.148	0.187	0.276	0.032	0.084	0.145	0.212	0.287
60	0.009	0.059	0.094	0.121	0.234	0.018	0.063	0.126	0.134	0.257	0.027	0.062	0.133	0.146	0.265
70	0.006	0.048	0.084	0.111	0.226	0.014	0.051	0.112	0.109	0.223	0.018	0.054	0.119	0.118	0.246
80	0.003	0.041	0.076	0.096	0.215	0.011	0.045	0.087	0.093	0.201	0.015	0.044	0.096	0.107	0.211
10^{-4} (k_{obs}) (s^{-1})	5.45	4.96	4.76	4.38	3.55	6.03	5.68	4.90	4.84	3.90	6.24	5.86	5.17	4.94	4.08

TABLE-2
EFFECT OF VARIATION OF [L-PROLINE] ON THE REACTION RATE AT 298 K, 308 K AND 318 K
[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3}, [L-proline] = 1.0 × 10^{-2} to 5.0 × 10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [Mn(II)] = 2.0 × 10^{-3}mol dm^{-3}

Time (min)	298 K					308 K					318 K				
	10^{-2} [L-Proline]														
	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0
	Absorbance														
0	0.392	0.374	0.345	0.306	0.277	0.685	0.623	0.578	0.488	0.421	0.756	0.687	0.612	0.567	0.489
10	0.364	0.343	0.314	0.271	0.239	0.601	0.523	0.476	0.371	0.304	0.645	0.546	0.487	0.421	0.339
20	0.339	0.321	0.293	0.256	0.221	0.578	0.498	0.456	0.321	0.278	0.612	0.526	0.466	0.367	0.301
30	0.321	0.305	0.278	0.242	0.212	0.553	0.476	0.423	0.317	0.254	0.598	0.511	0.423	0.345	0.289
40	0.308	0.291	0.268	0.232	0.201	0.521	0.459	0.402	0.301	0.232	0.576	0.478	0.401	0.321	0.245
50	0.296	0.283	0.259	0.221	0.192	0.502	0.439	0.383	0.283	0.211	0.545	0.443	0.387	0.301	0.212
60	0.287	0.271	0.247	0.211	0.187	0.488	0.421	0.371	0.267	0.196	0.521	0.421	0.356	0.287	0.193
70	0.278	0.266	0.242	0.202	0.181	0.467	0.401	0.353	0.245	0.176	0.501	0.398	0.342	0.246	0.178
80	0.272	0.257	0.236	0.197	0.176	0.454	0.391	0.341	0.232	0.159	0.478	0.376	0.321	0.231	0.165
10^{-4} (k_{obs}) (s^{-1})	0.9	1.03	1.08	1.24	1.42	1.21	1.48	1.68	2.39	2.85	1.36	1.82	1.95	2.69	3.27

The reaction of Ce(IV) with L-proline in acidic medium show's a slow redox reaction. The concentration of H_2SO_4 increases when the concentration of HSO_4^- decreases. Similarly the concentration of H^+ increases the rate of reaction decreases. It is inversely dependent on the HSO_4^- ion concentration rate [22,23].

The oxidation of Ce(IV) in aqueous acidic media and L-proline is slow in the absent of catalyzes but the rate of reaction is accelerated in the presence of Ce(IV) in aqueous acidic media and the oxidation of L-proline in the presence of Mn(II) catalysis. This is probably due to the presence of active Ce(IV) species $Ce(SO_4)_2$ in the medium. The reaction rate is the first in relation to the Ce(IV) and the concentration of Mn(II). The completed study was all done in presence of sulphuric acid. Thus the effect of sulphuric acid was studied on the rate of reaction by adding (H^+) ionic. The rate of the reaction decrease as the concentration of sulphuric acid in the reaction mixture increases. This is due to the formation of HCe activated and blocker. The order was less than unity and negative with (H^+) ion concentration. Such information is obtained through oxidation Ce(IV). The dependence of the amino acid can be determined to first order complexes with Ce(IV) and Mn(IV) [24]. The rate of reaction decrease with increasing concentration of sulphuric acid. Thus the rate of the reaction is inversely proportion of concentration of sulphuric acid. Complex formation was reported between the Mn(II) and L-proline. The L-proline adds the catalysis to from an [adduct] of Mn(II) and the product from the Ce(IV) to Ce(III) ion would slowly convert from Mn(II) to Mn(III) ion. Thus results in the rate of the reaction. The $[adduct]^+$ is converted into free radicals obtained from the L-proline and Mn(II) catalysis, where the catalysis is regenerated. The free radical then reacts with another mole $Ce(SO_4)_2$ in a further fast step to give Ce(III), 1-butanal, ammonia and carbon dioxide. The results are accommodated in **Scheme-II**.

The proposed mechanism leads to the rate law (eqn. 5):

$$\frac{-d[Ce(IV)]}{dt} = \frac{kK[Ce(IV)][L\text{-}pro][Mn(II)]}{1+K[H^+][L\text{-}pro]} \qquad (5)$$

$$\frac{-d[Ce(IV)]/dt}{[Ce(IV)]} = k_{obs} = \frac{kK[L\text{-}pro][Mn(II)]}{1+K[H^+][L\text{-}pro]} \qquad (6)$$

where k_{obs} is pseudo first-order rate constant. Since the order with respect to Mn(II) rate law further change to eqn. 7:

$$k_{obs} = \frac{kK[L\text{-}pro]}{1+K[H^+][L\text{-}pro]} \qquad (7)$$

After rearranging eqn. 7:

$$k_{obs} = \frac{kK[L\text{-}pro]}{1} + \frac{k}{[H^+]} \qquad (8)$$

The eqn. 8 is obtained on the concentration of the [H^+] ion in the plots straight lines between Ce(IV) *versus* L-proline with non-zero intercept (Fig. 1), where is L-proline and Mn(II) in this an intermediate has been created between the equilibrium. The value of the rate constant (k) of the slow step of **Scheme-II** has obtained from the intercept.

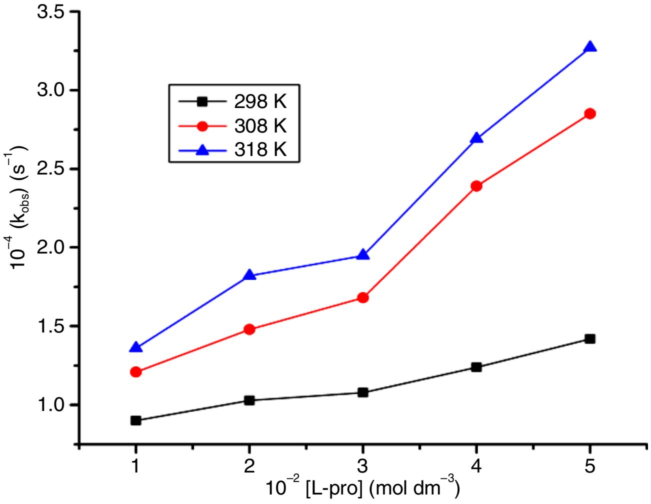
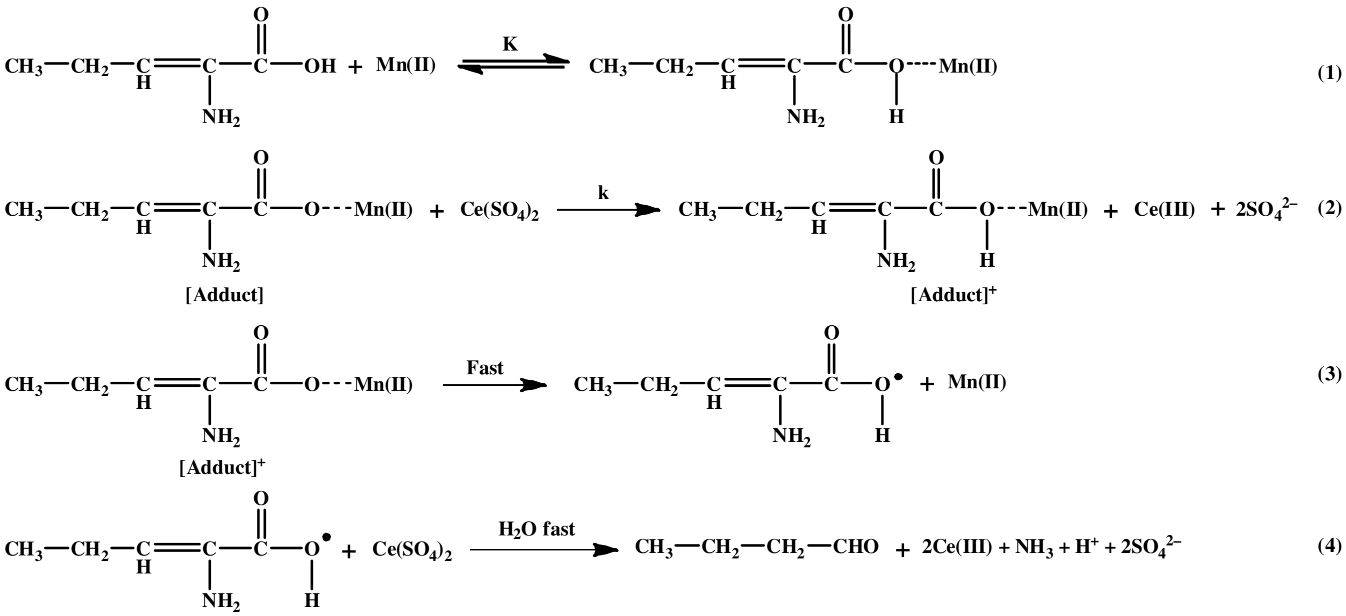


Fig. 1. Plot of 10^{-4} (k_{obs}) (s^{-1}) *versus* 10^{-2} [L-pro] (mol dm^{-3})

Manganese(II) dependence: The effect of Mn(II) catalyst concentration from 1.0 × 10^{-3} to 5.0 × 10^{-3} mol $dm^{-3}$and constant concentration of [Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3}, [L-proline] = 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 Mn(II) as fast as the L-proline is converted into product. It we found out here that is the first order of Mn(II) reaction (Table-3).



Scheme-II

TABLE-3
EFFECT OF VARIATION OF [Mn(II)] ON THE REACTION RATE AT 298 K, 308 K AND 318 K
[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3}, [L-proline] = 2.0 × 10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [Mn(II)] = 1.0 × 10^{-3} to 5.0 × 10^{-3} mol dm^{-3}

Time (min)	298 K					308 K					318 K				
	10^{-3} [Mn(II)]														
	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0	1.0	2.0	3.0	4.0	5.0
	Absorbance														
0	0.666	0.538	0.343	0.256	0.179	0.666	0.538	0.343	0.256	0.179	0.834	0.756	0.721	0.656	0.547
10	0.567	0.449	0.264	0.183	0.109	0.567	0.449	0.264	0.183	0.109	0.668	0.601	0.511	0.443	0.321
20	0.546	0.389	0.227	0.142	0.087	0.546	0.389	0.227	0.142	0.087	0.621	0.535	0.447	0.319	0.246
30	0.521	0.441	0.198	0.119	0.076	0.521	0.441	0.198	0.119	0.076	0.571	0.486	0.401	0.264	0.211
40	0.501	0.411	0.173	0.107	0.065	0.501	0.411	0.173	0.107	0.065	0.532	0.421	0.357	0.214	0.187
50	0.481	0.386	0.158	0.091	0.054	0.481	0.386	0.158	0.091	0.054	0.501	0.401	0.323	0.167	0.151
60	0.472	0.367	0.145	0.069	0.041	0.472	0.367	0.145	0.069	0.041	0.487	0.378	0.309	0.134	0.123
70	0.458	0.375	0.131	0.053	0.036	0.458	0.375	0.131	0.053	0.036	0.456	0.345	0.297	0.112	0.102
80	0.443	0.354	0.126	0.044	0.031	0.443	0.354	0.126	0.044	0.031	0.437	0.321	0.277	0.089	0.087
10^{-4} (k_{obs}) (s^{-1})	1.33	1.47	2.88	4.07	4.77	1.92	2.34	3.01	4.21	5.10	2.01	2.41	3.13	4.95	5.19

Effect of CTAB: The effect of the reaction has been studied in the rate of the reaction due o change of concentration 1.0 × 10^{-4} to 5.0 × 10^{-4} mol dm^{-3} of [CTAB] cationic surfactant in this fixed concentration of [Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3}, [L-proline] = 2.0 × 10^{-2} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and Mn(II) = 2.0 × 10^{-3} mol dm^{-3} at 298 K to 318 K for catalytic reaction. The rate of reaction is decrease with increase in the concentration of surfactant CTAB (Table-4). This indicates that CTAB is a first order of reaction.

Effect of SDS surfactant: The rate of the reaction in which the reaction has been studies at various concentrations of surfactant [SDS] = 1.0 × 10^{-4} to 5.0 × 10^{-4} mol dm^{-3} with fixed concentration [Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3}, [L-proline] = 2.0 × 10^{-2} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and [Mn(II)] = 2.0 × 10^{-3} mol dm^{-3} at 298 K to 318 K. It indicates that the rate of reaction proceed fast due to the presence of SDS. The results are shown in Table-5.

TABLE-4
EFFECT OF VARIATION OF [CTAB] ON THE REACTION RATE AT 298 K {[Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3}, [L-proline] = 2.0 × 10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 M, [CTAB] = 1.0 × 10^{-4} to 5.0 × 10^{-4} mol dm^{-3}, [Mn(II)] = 2.0 × 10^{-3} mol dm^{-3}}

Time (min)	10^{-4} [CTAB]				
	1.0	2.0	3.0	4.0	5.0
	Absorbance				
0	0.169	0.131	0.119	0.105	0.095
10	0.112	0.101	0.096	0.086	0.079
20	0.097	0.087	0.081	0.075	0.068
30	0.082	0.076	0.076	0.068	0.062
40	0.076	0.065	0.067	0.061	0.057
50	0.068	0.056	0.059	0.054	0.051
60	0.061	0.049	0.052	0.051	0.047
70	0.054	0.043	0.046	0.047	0.044
80	0.047	0.037	0.041	0.043	0.041
10^{-4} (k_{obs}) (s^{-1})	3.76	3.06	2.59	2.35	2.24

Effect of salt KCl: The rate of reaction ionic strength univalent has been studies by fixed concentration [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} located in it at different concentration from surfactant [KCl] = 1.0 × 10^{-3} to 5.0 × 10^{-3} mol dm^{-3} at temperature raining from 298 K to 318 K. The effect of ionic strength on the rate has been studies and

TABLE-5
EFFECT OF VARIATION OF [SDS] ON THE REACTION RATE, AT 298 K {[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}, [L-proline] = 2.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 M, [SDS] = 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 2.0×10^{-3} mol dm^{-3}}

Time (min)	10^{-4} [SDS]				
	1.0	2.0	3.0	4.0	5.0
	Absorbance				
0	0.122	0.104	0.094	0.086	0.074
10	0.101	0.082	0.073	0.063	0.051
20	0.086	0.071	0.061	0.054	0.043
30	0.076	0.059	0.053	0.045	0.036
40	0.069	0.049	0.044	0.037	0.029
50	0.056	0.041	0.036	0.031	0.024
60	0.043	0,035	0.029	0.026	0.021
70	0.038	0.031	0.025	0.023	0.016
80	0.032	0.027	0.021	0.019	0.011
10^{-4} (k_{obs}) (s^{-1})	2.67	3.15	3.36	3.64	4.18

found that the reaction has slightly increase due to effect of ionic strength (Table-6), which confirmed the first order of reaction.

TABLE-6
EFFECT OF VARIATION OF [KCl] ON THE REACTION RATE AT 298 K {[Ce(IV)] = 3.0×10^{-4} mol dm^{-3}, [L-proline] = 4.0×10^{-2} mol dm^{-3}, [H_2SO_4] = 1.0 M, [KCl] = 1.0×10^{-3} to 5.0×10^{-3} mol dm^{-3}, [Mn(II)] = 2.0×10^{-3} mol dm^{-3}}

Time (min)	10^{-3} [KCl]				
	1.0	2.0	3.0	4.0	5.0
	Absorbance				
0	0.098	0.089	0.081	0.078	0.068
10	0.076	0.074	0.069	0.069	0.061
20	0.068	0.068	0.063	0.061	0.057
30	0.058	0.061	0.058	0.056	0.053
40	0.051	0.056	0.053	0.051	0.049
50	0.044	0.051	0.048	0.047	0.046
60	0.039	0.047	0.044	0.044	0.043
70	0.035	0.043	0.041	0.041	0.039
80	0.031	0.039	0.037	0.038	0.036
10^{-4} (k_{obs}) (s^{-1})	2.87	2.05	1.88	1.74	1.49

The thermodynamic parameter values of $\Delta H^{\#}$, $\Delta G^{\#}$, $\Delta S^{\#}$ and the activated complex ($Ea^{\#}$) is given in Table-7, which indicated that the reaction is endothermic ($\Delta H > 0$). The moderate value of $\Delta H^{\#}$ and $\Delta S^{\#}$ were favourable for electron transfer processes [25,26].

TABLE-7
KINETIC AND THERMODYNAMIC ACTIVATION PARAMETER FOR CATALYSES REACTION

Parameter	L-proline
$E_a^{\#}$ (kJ mol^{-1})	31.67
$\Delta H^{\#}$ (kJ mol^{-1})	90.26
$\Delta S^{\#}$ (J mol^{-1})	-29.15
$\Delta G^{\#}$ (kJ mol^{-1})	99.24

Conclusion

The rate of reaction between the Ce(IV) and L-proline was increased in the presence of catalyst Mn(II) as the temperature increased from 298 K to 318 K. It is found that rate of the process increased if a catalyst is added between the oxidant Ce(IV) and L-proline in the form of oxidation. The main active species of cerium(IV) is considered as $Ce(SO_4)_2$, although other species are also present but in lesser extent. The oxidant and substrate under uncatalyst condition is found to be first order.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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