Kinetics and mechanistic study of oxidation of alanine by cerium (IV) using Mn^{+2} as catalyst.

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Abstract

Metal ion Mn^{+2} as homogeneous catalyst has been used in the oxidation of alanine in acid medium. The reaction shows first order kinetics with respect to Ce(IV), the reactions also showedfraction order kinetics with respect to Mn^{+2} and alanine and inverse first order with respect to $[H^+]$. The reaction product (Cerium(III) Sulphate ($Ce_2(SO4)_3$) was added to the reactions and had no effect on the rate of oxidation of alanine by Ce(IV). Changing ionic strength, dielectric constant and chloride ion of the medium has no effect on the rate of oxidation. Ce^{+2} and Mn^{+2}have been suggested to be the reactive species. A reaction mechanism was suggested and rate law had been derived . Aldehyde have been identified to be the oxidation products of the reaction

Introduction:

The studies of the amino acids by various oxidants[1-5]both in acidic and alkaline media have been reported. Many reagents have been investigated towards oxidative decarboxylation of α-amino acids, which give nitrile[6-7]or a mixture of nitrile and aldehyde[8-11]as the products depending on the reaction conditions and reagents employed. Beside aldehyde and nitriles, α-keto-acids are also reported to be formed asoxidationproduct[12].The kinetic and mechanistic features of a particular oxidation reaction of amino-acids are likely to be affected by the polar and nonpolar nature of the side chain of amino acid in solution and the active species of the oxidant[13-14]. Amino acids are very attractive natural ligands for both toxic and essential metal ions. Besides acting simply as effective chelators[15-16], in many cases they are also reducing agents; e.g. for metal ions such as Ce(IV), V(V),Co(III) and Fe(III).
Gowda and co-workers have studied the oxidation of amino acids by varioushalogen oxidants viz. chloramineT[17-18], its dimer dichloramines[19]andbromamine T[20]. The oxidation product is aldehyde via hydrolysis of imine intermediate. However, Vivekanandam et al.[21]showed for the oxidation of imine by another molecule of chloramineT to nitrile.Cerium has a property, unique among the lanthanides, which explain its ability to participate in one electron transfer reactions, its ability to exist in two stable adjacent oxidation states +3 and +4[22-23]. Ce(IV) is well known oxidant in acid

media having the reduction potential of the couple Ce(IV)/Ce(III) 1.70 V[24-25]. Cerium(IV) is one of the most important one equivalent oxidant in acid medium which has been used in numerous kinetic, mechanistic and analytic studies, the basic advantage of cerium(IV) over other oxidants is its reduction to a single substance cerium(III)[22]. The cerium(IV) species in perchloric acid[26-27]medium and sulphuric acid medium[28]have been established and equilibrium constants calculated.

This work study the kinetics of the reaction and finding the order of the reaction and rate constants and suggesting reaction mechanism.

Experimental work

Hana digital pH meter**,** was used for the determination of pH of the reaction mixtures with the maximum uncertainity in pH of ± 0.01 unit. PyeUnicamUV spectrophotometerwas used for spectrophotometric measurements. Spectrophotometer can be used to determine kinetics and the rate constant of a chemical reaction. The rate constant of a particular reaction can be determined by measuring visible absorbance at specific time intervals. Since the rate of reaction is directly proportional to the concentration of the cerium(IV), it was necessary to find out the range of concentration of cerium(IV) in sulphuric acid in the presence of amino acid over which Beer's law was applicable. The spectrophotometeric study of the solution containing all the reagents with Ce(IV) in sulphuric acid medium showed that the reaction can be monitored spectrophotometrically by measuring the absorbance of cerium(IV) at 390 nm where cerium(IV) has considerable absorbance and other ions have no contribution towards absorbance. At this wavelength absorbance values were obtained for different concentration of cerium(IV) solution with other reagent between the concentration range 5×10-5 to 5×10-4 mol dm-3.

Thermostat, Water bath (Macro Scientific) temperature range 30◦C -110◦C was used. All kinetic studies were done using thermostated at temperature varying from 350˚C to 50˚C.
Electronic Balance**,**Shimadzu electronic Balance, A × 200 was used for weighing works. The least count of balance is 0.0001 mg.

All other reagents were either of Anala R or guaranteed reagent grade and used as supplied. Doubly distilled water, second distillation being from alkaline potassium permanganate solution in all glass assembly, was employed in all the preparations and kinetic studies.

Kinetic Measurements

Appropriate quantities of the solution were placed in separate glass vessels and kept for at least 15 minutes in a thermo stated water bath at 35◦C. The calculated amounts of each reactant were then added together in a particular glass vessel followed by the requisite amount of double distilled water. The reaction mixture was then placed in a thermostatted water bath maintained at constant temperature of 35◦C (±5%) and the reaction was initiated by adding the requisite amount of oxidant solution placed separately in the same water bath. The reaction was followed by measuring the absorption of cerium(IV) at 390 nm with time in a 1 cm cell placed in the Pye All kinetic measurements were performed under pseudo first order conditions with alanine concentration in excess over cerium(IV) at a constant ionic strength of 1.50 mol dm-3. The pseudo first order rate constants (kobs) were obtained from the slope of the plots of log absorbance versus time. The observed rate constants were reproducible within the experimental error ±5%. The cerium(IV) solution was thermally stable in the visible region and undergoes photochemical decomposition only in the UV region.

Stoichiometry and Product Analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [alanine] at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24 hours at 308 K. After completion of the reaction, the remaining Ce(IV) was estimated in different sets of the experiment. The results indicated that two moles of Ce(IV) were consumed by one mole of alanine since,
The oxidation products were identified as Ce(III), 2-hydroxyethanal, ammonia and carbon dioxide. The reaction mixture was treated with acidified 2,4−dinitrophenyl hydrazine solution, which yielded a hydrazine.

Results and Discussion

Effect of Cerium (IV).Ceric (IV) Ammonium Sulphate [$(NH_4)_4Ce(SO_4)_4.2H_2O$]

The concentration of Cerium (IV) was varied from $5.0 \times 10^{-5}$to 5.0×10^{-4}mol dm^{-3}at fixed concentration of [Ala] =5×10^{-3}mol dm^{-3}, [H+] =1.0 mol dm^{-3}, I=1.5mol dm-3and [Mn(II)]=$5\text{x}10^{-5}$mol dm^{-3} at 35^{o}C. The pseudo first order rate constant (kobs) are independent of the initial concentration of Cerium(IV) (Table1).

Effect of Alanine

The concentration of alanine was varied from 0.003-0.009mol dm^{-3} at fixed concentration of Cerium (IV) =5.0×10^{-4}mol dm^{-3} [H+] =1.0 mol dm^{-3}, I=1.5 mol dm^{-3},and [Mn (II)]= 5×10^{-5}mol dm^{-3}.Pseudo first order constant (kobs) increases with the increase of concentration of alanine (Table-2. and figures 1-4) The reaction order of alanine is 0.5 obtained from the linear regression of log kobs versus log [Ala], indicating fractional order with respect to alanine (figure 5).

Effect of Mn (II). Manganese Sulphate ($MnSO_4$)

Manganese (II) concentration was varied from 2.0×10^{-5} to 2.0×4 mol dm^{-3}at constant concentration of Ce (IV)= 5.0×10^{-4}mol dm^{-3}[Ala] =5×10^{-3}moldm^{-3},(H+) =1.0 mol dm^{-3}, I =1.5mol dm^{-3} (Table 3and figure 6).

Effect of Hydrogen ion

Hydrogen ion concentration was varied from 0.2 to1.0 mol dm-3 at fixed [HSO4-] {[HSO4-]=1.0 mol dm-3 from H2SO4 and NaHSO4}, [Ala], [Mn(II)],[H+] was calculated ignoring the dissociation of [HSO4-] and assuming [H+]=[H2SO4] the rate constant decrease with increase of [H+] (Table 4, Figure 7).

Effect of [HSO4-]

The concentration of bisulphate (HSO4-) ion was varied in the range of 0.2 to1.0 mol dm-3 at fixed [H+] {[H+] =0.2 moldm-3][(Ce(IV)], [Ala], [Mn(II)], at 35^{o}C. Here [HSO4-] = [NaHSO4+H2SO4] ignoring the dissociation of [HSO4-] in strongly acidic medium. The rate shows a rate retarding effect.

Effect of ionic strength

At fixed [Ce (IV)], [Ala], [H2SO4], [Mn (II)] and temperature the ionic strength (µ) was varied 1.2-2.0 mol dm-3, employing Sodium perchlorate for adjusting ionic strength. The rate of reaction increases slightly with increasing ionic strength.

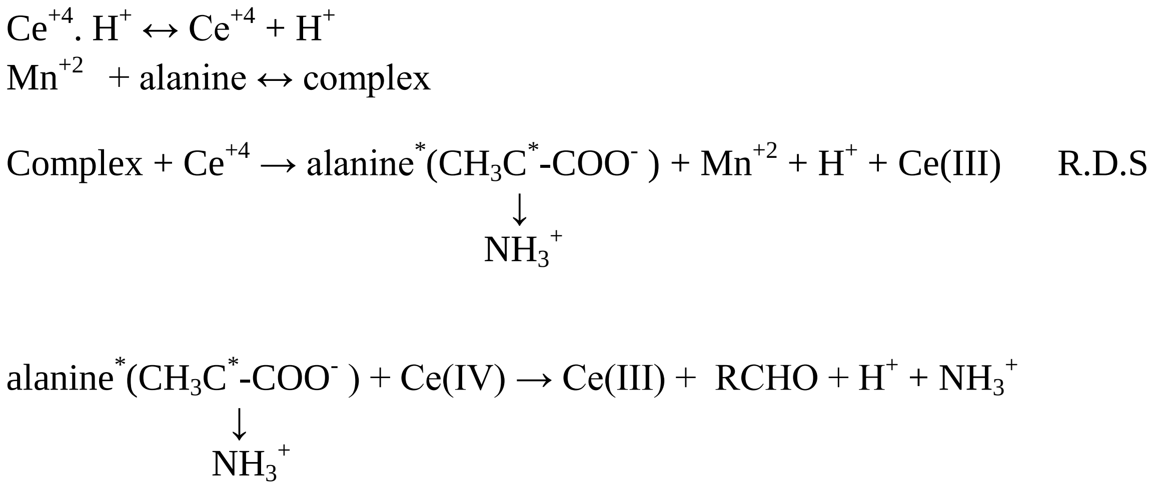
Effect of added product.(Cerium(III) Sulphate ($Ce_2(SO_4)_3$)

The effect of Cerium (III) on the rate was alsostudied and was found to be independent of Cerium (III) concentration, ruling out any possibility of the rate limiting step preceded by the reversible equilibrium involving Cerium (III).
Test for free radicalsIn the reaction mixture, acrylonitrile solution was added in an inert atmosphere for 4 hour. Then dilution with methanol, a white precipitate resulted suggesting the participation of free radicals in the reaction.

Discussion

Under the kinetic conditions in presence of catalyst, excess of alanine over Cerium (IV) constant ionic strength and acidity in a thermostated water bath at 35^{o}C for 24 hour. The products were extracted from the reaction mixture with ether. An addition of 2, 4- dinitrophenylhydrazine in the reaction mixture yield brown precipitate of hydrazone derivative of aldehyde[29].
The kinetic results, 1/kobs versus1/[Ala] fits well with the MichaelisMenen model (Figure 8), suggesting that1:1 type complex of (Ala) and Mn(II) is formed in the first pre-equilibrium step. Alanine is protonized in acid media, indicating involvement of H+ is the reaction in the pre-equilibrium step. To explain the first order dependence on Ce(IV), it is assumed that the complex is oxidized by cerium(IV) is a slow step to produce Mn(II) substrate complex which collapses in a fast step to produce catalyst and free radical, which is responsible for product [30]. The condition employed in the present investigation appears to be $Ce(SO4)_2$ as the reactive species of Cerium (IV).
Scheme 1 shows the suggested mechanism and the derived rate law was suggested.
The uncatalysed cerium(IV) oxidation of alanine is very slow in sulphuric acid under the present experimental conditions. However, the reaction is appreciably faster in the presence of a minute quantity (10^{-5}mol dm-3) of manganese(II) in sulphuric acid . In the presence of perchloric acid, manganese(II) catalysis is much less efficient, possibly due to presence of active cerium(IV) species, $Ce(OH)^{3+}$ in such media. Hence, the present study was undertaken in sulphuric acid medium. The reaction is first order with respect to cerium(IV) and manganese(II) concentrations, and the order with respect to alanine was first order. The effect of hydrogen ions on the rate was studied by adding sulphuric acid and it was found that as the sulphuric acid concentration increased in the reaction mixture, the rate of reaction decreased. This is due to formation[31]of an active inhibitor $H_2Ce(SO4)_2^{2-}$. 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 HSO4− ion concentration. Since the rate is inversely dependent on the HSO4−

concentration, the overall effect of adding sulphuric acid would be to lower the rate.



$$Ce^{+4}.\ H^{+} \leftrightarrow Ce^{+4} + H^{+}$$

$$Mn^{+2}\ \ + \text{alanine} \leftrightarrow \text{complex}$$

$$\text{Complex} + Ce^{+4} \rightarrow \text{alanine}^{*}(CH_3\underset{\substack{\downarrow\\ NH_3^{+}}}{C^{*}}\text{-}COO^{-}) + Mn^{+2} + H^{+} + Ce(III) \qquad \text{R.D.S}$$

$$\text{alanine}^{*}(CH_3\underset{\substack{\downarrow\\ NH_3^{+}}}{C^{*}}\text{-}COO^{-}) + Ce(IV) \rightarrow Ce(III) + RCHO + H^{+} + NH_3^{+}$$

Scheme 1

$$\text{Rate} = k_5\,[\text{Complex}][Ce^{+4}] \qquad \rightarrow 1$$

$$-d[\text{complex}]/dt = k_3[\text{alanine}][Mn^{+2}]-k_4[\text{complex}]-k_5[\text{complex}][Ce^{+4}]=0 \quad \rightarrow\ 2$$

$$[\text{complex}] = k_3[\text{alanine}][Mn^{+2}]/(k_4 + k_5[Ce^{+4}] \qquad \rightarrow\ 3$$

$$K = [Ce^{+4}][\ H^{+}]/[Ce^{+4}.\ H^{+}] \qquad \rightarrow\ 4$$

$$\text{Rate} = Kk_5k_3[\text{alanine}][Mn^{+2}]^{+}][Ce^{+4}.\ H^{+}]/(k_4 + k_5[Ce^{+4}])[H^{+}] \qquad \rightarrow\ 5$$

Table 1: The effect of variation of Ce(IV) concentration on the rate constants

[alanine]=0.005M, [H^+]=1M, I=1.5M, and [Mn^{+2}]=2x10^{-5}M. temp.=35^{o}C

k/min^{-1}	0.168	0.173	0.159
10^4[Ce(IV)]/M	0.5	1.0	5.0

Table 2: The effect of variation of alanine concentration on the rate constants [Ce(IV)]=0.0005M, [H^+]=1M, I=1.5M, and [Mn^{+2}]=2x10^{-5}M. temp.=35^{o}C

k/min^{-1}	0.148	0.168	0.194	0.267
10^3[alanine]/M	3.0	5.0	7.0	9.0

Table 3: The effect of variation of Mn^{+2} concentration on the rate constants [Ce(IV)]=0.0005M, [H^+]=1M, I=1.5M, and [alanine]=0.005M. temp.=35^{o}C

k/min^{-1}	0.168	0.181	0.199	0.29
10^4[Mn^{+2}]/M	0.2	0.9	2.0	5.0

Table 4: The effect of variation of H^+ concentration on the rate constants [Ce(IV)]=0.0005M, [Mn^{+2}]=2x10^{-5} M, I=1.5M, and [alanine]=0.005M. temp.=35^{o}C

k/min^{-1}	0.168	0.111	0.097	0.074
[H^+]/M	1.0	1.3	1.5	2.0

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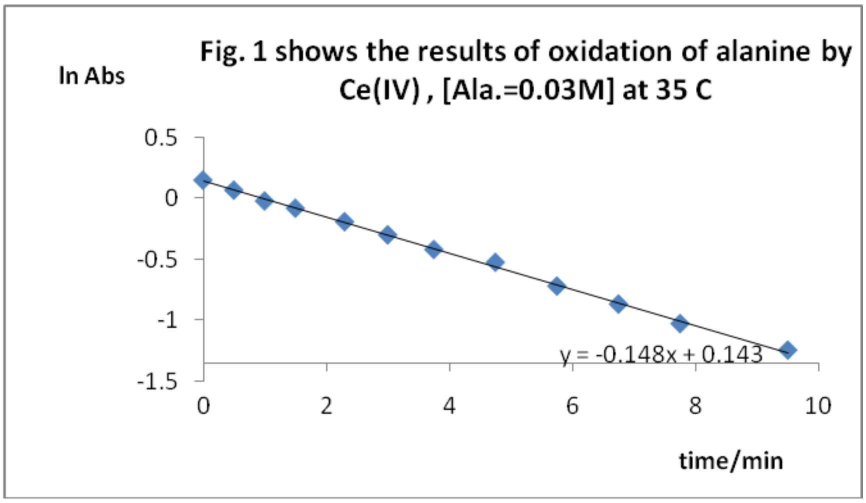

Fig. 1 shows the results of oxidation of alanine by Ce(IV) , [Ala.=0.03M] at 35 C

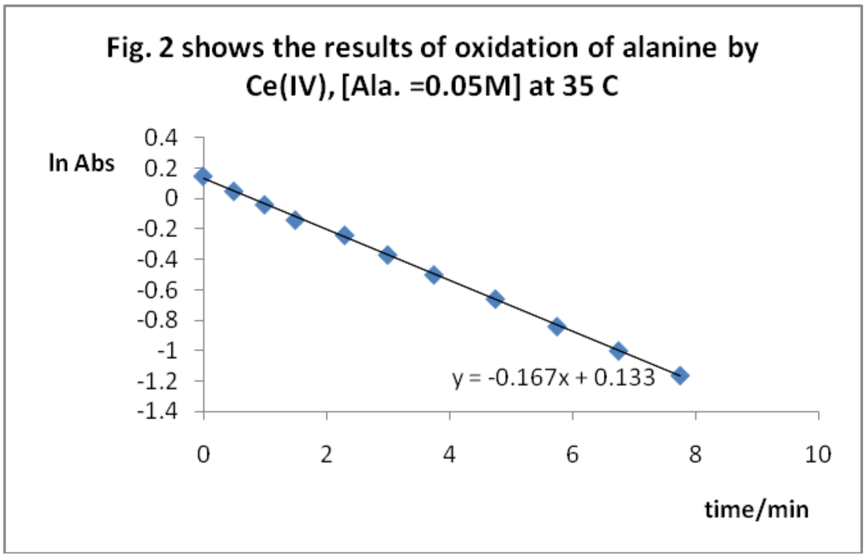

Fig. 2 shows the results of oxidation of alanine by Ce(IV), [Ala. =0.05M] at 35 C

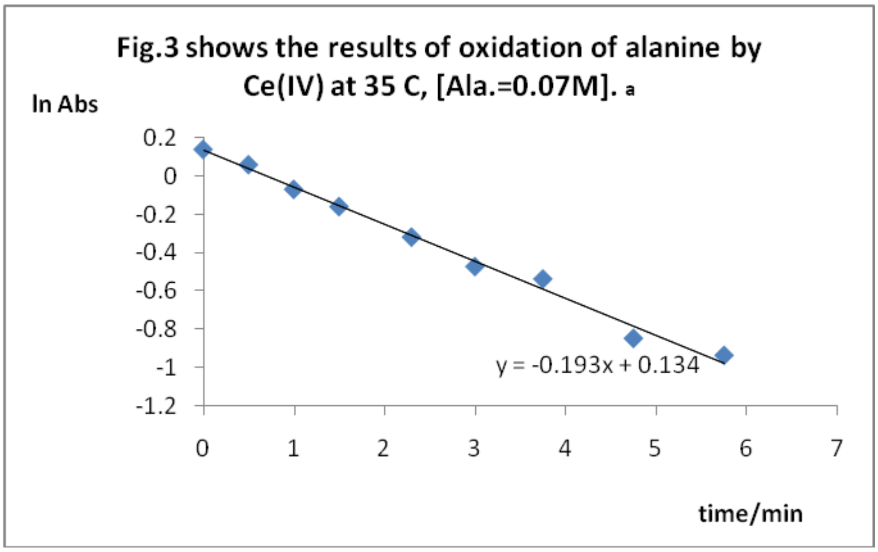

Fig.3 shows the results of oxidation of alanine by Ce(IV) at 35 C, [Ala.=0.07M]. a

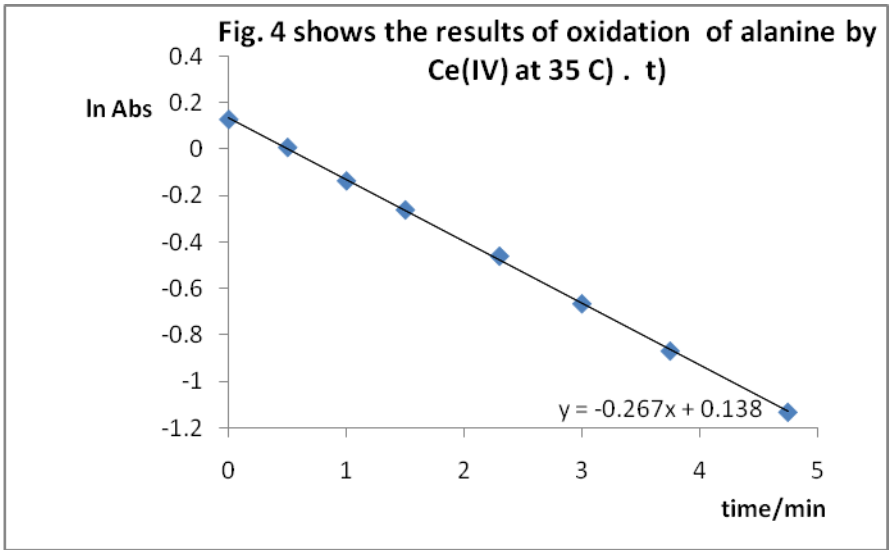

Fig. 4 shows the results of oxidation of alanine by Ce(IV) at 35 C) . t)

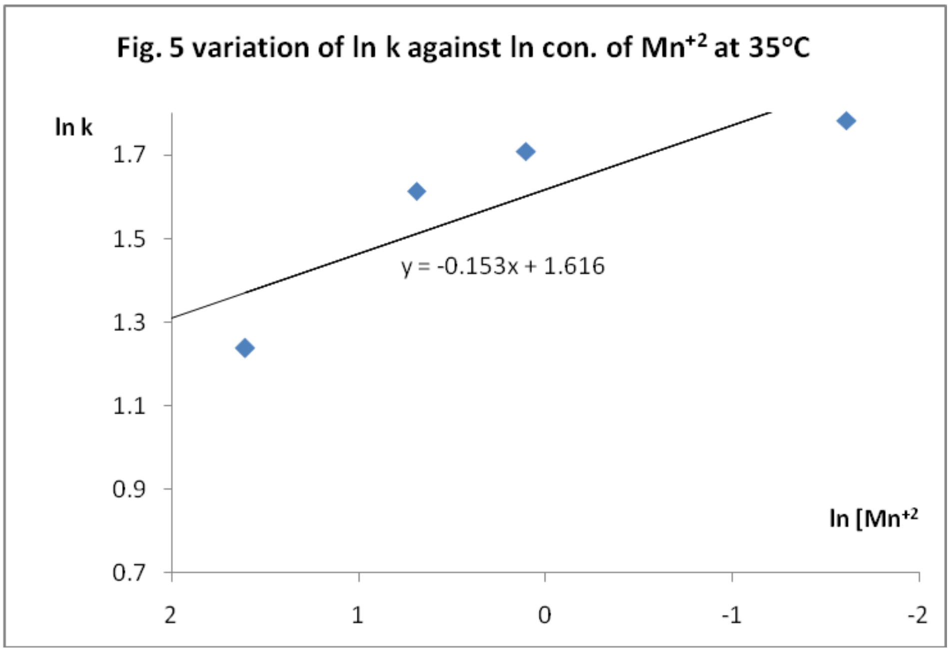

Fig. 5 variation of ln k against ln con. of Mn^{+2} at 35°C

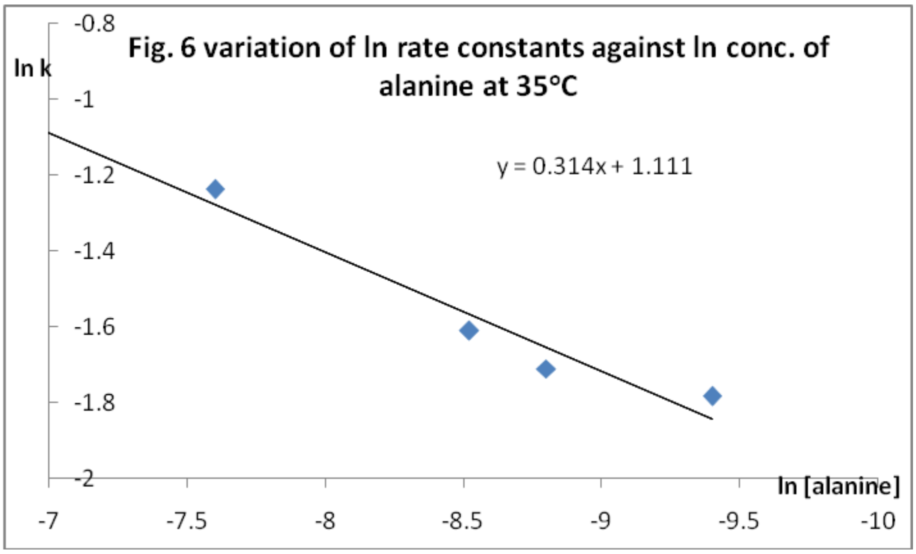

Fig. 6 variation of ln rate constants against ln conc. of alanine at 35°C

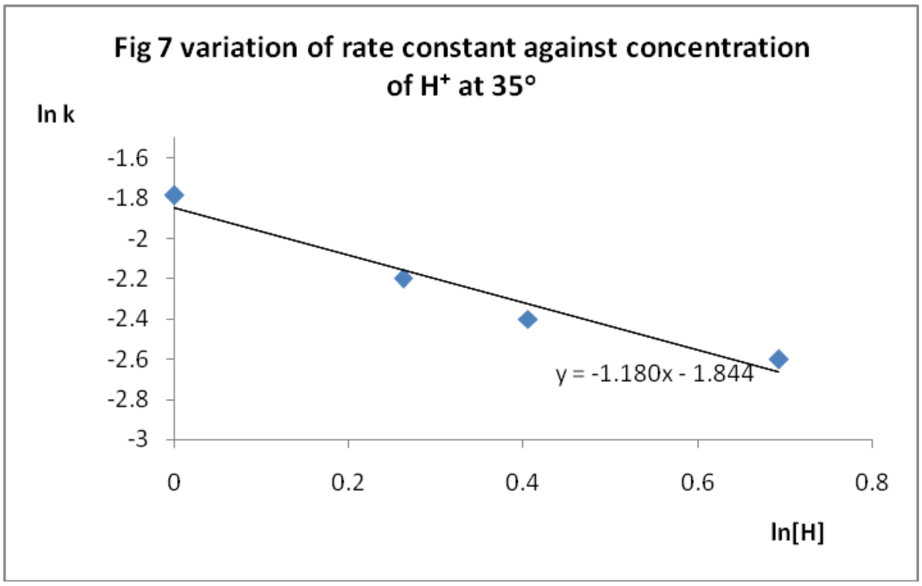

Fig 7 variation of rate constant against concentration of H^+ at 35°

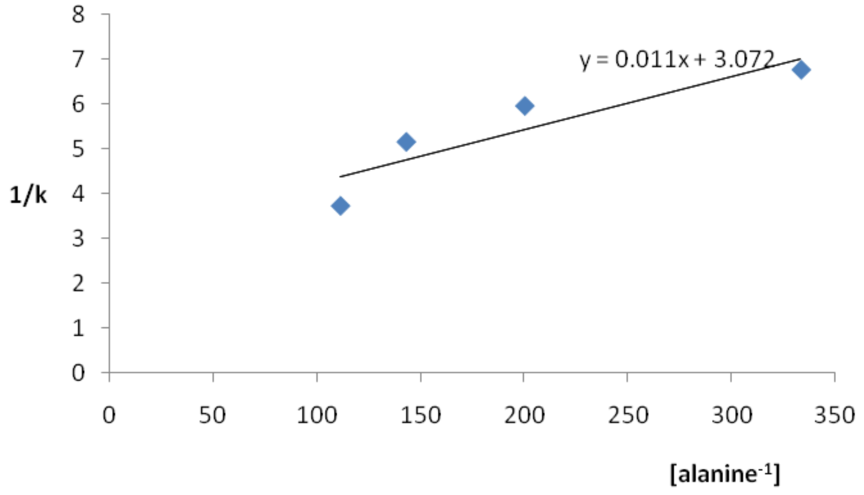

Fig.8 Relation between 1/k against 1/[alanine] at 35°

الخلاصة:-

تم استخدام ايون Mn^{+2} كعامل مساعد في عملية اكسدة الالنيين في الوسط الحامضي, اظهر التفاعل من الدرجة الاولى في Ce(IV) كما اظهر التفاعل من الدرجة الكسرية في كل من ايون المنغنيز والالنيين ومن المرتبة الاولى السالبة في ايون الهيروجين. كما تم اضافة ناتج التفاعل (Cerium(III) Sulphate ($Ce_2(SO4)_3$) الى التفاعل ولم يلاحظ اي تاثيرعلى سرعة التفاعل. كما درس تاثير كل من القوة الايونية وثابت عزل الوسط وايون الكلوريد على وسط التفاعل ولم يلاحظ اي تاثيرعلى سرعة التفاعل . تم اقتراح ميكانيكية للتفاعل وتم اشتقاق قانون سرعة للتفاعل و كما تم تشخيص ناتج التفاعل وكان مركب الدهايدي