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"COMPARATIVE STUDY OF KINETICS OF CHROMIUM CATALYSED OXIDATION OF L-LEUCINE AND L-ISOLEUCINE BY ALKALINE POTASSIUM PERMAGANATE"

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Abstract:- The kinetics of oxidation of L-Leucine and L- Isoleucine by alkaline potassium permagnate catalysed by chromium was studied spectrophotometrically. The reaction was found to be of first order with respect to permagnate and catalyst and less than unity with respect to substrate .There was a good agreement between observed and calculated rate constants. Formation of a complex between the amino acid and the hydroxylated species of chromium(III) is suggested.In rate determining step complex reacts further with permanganate , results in the formation of a free radical , which again reacts with the permanganate in a subsequent fast step to yield products. A plausible mechanism for the reaction is proposed and the activation parameters are calculated and discussed with respect to slow step of the reaction mechanism. It was found that of the two amino acids leucine oxidized faster than that of isoleucine.

Keywords: kinetics , oxidation ,Leucine , Isoleucine , rate constant

Introduction :Amino acids play a significant role not only in protein synthesis but also in metabolism. In metabolism amino acids undergo many reactions and can supply precursors for many endogenous substances. Among all the oxidizing agents potassium permanganate is most widely and commonly used as oxidant in organic and analytical chemistry and also as a disinfectant. Above all, it is a strong, vividly colored oxidant, serving as its own indicator**.** Oxidation by permanganate is applied extensively in organic synthesis**.[1-7**] .The manganese chemistry involved in this reaction because the manganese intermediates are relatively easy to identify as they have sufficiently long life times and oxidation states of intermediates permit useful conclusion to be drawn as to the possible reaction mechanism. Oxidation is affected by many factors such as pH , catalyst , temperature etc. It is also used as disinfectant. There are six oxidation states of manganese (+2 to +7), of which Mn(VII) is the most potent oxidation state in acid as well as in alkaline medium **[8-9].**Leucine and Isoleucine are essential amino acids and are active binding site residues of enzymes. They help in maintaining

the correct conformation of enzymes by keeping them in their proper ionic states. Thus oxidation of these amino acids may help in understanding enzyme kinetics**.** study of oxidation of amino acids is of interest because the products differ depending on the oxidants[**10-12].** Chromium (III) is an essential trace metal in mammalian metabolism. chromium (III) is the cheapest transition metal that can be used as catalyst, its microscopic amount is sufficient for catalysis.The chemistry of chromium(III) is well developed in acid medium than that of alkaline medium It has been reported that the solubility of chromium(III) in solutions of pH >11.5 is due to species such as] $Cr(OH)_4$[13-14] A variety of mechanisms has been proposed to explain the mechanism .The uncatalysed reaction between the said amino acid and permanganate in alkaline medium has been studied previously.[15].Here we will study the results of the title reaction to determine the active species of oxidant ,reductant and catalyst to find the plausible mechanism.

Experimental Details:

Materials :

Stock solutions of L-leucine and L-isoleucine (merck co.) were prepared by dissolving the appropriate amount of sample in double distilled water.

The $KMnO_4$ Solution was prepared as described by[Carrington and Symons] and standardized with oxalic acid**.[16]** The solution was standardized by measuring the absorbance in UV – VIS spectrophotometer with 1 cm quartz cell at 525 nm.

The chromium solution was prepared by dissolving Chromium (III)potassium sulfate (Anala R) $(Cr_2(SO4)_3 \cdot K_2SO_4 \cdot 24H_2O)$ in H_2O.and was standardized **[17]** by oxidizing it to chromium(VI) with excess if persulfate in presence of one or two drops of 1.0×10^{-2} mol/ dm^3silver nitrate. The excess of persulfate was boiled off .

All other reagents were of analytical grade and were prepared by dissolving requisite amount of the sample in doubly distilled water . NaOH and $NaClO_4$, were prepared to provide required alkalinity and to maintain the ionic strength., respectively.

Kinetic Procedure:

In order to study all the absorbance at λ_{max} ,It was determined by taking solution of potassium permanganate of any concentration. Then solutions of amino acid, potassium permanganate,catalyst are mixed in proper proportions (as given in table) to study the effect of change in concentration of oxidant, alkali, catalyst on rate constant and their absorbance are studied through UV-VISIBLE spectrophotometer. Effect of temperature is also studied by giving run at different temperature. In view of ubiquitous contamination of basic solutions by carbonate, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rate. Nevertheless , as a precaution fresh solutions were used while conducting kinetic experiments.

Table1:- **Effect of variation in concentration of permanganate ion , amino acids,Chromium(III), and hydroxide ion concentration on oxidation of Leucine and Isoleucine , catalysed by Chromium in Alkaline Medium**.

S.No.	10^4 [MnO4 −] (mol dm−3)	10^3 [AA] (mol dm−3)	10^2 [OH−] (mol dm−3)	10^5 [Cr(III)] (mol dm−3)	10^3 × kobs (s−1) Experimental leu	10^3 × kobs (s−1) Experimental I-leu
1	1	2	5	5	2.23	1.61
2	2	2	5	5	2.25	1.64
3	3	2	5	5	2.26	1.66
4	4	2	5	5	2.27	1.67
5	5	2	5	5	2.28	1.72
6	2	1	5	5	1.28	0.92
7	2	2	5	5	1.77	1.32
8	2	3	5	5	2.21	1.66
9	2	4	5	5	2.59	2.14
10	2	5	5	5	3.10	2.57
11	2	5	2.5	5	2.21	1.62
12	2	5	5.0	5	2.22	1.64
13	2	5	10.0	5	2.24	1.67
14	2	5	17.5	5	2.25	1.68
15	2	5	25.0	5	2.27	1.70
16	2	5	5	1	0.47	0.32
17	2	5	5	2	0.96	0.71
18	2	5	5	5	2.19	1.66
19	2	5	5	7.5	3.3	2.42
20	2	5	5	10.0	4.61	3.44

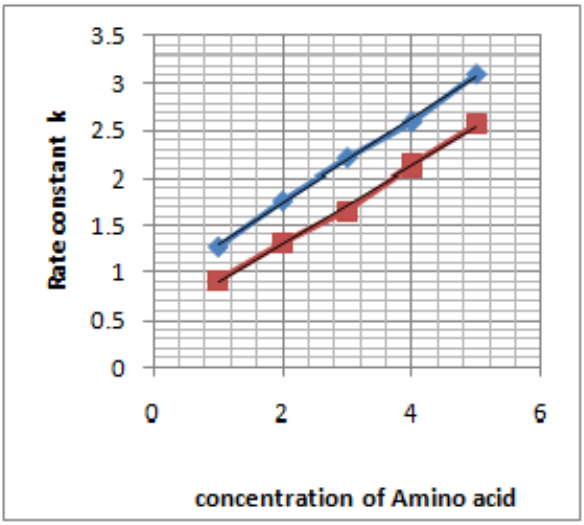


Fig 1 :-comparison of effect of change in concentration of[Amino acid] on Rate constant **k**

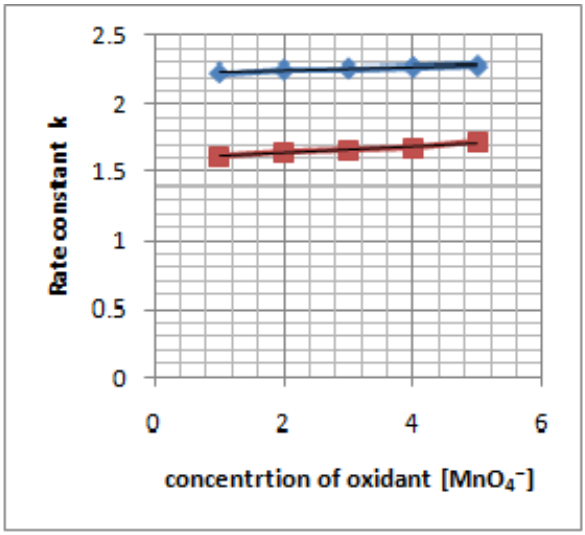


Fig 2 :-comparison of effect of change in concentration of oxidant **[MnO_4^-]** on Rate constant **k**

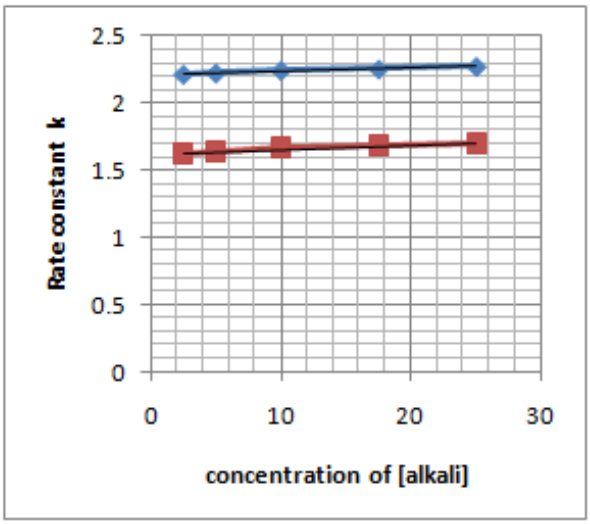


Fig 3 :-comparison of effect of change in concentration of[alkali]on Rate constant **k**

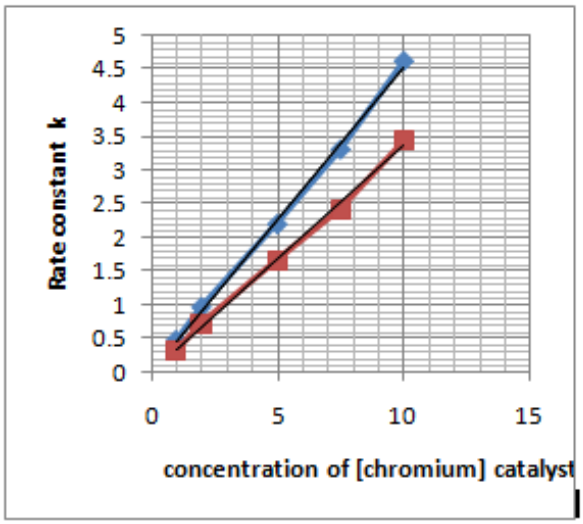


Fig 4 :-comparison of effect of change in concentration of[Chromium catalyst]on Rate constant **k**

Results :

Stoichiometry :

The reaction mixtures , containing an excess of permagnate over amino acids , a constant amount of Chromium (III) and .05 mol dm^{-3} sodium hydroxide at constant ionic strength of 0.35 mol dm^{-3} was allowed to react for about 6 hour at 30 ± 0.1 °. After completion of reaction the remaining MnO_4^- was then analysed spectrophotometrically. Some results indicated that one mole of amino acid consumed two moles of amino acid , other results indicated that four moles of MnO_4^- were consumed by one mole of amino acids amino acids each .Products were identified as aldehydes **[18]**for first series of reactions and ammonia **[19]** was tested

by Nessler's reagent and manganate by its visible spectrum. CO_2 was qualitatively detected by bubbling N_2 gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water**.[20]** About 72% aldehyde was quantitatively estimated which is evidenced by its 2,4-DNP derivative**.[21]** The nature of the aldehyde was confirmed by its IR spectra. **[22]** Carbonyl stretching at 1729 cm−1 and a band at 2928 cm−1 is due to aldehydic stretching.

The reaction product for the second series were identified as carboxylic acid by its b.p. spot test.**[23]** ammonia by Nessler's reagent and manganate by its visible spectrum. The nature of the carboxylic acid was confirmed by by its IR spectrum , which showed a carbonyl (C=O) stretch at 1657 cm−1 and OH− stretch at 2854 cm−1. It was also observ Cr(II) he aldehydes does not undergo oxidation under present kinetic condition

$$R\text{-}\underset{\underset{NH_2}{|}}{CH}\text{-}COOH + 2\,MnO_4^- + 2\,OH^- \longrightarrow RCHO + 2\,MnO_4 + NH_3 + CO_2 + H_2O$$

Where :-R= CH_2-CH.Me_2 For L – Leucine

R= CH(Me)Et For Iso leucine

During kinetic study it has been observed that the colour of the permagnate solution changes from violet to blue and then green. The change of colour of solution is due to change in oxidation states of Manganese .Violet colour is due to Mn(VII), blue Colour (V),and dark green is due to Mn(VI) oxidation state. It has been observed that absorbance of Mn(VII) decreases at 526nm, whereas Mn (VI) increase at 608 nm during the reaction. The course of reaction was followed by monitoring the decrease in absorbance of permanganate ion.[24]

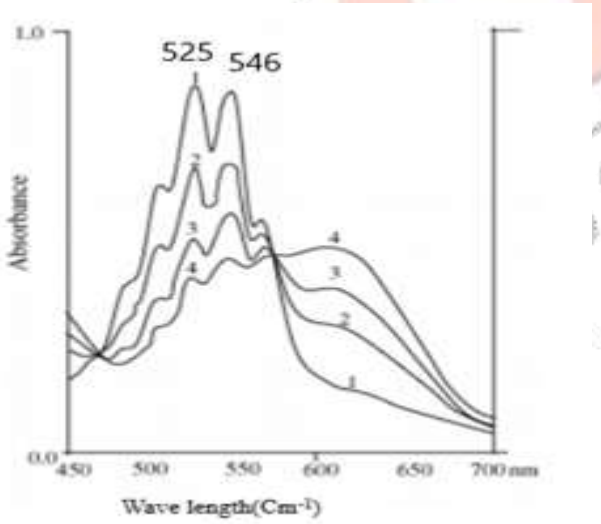


Fig:- UV Spectral changes during the oxidation of Amino acids by alkaline Potassium permanganate

Reaction Order:-

Order of the reaction can be determined, by plotting graph between log k_{obs} versus log $_C$,by varying the concentration of reductant , catalyst and alkali , while keeping others constant.

The oxidant ($KMnO_4$) concentration was varied in the range of 0.5 × 10−4 mol dm−3 to 5.0 × 10−3 mol dm−3 . The plot of log [At − A∞] versus time, for different initial concentration of [MnO_4^-] are found to be linear, and fairly constant , indicating order of the reaction with respect to [MnO_4^-] was unity**.[25,26]**

The concentration of substrates L-Leucine and L-Isoleucine were varied from 0.5×10^{-3} mol dm^{-3} to 5.0×10^{-3} mol dm^{-3} at $30^{\cdot c}$. By keeping all other concentrations and catalyst concentration constant.with increase in concentration of substrates , it was observed that the rate constant k_{obs} increased.,Indicating fractional order dependence on both the substrates. Which is also confirmed by the intercept of the plot of $\log_{kobs}$ versus [amino acid].

Effect of alkali:

By keeping others concentration constant , concentration of alkali varied . No change in rate constant was observed, Hence order of the reaction with respect to alkali was considered to be zero.

Effect of catalyst :

The concentration of chromium(III) was varied in 1.0×10^{-5} mol dm−3 to 1.0×10^{-4} mol dm−3 range. A linear plot between log $_{kobs}$ versus log[Cr(III)] with unit slope showed , unit order dependence on the catalyst.

Effect of Ionic Strength:

By varying the concentration of sodium perchlorate from 0.25 to 1.0 mol dm^{-3} and keeping others concentration constant , it was observed that rate constant increasd with increase in concentration of $NaClO_4$ and the plot of logk versus $I^{1/2}$ was linear with positive slope.

Test for Free Radical :

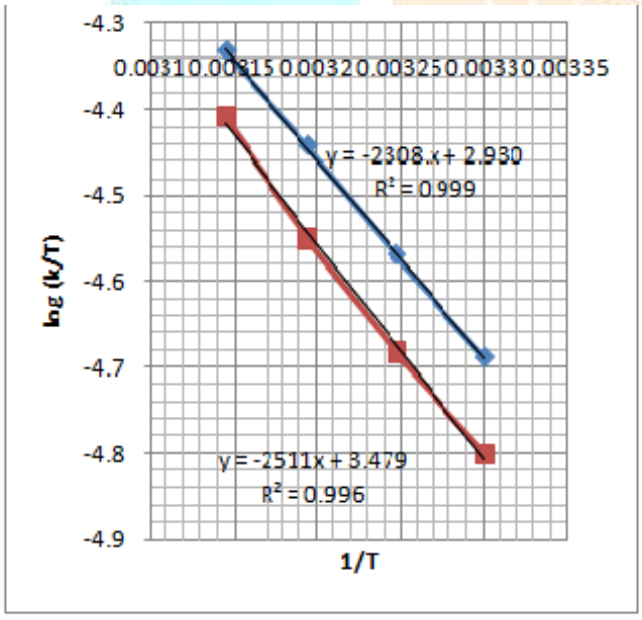
The reaction mixture was mixed with Acrylonitrile monomer and kept for 2 hours in an inert atmosphere. On diluting with methanol ,formation of white precipate indicates intervention of free radical in the reaction. However it is noteworthy that the blank experiments with reactant in presence of Acrylonitrile did not respond positive test for free radical formation.

Effect of Temperature :

The rate of the reaction was measured at four different temperatures with varying amino acids (as in Table 1) keeping other conditions constant. It was observed that The rate increases with increasing temperature. The rate constants, k of the slow step of Scheme 1 were obtained from the intercept of the plots of $[Cr(III)]/k_{obs}$ versus 1/[lleu] for different temperatures. The values of $k \times 10^{-1}$ for leucine at 303 K, 308 K, 313 K and 318 K were 6.2 dm3 $mol^{-}1$ s^{-1}, 8.3 dm^3 mol^{-1} s^{-1}, 11.3 dm^3 mol^{-1} s^{-1} and 14.8 dm^3 mol^{-1} $s^{-1,}$ respectively. The values of $k \times 10^{-1}$ for isoleucine at 303 K, 308 K, 313 K and 318 K were 4.8 dm3 mol^{-1} s^{-1}, 6.4 dm3 mol^{-1} s^{-1}, 8.8 dm3 mol−1 s^{-1} and 12.9 dm^3 mol^{-1} s^{-1}, respectively. The energy of activation corresponding to these constants was evaluated from the plot of log k versus 1/T, from which the activation parameters were calculated and are given in Table 2.

Table 2 :- Effect of Temperature on Rate costant for leucine and isoleucine amino acids

Temperature	k of leucine	log(k/T) for leucine	k of isoleucine	log(k/T) for isoleucine
303	$6.2*10^{-3}$	-4.689	$4.8*10^{-3}$	-4.800
308	$8.3*10^{-3}$	-4.569	$6.4*10^{-3}$	-4.682
313	$11.3*10^{-3}$	-4.442	$8.8*10^{-3}$	-4.551
318	$14.8*10^{-3}$	-4.332	$12.4*10^{-3}$	-4.409



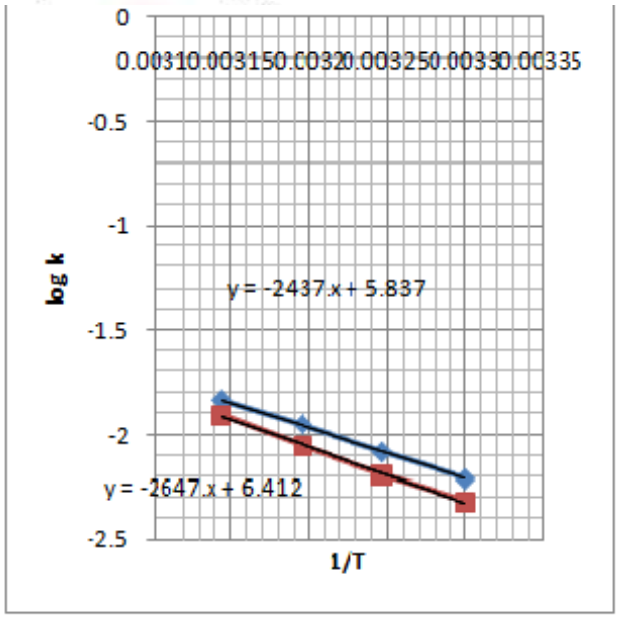


Fig5:- logk/T vs 1/T

Fig6 :- logk Vs 1/T

Table 2:Activation Parameters with respect to slow step of scheme 1

Activation Parameters	**Leucine Cr (III) catalysed**	**Isoleucine Cr(III) catalysed**
Ea	50.68	46.7
Log A	6.412	5.837
ΔH **(kJ mol−1)**	-44.2	-48.1
ΔS **(J K−1 mol−1)**	-141.46	-130.9
ΔG (kJ mol−1)	42.81	39.615

Discussion:-

Permanganate ion MnO^{4-}, exhibits many oxidation states, is a powerful oxidant in an aqueous alkaline medium. pH of the reaction and the stoichiometric results play an important role.under experimental conditions at pH > 12, The reduction product of manganese(VII) is stable and further reduction of manganese(VI) might be stopped **[27]**.At pH > 12, the product of manganese(VII) is manganese(VI) and no further reduction was observed. However, manganese (VI) is reduced to manganese(IV) on prolonged standing. at pH > 11.5 the relatively high solubility of chromium(III) is due to the predominance of the species [Cr(OH)4**.[13].** Slow formation of polymeric species is apparently responsible for the observed precipitation with time. The solubility of chromium(III) increases with pH. **[28]**. The solutions are clear above pH 12, but the turbidity increases with decreasing pH**[29**]. The chromium(III) species $[Cr(OH)]^{2+}$, $[Cr(OH)_2]^{+}$, $[Cr(OH)_3]$ and $[Cr(OH)_4]^{-}$, in addition to this polymeric species are known to exist in aqueous solution **[30]**. In basic solutions in the pH 7–10, range, chromium(III) precipitates as $Cr(OH)_3$, but dissolves in excess of base owing to the likely formation of hydroxide species **[31]** $Cr(OH)_6]_3$. Recent work favours $[Cr(OH)_4]^{-}$ as the major species. Hence, this is the form in which almost the entire dissolved chromium(III) exists above pH 12 in this reaction . The spectrum of chromium(III) at pH > 12 is similar to that of aqueous chromium(III) except that of some hypochromicity. It is known that in aqueous solution, amino acid exists as zwitterionic **[32]** form, whereas in aqueous alkaline medium it exists as anionic form according to the following equilibria.. The reaction between permanganate and amino acids under study in alkaline medium has a 2:1 stoichiometry with a first order dependence on both [MnO4 −] and chromium(III), less than unit order dependence on [amino acid] and zero order with respect to [alkali**].** No effect ofadded products, such as aldehyde, Mn(VI) and ammonia was observed**.** The observed order of less than unity in amino acid concentration reveals that the substrate is involved in complex formation either with chromium(III) or alkali. Since the reaction rate is independent of (alkali), complexation between amino acid and chromium(III) species is expected. The complex formed between amino acid and chromium(III)species reacts with permanganate in a slow step to give a free radical derived from decarboxylated amino acid, which further reacts with another molecule of permanganate in fast step to yield productas shown in scheme I.such complex formation has also been reported in earlier work**.[33]**The spectral evidence for complex formation between catalyst and substrate was obtained from the UV–vis spectra of the catalyst and a mixture of catalyst and amino acid in the alkaline medium.. A bathochromic shift of 4 nm from 431 to 435 nm is observed for leucine and a hypsochromic shift of 7 nm from 431 to 424 nm is observed for isoleucine. The formation of the complex was also proved kinetically by the non-zero intercept of the plot of [Cr(III)]/kobs versus 1/[amino acid]. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step,

$RCH(NH_2)COOH \rightleftharpoons RCH(+NH_3)\,COO^-$

(Zwitter ion)

$RCH(NH_2)COOH + OH^- \rightleftharpoons RCH(NH_2)COO^- + H_2O$

$R\text{-}CH(NH_2)\text{-}COO^- + [Cr\,(OH)_4(H_2O)_2]^- \underset{}{\overset{K^-}{\rightleftharpoons}}$ Complex (C) $+ H_2O$

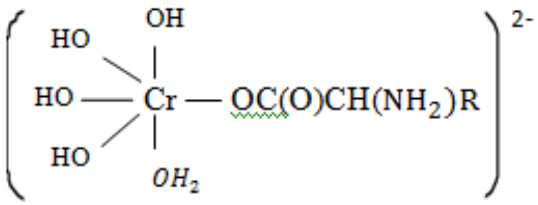
Complex (C) $+ MnO_4^- \xrightarrow[\text{Slow}]{k} R\text{-}\dot{C}H(NH_2) + MnO_4^{2-} + [Cr\,(OH)_4(H_2O)]^- + CO_2$

$R\text{-}\dot{C}H(NH_2) + MnO_4^- + OH^{\cdot} \xrightarrow{\text{fast}} R\text{-}CHO + MnO_4^{2-} + NH_3$

Where R = $-CH_2 - CH\,Me_2$ for L-Leucine and

And, R = $-CH\,Me\,Et$ for L-Isoleucine

The probable structure of the complex (C) is,



Scheme-1

According to Scheme 1,

$\text{Rate} = k[MnO_4]^- \times C = kK\,[AA]f\,[Cr(III)]f[MnO_4]^-$ (1)

The total concentration of amino acid is given by,

$[AA]_T = [AA]f + [C] = [AA]_f + K\,[AA]_f\,[Cr(III)]^*$

$= [AA]_f + K[AA]_f[Cr(III)]$

$= [AA]_f\,\{1 + K\,[Cr(III)\}$

Therefore,

$[AA]_f = \frac{[AA]_T}{1+K[Cr(III)]_f}$ (a)

and

$$[Cr(III)]_f = \frac{[Cr(III)]_T}{1+K[Cr(III)]_f} \qquad (b)$$

Substituting Eqs. (a) and (b) in Eq. (1), we get

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = \frac{kK(MnO_4^-)[Cr(III)]_T[AA]_T}{\{1+K[Cr(III)]_T\}\{1+K[AA]_T\}} \qquad (c)$$

The terms $(1 + K\,[Cr(III)]_T)$ in the denominator of Eq.

(c) approximate to unity in view of low concentration of

chromium (III) used.

Therefore, Eq. (c) becomes Eq. (2).

$$k_{obs} = \frac{\text{Rate}}{[MnO_4^-]} = \frac{kK[Cr(III)]_T[AA]_T}{\{1+K\,[AA]_T\}} \qquad (2)$$

In the above equation, the subscripts T and f stands for total and free, respectively.

The moderate ΔH and ΔS values are both favorable for electron transfer reactions. Negative ΔS values for radical reactions have been ascribed to the nature of electron pairing and unpairing reactions and to the loss of degrees of freedom by formation of a rigid transition state **[31,32]**. The activation parameters for the oxidation of some amino acids by [MnO_4^-] are summarized in Table 2. The entropy of activation for the title reaction falls within the observed range**[33]**. Changes in rate are caused by changes in both ΔHand ΔS but these quantities vary extensively in a parallel fashion.[**34-37**]

Conclusion:

From this experiment It is observed that the oxidant species [MnO_4^-] requires

pH > 12, below which the system becomes disturbed and the reaction proceeds further to give a reduced oxidation product as manganese(IV), which was seen observed by appearance of yellow turbidity. Hence, we can conclude that the role of pH in carrying out this experiment is crucial.In alkaline medium chromium(III) is found to be an efficient catalyst. which catalyses the reaction with a measurable velocity at a concentration of 10^{-5} mol $dm^{-3.}$ It is also noteworthy that, under the experimental conditions, the reaction occurs in two successive one-electron reduction steps rather than a two-electron reduction in a single step.

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