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# Comparative study of the chromium(III) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate: A kinetic and mechanistic approach

Dinesh Bilehal, Raviraj Kulkarni, Sharanappa Nandibewoor*

*Post Graduate Department of Studies in Chemistry, Karnatak University, Dharwad 580003, India*

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**Abstract**

The kinetics of the chromium(III) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate were studied and compared, spectrophotometrically. The reaction is first order with respect to (oxidant) and (catalyst) with an apparently less than unit order in (substrate) and zero order with respect to (alkali). The results suggest the formation of a complex between the amino acid and the hydroxylated species of chromium(III). The complex reacts further with the permanganate in a rate-determining step, resulting in the formation of a free radical, which again reacts with the permanganate in a subsequent fast step to yield the products. The reaction constants involved in the mechanism were obtained. There is a good agreement between observed and calculated rate constants under different experimental conditions. The activation parameters with respect to slow step of the mechanism for both the amino acids were calculated and discussed. Of the two amino acids, leucine is oxidised at a faster rate than the isoleucine.


*Keywords:* Chromium(III); Catalytic study; L-Leucine; L-Isoleucine; Kinetic study; Permanganate

## 1. Introduction

Potassium permanganate is widely used as an oxidising agent in synthetic as well as in analytical chemistry, and also as a disinfectant. The permanganate reactions are governed by the pH of the medium. Among the six oxidation states of manganese (+2 to +7), permanganate, Mn(VII) is the most potent oxidation state in acid as well as in alkaline medium [1–4].

The mechanism by which the multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium [5] used for the study. In strongly alkaline medium, the stable reduction product [6,7] of the permanganate ion is manganate ion, $MnO_4^{2-}$. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion [8].

Leucine and isoleucine are essential amino acids. They are active site residues of enzymes, and help in maintaining the correct conformation of enzymes by keeping them in their proper ionic states. Thus, oxidation of these may help in understanding enzyme kinetics. The oxidation of amino acids is of interest as the products differ depending on the oxidants [9,10].

Chromium(VI) compounds irritate the skin and mucous membranes, whereas chromium(III) appears to be an essential trace metal in mammalian metabolism. To determine the chemical processes that affect biological systems the aqueous species of chromium(III) at all pH conditions must be identified. Chromium(III) is the cheapest transition metal, which can be used for catalysis. The chemistry of chromium(III) in alkaline medium is not so well developed as that in acid [11]. Recently, it has become known that the relatively high

* Corresponding author. Tel.: +91 836 2770524; fax: +91 836 2747884.
*E-mail address:* stnandibewoor@yahoo.com (S. Nandibewoor).

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solubility of chromium(III) in solutions of pH > 11.5 is due to species, such as [12] $Cr(OH)_4$. The uncatalysed reaction between the said amino acids and permanganate in alkaline medium has been studied previously [13]. A microscopic amount of chromium(III) is sufficient to catalyse the reaction in alkaline medium and a variety of mechanisms are possible. Herein, we describe the results of the title reaction in order to determine the active species of oxidant, reductant and catalyst in such media and to arrive at a plausible mechanism.

## 2. Experimental details

### 2.1. Materials

Stock solutions of L-leucine and L-isoleucine (S.D. Co., fine chemicals) were prepared by dissolving the appropriate amount of sample in doubly distilled $H_2O$. The solution of $KMnO_4$ (BDH) was prepared and standardized with $(CO_2H)_2$ [14]. Potassium manganate solution was prepared as described by Carrington and Symons [15]. The solution was standardized by measuring the absorbance on a Varian CARY 50 Bio UV–vis spectrophotometer with a 1 cm quartz cell at 608 nm ($\varepsilon = 1530 \pm 20\,dm^3\,mol^{-1}\,cm^{-1}$).

The chromium(III) solution was prepared by dissolving chromium(III) potassium sulfate (BDH, AnalaR) ($Cr_2(SO_4)_3{\cdot}K_2SO_4{\cdot}24H_2O$) in $H_2O$ and was standardized [16] by oxidising it to chromium(VI) with excess if persulfate in presence of one or two drops of $1.0 \times 10^{-2}$ mol dm$^{-3}$ silver nitrate. The excess of persulfate was boiled off and the chromium(VI) thus obtained, was determined against iron(II) ammonium sulfate solution.

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of the samples in doubly distilled $H_2O$. NaOH and $NaClO_4$ were used to provide the required alkalinity and to maintain the ionic strength, respectively.

### 2.2. Kinetic procedure

The kinetic procedure followed as given in earlier paper [17]. The effect of dissolved oxygen on the reaction rate was checked by preparing the mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under the nitrogen and in the presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. Nevertheless, as a precaution, fresh solutions were used when conducting kinetic experiments.

## 3. Results

### 3.1. Stoichiometry

The reaction mixtures, containing an excess of permanganate over amino acids, a constant amount of chromium(III) and 0.05 mol dm$^{-3}$ NaOH at a constant ionic strength of 0.35 mol dm$^{-3}$ was allowed to react for ca. 8 h at 30 ± 0.1 °C under nitrogen atmosphere. After completion of the reaction, the remaining $MnO_4^-$ was then analysed spectrophotometrically. Some results indicated that two moles of $MnO_4^-$ were consumed by one mole of amino acid each. Other results indicated that four moles of $MnO_4^-$ were consumed by one mole of amino acid each. The reaction products for the first series were identified as aldehyde [18], by b.p., spot test and ammonia [19] 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 limewater [20]. The product aldehyde was quantitatively estimated to about 76%, which is evidenced by its 2,4-DNP derivative [21]. The nature of the aldehyde was confirmed by its i.r. spectrum [22] carbonyl stretching at 1729 cm$^{-1}$ and a band at 2928 cm$^{-1}$ due to the aldehydic –CH-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. $CO_2$ was qualitatively detected by bubbling $N_2$ gas through the acidified reaction mixture and passing the liberated gas through a tube, containing limewater. The nature of the carboxylic acid was confirmed by its i.r. spectrum which showed a carbonyl (C=O) stretch at 1657 cm$^{-1}$ and $OH^-$ stretch at 2854 cm$^{-1}$. The same type of aldehyde as above was obtained when the product analysis was carried under pseudo-first order conditions for leucine and isoleucine separately. It was also observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. A test for corresponding acid was negative, so, it is concluded that the stoichiometry of the reaction under kinetic study is:

$$\text{R-CH(NH}_2\text{)-CO}_2\text{H} + 2MnO_4^- + 2OH^- \xrightarrow{Cr(III)} \text{R-CHO} + 2MnO_4^{2-} + NH_3 + CO_2 + H_2O$$

Where R = -$CH_2$- CH $Me_2$ for L-leucine

And, R = - CH Me Et for L-isoleucine

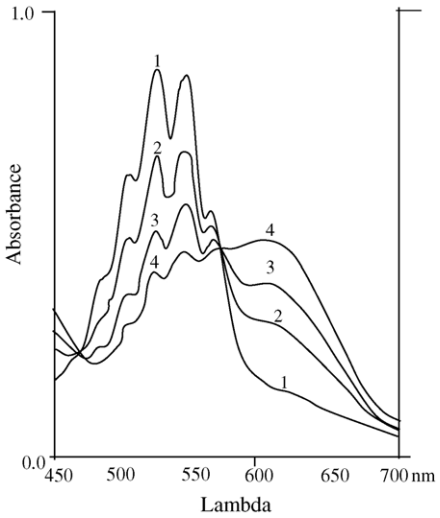



Fig. 1. UV–vis spectral changes during the oxidation of amino acid by aqueous alkaline permanganate at 30 °C, scanning time interval, 2 min.

The permanganate in alkaline medium exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The solution changed from violet to blue and then to green, excluding the accumulation of hypomanganate. The violet colour originates from the pink of permanganate and blue from hypomanganate. The change of $KMnO_4$ solution from violet Mn(VII) ion to dark green Mn(VI) ion through the blue Mn(V) ion has been observed. The spectral changes during the reaction are shown in Fig. 1. It is evident that [Mn(VII)] decreases at 526 nm, whereas [Mn(VI)] increases at 608 nm during the reaction.

Regression analysis of experimental data to obtain the regression coefficient $r$, and standard deviation $\sigma$, of points from the regression line was performed using a Pentium-III personnel computer.

### 3.2. Reaction orders

The reaction orders were determined from the slopes of log $k_{obs}$ versus log concentration plots, by varying the concentration of reductant, catalyst and alkali, while keeping others constant.

The oxidant (potassium permanganate) concentration was varied in the range $0.5 \times 10^{-4}$ mol dm$^{-3}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ as shown in Table 1. The plots of log $[A_t - A_\infty]$ versus time, for different initial concentrations of $MnO_4^-$ are found to be linear ($r > 0.9954$, $\sigma < 0.022$), and the fairly constant $k_{obs}$ values indicate that the order with respect to $[MnO_4^-]$ was unity. This fact was also confirmed by varying $[MnO_4^-]$ which did not show any change in pseudo-first order constants ($k_{obs}$) values as shown in Table 1.

The substrates, L-leucine and L-isoleucine were varied in the $0.5 \times 10^{-3}$ mol dm$^{-3}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ range at 30 °C, keeping all other concentrations and the catalyst concentration constant. The rate constant, $k_{obs}$ increased with increase in concentration of amino acids, indicating a less than unit order dependence on both the substrates concentration. This is also confirmed

Table 1
Effect of variation of $[MnO_4^-]$, [amino acid], [Cr(III)] and $[OH^-]$ on chromium(III) catalysed oxidation of leucine and L-isoleucine by $KMnO_4$ in aqueous alkaline medium at 30 °C and $I = 0.35$ mol dm$^{-3}$

| $10^4$ $[MnO_4^-]$ (mol dm$^{-3}$) | $10^3$ [AA] (mol dm$^{-3}$) | $10^2$ $[OH^-]$ (mol dm$^{-3}$) | $10^5$ [Cr(III)] (mol dm$^{-3}$) | $10^3 \times k_{obs}$ (s$^{-1}$) | |
|---|---|---|---|---|---|
| | | | | Experimental leu (I-leu) | Calculated leu (I-leu) |
| 0.5 | 2.0 | 5.0 | 5.0 | 2.22 (1.63) | 2.24 (1.76) |
| 1.0 | 2.0 | 5.0 | 5.0 | 2.27 (1.60) | 2.24 (1.76) |
| 2.0 | 2.0 | 5.0 | 5.0 | 2.20 (1.67) | 2.24 (1.76) |
| 3.0 | 2.0 | 5.0 | 5.0 | 2.28 (1.64) | 2.24 (1.76) |
| 5.0 | 2.0 | 5.0 | 5.0 | 2.21 (1.68) | 2.24 (1.76) |
| 2.0 | 0.5 | 5.0 | 5.0 | 1.08 (0.93) | 1.16 (0.91) |
| 2.0 | 1.0 | 5.0 | 5.0 | 1.78 (1.33) | 1.71 (1.34) |
| 2.0 | 2.0 | 5.0 | 5.0 | 2.20 (1.67) | 2.24 (1.76) |
| 2.0 | 3.0 | 5.0 | 5.0 | 2.62 (2.16) | 2.65 (2.08) |
| 2.0 | 5.0 | 5.0 | 5.0 | 3.12 (2.59) | 2.76 (2.16) |
| 2.0 | 2.0 | 2.5 | 5.0 | 2.22 (1.63) | 2.24 (1.76) |
| 2.0 | 2.0 | 5.0 | 5.0 | 2.26 (1.64) | 2.24 (1.76) |
| 2.0 | 2.0 | 10.0 | 5.0 | 2.20 (1.67) | 2.24 (1.76) |
| 2.0 | 2.0 | 17.5 | 5.0 | 2.27 (1.69) | 2.24 (1.76) |
| 2.0 | 2.0 | 25.0 | 5.0 | 2.28 (1.70) | 2.24 (1.76) |
| 2.0 | 2.0 | 5.0 | 1.0 | 0.48 (0.31) | 0.45 (0.35) |
| 2.0 | 2.0 | 5.0 | 2.0 | 0.98 (0.70) | 0.90 (0.70) |
| 2.0 | 2.0 | 5.0 | 5.0 | 2.20 (1.67) | 2.24 (1.76) |
| 2.0 | 2.0 | 5.0 | 7.5 | 3.13 (2.43) | 3.36 (2.64) |
| 2.0 | 2.0 | 5.0 | 10.0 | 4.62 (3.45) | 4.48 (3.51) |

Leu.: L-leucine.
I-leu.: L-isoleucine.
AA: amino acid.

by the intercept of the plot of $\log k_{obs}$ versus [amino acid].

### 3.2.1. Effect of alkali

The effect of alkali on the reaction was studied at constant amino acids (L-leucine and L-isoleucine), constant chromium(III) and potassium permanganate concentrations and at a constant ionic strength of 0.35 mol dm$^{-3}$ at 30 °C. The rate constants are almost constant with increase in (alkali). Hence, the order with respect to (alkali) was considered to be effectively zero (Table 1).

### 3.2.2. Effect of catalyst

The chromium(III) concentration was varied in $1.0 \times 10^{-5}$ mol dm$^{-3}$ to $1.0 \times 10^{-4}$ mol dm$^{-3}$ range. The linearity of plots ($r > 0.9973$, $\sigma < 0.0342$) of $\log k_{obs}$ versus log[Cr(III)] with unit slope showed unit order (Table 1) dependence on [Cr(III)]. Under the conditions used, the uncatalysed reaction rate is very much lesser compared to the catalysed reaction rate.

### 3.2.3. Effect of initially added products

The externally added products, such as manganate, ammonium hydroxide and aldehyde did not show any significant effect on the rate of the reaction.

### 3.2.4. Effect of ionic strength and dielectric constant

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.25 to 1.0 mol dm$^{-3}$ at constant permanganate, amino acids, alkali and catalyst concentrations. It was found that the rate constants increased with increase in concentration of $NaClO_4$ and the plot of log $k_{obs}$ versus $I^{1/2}$ was linear with positive slope ($r > 0.9973$, $\sigma < 0.0134$). The effect of relative permittivity ($D$) on the rate constant has been studied by varying the $t$-butanol–water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids [24]. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. It was found that the rate constants increased with increase in the dielectric constant of the medium and the plot of $\log k_{obs}$ versus $1/D$ was linear with negative slope ($r > 0.9985$, $\sigma < 0.0312$).

### 3.2.5. Test for free radicals

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 h in an inert atmosphere. On diluting with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. However, the blank experiments with reactants in presence of acrylonitrile did not responded to positive test for free radical formation.

### 3.2.6. Effect of temperature

The reaction rate was measured at four different temperatures with varying (substrate) (as in Table 1) keeping other conditions constant. The rate was found to increase 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/[L-leu] for different temperatures. The values of $k \times 10^{-1}$ for leucine at 303 K, 308 K, 313 K and 318 K were 6.5 dm$^3$ mol$^{-1}$ s$^{-1}$, 8.5 dm$^3$ mol$^{-1}$ s$^{-1}$, 11.5 dm$^3$ mol$^{-1}$ s$^{-1}$ and 15.0 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 5.1 dm$^3$ mol$^{-1}$ s$^{-1}$, 6.6 dm$^3$ mol$^{-1}$ s$^{-1}$, 9.0 dm$^3$ mol$^{-1}$ s$^{-1}$ and 13.0 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.

The thermodynamic quantities of the first step of Scheme 1 can be evaluated as follows. The equilibrium constants, $K$ of Scheme 1 were obtained from the slope of the plots of [Cr(III)]/$k_{obs}$ versus 1/[L-leu] for different temperatures. The values for leucine at 308 K, 313 K and 318 K are, $2.1 \times 10^3$ dm$^3$mol$^{-1}$, $4.3 \times 10^3$ dm$^3$mol$^{-1}$ and $8.2 \times 10^3$ dm$^3$mol$^{-1}$, respectively. The values for isoleucine at 308 K, 313 K and 318 K are $3.5 \times 10^3$ dm$^3$ mol$^{-1}$, $7.2 \times 10^3$ dm$^3$mol$^{-1}$ and $16.6 \times 10^3$ dm$^3$mol$^{-1}$ respectively. The van't Hoff plot was drawn for the variation of $K$ with temperature ($\log K$ versus $1/T$; $r > 0.9974$, $\sigma < 0.0231$). The values of thermodynamic quantities are given in Table 3. A

Table 3
Thermodynamic quantities with respect to first step of scheme 1

| Thermodynamic quantities | Leucine | Isoleucine |
|---|---|---|
| $\Delta H$ (kJ mol$^{-1}$) | 107 ± 6 | 142 ± 7 |
| $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | 128 ± 7 | 164 ± 8 |
| $\Delta G$ (kJ mol$^{-1}$) | −21 ± 1 | −22 ± 1 |

Table 2
Activation parameters with respect to slow step of scheme 1

| Activation parameters | Leucine Cr(III) catalysed | Isoleucine Cr(III) catalysed | Leucine Ru(III) catalysed | Isoleucine Ru(III) catalysed |
|---|---|---|---|---|
| $E_a$ (kJ mol$^{-1}$) | 44.9 ± 2.5 | 49.7 ± 2.5 | 39.3 ± 3.0 | 31.2 ± 3.0 |
| log $A$ | 9.5 ± 0.5 | 10.3 ± 0.5 | | |
| $\Delta H^{\#}$ (kJ mol$^{-1}$) | 42.3 ± 2.0 | 47.2 ± 2.5 | 30.7 ± 3.0 | 28.8 ± 3.0 |
| $\Delta S^{\#}$ (J K$^{-1}$ mol$^{-1}$) | −16.8 ± 1.0 | −13.6 ± 0.5 | −62.0 ± 10 | −71.0 ± 10 |
| $\Delta G^{\#}$ (kJ mol$^{-1}$) | 47.5 ± 2.5 | 51.4 ± 2.5 | 49.2 ± 3.0 | 49.3 ± 3.0 |
| Reference | Present work | Present work | [41] | [41] |

comparison of these values with those values obtained for the slow step shows that the reaction before the rate-determining step is fairly slow in case of both leucine and isoleucine.

## 4. Discussion

Permanganate ion, $MnO_4^-$, is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH > 12, the reduction product of manganese(VII) is stable and further reduction of manganese(VI) might be stopped [12,13]. Diode Array Rapid Scan Spectrophotometric (DARSS) studies have shown that at pH > 12, the product of manganese(VII) is manganese(VI) and no further reduction was observed as reported [12,13] by Simandi et al. However, on prolonged standing, green manganese(VI) is reduced to manganese(IV) under our experimental conditions.

The relatively high solubility of chromium(III) in alkaline medium at pH > 11.5 is due to the predominance of the species $[Cr(OH)_4]^-$ at 27 °C [16]. Slow formation of polymeric species is apparently responsible for the observed precipitation with time. The solubility of chromium(III) increases with pH. As monitored by nephelometer [25], the solutions are clear above pH 12, but the turbidity increases with decreasing pH and precipitation occurs below pH 12. Hence, only pH > 12 have been studied in this work. 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 [16]. 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 [26] $[Cr(OH)_6]^{3-}$. Interestingly, this is widely believed to be responsible for the amphoterism of chromium(III), and is not one of the reactive species present in alkaline medium [16]. However, the latter or even the $[Cr(OH)_5]^{2-}$ species [26] has not been identified with certainty in such solutions, and recent work [12,25,27] 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 under the conditions employed in this reaction. The spectrum of chromium(III) at pH > 12 is similar to that of aqueous chromium(III) except that of some hypochromicity is found in the former [$\varepsilon = 25 \pm 1$ (pH > 12) versus 17 $dm^3\,mol^{-1}\,cm^{-1}$ in aqueous chromium(III)].

It is known that in aqueous solution, amino acid exists as zwitterionic [28] form, whereas in aqueous alkaline medium it exists as anionic form according to the following equilibria.

$$RCH(NH_2)COOH \rightleftharpoons \underset{\text{(Zwitterion)}}{RCH(\overset{+}{N}H_3)COO^-}$$

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

The reaction between permanganate and amino acids under study in alkaline medium has a 2:1 stoichiometry with a first order dependence on both $[MnO_4^-]$ and chromium(III), less than unit order dependence on [amino acid] and zero order with respect to [alkali]. No effect of added 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 a subsequent fast step to yield the products as shown in Scheme 1. Such complex formation between substrate and catalyst has also been observed in earlier work [29].

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 $[Cr(III)]/k_{obs}$ 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, indicate that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation [30]. Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work on the alkaline permanganate oxidation of amino acids [31].

Scheme 1 leads to rate law (2)

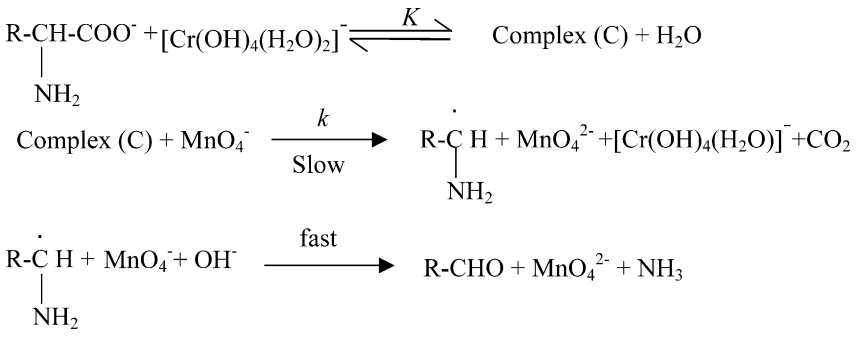
$$\text{Rate} = \frac{-\mathrm{d}[MnO_4^-]}{\mathrm{d}t} = \frac{kK[MnO_4]^-[Cr(III)]_T[AA]_T}{\{1 + K[Cr(III)]_T\}\{1 + K[AA]_T\}} \quad (1)$$

The term $(1 + K[Cr(III)]_T)$ in the denominator of Eq. (1) approximates to unity in view of the low concentration of chromium(III) used. Therefore, Eq. (1) becomes Eq. (2).

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

Further, the Eq. (2) can be rearranged to (3) (by omitting the subscript '*T*') which is suitable for the verification

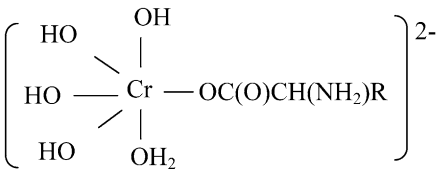
$$\frac{[Cr(III)]}{k_{obs}} = \frac{1}{kK[AA]} + \frac{1}{k} \quad (3)$$




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 Eq. (3), the plots of $[Cr(III)^{III}]/k_{obs}$ versus 1/[amino acid] is linear with non-zero intercepts which are verified in Fig. 2. From slopes and intercepts of such plots $k$ and $K$ values are obtained at 30 °C as 65 $dm^3\ mol^{-1}\ s^{-1}$ and $1.10 \times 10^3\ dm^3\ mol^{-1}$, respectively for leucine and 51 $dm^3\ mol^{-1}\ s^{-1}$ and $1.10 \times 10^3\ dm^3\ mol^{-1}$ for isoleucine. Using these values the calculated rate constants are in reasonable agreement with the experimental values as given in Table 1. The rate constants indicate that leucine is oxidised at a faster rate than the isoleucine.

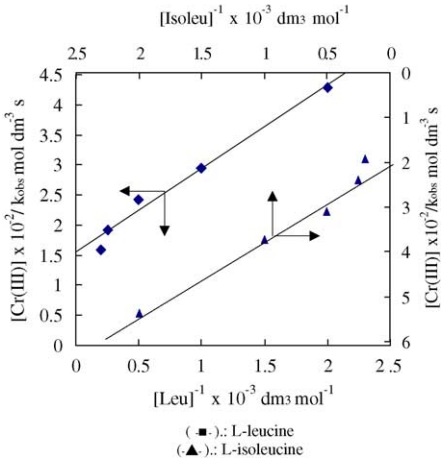



Fig. 2. Verification of rate law (2) in the form of (3) for the permanganate oxidation of L-leucine and L-isoleucine in aqueous alkaline medium at 30 °C.

The effect of increasing ionic strength on the rate qualitatively explains the reaction between similar charged ions as seen in Scheme 1. The effect of solvent on the reaction kinetics has been described in earlier literature [32–36]. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Leffler [40] has shown that a plot of log $k_{obs}$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction. However, in the present study, an increase in the content of $t$-butanol in the reaction medium leads to the decrease in the reaction rate, which is not in agreement with Amis theory [37]. Applying the Born equation, Laidler and Eyring derived the Eq. (4).

$$\ln k = \ln k_0 + \frac{NZ^2e^2}{2DRT}\left(\frac{1}{r} - \frac{1}{r^*}\right) \quad (4)$$

where $k_0$ is the rate constant in a medium of infinite dielectric constant and $r$ and $r^*$ refer to the radius of the reacting species and the activated complex, respectively. It can be seen from the Eq. (4) that the rate should be greater in a medium of lower dielectric constant when $r^* > r$. Intermolecular hydrogen bonding, that could stabilise the transition state, increasing the size of the activated complex by attracting solvent molecules due to a solvation effect is possible. It is likely that $r^* > r$ for amino acid, thus explaining the experimental observation. Hence, one can expect intermolecular hydrogen bonding [38] in amino acid since it contains $NH_2$, COOH groups on the same carbon atom. Such hydrogen bonding is

common for molecules having COOH and $NH_2$, COOH and $OH^-$ groups at either on the adjacent carbon atom or on the same carbon atom of the molecule as found in simple amino acids [38].

The moderate $\Delta H^{\#}$ and $\Delta S^{\#}$ values are both favourable for electron transfer reactions. Negative $\Delta S^{\#}$ 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 [39].

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. Variation in the rate within a reaction series may be caused by changes in the enthalpy and/or entropy of activation. Changes in rate are caused by changes in both $\Delta H^{\#}$ and $\Delta S^{\#}$, but these quantities vary extensively in a parallel fashion. A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ is linear according to equation,

$$\Delta H^{\#} = \beta \Delta S^{\#} + \text{constant}$$

where $\beta$ is called the isokinetic temperature

We have calculated the isokinetic temperature by plotting $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Fig. 3). The value of $\beta$ is 293.5 K. The value of $\beta$ is lower than the experimental temperature. This indicates that the rate is being governed by the entropy of activation [40]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested. Among the two amino acids leucine and isoleucine the former is found to be oxidised faster than the latter. This is due to the presence of the branched chain, making molecules less reactive because of the increase in the steric crowding.

The difference in the activation parameters for the catalysed and uncatalysed reactions [13], explains the catalytic effect on the reaction. The catalyst, Cr(III) alters the reaction path by lowering the energy of barrier, i.e. it provides an alternative pathway with lower activation parameters for the reaction, involving the formation of an intermediate complex as proposed in Scheme 1.

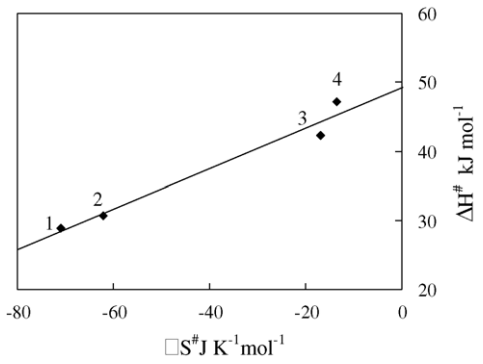



Fig. 3. Isokinetic relationship of oxidation of some amino acids by $MnO_4^-$.

## 5. Conclusion

It is interesting 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 slowly develops a yellow turbidity. Hence, it becomes apparent that, in carrying out this reaction, the role of pH in the reaction medium is crucial. Chromium(III) is found to be an efficient catalyst (especially in alkaline medium) which catalyses the reaction with a measurable velocity at a concentration of $10^{-5}$ mol dm$^{-3}$. It is also noteworthy that, under the conditions studied, the reaction occurs in two successive one-electron reduction steps rather than a two-electron reduction in a single step.

## Appendix A

According to Scheme 1,

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

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,

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

and

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

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

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

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).

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

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

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