Kinetics and mechanism of oxidation of L-proline by heptavalent manganese: a free radical intervention and decarboxylation

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The kinetics of oxidation of L-proline by permanganate in alkaline medium was studied spectrophotometrically. The reaction is first order with respect to $[MnO_4^-]$ and is an apparent less than unit order, each in [L-proline] and [alkali] under the experimental conditions. The reaction rate increases with increase in ionic strength and decrease in solvent polarity of the medium. Addition of reaction products has no effect on the reaction rate. A mechanism involving the formation of a complex between the oxidant and substrate has been proposed. The reaction constants involved in the mechanism were evaluated. There is a good agreement between the observed and calculated rate constants under varying experimental conditions. The activation parameters with respect to the slow step of the proposed reaction scheme were evaluated and discussed.

Permanganate ion oxidises a great variety of substrates and finds extensive applications in organic syntheses,[1,2] especially after the advent of phase transfer catalysis[3,4] which permits the use of solvents such as methylene chloride and benzene. Kinetic studies constitute an important source of mechanistic information on the reaction, as demonstrated by results referring to unsaturated acids in both aqueous[1,3] and non-aqueous media.[5]

During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which this multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium[6] used for the study. In strongly alkaline medium, the stable reduction product[7] is the 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 step followed by a rapid reaction.[7] Amino acids have been oxidised by a variety of oxidising agents.[8] The oxidation of amino acids is of interest as the oxidation products differ for different oxidants.[9,10]

L-proline is a non-essential amino acid and is an important constituent of collagen. As per a recent report,[11] L-proline is considered to be the world's smallest natural enzyme and it is used in catalysing the aldol condensation of acetone to various aldehydes with high stereo-specificity. Although some work on the oxidation of organic[12] and inorganic[13] substrates by permanganate in aqueous alkaline medium has been carried out, there has been no report on the oxidation of L-proline in such media. Here the title reaction has been carried out in order to elucidate the redox chemistry of permanganate in alkaline media and to arrive at a plausible mechanism.
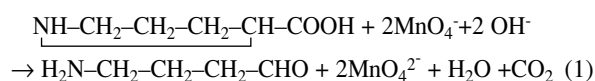
Experimental

Materials and reagents: Stock solutions of L-proline (sd-fine chemicals) and KMnO₄ (BDH) were prepared by dissolving the appropriate amounts of samples in double distilled water. The preparations of other stock solutions are as described previously.[7]

Kinetic measurements: Since the initial reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12). All kinetic measurements and other experiments are as given in an earlier paper.[7]

Results

Stoichiometry and product analysis: The reaction mixtures containing an excess of permanganate over L-proline, NaOH and adjusted ionic

strength of 0.50 mol dm⁻³, was allowed to react for 2 h at $25 \pm 0.1°$ C. The remaining permanganate was then analysed spectrophotometrically. The results indicated that two moles of MnO_4^- were consumed by one mole of L-proline as given by Eqn (1).

$$NH–CH_2–CH_2–CH_2–CH–COOH + 2MnO_4^- + 2\ OH^-$$
$$\rightarrow H_2N–CH_2–CH_2–CH_2–CHO + 2MnO_4^{2-} + H_2O + CO_2 \quad (1)$$

The products were eluted with solvent ether and the organic product was submitted to spot tests. The main reaction products were identified as aminobutaraldehyde the by spot test[14] for amine and aldehyde groups and manganate by its UV-Vis spectrum. The presence of aldehyde was also confirmed by IR spectroscopy,[15] which showed bands at 3444 cm⁻¹ for –NH stretching, 1733 cm⁻¹ for aldehydic-CO stretching, and 2919 cm⁻¹ for aldehydic-CH stretching respectively. The only organic product obtained by oxidation was aminobutaraldehyde, the yield obtained was found to be about 70% from its 2,4-DNP derivative. It was further observed that the aldehyde does not undergo further oxidation under prevailing kinetic conditions. Test for the corresponding acid was negative.

Reaction order: The reaction orders were determined from the slopes of log k_{obs} vs log (concentration) plots by varying the concentration of the reductant and OH⁻ in turn while keeping others constant. The potassium permanganate concentration was varied in the range of $5.0 \times 10^{-5} – 5.0 \times 10^{-4}$ mol dm⁻³ and the linearity of plots of log $[MnO_4^-]$ versus time ($r > 0.9985$, $s \le 0.027$) indicated a reaction order of unity in $[MnO_4^-]$. This was also confirmed by variation of $[MnO_4^-]$, which did not result any change in the pseudo first-order rate constants, k_{obs} (Table 1). The substrate, L-proline concentration was varied in the range $5.0 \times 10^{-4} – 5.0 \times 10^{-3}$ mol dm⁻³ at 25°C while keeping all other reactant concentrations and conditions constant. The reaction order in [L-proline] was found to be less than unity (Table 1). The effect of alkali on the reaction has been studied at constant concentrations of L-proline and potassium permanganate and a constant ionic strength of 0.50 mol dm⁻³. The rate constants increased with increasing [OH⁻] (Table 1) ($r > 0.9978$, $s \le 0.018$).

Effect of ionic strength and solvent polarity: The effect of ionic strength was studied by varying the NaClO₄ concentration in the reaction medium. The ionic strength was varied from 0.1 to 1.0 mol dm⁻³ at constant concentrations of permanganate, L-proline and alkali. It was found that the rate constant increased with increasing concentration of NaClO₄; the plots of log k_{obs} versus $I^{1/2}$ was linear with a positive slope (Fig. 1) ($r > 0.9978$, $s \le 0.018$).
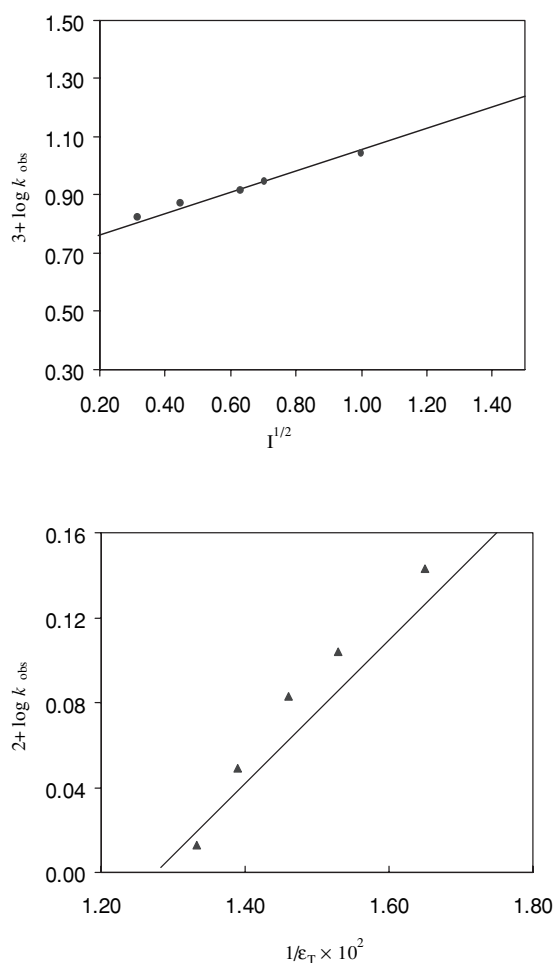
The effect of relative permitivity (ε_T) on the rate constant was studied by varying the *t*-butanol-water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the relative permitivities were not successful. However, they were computed from the values of the pure liquids.[16] No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant, k_{obs} increased with decreasing dielectric constant of the medium. The plot of log k_{obs} versus $1/\varepsilon_T$ was linear with a positive slope (Fig.1).

Effect of initially-added products: Initially-added reaction products such as manganate and aminobutaraldehyde did not show any significant effect on the rate of the reaction.

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Table 1 Effect of variation of [MnO$_4^-$], [L-proline], and [OH$^-$] on oxidation of L-proline by alkaline permanganate at 25°C, I = 0.20 mol dm^{-3}

[MnO$_4^-$] x 10^4 /mol dm^{-3}	[L-proline] × 10^3 /mol dm^{-3}	[OH$^-$] /mol dm^{-3}	k_{obs} × 10^2 /s^{-1}	k_{cal} × 10^2 /s^{-1}
0.5	2.0	0.1	7.62	7.60
1.0	2.0	0.1	7.68	7.60
2.0	2.0	0.1	7.60	7.60
4.0	2.0	0.1	7.59	7.60
5.0	2.0	0.1	7.64	7.60
2.0	0.5	0.1	3.90	3.7
2.0	1.0	0.1	5.60	5.4
2.0	2.0	0.1	7.60	7.6
2.0	4.0	0.1	8.60	8.4
2.0	5.0	0.1	9.20	8.7
2.0	2.0	0.02	3.45	3.74
2.0	2.0	0.04	5.29	5.31
2.0	2.0	0.08	7.13	7.10
2.0	2.0	0.10	7.60	7.60
2.0	2.0	0.20	9.68	9.57

Fig. 1 Plots of (a) log k_{obs} versus $I^{1/2}$ and (b) log k_{obs} versus $1/\varepsilon_T$.
(a) [MnO$_4^-$] = 2.0 × 10^{-4} , [L-proline] = 2.0 × 10^{-3}, [OH$^-$] = 0.10;
(b) [MnO$_4^-$] = 2.0 × 10^{-4}, [L-proline] = 2.0 × 10^{-3},[OH$^-$] = 0.10, [I] = 0.20 mol dm^{-3}.

Polymerisation study: The reaction mixture was mixed with acrylonitrile monomer and kept for 3 h in a dinitrogen atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either permanganate or L-proline with acrylonitrile alone did not induce polymerisation under the same conditions as those induced with reaction mixtures. Initially-added acrylonitrile decreases the rate, indicating free radical intervention, which was the case in earlier work.[17]

Effect of temperature: The rate constants, k, of the slow step of the mechanism were obtained from the plots of $1/k_{obs}$ versus $1/$[proline] at four different temperatures. The values of k at different temperatures are given in Table 2. From the plot of log k versus $1/T$ ($r \geq 0.999$ and $s \leq 0.0063$) with least square analysis, the activation parameters are calculated and are given in Table 2.

The thermodynamic parameters of the first step of Scheme 1 and the activation parameters for the rate-determining step of Scheme 1 could be evaluated as follows: the hydroxyl ion concentration was varied at several temperatures and values of K_1 were determined. The values of K_1 obtained are 3.80, 4.25, 4.80 and 5.40 dm^3 mol^{-1} at 25, 30, 35 and 40°C, respectively. A vant Hoff's plot was drawn for the variation of K_1 with temperature (log K_1 versus $1/T$; $r>0.9996$, $s\leq0.0173$), and values for ΔH, ΔS and ΔG of 18.6±1.0 kJ mol^{-1}, 72.4±2 JK^{-1} mol^{-1}, and-3.3±0.2 kJ mol^{-1} were derived. An Arrhenius plot of log k versus $1/T$ ($r>0.9996$, $s \leq0.0173$) yielded the activation parameters for the rate limiting step of Scheme 1 which are given in Table 2. A comparison of the values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly rapid and involves little activation energy.[18]

Discussion

The permanganate ion, MnO$_4^-$ is a powerful oxidant in aqueous alkaline medium. As it exhibits multitude oxidation states, the stoichiometric results and pH of reaction media play a significant role. At pH>12, the reduction product of Mn(VI) might be stopped.[7] The diode array rapid scan spectrophotometer (DARSS) studies have show that at pH>12 the product of the reaction of Mn(VII) is Mn(VI) and no further reduction was observed as reported by earlier work.[13] However, on long standing for about 16 h, Mn (VI) is slowly reduced to Mn(IV) under our experimental conditions.

The reaction between L-proline and permanganate in alkaline medium has stoichiometry of 1:2 with unit order in [permanganate] and less than unity in [L-proline] and [OH$^-$]. No products effect was observed. It is known that L-proline exists in the form of

Table 2 Activation parameters for the oxidation of L-proline by permanganate in aqueous alkaline medium with respect to slow step of Scheme 1

(a) Effect of temperature

Temperature /°C	k x 10^2 /s^{-1}
25	1.03
30	1.72
35	3.20
40	4.40

(b) Activation parameters

| E_a /kJ mol^{-1}	$\Delta H^{\#}$ /kJ mol^{-1}	$\Delta S^{\#}$ /JK^{-1} mol^{-1}	log A	$\Delta G^{\#}$ /kJ mol^{-1}
76 ± 2	74 ± 2	−34 ± 1	11 ± 1	84 ± 4
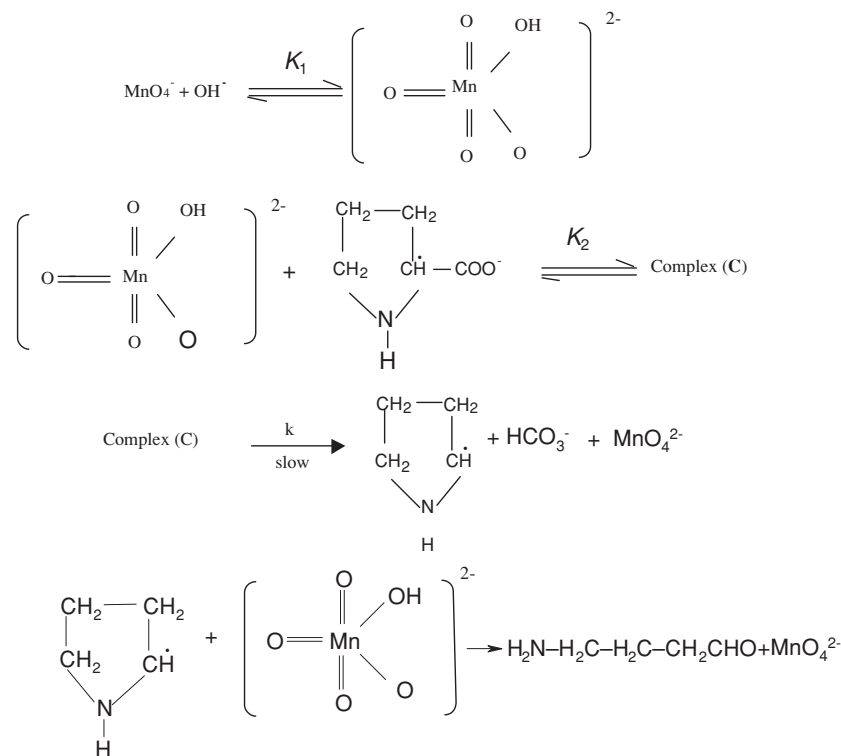
Scheme 1

a Zwitter ion[19] in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium, it is in the fully deprotonated form.

$$NH–CH_2–CH_2–CH_2–CH–COO^-$$
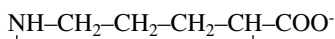
The observed fractional order in [OH$^-$] indicates that first alkali combines with permanganate to form an alkali-permanganate species [MnO$_4$.OH]$^{2-}$ in a pre-equilibrium step,[20] which is also supported by the Michaelis–Menton plot (Fig 3) which is linear with a positive intercept. L-proline in the deprotonated form reacts with alkali-permanganate species [MnO$_4$.OH]$^{2-}$ to form a complex (**C**). C decomposes in a slow step to give a free radical derived from decarboxylated L-proline.

The probable structure of complex (**C**) is
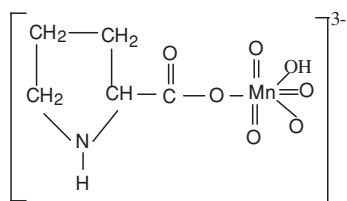
This radical in turn reacts with another molecule of permanganate species in a fast step to yield the products (Scheme 1).

Spectral evidence for complex formation between oxidant and substrate was obtained from the UV-Vis spectra of the alkali permanganate species and L-proline. A bathochromic shift, λ_{max}, of *ca* 6nm from 304 to 310nm is observed, together with hyperchromicity at λ_{max} 310 nm. Analogous effects upon complex formation between a substrate and an oxidant have been observed in other investigations.[20] Furthermore, the formation of the complex is proved kinetically by the non zero intercept of the plot of $1/k_{obs}$ *vs* 1/[proline] (Fig.2) ($r > 0.9935$, $s \leq 0.043$). The observed modest enthalpy of activation and a relatively low value of the entropy of activation indicate that oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work.[21] Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the reaction would involve a radical intermediate. A free radical scavenging experiment revealed such a possibility (*vide infra*).
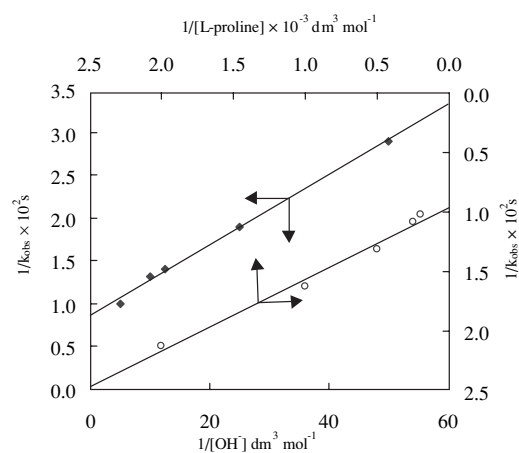

Fig. 2 Verification of rate law(8): Plots of $1/k_{obs}$ versus 1/[L-proline] and $1/k_{obs}$ versus 1/[OH$^-$] (conditions as in Table 1).
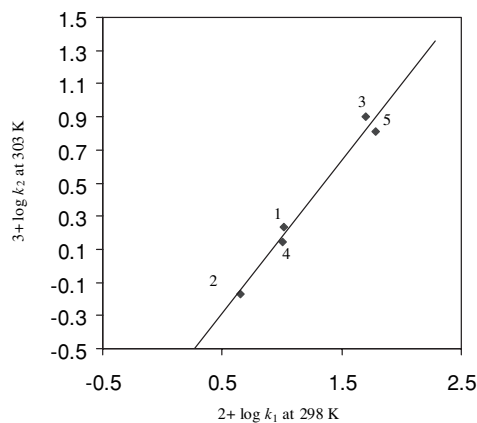

Fig. 3 Plot of log k_2 at 303 K versus log k_1 at 298 K for isokinetic temperature. (conditions as in Table 3). 1, L-Proline; 2, L (+) Lysine; 3, L–hydroxy proline; 4, Rac-serine; and 5, L-cystine.

Table 3 Activation parameters for some amino acids (for isokinetic temperature)

Amino acids	$k \times 10^2$/dm^3 mol^{-1}s^{-1} at 298 K	$k \times 10^2$/dm^3 mol^{-1}s^{-1} at 303 K	$\Delta S^{\#}$ /JK^{-1}mol^{-1}	$\Delta H^{\#}$ /kJ mol^{-1}	$\Delta G^{\#}$ /kJ mol^{-1}	Ref.
L-Proline	1.03	1.72	−34 ± 1	74 ± 2	84 ± 4	Present work
L(+) Lysine	0.45	0.68	−28 ± 1	51 ± 2	60 ± 3	29
L-Hydroxy proline	5.0	8.0	−78 ± 4	57 ± 3	81 ± 4	30
Rac-serine	1.0	1.4	−28 ± 2	49 ± 3	58 ± 3	31
L-Cystine	6.1	6.5	−105 ± 10	48.5 ± 2.5	80 ± 4	32

This type of radical intermediate has also been observed in earlier work[22] on alkaline-permanganate oxidations of amino acids.

Scheme 1 leads to the rate law as follows,

$$\text{Rate} = k\,[\text{C}] = kK_1 K_2 \,[\text{L-proline}]_f \,[\text{MnO}_4^-]_f \,[\text{OH}]_f. \quad (2)$$

Now,

$$[\text{MnO}_4^-]_t = [\text{MnO}_4^-]_f + [\text{MnO}_4 \cdot \text{OH}]^{2-} + [\text{C}]$$
$$= [\text{MnO}_4^-]_f (1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{L-proline}][\text{OH}^-]) \quad (3)$$

Where t and f stand for total and free,

$$[\text{MnO}_4^-]_f = \frac{[\text{MnO}_4^-]_t}{1 + K_1[\text{OH}^-] + K_1 K_2 \,[\text{L-proline}][\text{OH}^-]} \quad (4)$$

Similarly,

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_t}{1 + K_1[\text{MnO}_4^-] + K_1 K_2 \,[\text{L-proline}][\text{MnO}_4^-]} \quad (5)$$

and

$$[\text{L-proline}]_f = \frac{[\text{L-proline}]_t}{1 + K_1 K_2 \,[\text{MnO}_4^-] \,[\text{OH}^-]} \quad (6)$$

Substituting the values of Eqns (4), (5) and (6) in Eqn (2) and omitting subscripts t and f, we get Eqn (7)

$$\text{rate} = -\frac{d[\text{MnO}_4^-]}{dt} = \frac{kK_1 K_2 \,[\text{L-proline}]\,[\text{OH}^-][\text{MnO}_4^-]}{(1 + K_1[\text{OH}^-] + K_1 K_2 \,[\text{OH}^-][\text{L-proline}])}$$
$$\times \frac{1}{(1 + K_1 K_2 [\text{MnO}_4^-][\text{OH}^-])(1 + K_1[\text{MnO}_4^-] + K_1 K_2[\text{L-proline}][\text{MnO}_4^-])} \quad (7)$$

The terms $(1 + K_1 K_2 [\text{MnO}_4^-][\text{OH}^-])$ and $(1 + K_1[\text{MnO}_4^-] + K_1 K_2 [\text{L-proline}][\text{MnO}_4^-])$ in the denominator of Eqn (7) approximate to unity in view of the low concentration of MnO$^-_4$ used ($K_1 = 3.80$ and $K_2 = 4045$). Therefore Eqn (7) becomes

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{MnO}_4^-]} = \frac{kK_1 K_2 \,[\text{L-proline}]\,[\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1 K_2 \,[\text{OH}^-][\text{L-proline}]} \quad (8)$$

Eqn (8) can be rearranged to the following form (9), which is suitable for the verification of the rate law:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1 K_2 \,[\text{L-proline}][\text{OH}^-]} + \frac{1}{kK_2[\text{L-proline}]} - \frac{1}{k} \quad (9)$$

According to Eqn (9), the plots of $1/k_{\text{obs}}$ versus $1/[\text{L-proline}]$ ($r > 0.9988$, $s \leq 0.045$) and $1/k_{\text{obs}}$ vs $1/[\text{OH}^-]$ ($r > 0.9928$, $s \leq 0.052$) should be linear which is verified in Fig. 2. The slopes and intercepts of the plots lead to the values of k, K_1 and K_2 at 25 °C of 1.03 ± 0.04 × 10^{-2} s^{-1}, 3.80 ± 0.16 dm^3 mol^{-1}, and 4.05 ± 0.10 × 10^3 dm^{3}mol^{-1}, respectively. Using these values, the rate constants under different experimental conditions were calculated by Eqn (8) and compared with experimental data (Table 1). Experimental and calculated values agree reasonably well, supporting the assumptions of Scheme 1. The value of K_1 is in good agreement with that derived in earlier work.[7]

The effect of ionic strength and solvent polarity on the rate of reaction in the present case is entirely different from that of earlier studies on other amino acids. In case of oxidation of L-Asparagine–permanganate reaction,[23] there was no effect of ionic strength and relative permittivity on the rate of reaction. In case of L-phenylalanine[24] also the rate was independent of ionic strength. But in our present study the effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. However, increasing the content of t-butyl alcohol in the reaction medium leads to the increase in the reaction rate, contrary to the expected slower reaction between like ions in the media of lower relative permitivity. Perhaps the effect is countered substantially by the formation of active reactive species to a greater extent in low relative permitivity media leading to the net increase in rate.[25] The entropy of activation ($\Delta S^{\#}$) in earlier work[23] on L-Asparagine was found to be positive indicating the complex is less ordered than reactant molecules, whereas in case[24] of L-phenyl-alanine, negative value of $\Delta S^{\#}$ and high value of frequency factor indicates that the electrostatic effects are un important. However, in the present study, the negative value of $\Delta S^{\#}$ indicates that the complex is more ordered than the reactants. The activation parameters for the oxidation of some amino acids by alkaline permanganate are summarised in Table 3. The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy or entropy of activation. Changes in the 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,

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

β is called the isokinetic temperature; it has been asserted that apparently linear correlation of $\Delta H^{\#}$ with $\Delta S^{\#}$ are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity.[26] Exner[27] advocates an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and log k_2 (at T_2) is linearly related to log k_1 (at T_1) i.e. log $k_2 = a + b$ logk_1, he proposes that β can be evaluated from the equation,

$$\beta = T_1 T_2 \,(b-1)/T_2 b - T_1$$

We have calculated the isokinetic temperature as 235 K by plotting log k_2 at 303 K vs log k_1 at 298 K (Fig.3) ($r \geq 0.998$ and $s \leq 0.0067$). The value of β (235 K) is lower than experimental temperature (298 K). This indicates that the rate is governed by the entropy of activation.[28] The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested.

Conclusion

It is interesting to note that the oxidant species [MnO$_4^-$] required a pH > 12, below which the system becomes disturbed and the reaction will proceed further to give a reduced product of the oxidant as Mn (IV), which slowly develops yellow turbidity in the reaction solution. Hence, it is apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reductions rather than a single two-electron step. The rate constant of the slow step and other equilibrium constants involved in the mechanism have been evaluated and activation parameters with respect to the slow step of the reaction were computed.

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