Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 11 (4) 197-205: Winter 2015
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Kinetics and mechanism of the reaction of lysine with permanganate ion at different ionic strengths and temperatures

Farrokh Gharib[1,]*, Dariush Ehsanipour [2] and Kasra Karroubi[3]

[1] Department of Chemistry, Shahid Beheshti University, G. C., Tehran, Evin, Iran
[2] Department of Petroleum Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received October 2014; Accepted November 2014

ABSTRACT

The kinetics of Mn(VII) oxidation of lysine in moderately sulfuric acid solutions was studied spectrophotometrically in the presence and absence of Mn(II) as catalyst. The reaction was arranged to be under pseudo first-order condition with respect to Mn(VII). The results showed that the pseudo first-order rate constant increases with increasing [H_2SO_4], [(Mn)II], and [lysine]. The dependence of the reaction rate on temperature (20 to 40 °C) and on ionic strength (0 to 0.12 mol dm^{-3} NaCl) was also studied. The obtained results showed that the activation energy and $\Delta H^{\#}$ decrease but $\Delta S^{\#}$ increases by increasing the ionic strength. Finally, an equation was derived to calculate the activation energy dependence on ionic strength based on a Debye-Huckel type equation and a mechanism was proposed consistent with the observed results.

Keywords: Kinetics; Lysine; Potassium permanganate; Ionic strength;Temperature

INTRODUCTION

Among the different oxidation states of manganese (2 to 7), manganese (VII) is extensively used as a potent oxidant for studying the oxidation kinetics of both organic and inorganic substrates in acid as well as in alkaline medium [1]. Permanganate ion is widely used in synthetic and analytical chemistry not only as a strong oxidizing agent, but also due to its color which serves as its own indicator. Of these, oxidation of amino acids by manganese ion in heptavalent is of special importance [2-4]. Amino acids act not only as the building blocks in protein synthesis but also they play a significant role in metabolism of all living creatures. Although, the extent ofoxidation of amino acids by permanganate ion depends on the nature of the substrate, the mechanism of the reactions depends on the acidity and the nature of the medium [5-8]. In some cases, the mechanistic approach has been based on the intermediate complex formation and in some others the results have been interpreted by a free radical mechanism. The mechanisms suggested by these authors are not uniform, indicating that a variety of mechanisms are possible to interpret the obtained results. Further, in neutral medium or weakly alkaline, it is

---

[*] Corresponding author: f-gharib@sbu.ac.ir

believed the appearance of an autocatalytic effect and a mechanism with no free radicals involved has been suggested [9-10].

This work deals with the study of the kinetics and mechanism of lysine oxidation by manganese (VII) in moderately sulfuric acid medium. The substrate chosen, lysine, is an essential amino acid in human beings and serves important function in our biological systems such as: calcium absorption, building muscle protein, recovering from surgery or sports injuries, body's production of hormones and antibodies, etc [11]. The reaction kinetics is studied at different ionic strengths and various temperatures. The dependence of activation energy and other thermodynamic parameters of the reaction on ionic strength were determined. In catalytic pathway, Mn(II) ion has been determined to be responsible for the oxidation and finally a mechanism has been suggested both in absence and in presence of Mn(II).

EXPERIMENTAL

Reagents

All the chemicals were obtained from Merck or Fluka as analytical reagent grade materials and used as received. Doubly distilled water with a conductance equal to 1.2 ± 0.1 µS was used to prepare all the solutions. The DL-lysine solution (0.02-0.1 mol dm^{-3}) was prepared daily by dissolving 7.45×10^{-2}-3.73×10^{-1} g solid $C_6H_{14}N_2O_2$ in a total volume of 25 mL. The stock solution of potassium permanganate was prepared as described in literature and its concentration was determined by titration with a standard oxalic acid solution in sulfuric acid medium [12].

Kinetics measurements

Mixtures of solutions containing requisite amounts of lysine (enough to maintain a large excess over the oxidant, at least 100 times), sulfuric acid (to maintain a known acid concentration, 3.33 mol dm^{-3}), sodium chloride (to maintain the ionic strength, 0-0.12 mol dm^{-3}), and manganese(VII) were syringed out and poured into the reaction cell of the spectrophotometer. The course of the reaction was followed by recording the decrease in absorbance of manganese (VII) at 525 nm against time. The molar absorption coefficient of potassium permanganate in 3.33 mol dm^{-3} sulfuric acid was determined as 2.396×10^3 dm^3 mol^{-1} cm^{-1} at 525 nm. It was verified that there is no interference from other reagents at this wavelength. The absorption measurements were made in a thermostated cell compartment at the desired temperature (20-40°C) on a Cecil CE 7200 UV-Vis double-beam spectrophotometer supported with a Pentium 4 computer and using quartz cells of path 10 mm. Application of Beer's law was verified in $(0.1\text{-}0.6)\times10^{-3}$ mol dm^{-3} of Mn(VII) in the wavelength used and in sulfuric acid concentration ranging between 2.0 and 4.0 mol dm^{-3} under the reaction conditions. The reaction mixtures remain homogeneous in the solutions used. All measurements were carried out at the desired temperature by circulating a thermostated liquid through hollow, thermospacer plates on either side of the cell compartment. Repetitive scans of the spectra during the course of the reaction showed only a decrease in the absorbance with no evidence of a shift in the peaks. The observed pseudo first-order rate constants, k_{obs}, with respect to the Mn(VII) ion were calculated from the slopes of the linear plots of $\ln(\frac{a}{a-x})$ versus time, where a

is the initial concentration of Mn(VII) and (*a*-*x*) is the concentration of Mn(VII) at different time intervals. The pseudo first-order plots, in all cases, were linear over 75 % completion of the reaction. The k_{obs} values in different concentrations of sulfuric acid and the substrates were reproducible within ±4 % and are the average of at least three independent kinetic runs.

Stoichiometry of reaction and product analysis

Reaction mixtures containing a known amount of lysine with a large excess on potassium permanganate (0.01 mol dm^{-3}) 1:10 and 1:20 ratios in the presence of 3.33 mol dm^{-3} sulfuric acid were allowed to react completely in dark (about 2 h) at room temperature. Estimation of the unreacted [MnO_4^-] showed that one mole of MnO_4^- consumed 2.5 moles of the amino acid.

Product analysis indicated the formation of ammonium ion and an aldehyde as described elsewhere [13-14]. The result confirms that the stoichiometry of the overall reaction is as in Eq. (1).

$$2MnO_4^- + 5R\text{-}CH(NH_2)COOH + 11H^+T\ 5R\text{-}CHO + 5CO_2 + 5NH_4^+ + 2Mn^{2+} + 3H_2O` \qquad (1)$$

where R is $NH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2$.

RESULTS AND DISCUSSION

The reaction order with respect to Mn(VII) was determined by studying the oxidation reaction at 25 °C, [lys] = 4.66×10^{-2} mol dm^{-3}, [H_2SO_4] = 3.33 mol dm^{-3}, and [Mn(VII)] ranging from 0.2×10^{-3} to 0.6×10^{-3} mol dm^{-3}. The plots of the $\ln(\frac{a}{a-x})$ versus time were linear to about 75 % completion of the reactions with correlation coefficients of more than 0.99. The values of the rate constant, k_{obs}, slightly decreased with increasing the initial concentration of [Mn(VII)], and are listed in Table 1 and shown in Fig. 1. The linearity of the plots show that the reaction is first-order in Mn(VII).

The reaction rate constant was investigated at 25 °C, [H_2SO_4] = 3.33 mol dm^{-3}, [Mn(VII)] = 0.4×10^{-3} mol dm^{-3}, and [lys] ranging from 4.66×10^{-2} to 7.33×10^{-2} mol dm^{-3}. Under the above conditions, the rate constant increased with increasing the initial concentration of the amino acid, Table 1. The plot of $1/k_{obs}$ versus 1/[lys] (not shown here) is linear ($r^2 > 0.99$) passing through the origin showing the order in the amino acid as one.

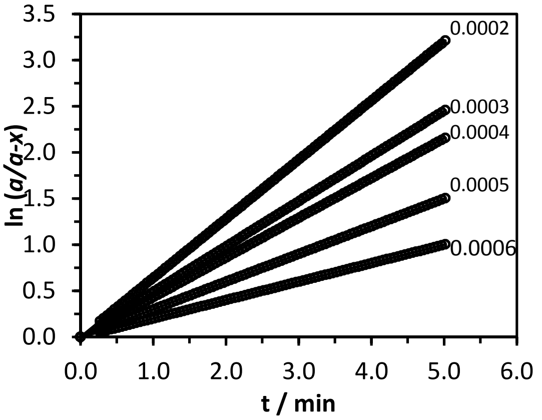


Fig. 1. The plots of ln(*a*/*a*-*x*) versus time (min) at 25 °C, different concentrations of Mn(VII), [lys] = 4.66×10^{-2} mol dm^{-3}, and [H_2SO_4] = 3.33 mol dm^{-3}.

The effect of sulfuric acid concentration on the rate of oxidation was also studied at different solutions of sulfuric acid concentration ranging from 2.66 to 4.0 mol dm^{-3} at 25 °C while the other substrates were kept constant: [Mn(VII)] = 0.4×10^{-3} mol dm^{-3} and [lys] = 4.66×10^{-2} mol dm^{-3}. The obtained results have shown that an increase in sulfuric acid concentration causes an increase of the oxidation rate of lysine, Table 1. It was suggested the faster rate of oxidation in more concentrated sulfuric acid is most probably due to protonation of the oxidant.The observation leads us to suggest that $HMnO_4$ is the active oxidizing species in acidic medium. Similar observation was observed in oxidation of alcohols and some other substrates [15]. The plots of k_{obs} versus $1/[H_2SO_4]$ and $1/[H_2SO_4]^2$ are shown in Fig. 2. In this Fig., the first plot (k_{obs} versus $1/[H_2SO_4]$) gives a better fit in comparison with the second plot (k_{obs} versus $1/[H_2SO_4]^2$). Although, previous reports demonstrated that the latter plot in Fig. 2 should give a better fit.

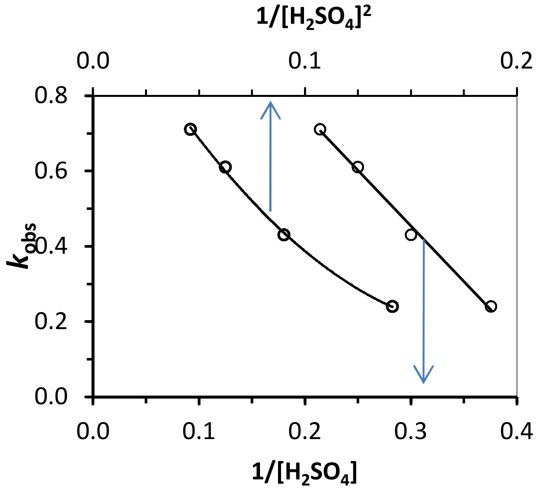


Fig. 2. The plots of k_{obs} versus $1/[H_2SO_4]$ and $1/[H_2SO_4]^2$, at 25 °C, $[Mn(VII)] = 4.0\times10^{-4}$ mol dm^{-3}, and $[lys] = 4.66\times10^{-2}$ mol dm^{-3}.

In this work, the effect of [Mn(II)] was studied on the rate of reaction. The results showed that the increasing of the initial concentration of [Mn(II)] was caused by an increase in the rate constant of the reaction, Table 1. Similar results were reported in oxidation of some other amino acids [8,16-17].

On the basis of the results obtained in this work, the following mechanism is proposed for oxidation of lysine by potassium permanganate in the absence of Mn(II).

$$MnO_4^- + H^+ \xrightleftharpoons{K_1} HMnO_4 \qquad (2)$$

$$K_1 = \frac{[HMnO_4]}{[MnO_4^-][H^+]}$$

$$[Mn(VII)]_t = [MnO_4^-] + [HMnO_4] \qquad (3)$$

Substituting $[MnO_4^-]$ from Eq. (2) in Eq. (3) and solving for permanganic acid, gives

$$[HMnO_4] = \frac{[Mn(VII)]_t K_1[H^+]}{1+K_1[H^+]} \qquad (4)$$

The amino acid exists as the protonated species in moderately sulfuric acid medium, so

$$H_3L^{2+} + HMnO_4 \xrightleftharpoons[k_{-1}]{k_1} X_1 \xrightarrow{k_2} \text{products} \qquad (5)$$

where H_3L^{2+} and X_1 are the protonated species of lysine and the produced complex, respectively.

On this basis, $[lys]_o = [H_3L^{2+}] + [X_1]$ and the rate equation can be proposed as: $R = k_2[X_1]$.

Applying steady-state approximation to eliminate X_1 and substituting the values in the rate equation, gives R:

$$\frac{k_1k_2[lys]_o[Mn(VII)]_t K_1[H^+]}{(k_{-1}+k_2)(1+K_1[H^+])+k_1[Mn(VII)]_t K_1[H^+]} \qquad (6)$$

The reciprocal of the rate equation results:

$$\frac{1}{R} = \frac{(k_{-1}+k_2)(1+K_1[H^+])}{k_1k_2[lys]_o[Mn(VII)]_t K_1[H^+]} + \frac{1}{k_2[lys]_o} \qquad (7)$$

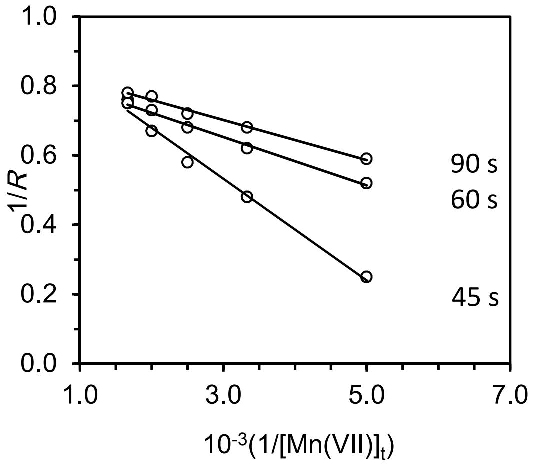


Fig. 3. The plots of $1/R$ versus $1/[Mn(VII)]_t$ at 25 °C, different times (s), [lys] = 4.66×10^{-2} mol dm^{-3}, and $[H_2SO_4]$ = 3.33 mol dm^{-3}.

Equation (7) predicts the plot of $\frac{1}{R}$ versus $\frac{1}{[Mn(VII)]_t}$ should be a straight line with a positive intercept, $\frac{1}{k_2[lys]_o}$. This equation is consistent with our experimental findings, Fig. 3, which support the proposed mechanism. The values of k_2 in different conditions can be determined from the intercept of Eq. (7) (not listed here).

Dependence of reaction rate on [Mn(II)]

It was reported [6] that acidified permanganate ion in the presence of Mn(II) is reduced to Mn(III) and Mn(IV), according to Eq. (8).

$$MnO_4^- + 3Mn^{2+} + 8H^+T\ 3Mn^{3+} + Mn^{4+} + 4H_2O \qquad (8)$$

It was found that by increasing the initial concentration of Mn(II) the rate of reaction progressively increased too. The data are summarized in Table 1. The results indicate that neither Mn(III) nor Mn(IV) is involved in the oxidation process. The mechanism of the reaction in the presence of Mn(II) is proposed as follow:

$$H_3L^{2+} + Mn(II) \overset{K_2}{\rightleftarrows} X_2$$

$$K_2 = \frac{[X_2]}{[H_3L^{2+}][Mn(II)]} \qquad (9)$$

$$X_2 + HMnO_4 \xrightarrow{k_3} \text{Products} \qquad (10)$$

So,

$$[lys]_o = [H_3L^{2+}] + [X_1] + [X_2] \qquad (11)$$

Applying steady-state approximation to eliminate $[X_2]$ and substituting this value and $[X_1]$ as before in Eq. (11), gives $[H_3L^{2+}]$:

$$\frac{[lys]_o}{1+\frac{k_1[HMnO_4]}{k_{-1}+k_2}+K_2[Mn(II)]} \qquad (12)$$

Substituting all the values from Eqs. (11) and (12) in the rate equation, $R = \frac{-d[Mn(VII)]}{dt} = k_3[X_2][HMnO_4]$, canceling like terms, rearranging and make it reciprocal, gives

$$\frac{1}{R}=\left(\frac{1+K_1[H^+]}{k_3K_1K_2[lys]_o[Mn(VII)]_o[H+]}+\frac{k_1}{k_3K_2[lys]_o(k_{-1}+k_2)}\right)\left(\frac{1}{[Mn(II)]}\right)$$

$$+\frac{1+K_1[H^+]}{k_3K_1[lys]_o[Mn(VII)]_o[H^+]} \qquad (13)$$

Equation (12) predicts the plot of $\frac{1}{R}$ versus $\frac{1}{[Mn(II)]}$ should be linear. This equation is consistent with our experimental findings, Fig. 4, which support the proposed mechanism.

To determine the pseudo first-order rate constant, k_{obs}, the rate equation is derived as:

$$\ln\left(\frac{b+x}{a-x}\right) = \ln\left(\frac{b}{a}\right) + (a+b)k_{obs}t \qquad (14)$$

where a and b are the initial concentrations of permanganate and Mn(II) ions, respectively, and x represents the amount of permanganate ion consumed at each time, t. The plot of $\ln(\frac{b+x}{a-x})$ versus t is linear (not shown, r^2 is more than 0.99) and k_{obs} can be determined from the slope of Eq. (14) and are listed in Table 1.

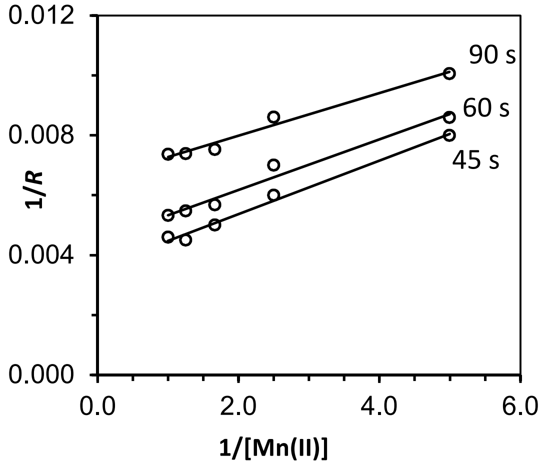


Fig. 4. The plots of $1/R$ versus 1/[Mn(II)] at 25 °C, different times (s), [lys] = 4.66×10^{-2} mol dm^{-3}, [Mn(VII)] = 6.0×10^{-4} mol dm^{-3}, and [H_2SO_4] = 3.33 mol dm^{-3}.

Dependence of the reaction rate on ionic strength and temperature

The reaction was studied at different temperatures, 20-40 °C, and five ionic strengths, 0.0 to 0.12 mol dm^{-3} NaCl in each temperature keeping the other substrates constant: [lys] = 3.33×10^{-2} mol dm^{-3}, [MnO_4^-] = 3.33×10^{-4} mol dm^{-3} and [H_2SO_4] = 3.33 mol dm^{-3}. The rate constant, k_{obs}, was obtained at different temperatures and various ionic strengths as before, Table 2, and was used to calculate the activation energy using Arrhenius and Eyring equations (at different ionic strengths), Fig. 5. The enthalpy and entropy of activations were computed from the slope and the intercept of the line, Fig. 5, and are listed in Table 3 for the overall reaction at different ionic strengths of sodium chloride.

The obtained values of $\Delta H^{\#}$ and $\Delta S^{\#}$ from the Eyring equation at different ionic strengths are both favorable for electron transfer processes. Negative value of $\Delta S^{\#}$ has been ascribed to the loss of degree of freedom [18]. In similar works Moore and Hicks [19] observed that the entropy of activation for a group of permanganate ion reaction is negative for the reactions that proceed via complex formation and presumably occurs by an inner-sphere mechanism, while the $\Delta S^{\#}$ values for the outer-sphere reactions tend to be positive.

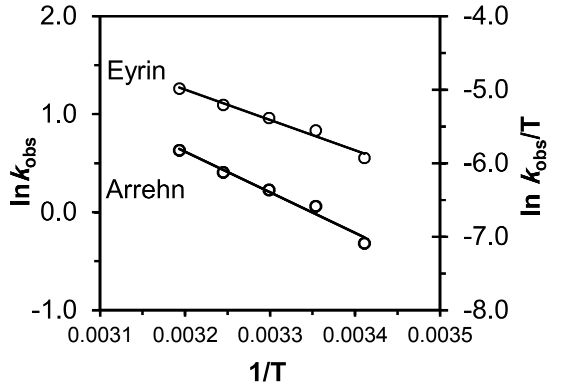


Fig. 5. The Eyring and Arrhenius plots at zero ionic strength of NaCl, [Mn(VII)] = 3.33×10^{-4} mol dm^{-3}, [lys] = 3.33×10^{-2} mol dm^{-3}, and [H_2SO_4] = 3.33 mol dm^{-3}.

The values of k_{obs} were found to increase with increasing the ionic strength, thus, showing a positive salt effect for the reaction, Table 2. To find out the dependence of activation energy on ionic strength, we used an equation derived for the enthalpy change of a reaction on ionic strength based on a Debye-Huckel type equation [20]. It is known, that the enthalpy change of the reaction is related to its activation energy, E_a, so by introducing an appropriate coefficient, F, Eq. (15) is derived.

$$E_a = E^{o}_{a} - \frac{Z^*}{F}\frac{1.5\sqrt{I}}{1+1.5\sqrt{I}} + p.I \qquad (15)$$

where E^o_a is the activation energy at infinite dilution, $p = 2.303RT^2(\frac{d\Delta C}{dT})$, $Z^* = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma(\text{charges})^2_{\text{products}}$, I is the ionic strength in mol kg^{-1}, and C is the parameter for the dependence of the activation energy on the ionic strength when the molal concentration scale is used. Therefore, the plot of E_a versus I should be linear, Fig. 6, and E^o_a can be calculated from the intercept of Eq. (15). It is interesting to note that the calculated E^o_a from Eq. (15) (33.79 kJ mol^{-1}) is consistent and very close to the value was obtained from Arrhenius equation (34.91 kJ mol^{-1}) at zero ionic strength of NaCl.

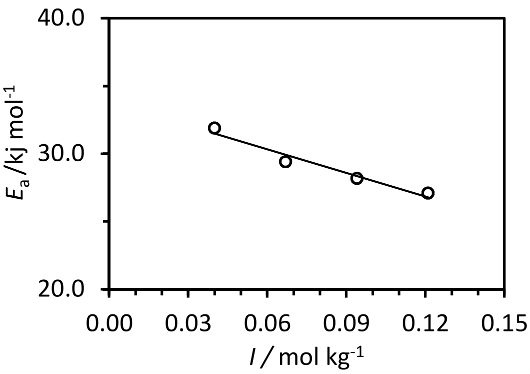
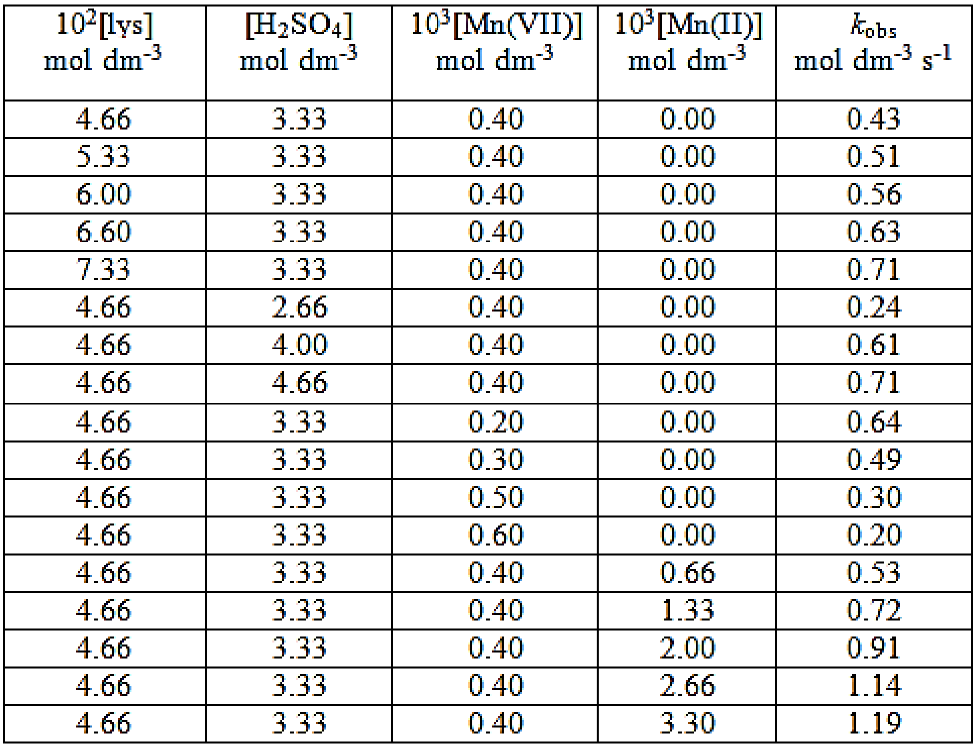


Fig. 6. The plot of activation energy versus ionic strengths of NaCl (in molal scale), [Mn(VII)] = 3.33×10^{-4} mol dm^{-3}, [lys] = 3.33×10^{-2} mol dm^{-3}, and [H_2SO_4] = 3.33 mol dm^{-3}.

Table 1. Pseudo first-order rate constants (k_{obs}) for the oxidation of lysine by Mn(VII) at 25 °C and different concentrations of lysine, H_2SO_4, Mn(VII), and Mn(II)



10^2[lys] mol dm^{-3}	[H_2SO_4] mol dm^{-3}	10^3[Mn(VII)] mol dm^{-3}	10^3[Mn(II)] mol dm^{-3}	k_{obs} mol dm^{-3} s^{-1}
4.66	3.33	0.40	0.00	0.43
5.33	3.33	0.40	0.00	0.51
6.00	3.33	0.40	0.00	0.56
6.60	3.33	0.40	0.00	0.63
7.33	3.33	0.40	0.00	0.71
4.66	2.66	0.40	0.00	0.24
4.66	4.00	0.40	0.00	0.61
4.66	4.66	0.40	0.00	0.71
4.66	3.33	0.20	0.00	0.64
4.66	3.33	0.30	0.00	0.49
4.66	3.33	0.50	0.00	0.30
4.66	3.33	0.60	0.00	0.20
4.66	3.33	0.40	0.66	0.53
4.66	3.33	0.40	1.33	0.72
4.66	3.33	0.40	2.00	0.91
4.66	3.33	0.40	2.66	1.14
4.66	3.33	0.40	3.30	1.19

Uncertainties in the pseudo-rate constants are 0.04 or lower.

Table 2. Pseudo first-order rate constants (k_{obs}) for the oxidation of lysine by Mn(VII) at different temperatures and various ionic strengths of NaCl, [Mn(VII)] = 4.0×10^{-4}mol dm^{-3}, [lys] = 3.33×10^{-2} mol dm^{-3}, and [H_2SO_4] = 3.33 mol dm^{-3}

T / °C	k_{obs} /mol dm^{-3} min^{-1}				
	I = 0.0 (NaCl) mol kg^{-1}	I = 0.04 (NaCl) mol kg^{-1}	I = 0.067 (NaCl) mol kg^{-1}	I = 0.094 (NaCl) mol kg^{-1}	I = 0.121 (NaCl) mol kg^{-1}
20	0.73	1.75	2.18	2.36	2.63
25	1.06	2.58	2.71	2.92	3.37
30	1.25	2.98	3.23	3.39	3.62
35	1.50	3.58	3.69	4.00	4.37
40	1.88	4.12	4.78	4.98	5.50

Uncertainties in the pseudo-rate constants are 0.04 or lower

Table 3. Thermodynamic parameters for oxidation of lysine by Mn(VII) in different ionic strengths (NaCl), [Mn(VII)] = 3.33×10^{-4} mol dm^{-3}, [H_2SO_4] = 3.33 mol dm^{-3}, and [lys] = 3.33×10^{-2}mol dm^{-3}

I (NaCl) mol kg^{-1}	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J $K^{-1}mol^{-1}$
0	34.91	32.27	-136.77
0.04	31.88	29.27	-139.56
0.067	29.40	26.80	-146.88
0.094	29.16	25.56	-150.43
0.121	27.09	24.48	-153.11

Uncertainties in the activation parameters are 0.10 or lower

CONCLUSIONS

The kinetics of oxidation of L-lysine by potassium permanganate was investigated in moderately sulfuric acid medium, using spectrophotometric technique. Addition of manganese sulfate(II) to the reaction mixture raised the reaction rate. The pseudo first-order rate constants obtained for both the catalytic and non-catalytic pathway in different concentrations of the substrate, sulfuric acid and various temperatures and ionic strengths of NaCl. The obtained results showed that the activation energy and enthalpy of activation decrease but the entropy of activation increases by increasing the ionic strength. An equation was derived to calculate the activation energy dependence on ionic strength based on a Debye-Huckel type equation and a mechanism has been proposed consistent with the observed result.

REFERENCES

[1]. R.M. Hassan, M.A. Mousa, M.H. Wahdan, *J. Chem. Soc. Dalton Trans*. (1988) 605.

[2]. J.F. Perez-Benito, F.Mata-Perez, E. Brillas, *Can. J. Chem*. 65(1987) 2329.

[3]. S. Chandraju, B.S. Sherigara, *Int. J. ChemKinet*. 26 (1994) 1105.

[4]. S. Chandraju, D.S. Mahadevappa, K.S. Rangappa, *Indian J. Chem. Sec. A* 36 (1997) 974.

[5]. M.J. Insausti, F. Mata-Perez, P. Alvarez-Macho, *Int. J. Chem.Kinet*.24 (1992) 411.

[6]. R.M. Hassan, *Can. J. Chem*.69 (1991) 2018.

[7]. M. Zahedi, H. Bahrami, *Can. J. Chem.* 82 (2004) 1.

[8]. M.J. Insausti, F. Mata-Perez, M.P. Alvarez-Macho, *Int. J. Chem.Kinet.*27 (1995) 507.

[9]. A. Arrizabalaga, F.J. Andres Ordax, M.Y. Fernandez Aranguiz, R. Peche, *Int. J. Chem. Kinet.*28 (1996) 799.

[10]. A. Arrizabalaga, F.J. Andres Ordax, M.Y. Fernandez Aranguiz, R. Peche, *Int. J. Chem.Kinet.*29 (1997) 181.

[11]. A.L. Lehninger, *Principles of Biochemistry*, Worth Publishers Inc, New York (1982).

[12]. A.I. Vogel, *Quimica analytica quantitative*, Kapelusz, Buenos Aires, (1960).

[13]. F. Felig, *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam (1972).

[14]. F. Felig, *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam (1976).

[15]. S.V. Radhey, J.R. Madhusudana, R.S. Vyayendra, *J. Chem. Soc. Perkin II* (1976) 469.

[16]. H.V. Rajeshwari, K.S. Byadagi, S.T. Nandibewoor, S.A. Chimatadar, *J. Chem. Eng. Mater.Sci.*3 (2012) 65.

[17]. O.A. Babatunde, *World J. Chem.* 3 (2008) 27.

[18]. A.L. Harihar, M.R. Kembhavi, S.T. Nandibewoor, *Indian J. Chem.A*(2000) 769.

[19]. F.M. Moore, K.W. Hicks, *Inorg.Chem.*14 (1975) 413.

[20]. C. Bretti, F. Crea, O. Giuffre, S. Sammartano, *J. Solution Chem.*37 (2008) 183.