Kinetic study for the oxidation of amino acids Schiff-base using permanganate ion

Mahmoud Shakir Saieed* and Mayyada Abd- Al-Kareem Zaidan**
Chemistry Department , College of Education , University of Mosul , Mosul , Iraq
*e-mail:m.s.said2001@yahoo.com
**e-mail:mayyadaalzedan@yahoo.com

(NJC)

(Recevied on 15/7 /2012) (Accepted for publication 23/10/2012)

Abstract

In the present investigation the kinetics study of amino acids Schiff-base oxidation by permanganate ion have been studied at different pH (ranged between6-8) and different temperatures (ranged between 278.16- 298.16K^o). The Schiff-bases were prepared from the condensation between amino acids (glycine, alanine, valine , leucine, phenyl alanine , serine and aspartic acid), and salicyldehyde. The rate were studied under pseudo order condition with an excess in the concentration of schiff-base 10 times over the oxidant. The kinetics were followed by monitoring the disappearance of permanganate ion spectrophotometrically at two wavelength 418 and 526 nm , respectively. The results showed that the observed rate is second- order in oxidant concentration , first- order in Schiff- base concentration and inverse-order in hydrogen ion concentration. In all studied cases no auto catalytic effect has been observed. The variation of the ionic strength of reaction medium have no significant effect on the reaction rate. This observation suggested that in the rate-determining-step one or more of the reactants are neutral molecule. The effect of temperature on the rate constant has been studied and activation parameters were evaluated. The isokinetic theory was applied for the activation parameters. The results showed presence of isokinetic temperature and a compensation effect between enthalpy and entropy of activation which support the idea of one mechanism domination.

Finally the stoicheiometry of the reaction shows that three moles of oxidant are consumed for each mole of schiff-base and the products contain ammonia, carbon dioxide and organic acids .

Keyword: kinetic ,oxidation ,Schiff-base ,permanganate ion ,isokinetic .

الخلاصة

تمت في هذا البحث دراسة حركية اكسدة قواعد شيف للاحماض الامينية بوساطة ايون البرمنكنات ، وذلك على مدى من الاس الهيدروجيني يقع بين (6- 8)ودرجات حرارة تتراوح (278.16- 298.16 مطلقة) . وقد حضرت قواعد شيف للاحماض الامينية من تفاعل الاحماض الامينية (كلايسين، الالنين، فالين، ليوسين، فينايل الانين، سيرين و الاسبارتيك) مع السلسلديهايد . وتمت متابعة الدراسة الحركية للتفاعل في ظروف المرتبة الكاذبة (حيث ان تركيز قاعدة شيف يكون عادة اكثر عشرة مرات من تركيز العامل المؤكسد) وذلك بمتابعة اختفاء العامل المؤكسد طيفيا مع الزمن . وظهر ان رتبة التفاعل هي الثانية بالنسبة للعامل المؤكسد والاولى

بالنسب لقاعدة شيف والاس السالب بالنسبة لايونات الهيدروجين . وفي جميع الحالات لم يظهر اي تحفيز ذاتي للنواتج . كما ان تغير القوة الايونية للوسط لم يظهر اي تأثير على سرعة التفاعل مما يدل على انه في الخطوة المحددة للتفاعل تكون المواد المتفاعلة او احداهما متعادل الشحنة الكهربائية ، ومن دراسة تأثير درجة الحرارة على سرعة التفاعل تم حساب الدوال التنشيطية لتفاعل الاكسدة . ومن ثم طبقت نظرية الاتزان الحركية (isokinetic) على النتائج وظهر وجود درجة حرارة مثلى تتساوى عندها جميع السرع مع وجود حالة التوازن بين الانتروبي والانثالبي للتنشيط مما يدل على سيادة ميكانيكية واحدة للتفاعل . واخيراً تم حساب جزيئية التفاعل وظهر ان مولا واحدا من قاعدة شيف يتفاعل مع ثلاثة مولات من العامل المؤكسد وظهر وجود كل من NH_3 و CO_2 بالاضافة الى الحامض العضوي في نواتج التفاعل.

الكلمة المفتاحية:الحركية, الأكسدة, قواعد شيف, ايون البرمنكنات, التماثل الحركي

Introduction

The permanganate ion [MnO_4^-] is one of the most important classic oxidation reagent in organic and inorganic chemistry . Many oxidation reactions for different organic compounds have performed using [MnO_4^-] in acidic or basic media(1-4). However among these compounds the oxidation of Schiff-bases (imine) have been studied , the oxidation leads to the formation of oxaziride with the possibility of their successive rearrengment to nitrone(5-7), depending on their structure and employed oxidant . On the other hand the kinetic studies of oxidation of amino acids Schiff-base are of great interest due to their biological importance . The present paper deals with the kinetics amino acids schiff-base oxidation prepared from the coupling between amino acids and salicylaldehyde by permanganate ion , in order to estimate the kinetic behavior of these reaction and highlights the effect of amino acids structure on the kinetic behavior of these reactions, which provides a useful information about the behavior of these oxidation reaction.

Experimetal

Materials:

A twice distilled water in an glass apparatus was used in the preparation of potassium permanganate (Fluka) . The Schiff bases were prepared as suitited in reference(8). A buffer solutions of KH_2PO_4- K_2HPO_4 (Fluka) were used to keep the pH of Medium constant , while the reaction was being monitored . The ionic strength of the medium has been modified by addition of potassium chloride .

Kinetic Measurement:

The permanganate ion was chosen as a rate monitoring species by monitoring the absorbance of the reaction mixture at two wavelengths (418, 526)nm using sperctometer model (CECILCE 1011, 1000 SERIES) coupled with thermostat model (Gerhard ± 0.1), in order to keep the temperature of the reaction mixture constant. The pH was determined by pH-meter (type WTW (82362-weiheim)) provided with combined electrode and calibrated with commertical glass electrode and calibrated with commertial buffers. It is necessary to mention that the inorganic product (MnO_2 absorbs light in whole visible region of the spectrum , so that the absorbance was corrected in order to find the concentration of permanganate ion , the absorbance at 418 nm (where only the product (MnO_2) absorbs light) and at 526nm (where both reactant and product absorbs light) by using equation (1)

$$C = A^{526} - (\varepsilon_p^{526} . A^{526} / \varepsilon_p^{418}) / \varepsilon_R^{526} \cdots\cdots (1)$$

Where the subscripts R and P stand for reactant and product respectively . The molar extinction coefficient ε_R of permanganate at 526 is equal to $2.4*10^3$ dm^3 mol^{-1}. cm^{-1}(9) and the extinction coefficients of the product at 418 and 526 nm (ε_R^{418} and ε_R^{526}) can be obtained from the absorbance at the end of the reaction .

Results and Discussion

Reaction order :

All experiments where carried out with Schiff base concentrations [SB] always greater than the oxidant , at least ten times greater , and at constant pH and temperature . Plots of $[MnO_4^-]$ versus the time showed an exponential decay in the $[MnO_4^-]$ with the time (Fig.1).

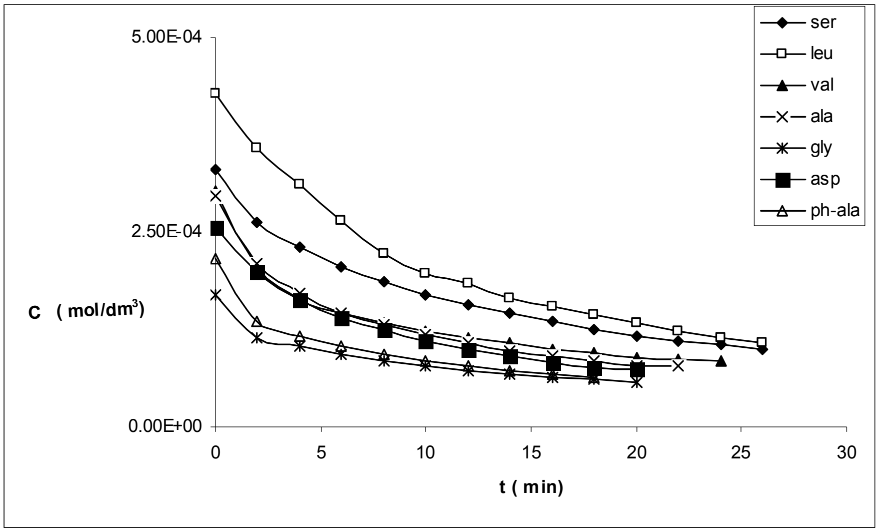


Figure 1: The relation between $[MnO_4^-]$ and time for oxidation of Schiff-base, pH=7 , T=25C°, [SB]= $2.5 * 10^{-2}$ mol/dm^3.

The first – order plot between logarithm of the concentration of the oxidant and the time showed a curvature tower the x-axis (fig.2).

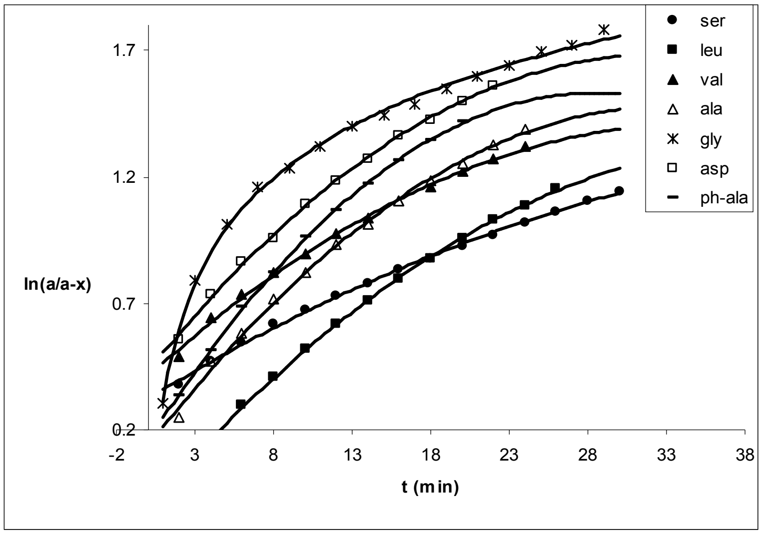


Figure 2: The first order plot for oxidation Schiff-bases, pH=7, [SB]= $2.5*10^{-2}$ mol/dm^3 , T = 25C°.

On the other hand a second – order plot between the inverse the concentration of the oxidant and time showed a linear relationship up to 80% of the reaction as shown in (fig.3) which indicates that the reaction is second-order .

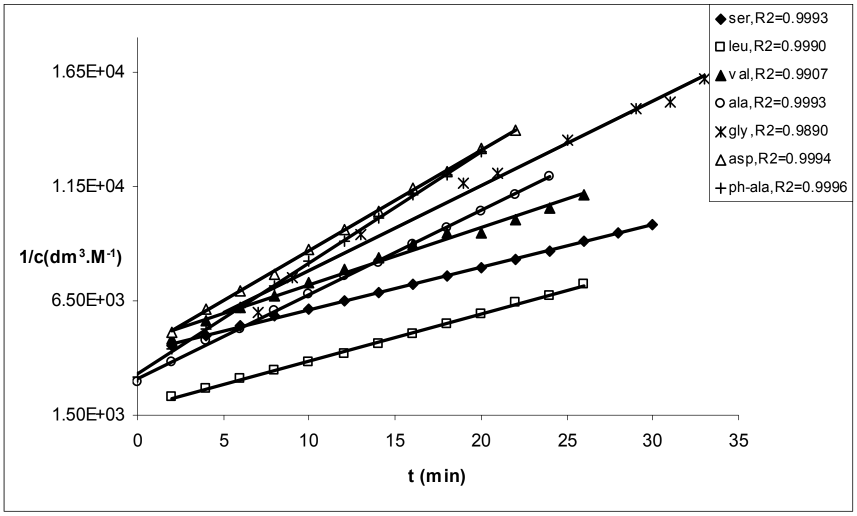


Figure 3: The second order plot between [MnO_4^-] and the time ,pH=7 , T=25C° , [SB]= $2.5*10^{-2}$ mol/dm^3

The log $t_{1/2}$ versus log the initial concentration of oxidant (log a) also proved that the oxidation is second-order as shown in (Fig.4). with respect to the oxidant.

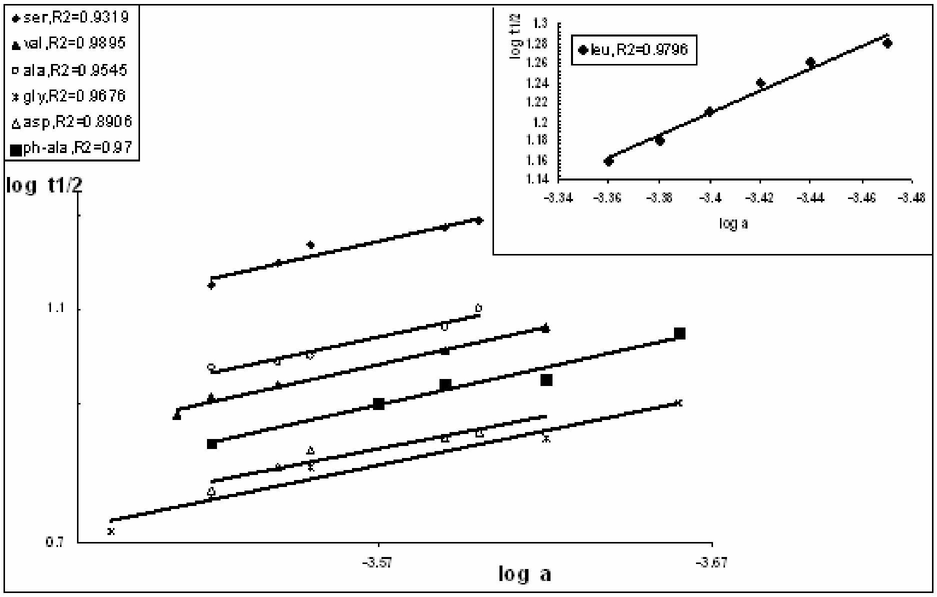


Figure 4: Half-life time plot for Schiff base at [SB]=2.5*10^{-2} mol/dm^3, T= 25C^o, pH=7

Application of initial rate method by plotting log r_o versus the initial concentration proved that the oxidation is also second order with respect to the [MnO_4^-] ,and the reaction rate does not effect by any of the reaction products. On the other hand the order of the reaction with respect to Schiff-base concentration was estimated from the fact that the value of k_{obs} increased by increasing the concentration of Schiff-base. Plot between concentrations of schiff-bases and the values of k_{obs} showed a linear relationship and passed through the origin which proves that oxidation reaction is first-order with respect to the Schiff-base (Fig.5) and oxidation occured through one oxidation path way .

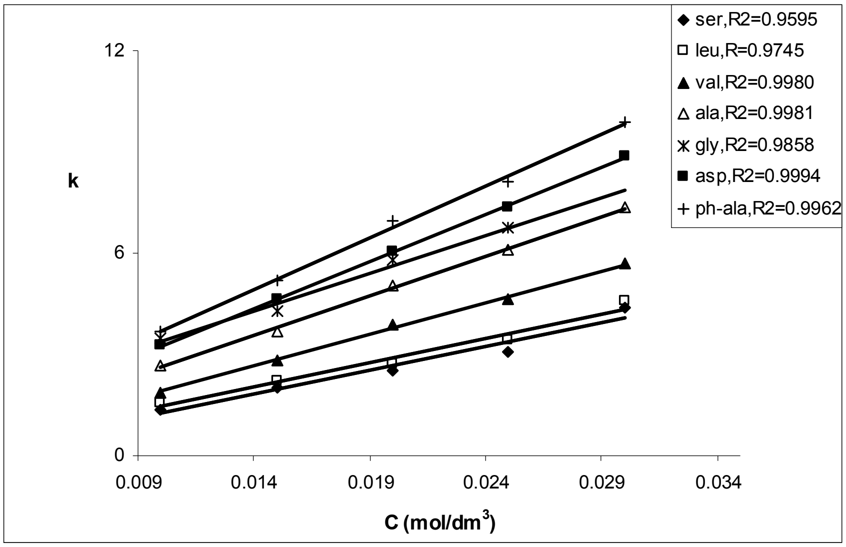


Figure 5: The relation between k_{obs} and [SB] at Temp.= 20C^o , pH= 7, [MnO_4^-] = 3 * 10^{-4} mol/dm^3

From the above results it can be expected that the disappearance rate of Schiff-bases , at constant pH and temperature can be expressed by equation 2

$$\frac{d[SB]}{dt} = k[SB]^1[MnO_4]^2 \quad \cdots\cdots (2)$$

Where the total order of the reaction is equal to three .

Effect of amino acid structure:

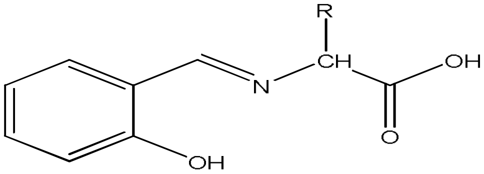
The values of pseudo-second order rate constants (k_{obs}) were evaluated as a mean of two runs and gathered in table 1. These values showed that the values of k_{obs} for Schiff-base toward the oxidation are in the following order :

$$\xrightarrow{\textbf{Decrease}}$$

Ph-alanine > aspartic > glycine>alanine>valine>leucine>serine

Which indicats in general that the presence of electron donating group deactivate the oxidation reaction while the presence of electron with-drowing groups increases the reaction rate.

Table(1): The rate constant of oxidation of schiff-bases derived from salicyldehyde and amino acids at pH=7,T=25C^o,[SB]=2.5*10^{-2}mol/dm^{-3}



No.	-R	k_{obs} (mol^{-1}.dm^3.sec^{-1})
1	$-CH_2OH$	4.3218
2	$-CH_2CH(CH_3)_2$	4.3557
3	$-CH(CH_3)_2$	5.5842
4	$-CH_3$	7.1657
5	-H	7.9988
6	$-CH_2CO_2H$	8.2628
7	-CH$_2$ph	8.8840

pH Effect :

The values of k_{obs} increase linearty with an increase in the pH values of the reaction mixture as shown in Fig.6.

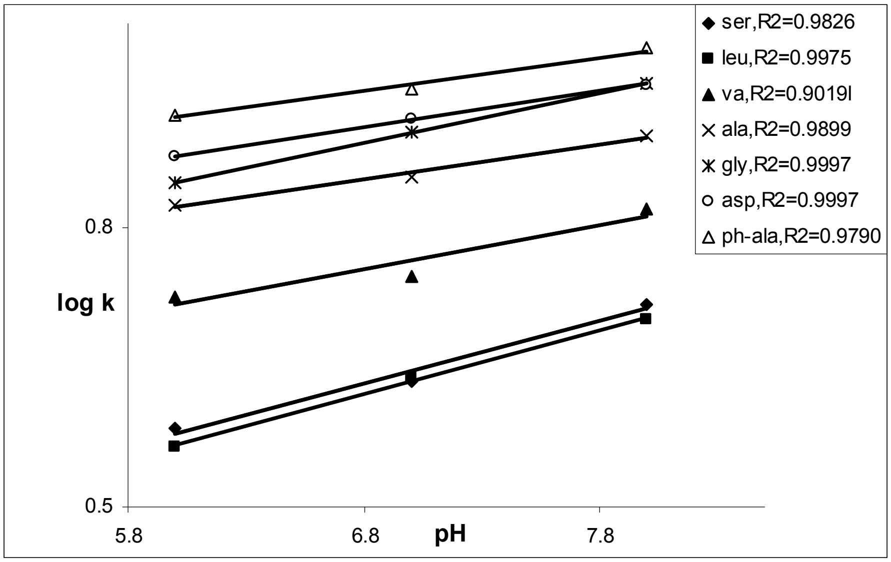


Figure 6: The relation between (log k) & pH of oxidation of Schiff-base , T=25C^{o}, [SB]= 2.5*10^{-2}mol/dm^{3}

This observation reveals that the rate of oxidation is deactivated by increasing the hydrogen ion concentration this may attributed to fact that the hydrogen ion from a quatanary salt with the nitrogen atom, which leads to deactivation of oxidation rate .

Effect of Ionic Strength:

No primary kinetic salt effect was abserved by adding neutral salts within the concentration limits demanded for the application of Bronested – Bjerrum equation the values of k_{obs} for different salt concentration were gathered in table 2.

This result implies that reaction involves two neutral molecules or neutral molecule with an ion in the rate-determining step.

Table(2):The effect of ionic strength on the oxidation reaction of Schiff-bases at pH=7 ,T=25 C ,[MnO_4]=3*10^{-4} ,[SB]=2.5*10^{-2} mol/dm^3

No.	R	[KCL] M	k_{obs} (mol-1.dm3.sec-1)	NO.	R	[KCL] M	k_{obs} (mol-1.dm3.sec-1)
1	$-CH_2OH$	0.1	4.3527	4	$-CH_3$	1.0	7.2058
		0.2	4.3889			1.5	7.2300
		0.5	4.2833	5	-H	0.1	7.9477
		1.0	4.2413			0.2	8.0537
		1.5	4.4412			0.5	8.0232
2	$CH_2CH(CH_3)_2$	0.1	4.3002			1.0	8.0413
		0.2	4.3703			1.5	7.9588
		0.5	4.4725	6	$-CH_2CO_2H$	0.1	8.1613
		1.0	4.2413			0.2	8.3525
		1.5	4.4203			0.5	8.2340
3	**$-CH(CH_3)_2$**	**0.1**	**5.6627**			**1.0**	**8.3290**
		0.2	**5.6760**			**1.5**	**8.2950**
		0.5	**5.7107**	**7**	**$-CH_2ph$**	**0.1**	**8.8038**
		1.0	**5.5380**			**0.2**	**8.9938**
		1.5	**5.4885**			**0.5**	**8.9273**
4	**$-CH_3$**	**0.1**	**7.0995**			**1.0**	**8.9387**
		0.2	**7.1202**			**1.5**	**8.8875**
		0.5	**7.0810**				

Effect of temperature :

The activation parameters associated with the oxidation of Schiff-bases were estimated according to Arrhenins equation 3, by studying the reaction at temperature range (5-25)C^{o} .

$$\ln k_{obs} = \frac{-Ea}{RT} + \ln A$$ **where R=8.314 J.K^{-1}.mol^{-1} …. (3)**

So that a plot of ln k_{obs} against the $\frac{1}{T}$ gave a striaght line as shown in figure 7, where the slope equals to –Ea/R and the intercept equals to ln A.

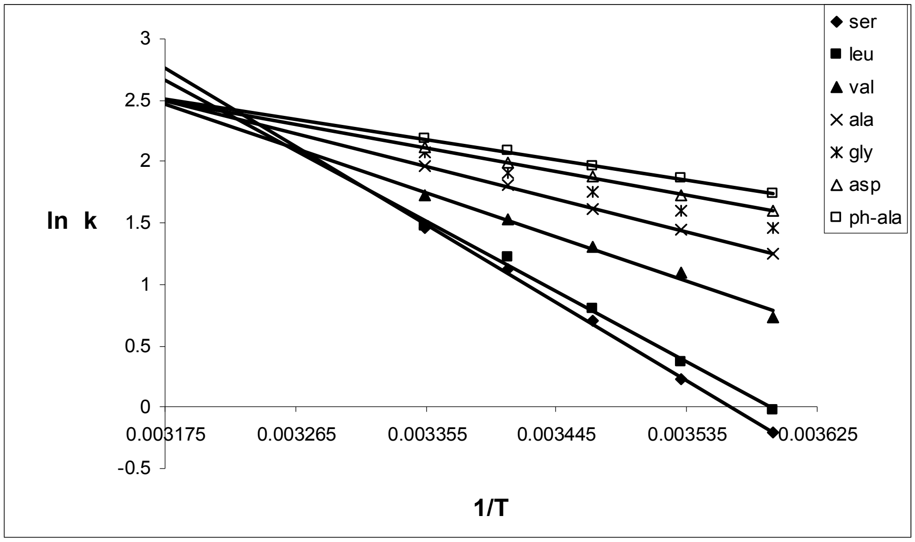


Figure 7: Arrhenius plots for oxidation of Schiff-base

The enthalpy and entropy of activation $\overset{\neq}{\Delta H}$ and $\overset{\neq}{\Delta S}$ can be calculated by applying Eyring equation 4.

$$\ln k_{obs} = \ln \frac{K_B T}{h} + \frac{\Delta S^{\neq}}{T} - \frac{\Delta H^{\neq}}{RT} \cdots\cdots \quad (4)$$

Where K_B = Boltzman's constant ($1.381 * 10^{-23}$ J.K°)
h=Plank's constant ($6.626*10^{-34}$ J.S)
Equation (4) can be rearranged in such a way that a plot of $\ln \frac{k_{obs}}{T} vs \frac{1}{T}$,gave a slope equals $\Delta \overset{\neq}{H}$/R and the intercept equals to $(\ln \frac{K_B}{h} + \frac{\overset{\neq}{\Delta S}}{R})$. The value of activation energy of oxidation decreases in same order of the rate constant increase which indicates that the reaction is conterolled . The activation parameters for the oxidation reaction at pH=7 are gathered in table 3.

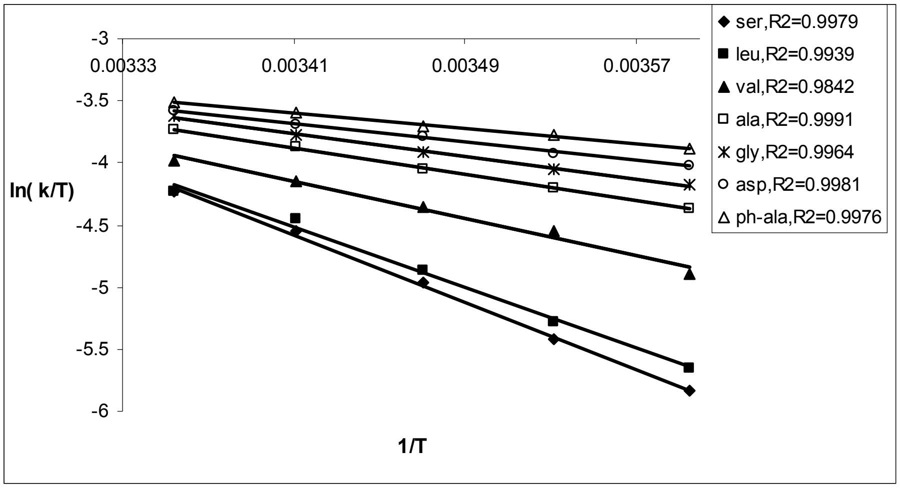


Figure 8: Eyring plots of the oxidation of Schiff-base.

Table(3):The activation energy and thermodynamic parameters of Schiff-bases derived from salicyldehyde and amino acids at pH=7

No.	Schiff-bases	Ea KJ/mole	$\Delta H^{\neq}$ KJ/mole	$\Delta S^{\neq}$ J/mole.°K	$\Delta G^{\neq}$ KJ/mole	A (mol^{-1}.dm^{3}.sec^{-1})
1	Sal-serine	58.669	56.2750	-43.7245	68.8747	8.2412 *10^{10}
2	Sal-leucine	53.147	50.7536	-62.0070	68.6219	9.0316 *10^{9}
3	Sal-valine	33.149	30.7552	-127.196	67.4079	3.4990 *10^{6}
4	Sal-alanine	24.723	22.3297	-153.638	66.6024	1.5420 *10^{5}
5	Sal-glycine	21.484	19.0906	-163.734	66.2725	4.6630 *10^{4}
6	Sal-aspartic	17.663	15.2695	-176.131	66.0239	1.0295 *10^{4}
7	Sal-ph-ala.	15.186	12.7928	-183.826	65.7587	0.4079 *10^{4}

Some isokinetic aspects of oxidation:

The isokinetic theory was applied in this work for mechanistic investigation. The kinetic parameter for Schiff-base oxidation have been calculated by application of activated complex theory using equation 3 and 4. The isokinetic theory states(10) that there is a linear relationship between the natural logrithm of activation factors of the oxidation and the activation energy. Also there is a linear relationship between enthalpies and entropies of activation for the reaction of a series of related compounds according to equations 5 and 6.

$$\ln A_i = \alpha + \frac{Ea_i}{R\beta} \quad \text{.............}(5)$$

$$\Delta H_i^{\neq} = \alpha + \beta\Delta S_i^{\neq} \quad \text{.............}(6)$$

Where α and β are constants. This behavior is called compensation effect or enthalpy – entropy compensation. The quantity β has a dimension of temperature and it is often defined as the isokinetic temperature and the corresponding behavior is referred as isokinetic behavior. The isokinetic shows that at the isokinetic temperature β, all reactions in the series showed the same value of rate. And has a same value of $\Delta G^{\neq}$ according to equations(11) 7 and 8

$$K_i(\beta) = A_i\, e^{(-Ea/R\beta)} = e^{\alpha} \quad \text{............}(7)$$

$$\Delta G_i^{\neq}(\beta) = \Delta H_i^{\neq} - \beta\Delta S_i^{\neq} = \alpha \quad \text{.........}(8)$$

Where α represents the value of ΔG_i at isokinetic temperature. In our results, Arrhenius plots showed the presence of a common point of intercept at temperature around 310 K° as showen in fig. 7 . On the other hand a linear relationship between the enthalpies and entropies of activation for the oxidation reactions where found according to equation 6 as shown in fig. 9 the value β is around 310K° .

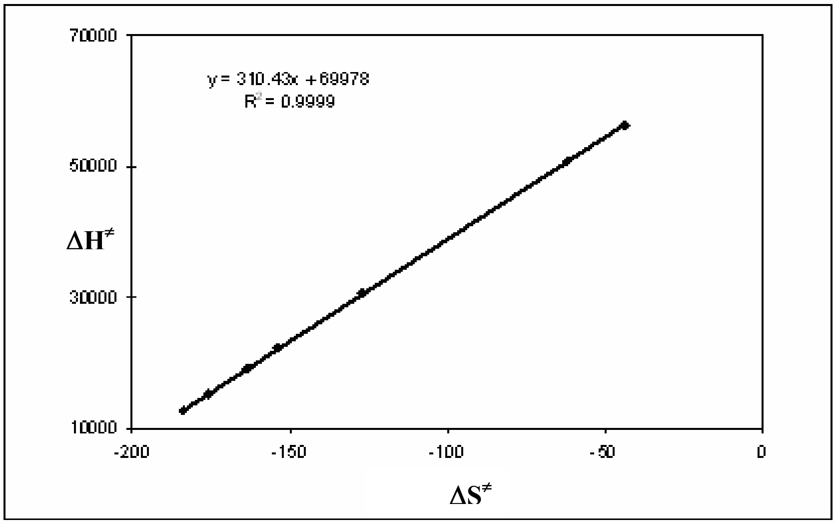


Figure 9: A plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for the oxidation of Schiff- base

On the other hand, also a linear relation were found between ln A and the activation energy and *β* value around 310k° as shown in fig. 10.

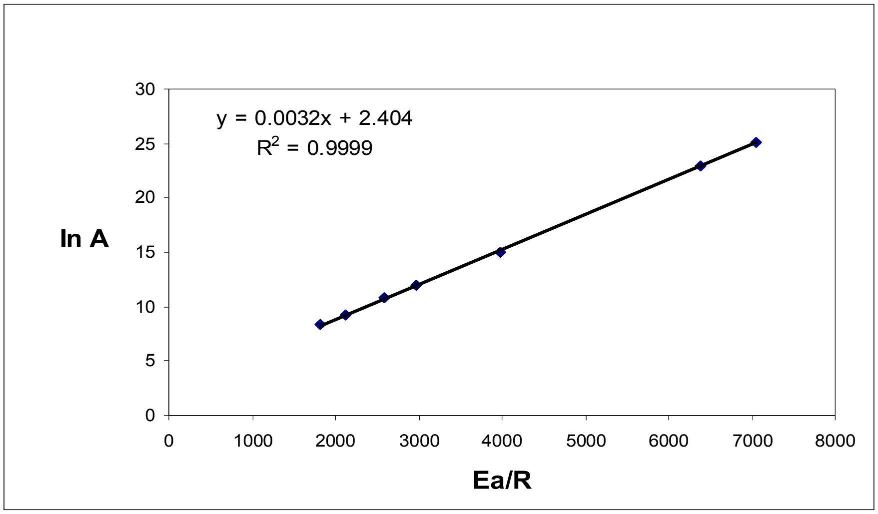


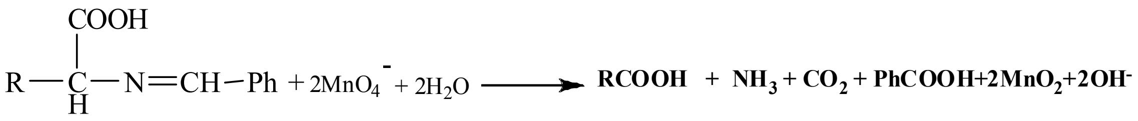
Figure 10: A plot of ln A versus Ea for oxidation of Schiff-base

The above results showed the presence of compensation effect between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and the presence isokinetic relationship at the isokinetic temperature *β*.

The presence enthalpy-entropy compensation indicates generally that the stronger inter molecular interaction or bonding (related enthalpy) would lead to a greater reduction of the configurational freedom and greater increase of the system order (related to the entropy). This might be the cause of the enthalpy- entropy compensation. On the other hand the presence of the isokinetic effect is evident for the dominant mechanism through the correlated series.

Stoichiometry and products analysis :

Reaction mixtures of schiff-base with excess quantity of the oxidant were kept for about 24hr. at 298K° in a thermostat in the reaction vessel. After that the remaining [MnO_4^-] was assayed spectrophotometrically. The results indicated that one mole of Schiff-base reacts with two moles of permanganate ion. Futhermore analysis of the products indicated the presence of ammonia, carbon dioxide and organic acids. So that according to the above results the stoichiometry of the oxidation could be expressed by equation 9.



$$R-\underset{H}{\overset{COOH}{C}}-N{=}CH-Ph + 2MnO_4^- + 2H_2O \longrightarrow RCOOH + NH_3 + CO_2 + PhCOOH + 2MnO_2 + 2OH^- \quad .....(9)$$

Conclusion

This study investigated the kinetics of oxidation of Schiff base by $KMnO_4$ in aqueous solution under different condition .The experimental results showed that reaction is second-order with respect to the permanganate ion and first-order with respect to the Schiff base with overall third-order reaction .The temperature dependency of the reaction rate constants followed Arrhenius equation and the activation energy values are ranging between (15.186-58.669) KJ/mole .

Finally ,the rate law was verified against the experimental data which obtained from this study .The effect of ionic strength on the reaction rate showed a little effect on the reaction.

Acknowledgement

The authors thank university of mosul and the chemistry department at college of education for their financial support and constant encouragement towards the successful completion of this research .We also acknowledge the referees for their suggestion and constructive criticisms .

References

1. R.S. Verma , M.J.Reddy and V.R.Shastry , ***J.C.S. Perkin II*** , 2000 , 469-473.
2. Sayyed Hussains, ***Int . J. of Chem. Tech . Research***, 2010, **2(1)**, 242-249.
3. C. Bungakan , T. Akuru and J, Chungsiripon., ***Int. Cof. on Engineering and Environment***, 2005, 9-21 may.
4. E.O. Odebunmi , S.A. Iwarere and S.O.Owalude, ***Int. J. Chem.***, 2006, **16(3)**, 167-176.
5. D. Christensen and K. A. Jorgensen., ***J. Org. Chem***., 1989, **54**, 126-131.
6. S. Manivarman, ***J. Serb. Chem. Soc.***, 2009, **74(5)**, 493-502.
7. L.Marting and K.A.Jorgensen , ***J. Chem.. Soc., Perkin Trans. I***, 1995, 699-704.
8. A.S.P.Azzouz and R.T. Ali , ***Nat.J. Chem.*** , 2010, **37**, 158-168.
9. J. Deandres, ***J. Chem. Soc. Trans II*** , 1988, 107-112.
10. J.E.Iffer, ***J. Org. Chem.***, 1955, **20**, 1202.
11. Lei Liu and Qing- Xiang Guo, ***Chem. Rev.***, 2001, **101**, 673-695.