



Kinetic Study for some effects on auto-catalyzed oxidation for Serine, Threonine and Tyrosene

Ahmed Y.Haydari *, Salah H.M. Sheet , Ahlaam M.Y.Albayati



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General Directorate of Education in Nineveh , Iraq

Abstract

In the present investigation. The kinetic of oxidation amino acids (Serine, Threonine and Tyrosene) by permanganate ion have been studied at different pH (pH=7&pH=9). The study showed that the oxidation rate constant for the non and auto-catalyzed reaction in the two different pH functions increases with the increase in pH. The effect of ionic strength on oxidation rate constants and at both pHs have been studied by using different concentrations of (NaCl). The study showed that the rate constant of non and auto-catalyzed oxidation reaction in both acidic functions increases as the ionic strength of the medium increase. The effect of dielectric constant of the medium was also studied at (pH=7&pH=9) by changing the ratio of the ethanol / water mixture in the reaction medium. The results showed that oxidation rate of non and auto catalyzed reaction increases as the dielectric constant of solvent decrease.

Keywords: oxidation kinetics, amino acids, dielectric constant, ionic strength.

1. Introduction

The oxidation process of organic compounds using different reagents depends greatly on the nature of the compounds to be oxidized and converted into other compounds, where many strong and weak oxidizing agents were used, such as potassium permanganate, dichromate, chromate, sulfuric acid, perchloric acid, nitric acid, chloramine-T and other oxidizing agents [1- 4].

The permanganate ion $[MnO_4^-]$ is one of the most important poly-electron oxidants in organic and inorganic chemistry. Where many oxidation reactions of different organic compounds were carried out using the permanganate ion $[MnO_4^-]$ [4]. It was found that it has the ability to interact with many active groups of organic compounds, including alcohols, aldehydes, ketones, amines and amino acids[5-7]. Also, the permanganate ion has many applications for oxidation reactions that depend on its use in acidic, basic and neutral media, so that its ability to oxidize in different media is different because during the oxidation process it becomes clear that the manganese ion (Mn^{+7}) in the permanganate ion is reduced to different oxidation states in the media. Acidic and basic as well as in the neutral medium.

Various kinetic studies on amino acid oxidation using different oxidizing agents have been carried out earlier[8-10] due to their biological importance and

understanding the mechanism of the biological oxidation reactions. In addition, it has wide and different applications in the field of pharmacy, as it is included in many pharmaceutical industry and various fields of medicine. The kinetics of the oxidation of amino acids by permanganate ion in an acidic medium was also studied[11]. Through it, the reaction rate was measured and the thermodynamic functions were calculated. The oxidation of DL-alanine by permanganate ion in concentrated solutions of sulfuric acid and perchloric acid was studied, and the reaction rate constant and the effect of acids on the kinetics of oxidation were calculated[12,13]. In basic and neutral medium[14,15] the kinetics of valine oxidation was studied by the same reagent as in neutral medium. The results showed that the reaction proceeds by two paths. The first is un-catalyzed and the second is spontaneously catalyzed by the colloidal manganese dioxide (MnO_2) produced by the un-catalyzed pathway. At a high concentration of amino acids (under pseudo-first-order conditions) the reaction rate (r)[5] was obtained and it was found that it follows the following equation:

$$r / C = (k_1 + k_2 C_0) - k_2 C \dots\dots\dots (1)$$

where (C and C_0) are the permanganate ion concentrations at time (t, 0) respectively and (k_1 and k_2) the rate constants of the un-catalyzed and spontaneously catalyzed oxidation reactions, respectively.

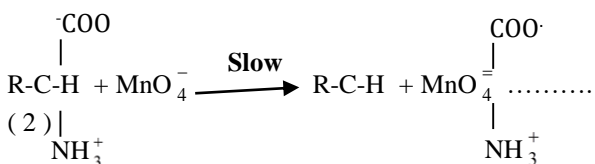
*Corresponding author e-mail: chem.mosul.research@gmail.com

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The proposed mechanism of the reaction assumes that the oxidation process is proceeded by electron transfer from the amino acid to the oxidizing agent in the slow step of the rate determining reaction as shown in equation (2):



In this work, the effect of pH, ionic strength and dielectric constant of the medium was studied on the reaction rate of the oxidation of three amino acids, namely (serine, threonine and tyrosine).

1. Experimental Part

Instrumentation

- 1- pH meter (BP 3001 Professional Benchop)
- 2- A water bath equipped with an accurate temperature regulator up to (± 0.1) type (Julabo SW-23)
- 3- Visible X-ray device (T92° UV Spectrophotometer PG Instruments) to track the change in the concentration of the permanganate ion.

Chemicals

Distilled water was used to prepare potassium permanganate (Merck). Buffered solutions of KH_2PO_4 - K_2HPO_4 (Fluka) were used to keep the pH of the solution constant. The amino acids (BDH) were also prepared by dissolving a certain amount of it in the buffer solution. While the reaction was followed up by changing the ionic strength of the medium by adding different concentrations of sodium chloride salt (NaCl).

Kinetic measurements

The kinetics of the oxidation reactions of the amino acids under consideration were studied by following the concentration of the permanganate ion with time by spectroscopic methods[16] under pseudo-order conditions (where the concentration of amino acids is always greater than the oxidizing agent at least ten times). Where it was found that the permanganate ion has a high absorbance at (526nm) and the inorganic product (MnO_2) absorbs light in the full visible spectrum. 526nm) where the product and the oxidizing agent absorb light so that the concentration of the oxidizing agent is calculated from equation (3) and as follows⁽⁵⁾:

$$C = \left(A^{526} - \frac{\epsilon P^{526} - A^{418}}{\epsilon P^{418}} \right) / \epsilon R^{526} \dots\dots\dots (3)$$

Where (ϵR , ϵP) represent the molar absorption coefficient of the oxidizing agent and the product, respectively. Where the ϵR of the oxidizing agent was estimated at a value equal to $2.4 \times 10^3 \text{ mol dm}^3\text{cm}^{-1}$ (9)

and the molar absorption coefficient of the product was estimated at (418nm) and (526nm) from the final absorbance readings.

The rates of reaction were also calculated by dividing the concentration differences over the time periods, as follows:

$$r_1 = \frac{C_0 - C_2}{2\Delta t} \dots\dots\dots(4)$$

where (r_1) is the rate of the reaction when the concentration of the permanganate ion is equal to (C_1). And (C_2 and C_0) represent the permanganate ion concentration before and after a period of time $2\Delta t$. And $2\Delta t$ represents the change in time from C_0 to C_2 .

2. Results and Discussion

Kinetic Study:

The kinetic study of the oxidation reaction of amino acids was carried out by following the change in the concentration of the permanganate ion with time. The kinetic results according to equation No. (1) showed that drawing a relationship between (r / C) versus (C) gives straight lines as shown in (Fig. 1), which indicates that the reaction takes place and is spontaneously moved by the colloidal product of the reaction (MnO_2) which allows to calculate the rate constant for the un-catalyzed reaction (k_1) and the auto-catalyzed reaction (k_2). The values of the rate constants for the oxidation of the three amino acids at a temperature of (298K) and (pH=7) are listed in Table (1):

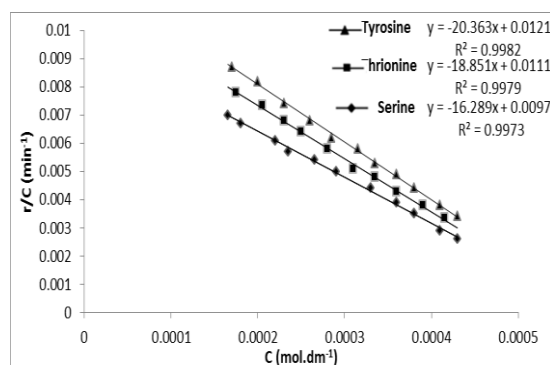


Fig.1. The relationship between (r/C) versus (C) for the oxidation of amino acids at (298K) and (pH=7).

Table 1: The values of the rate constants for the oxidation of amino acids at (298K) and pH = 7.

Amino acid	$k_1 \times 10^{-3}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)
Serine	2.0442	16.289
Threonine	2.4285	18.851
Tyrosine	2.7331	20.363

Effect of pH:

The study of the pH effect has to do with the fact that amino acids exist in different ionic forms depending on the pH of the medium[14]. Where the oxidation reactions of the three amino acids (Serine, Threonine and Tyrosine) were followed up in an

alkaline medium at (pH=9). When plotting the relationship between (r/C) versus (C) as shown in Figure (2). The values of the un-catalyzed reaction rate constants (k_1) and auto -catalyzed (k_2) for the oxidation of the amino acids under study were calculated and all results were included in Table (2).

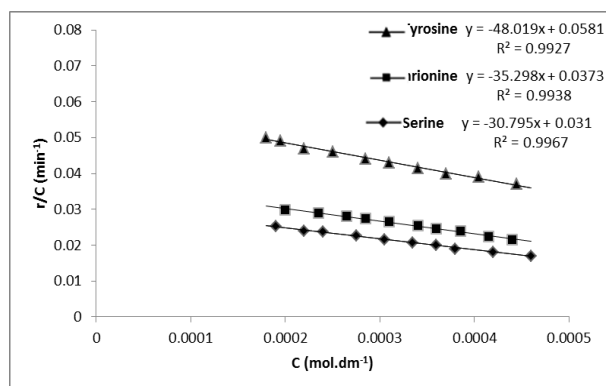


Fig.2. The relationship between (r/C) versus (C) for the oxidation of amino acids at (298K) and (pH=9).

Table 2: The values of the rate constants for the oxidation of amino acids at (298K) and pH = 9.

Amino acid	$k_1 \times 10^{-2}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)
Serine	1.6575	30.795
Threonine	2.1063	35.398
Tyrosene	3.5063	48.019

When comparing the values of the rate constants at pH = 7 listed in Table (1) with those at pH = 9 listed in Table (2), it is found that the values of the rate constant for the un-catalyzed and spontaneously catalyzed reaction increase as the pH of the medium increases. This is due to the fact that the rate constant is calculated under pseudo-order conditions and is equal to the sum of two terms. The first belongs to the oxidation of the neutral form of the amino acid (zwitter ion) and the second belongs to the oxidation of the anionic form of the amino acid (anion) as shown in equation (5).

$k_{\text{obs}} = k [\text{Amino acids}] = k_{\text{HA}} [\text{HA}] + k_{\text{A}^-} [\text{A}^-] \dots (5)$
Where (k_{HA} and k_{A^-}) are the rate constants of oxidation rate for the neutral (HA) and negative ionic (A^-) form of amino acids, respectively. This is due to the fact that the ionic forms of amino acids are oxidized faster than the neutral form. So that the increase in the pH value of the medium leads to an increase in the concentration of the negative ionic form of it, which led to an increase in the values of the rate constants of the rate of the un-catalyzed and auto-catalyzed reaction as shown by the above results[17].

Effect of ionic strength:

The study of the effect of the ionic strength on the rate of the reaction of the oxidation of amino acids is very important because it gives an idea about the nature of the interacting molecules[18], and thus helps in understanding the mechanism of the reaction. Where it was found that the mathematical relationship that links the ionic strength (μ) and the reaction rate constant (k) is the Bronsted and Bejerm equation, which is expressed in the following form[19]:

$$\log \frac{k}{k_0} = 1.02 Z_A Z_B \sqrt{\mu} \dots \dots (6)$$

Where (Z_A , Z_B) represents the charge of the reacting ions, (k) the rate constant of the reaction at a given ionic strength. And (k_0) is the reaction rate constant for very dilute solutions and (μ) represents the ionic strength of the solution. For this purpose, the oxidation of the three amino acids was carried out with different concentrations of sodium chloride salt, which ranged between (0.2-1.0 $\text{mol} \cdot \text{dm}^{-3}$) and at different pH levels (pH = 7 and pH = 9). The ionic strength of the solution (μ) at the mentioned concentrations was calculated according to the following equation:

$$\mu = \sum M_i \cdot Z_i^2 \dots \dots \dots (7)$$

Where (M_i) represents the molar concentration of the reacting ions and (Z_i) the charge of the reacting ions. The values of the rate constant for the un-catalyzed reaction (k_1) and the auto-catalyzed reaction (k_2) were also calculated from drawing the relationship between (r/C) versus (C) according to Equation (1) and the results were included in Tables 3, 4 and 5 for the three studied amino acids.

The results listed in Tables 2, 3 and 4 showed a clear increase in the rate constant for both the un-catalyzed and auto-catalyzed reaction at different pHs. Where in neutral medium at pH=7. The main dominant form of amino acids is the zwitter ion and the permanganate ion, such that the ionic strength does not affect the rate of oxidation according to the Bronsted equation[19]. The results mentioned in the above tables reveal an unexpected increase in the rate constant of oxidation, which is attributed to the presence of a small amount of anion at this pH.

On the other hand, in the basic medium pH = 9, the concentration of the negative ionic form increases and the main reaction occurs between two negative ions, which are the anionic form of amino acids and the negative permanganate ion (MnO_4^-). Therefore, the rate of the reaction should increase with increasing ionic strength of the medium according to the results shown in Tables 2, 3 and 4.

There is also a significant increase in the value of the rate constant for the auto-catalyzed reaction, and this is due to the fact that, in addition to this the increase comes from the Bronsted equation, another increase comes from the increase in the amount of amino acids adsorbed on the surface of the colloidal catalyst (MnO_2) as the concentration of the chloride salt increases sodium increases the rate of the reaction. In other words, the increase in the rate of the reaction resulted from two factors, the first from the Bronsted

equation and the second from the increase in the amount of amino acids adsorbed on the surface of the colloidal catalyst. When plotting (logk) against the

$\sqrt{\mu}$ according to equation (6), straight lines are obtained, as shown in Figures 3, 4, 5 and 6 for the three amino acids.

Table 3: Values of the oxidation rate constants (serine) in different ionic intensities at (298K).

NaCl mol.dm ⁻³	pH=7.00			pH=9.00		
	μ	$k_1 \cdot 10^3$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	$k_1 \cdot 10^2$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	
0.2	0.1	2.3094	20.5683	2.3637	46.892	
0.4	0.2	2.4311	22.7352	2.4991	59.873	
0.6	0.3	2.5521	25.4565	2.6212	81.1334	
0.8	0.4	2.6533	27.3338	2.7327	111.6606	
1.0	0.5	2.7083	29.3224	2.8761	146.3861	

Table 4: values of oxidation rate constants (threonine) in different ionic intensities at (298K).

NaCl mol.dm ⁻³	pH=7.00			pH=9.00		
	μ	$k_1 \cdot 10^3$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	$k_1 \cdot 10^2$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	
0.2	0.1	2.8477	22.3975	3.7948	52.7112	
0.4	0.2	3.0116	25.8285	4.1191	81.7334	
0.6	0.3	3.1702	29.5937	4.4606	108.168	
0.8	0.4	3.3319	32.5912	4.6708	141.123	
1.0	0.5	3.4237	35.9418	4.8809	207.348	

Table 5: Values of oxidation rate constants (tyrosine) in different ionic intensities at (298K)

NaCl mol.dm ⁻³	pH=7.00			pH=9.00		
	μ	$k_1 \cdot 10^3$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	$k_1 \cdot 10^2$ (min ⁻¹)	k_2 (mol ⁻¹ .dm ³ .min ⁻¹)	
0.2	0.1	3.4237	26.8411	4.2993	73.1475	
0.4	0.2	3.6619	30.9844	4.7665	115.106	
0.6	0.3	3.8716	35.4895	5.3272	163.042	
0.8	0.4	4.0355	40.4669	5.7332	229.298	
1.0	0.5	4.2305	46.3873	6.2201	317.394	

The relationship between logk vs. $\sqrt{\mu}$ presented in the plot in the Figures above show that the regression for auto-catalyzed oxidation reactions is always greater than the regression for un-catalyzed reactions (Table 6), according to the above assumptions.

Effect of the dielectric constant (D) of the medium:

The dielectric constant is related to the rate constant of the reaction according to the following equation (8)[20]:

$$\log k = \log k_0 - \frac{Z_A \cdot Z_B \cdot e^2}{D \cdot d_{AB} \cdot KT} \dots \dots \dots (8)$$

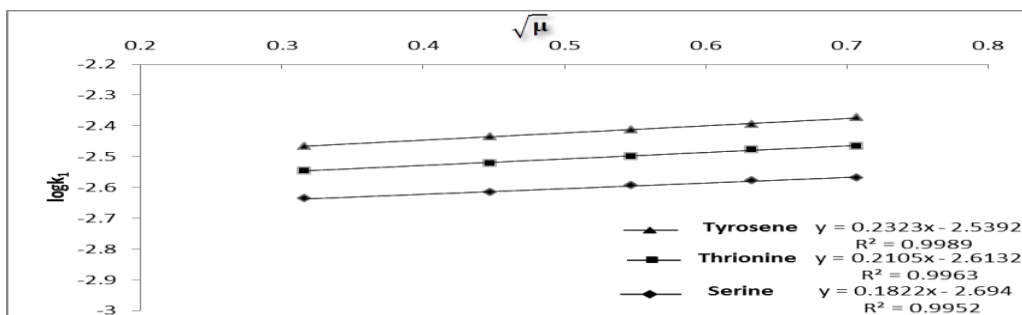
where Z_A , Z_B is the charge of the interacting ions and d_{AB} is the sum of the atomic radii of the interacting molecules.

From the above equation, it can be expected that, if one of the reacting molecules is neutral, there are no

significant effects of changing the dielectric constant of the medium on the kinetics of amino acid oxidation (as is the case in the neutral medium at pH = 7), and if both ions are the same in charge. The reaction rate constant must be inversely proportional to the value $1/D$ (as in the basic medium at pH = 9).

medium, where the dielectric constant of the medium was reduced by using solvent mixture of different percentages of (ethanol-water)[21-23] and at different pHs (pH=7) and (pH=9). Plotting the relation between (r/C) versus (C) , the rate constant of the uncatalyzed and auto-catalyzed reaction (k_1 and k_2)

were calculated. The results are included in Tables 7, 8 and 9.



The kinetics of the oxidation of amino acids was studied at a variable dielectric constant of the

Fig.3. Plotting the relationship between $\log k_1$ versus $\sqrt{\mu}$ for the three amino acid oxidation reaction at pH = 7 and (298K).

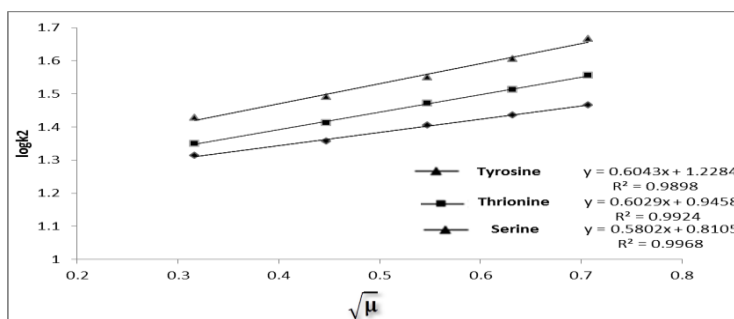


Fig.4. Plotting the relationship between $\log k_2$ versus $\sqrt{\mu}$ for the oxidation reaction of the three amino acids at pH = 7 and (298K).

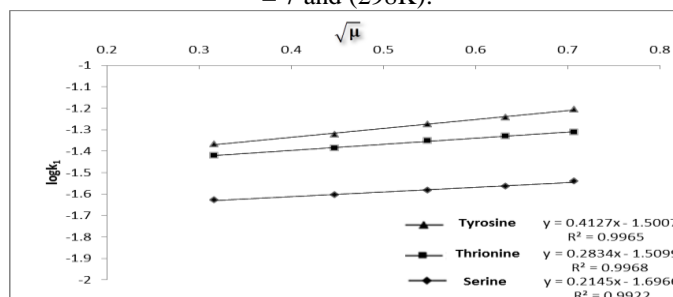


Fig.5. Plotting the relationship between $\log k_1$ versus $\sqrt{\mu}$ for the oxidation reaction of the three amino acids at pH=9 and (298K).

Table 6: Straight line regression of the relationship between $\log k$ vs $\sqrt{\mu}$.

amino acids	pH = 7.00		pH = 9.00	
	Slop k_1	Slop k_2	Slop k_1	Slop k_2
Serine	0.1822	0.5802	0.2145	1.8689
Threonine	0.2105	0.6029	0.3834	1.4642
Tyrosine	0.2323	0.6043	0.4127	1.6188

reactions, it gives straight lines as shown in Figure 6, 7, 8 and 9 for the three studied amino acids.

When plotting the relationship between (logk) versus (1/D) for both the un-catalyzed and auto-catalyzed

Table 7: Values of the dielectric constant of the medium and the oxidation rate constants (serine) at (298K).

Ethanol wt%	pH=7.00			pH=9.00		
	D	$k_1 \cdot 10^{-3}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	$k_1 \cdot 10^{-2}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	
4.72	78.062	2.1419	17.0255	2.3152	36.7028	
10.00	74.600	2.1953	18.0343	2.7108	44.4528	
16.10	71.036	2.2454	20.1094	3.1702	53.6908	
23.00	66.851	2.3046	23.1632	3.6974	75.2488	
31.00	62.016	2.3779	26.4181	4.4967	125.834	

Table 8: Values of the dielectric constant of the medium and the oxidation rate constants (threonine) at (298K).

Ethanol wt%	pH=7.00			pH=9.00		
	D	$k_1 \cdot 10^{-3}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	$k_1 \cdot 10^{-2}$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	
4.72	78.062	2.8398	21.5377	4.0784	55.106	
10.00	74.600	2.8946	22.9667	4.7369	74.7997	
16.10	71.036	3.0124	25.9776	5.3691	120.198	
23.00	66.851	3.1174	31.0742	6.4387	187.025	
31.00	62.016	3.3442	36.9062	9.1264	314.919	

Table 9: values of the dielectric constant of the medium and the oxidation rate constants (tyrosine) at (298K).

Ethanol wt%	pH=7.00			pH=9.00		
	D	$k_1 \cdot 10^3$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	$k_1 \cdot 10^2$ (min^{-1})	k_2 ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$)	
4.72	78.062	3.6107	28.8336	4.7852	85.8222	
10.00	74.600	3.6762	32.9533	5.9621	107.821	
16.10	71.036	3.8441	38.8061	6.9742	167.611	
23.00	66.851	4.0031	45.1961	8.6536	283.857	
31.00	62.016	4.3471	56.2211	11.171	565.067	

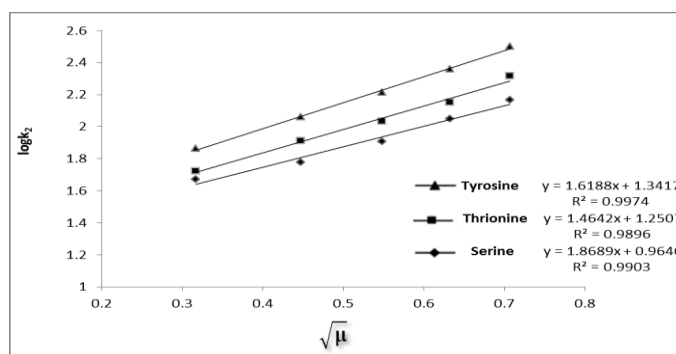


Fig.6. Plotting the relationship between $\log k_2$ versus $\sqrt{\mu}$ for the oxidation reaction of the three amino acids at pH = 9 and (298K).

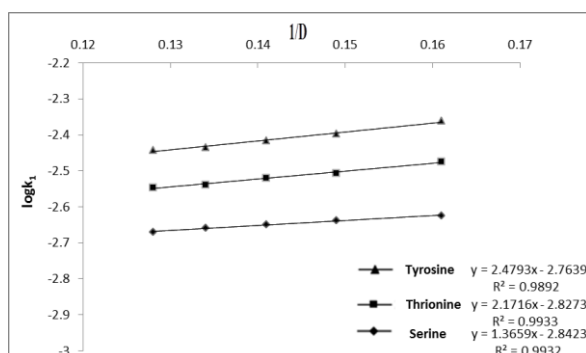


Fig.6. Plotting the relationship between $\log k_1$ versus $1/D$ for the oxidation reaction of the three amino acids at pH = 7 and (298K).

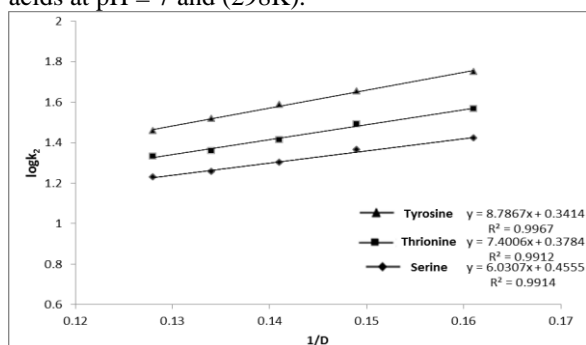


Fig.7. Plotting the relationship between $\log k_2$ versus $1/D$ for the oxidation reaction of the three amino acids at pH = 7 and (298K).

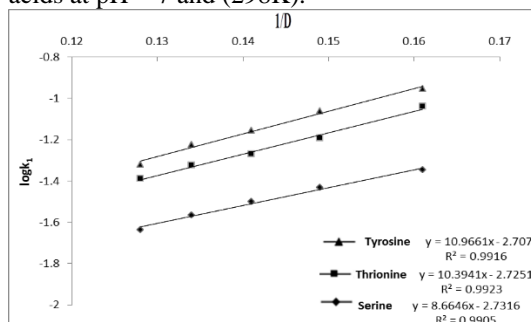


Fig.8. plots the relationship between $\log k_1$ versus $1/D$ for the oxidation reaction of the three amino acids at pH = 9 and (298K).

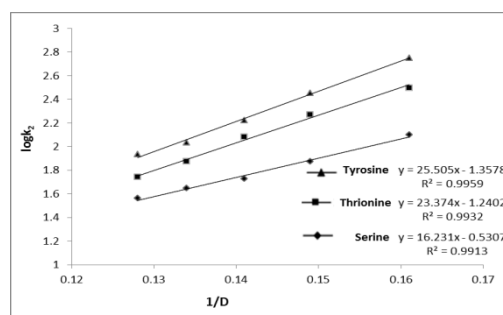
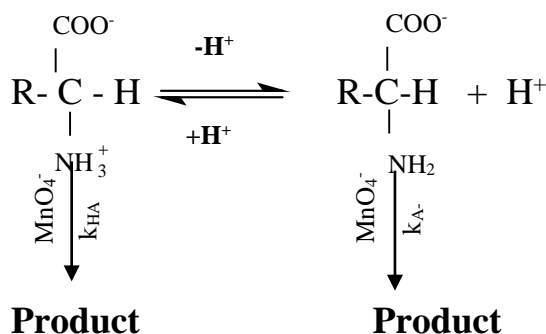


Fig.9 plotting the relationship between $\log k_2$ versus $1/D$ for the three amino acid oxidation reaction at pH = 9 and (298K).

All the above figures showed that, the slope of the straight line has a positive sign at pH=7 and pH=9 in contrast to the expected relationship from equation (8), such cases were presented in other study and attributed to the difference in the diameter of the reacting molecules and the activated complex[21-23]. In this study, this anomaly is related to the fact that the oxidation process was performed under pseudo-first-order conditions where the concentration of amino acid is much higher than the concentration of the permanganate ion so that the oxidation constant for the un-catalyzed and auto-catalyzed reaction results from multiplying the rate constant with the concentration of the amino acid[24,25].

($k_1 = k_{\text{non}}[\text{amino acid}]$, $k_2 = k_{\text{auto}}[\text{amino acid}]k_2$).

On the other hand, the amino acids present in two zwitter neutral ionic forms (HA) and the negative anion (A^-), so that the oxidation process occurs as follows:



According to equation (5) an increase in the concentration of the negative ionic form leads to an increase in the observed rate constant. As the percentage of alcohol increases, the dielectric constant of the medium decreases, which leads to a decrease in the concentration of the neutral ion and an increase in the concentration of the negative ion. This gives a greater value for the observed reaction rate constant. This assumption seems clear with the observed rate constant results for the un-catalyzed and auto-catalyzed reaction listed in Tables 6, 7 and 8 for the three amino acids. Therefore, at pH=9, the increase in alcohol concentration has two reversible effects, the first is an increase in the reaction rate constant as the alcohol concentration increases and the second is a decrease in the reaction rate constant due to the decrease in the dielectric constant of the solvent as a percentage of the alcohol increase

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