KINETICS AND MECHANISM STUDIES OF OXIDATION OF A-AMINO ACIDS BY N-BROMOSUCCINIMIDE

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Abstract

Kinetics and mechanism studies of oxidation of some α-amino acids (Proline, Arginine, Alanine) (AA) by N-Bromosuccinimide (NBS) by using conductivity method was carried out. The kinetic study showed that the reaction was first order with respect to NBS and AA. The effect of addition of $HClO_4$ to the reaction was negative on the rate of reaction. The reaction was carried out at different temperatures in which $(\Delta H^*, \Delta S^*, \Delta G^*)$ were calculated. The rate of reaction of AA was as follows: Proline > Arginine > Alanine

Key word: Kinetics , α-amino acids , N-Bromosuccinimide.

Introduction

NBS is considered as one of the oxidants that are used widely in oxidizing organic compounds[1-5]. It is also considered as important oxidant in oxidizing many coordination complexes [6-10] as well as oxidant in oxidizing biochemical compounds [11-12]. NBS is also used as initiator of polymerization in some reactions [13]. The literature presented

Many reports about oxidation of AA [14], but the kinetics of AA oxidation by NBS has not been reported.

Experimental

1. Material: NBS supplied by Fluka of 98% purity, Succinimide and Arginine supplied by Riedel-de Hean of 98% and 96% purity respectively, Proline and Alanine supplied by Aldrich of 98% purity and double distillated water had been used.
2. Method: Three different concentrations of NBS were prepared in dark bottles to avoid the photolysis of NBS. All kinetic measurements were recorded by using digital conductivity meter wTw-540 (0.000µS-02.000mS±5%). The reaction was followed up through conductivity variation at time intervals. The conductivity of the solution was increasing with time due to hydrogen ion generation as reaction product. All experiments were carried out at constant volume of final solution (50ml). The reaction was carried out by adding materials of certain concentrations in to the reaction cell. The conductivity was recorded directly after mixing the materials quickly then the conductivity was recorded in times intervals.

Results and Discussion

1- Kinetic measurements: The study showed that conductivity increased with time due to generation H^+ as reaction product, therefore:

$\kappa_\infty - \kappa_t$ Represents unreacted concentration of NBS

$\kappa_\infty - \kappa_o$ Represents initial concentration of NBS

where :

κ_∞ : the conductivity after completion.

κ_t : the conductivity at time (t).

κ_o : the conductivity before starting the reaction.

The kinetic study showed that the reaction was first order by using integral equations of reaction orders. Since the concentration of AA was several times more than the concentration of NBS, the reaction has been pseudo first order as follows:

$$\text{In}\,(\kappa_\infty - \kappa_t) = \text{In}\,(\kappa_\infty - \kappa_o) - k_t \;.............(1)$$

Equation (1) reveals the first order expression using the conductivity symbols.

Where:

k = constant of reaction rate

t = time

The results showed that the values of the rate constant for first order remained constant at changing the concentration of NBS with constant of other parameters as it is reported in Tables (1, 2, 3) and Figs. (1, 2, 3). This indicates that the reaction was first order with respect to NBS. The rate constant values were increases as AA concentration increased as shown in Tables (1, 2, 3).
Since the general equation of the rate is

$$R = k[NBS]^n [AA]^m \quad ....(2)$$

Since the concentration of AA was much more than NBS.Hence,

$$R = k_{exp}[NBS]^n \quad ....(3)$$

$$k_{exp} = k[AA]^m \quad ....(4)$$

To find order of reaction with respect to AA a plot log k_{exp} versus log [AA] was drawn utilizing the following equation:

$$\log k_{exp} = \log\ k + m\ \log\ [AA] \quad ....(5)$$

The plot exhibits a straight line with positive slop which represents the order of reaction with respect AA. The order of the reaction with respect AA was approximately of first order as it is shown in Figs. (4, 5, 6).

2- Effect of addition $HClO_4$ acid: The reaction was carried out by using different concentrations of $HClO_4$ acid with keeping other parameters constant. It was found that the value of rate constant decreasing with increasing concentration of $HClO_4$ acid as it is shown in Tables (1, 2, 3).
3- Effect of addition of Succinimide: Different concentrations of Succinimide were added to the reaction cell with keeping other parameters constant. It was found that the value of rate constant decreasing with increasing concentration of Succinimide as it is shown in Table (4).
4- Stoichiometry : Stoichiometric measurements, using iodometric titration, showed that each mole of AA reacts with 2 moles of NBS.
5- Effect of temperature: The reaction was carried out under different temperatures (25, 30, 35, 40) C°. It was found that the value of rate constants increasing with increasing temperature with keeping other parameters constant as it is shown in Table (5).

The Arrhenius equation:

$$\ln k_{exp} = \ln A - \frac{Ea}{RT} \quad ....(8)$$

has been used to implement the plot which is seen in Fig. (7).
Where
k_{exp} : experimental rate constant
A : frequency factor
Ea : activation energy
R : gas constant
T : temperature

By using the following thermodynamic equations[16] ; A, Ea, ΔH^*, ΔG^*, ΔS^* were calculated, as it is presented in Table (6)

$$\Delta H^* = Ea - RT$$

$$\ln A = \ln \frac{kT}{h} + \ln \frac{\Delta S^*}{R}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Where :
k : Boltzmann constant
h : Planck constant

6- Identification of the Product: The literature showed that the oxidation of AA using different oxidant would produce corresponded aldehyde[15]. The reaction was carried out by using high concentration of reacted materials .The appearance of CO_2 gas bubbles has been observed. The mixture was left 24 hours to ensure reaction completion. Test of carbonyl group[17] was carried out by 2,4-Dinitrophenylhydrazine. The test was positive. The Fehling test [17] carried out. The test was positive. These tests proved the presence of aldehyde as product.
7- Suggested Mechanism: Depending on kinetic results and literature[8,9], the following mechanism was suggested:

$$NBS + H_2O \overset{K_1}{\Longleftrightarrow} succinimide + HOBr \quad ...... (7)$$

$$\underset{\displaystyle NH_2}{R-CH-COOH} \overset{K_2}{\Longleftrightarrow} \underset{\displaystyle {}^{+}NH_3}{R-CH-COO^-} \quad .... (8)$$

(zwiterion)

$$\text{Zwiterion} + \text{HOBr} \xrightarrow[\text{Slow}]{K_3} \text{Complex} \quad ....(9)$$

$$\text{Complex} + \text{HOBr} \xrightarrow{K_4} \text{Product} \quad ....(10)$$

8- Suggested rate law

$$-\frac{d[\text{NBS}]}{dt} = k_3[\text{zwiterion}][\text{HOBr}] \quad .....(11)$$

From equation (7)

$$[\text{HOBr}] = \frac{K_1[\text{NBS}][H_2O]}{[\text{succinimide}]} \quad ....(12)$$

From equation (8)

$$[\text{Zwiterion}] = K_2[R-\underset{\underset{NH_2}{|}}{CH}-COOH] \quad ...(13)$$

Substituting (13) and (12) in (11) gives the final rate equation of the reaction:

$$-\frac{d[\text{NBS}]}{dt} = \frac{k_3K_1K_2[H_2O][\text{NBS}][R-\underset{\underset{NH_2}{|}}{CH}-COOH]}{[\text{succinimide}]} \quad ....(14)$$

$$-\frac{d[\text{NBS}]}{dt} = \frac{k_{exp}[\text{NBS}][R-\underset{\underset{NH_2}{|}}{CH}-COOH]}{[\text{succinimide}]} \quad ....(15)$$

Table (1)
The values of rate constant, pH and initial concentrations of the reactants NBS and Alanine at 298.15 K.

[NBS]/ *10^3M	[Alanine]/ *10^2M	pH (initial)	k_{exp} (s^{-1})/*10^4
1.0	1.0	7	4.85
1.5	1.0	7	4.9
2	1.0	7	4.9
1.0	0.2	7	9.0
1.0	0.3	7	15.0
1.0	0.4	7	22.5
1.0	1.0	9	8.0
1.0	1.0	3	3.0

Table (2)
The values of rate constant, pH and initial concentrations of the reactants NBS and Arginine at 298.15 K.

[NBS]/ *10^3M	[Arginine]/ *10^2M	pH (initial)	k_{exp} (s^{-1})/*10^4
1.0	1.0	7	20
1.5	1.0	7	19.8
2	1.0	7	20.1
1.0	0.2	7	43
1.0	0.3	7	50
1.0	0.4	7	80
1.0	1.0	9	56
1.0	1.0	3	9.7

Table (3)
The values of rate constant, pH and concentrations of the reaction between NBS and Proline at 298.15 K.

[NBS]/ *10^3M	[Proline]/ *10^2M	pH (initial)	k_{exp} (s^{-1})/*10^4
1.0	1.0	7	70.5
1.5	1.0	7	71
2	1.0	7	71
1.0	0.2	7	139
1.0	0.3	7	188
1.0	0.4	7	286
1.0	1.0	9	97
1.0	1.0	3	50

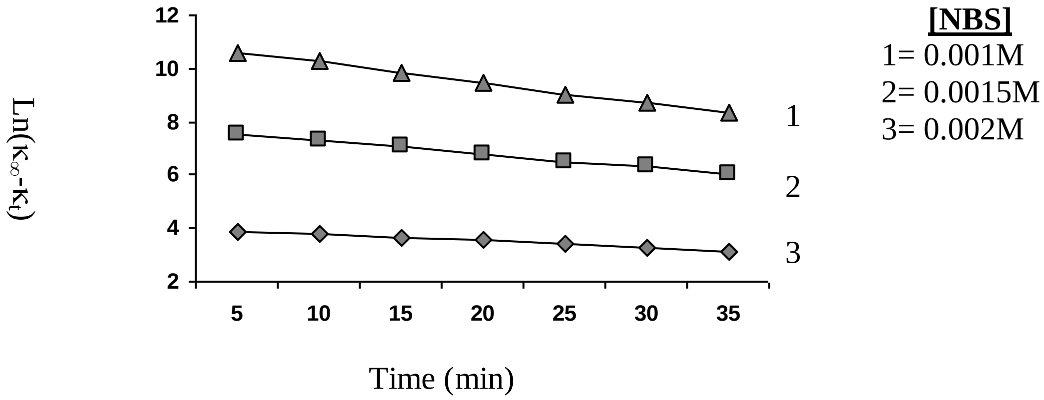

Fig. (1) : A plot of ln(κ_∞-κ_t) versus time of the reaction between NBS of different concentrations and 0.01M Alanine at 298.15K.

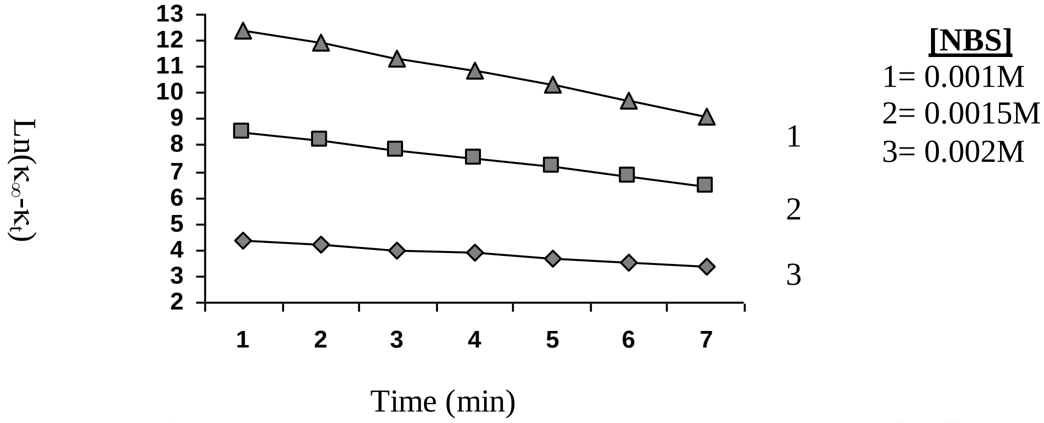

Fig. (2): A plot of ln(κ_∞-κ_t) versus time of the reaction between NBS of different concentrations and 0.01M Arginine at 298.15K.

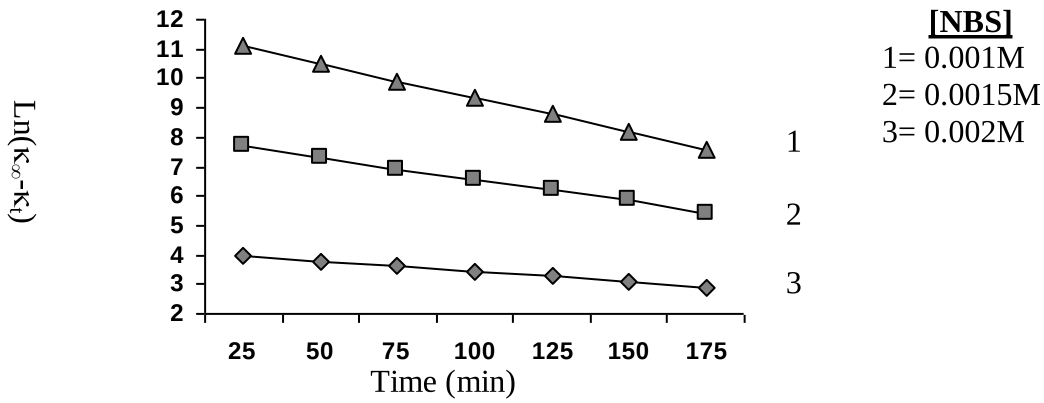

Fig. (3): A plot of ln(κ_∞-κ_t) versus time of the reaction between NBS of different concentrations and 0.01M Proline at 298.15K.

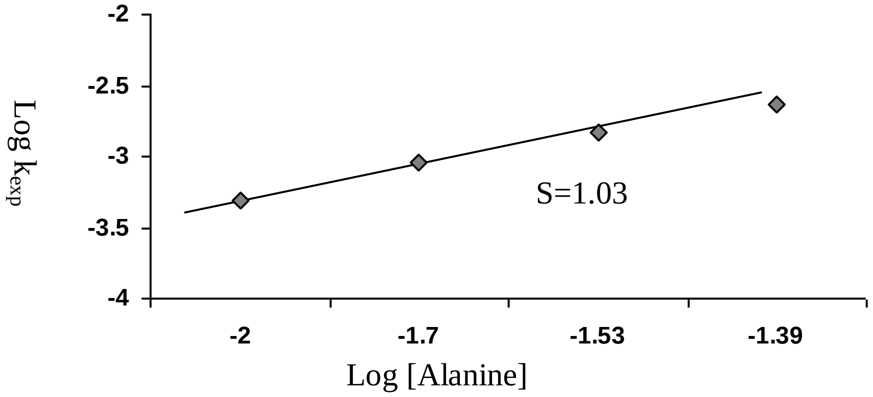

Fig. (4) : A plot to find out the order of the reaction with respect to Alanine concentration at 298.15K.

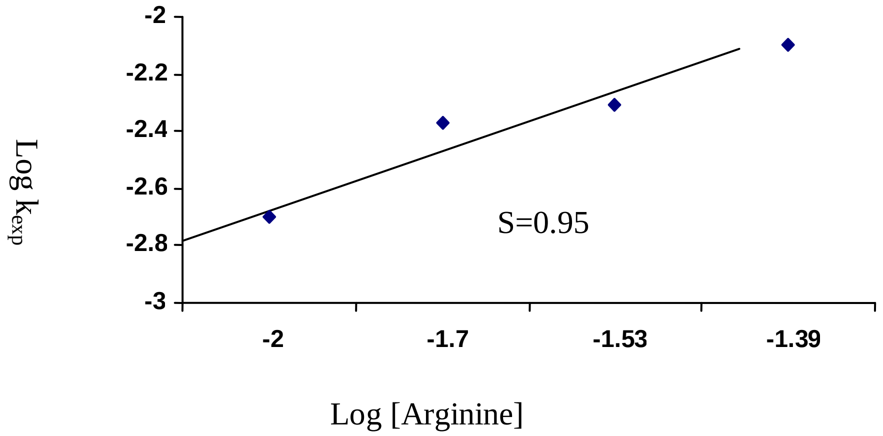

Fig. (5) : A plot to find out the order of the reaction with respect to Arginine concentration at 298.15K.

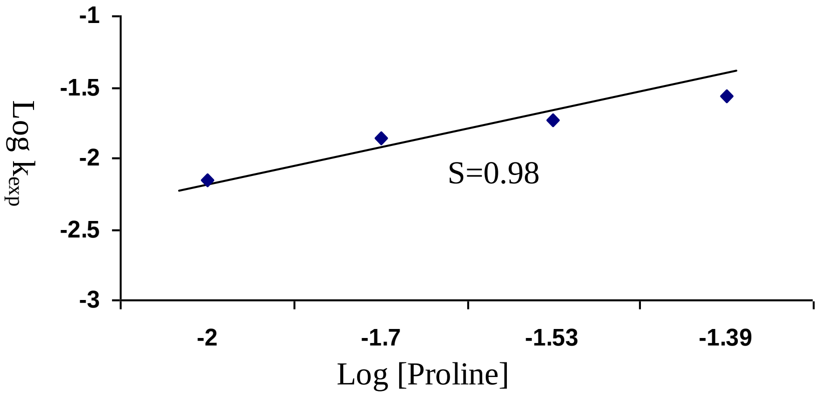

Fig. (6) : A plot to find out the order of the reaction with respect to Proline concentration at 298.15K.

Table (4)
The values of rate constants of AA and concentration of Succinimide at 298.15K.

[Succinimde]/ $*10^3$M	$k_{exp}(s^{-1})/*10^4$		
	Alanine (0.01M)	Arginine (0.01M)	Proline (0.01M)
0.0	4.8	20	71
0.5	4	16	61
1	3.5	13	52
1.5	3	11	48.2

Table (5)
The values of rate constants of AA at different temperatures.

Temp. K	$k_{exp}(s^{-1})/*10^4$		
	Alanine (0.01M)	Arginine (0.01M)	Proline (0.01M)
298.15	12	22	82
303.15	18	32	117
308.15	34	54	168
313.15	48	70	234

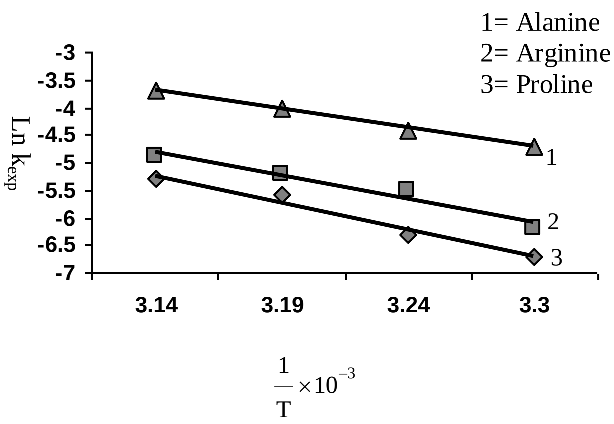

Fig. (7) : A plot of Arrhenius equation for the reaction of AA.

Table (6)
The values of some thermodynamic parameters of AA.

Parameters	Alanine	Arginine	Proline
k_{exp} / $s^{-1}x10^4$	12	22	82
Ea / KJ mol^{-1}	83.14	75	58.36
ΔH^* / KJ mol^{-1}	80.56	72.53	55.79
ΔS^* / J mol^{-1} K^{-1}	-76.5	-96	-128
ΔG^* / KJ mol^{-1}	103.73	101.6	94.57
A /s^{-1}	10^9	10^8	10^6

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الخلاصة

تـــم دراسة حركيـــة وميكانيكية أكسدة بعض الحوامض الفـــا- امينية بواسطـــة N-Bromosuccinimide بأستخدام التوصيلية . بينت الدراسة الحركية أن التفاعل من المرتبة الاولى لكل من الحوامض الفا-امينية و N-Bromosuccinimide . وجد أن إضافة حامض $HClO_4$ ذات تأثير سلبي على سرعة التفاعل. تم دراسة التفاعل بدرجات حرارة مختلفة وتم حساب الدوال الثرموديناميكية للتفاعل . وجد أن سرعة تفاعل الأكسدة للحوامض الامينية كانت بالترتيب الآتي:

Proline > Arginine > Alanine.