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Os (VIII) Catalyzed Oxidative Cleavage of Pyrrolidine Ring in L-Proline by Sodium Periodate ($NaIO_4$) in Alkaline Medium

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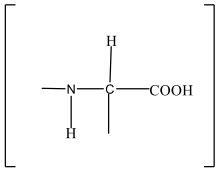
ABSTRACT

The present paper deals with the kinetic and mechanistic investigation of Os(VIII) catalyzed oxidation of proline by sodium periodate ($NaIO_4$) in alkaline medium in temperature range 30^0C to 45^0C. The experimental result shows a first order kinetics with respect to Os[VIII] and [Periodate] while positive effect with respect to substrate i.e., Proline was observed. The reaction showed negative effect for [OH^-]. Negligible effect of [$HgOAc)_2$] and ionic strength of the medium was observed. The reaction is carried out in presence of mercuric acetate as a scavenger. The reaction between sodium periodate and proline in alkaline medium shows 2:1 stoichiometry. The values of rate constants observed at different temperatures (30 to 45^0C) were utilized to calculate the activation parameters. A mechanism involving the complex formation between catalyst, substrate and oxidant has been proposed. L-glutamic acid has been identified as main oxidation product of the reaction chromatographically and spectroscopically. Based on kinetic data, reaction stiochiometry and product analysis of the reaction a feasible mechanism has been proposed. The rate law has been derived from obtained kinetic data.

Keywords: Kinetics, Os(VIII), Oxidation, Proline, Sodium Periodate, Alkaline Medium.

I. INTRODUCTION

Amino acids are the derivatives of protein in the diet or degradation of intracellular proteins is the final class of biomolecules and their oxidation makes a significant role in production of metabolic energy. Based upon the number of carbon atoms in the α–amino acids species, they get oxidized to α-keto glutamate, succinates, fumerate and oxaloacetate etc. L-proline is one among 20 α–amino acids with five-carbon atoms in pyrrolidine skeleton. This pyrrolidine ring is opened [1] by oxidation at the carbon atom most distant from the carboxylic group to produce a Schiff's base and hydrolysis of this Schiff's base produces a linear glutamic semi-aldehyde, which is further oxidized at the same carbon leads to glutamic acid. However, the earlier reports [2] reveal that L-proline undergoes oxidation with the cleavage of pyrrolidine ring at the nearest carbon atom from the carboxylic acid group followed by decarboxylation to produce 4-amino butanol or 4-amino butyric acid, whereas D- proline leads to keto acid. Since L-proline has a cyclic structure with an imino [3] group attached at one end by -CH_2 and at other end by >CH – COOH, the cleavage at the closest carbon atom from carboxylic group is unusual. This may also be due to the less reactivity of α-carbon/hydrogen. Hence, the ring opening takes place at a carbon atom of far end from carboxylic group. Moreover, when –NH_2 group is not present at α–carbon atom, there is no other driving force remains for decarboxylation to produce butaraldehyde, butyric acid or keto acids. Some reports about the oxidation of L-proline claimed that the ring cleavage took place between the N and C of, by retaining the -NH_2



group with the main moiety without liberating ammonia, and the decarboxylation was proposed as a mechanism for the oxidation [4]. L-proline is one among non-essential amino acid and is an important component of collagen. As per a report, [3] L-proline is considered to be the world's smallest natural enzyme and it plays important role in catalysing the aldol condensation of acetone to various aldehydes with high stereo-specificity.

Many transition and non-transition metal ions in their complex form perform as good oxidants in acidic, basic or neutral medium. However, oxidation capacity is depending upon their redox potential. It is also known that the redox potential of the couple is depending upon the pH of the medium. In recent years, the use of transition metal ion such as Osmium, Ruthenium and Iridium as catalyst in various redox processes has attracted considerable interest [5-6]. The mechanism of the catalysis is quite complicated because of the formation of different intermediate complexes, free radicals and different oxidation states of osmium. Although, both osmium and ruthenium belong to the same group, their compounds are stable in different oxidation states. Osmium compounds are highly stable in +8 oxidation state where as ruthenium compounds are in +3 or +4. Hence, their catalytic role varies to a large extent; in most of the oxidations [7] of organic compounds, the reaction was independent upon substrate concentration in Ru(III) catalysis and unity or fractional order in Os(VIII) catalysis. This may be due to the large difference in their redox potentials. The redox potentials of Ru(IV)/Ru(III) is +1.3 V which is unexpectedly higher than that of Os(VIII)/Os(VI) of + 0.85 V.

Periodate is a clean and relatively selective reagent for the oxidative cleavage of organic compounds containing -hydroxy, -oxo, -amino, or -carboxyl groups. There is extensive literature on the kinetics of the periodic acid oxidation of glycols [8-9] but the kinetics of the periodate oxidation of amino alcohols [10], dicarbonyl compounds [11], and amino acids [12], has received much less attention. Oxidation with periodate has been shown to cause denaturation of proteins and inactivation of enzymes and these findings have been interpreted on the basis of attack of periodate on essential amino acids. Periodate(Per) is a two electron oxidant with a redox potential of 0.70V in alkaline medium and is a more suitable reagent for the study of oxidation reactions of both organic and inorganic substrates [13]. Further we have isolated the oxidized products in a way to arrive at a suitable mechanism on the basis of kinetic and spectral results and to compute the thermodynamic quantities of various steps. An understanding of the mechanism allows the chemistry to be interpreted, understood and predicted.

II. MATERIAL AND PROCEDURE

2.1. *Materials*

Reagent grade chemicals and double-distilled water (from alkaline $KMnO_4$ in all-glass apparatus) were used. An aqueous solution of $NaIO_4$ was prepared by dissolving $NaIO_4$ (BDH) in water and was standardized iodometrically[14]. L-proline, a colorless crystalline compound (E-Merck) was used without further purification for the preparation of aqueous stock solution. The stock solution of osmium-(VIII) was obtained by dissolving osmic acid (OsO4) (Johnson-Matthey) in 0.5 mol dm^{-3} sodium hydroxide solution and its concentration was ascertained [15] against standard ceric ammonium sulfate solution in acid medium. Aqueous solution of NaOH and NaCl were used to maintain the $[OH^-]$ and ionic strength, respectively. In the present investigation, the effect of concentration of $[NaIO_{4]}$ was studied from 0.8×10^{-3} to 5.0×10^{-3} and [L-proline] was studied between 2.0×10^{-4} to 1.3×10^{-3}. The reaction stills were blackened from outside to prevent photochemical effects.

2.2. *Kinetic Procedure*

Appropriate volumes of the solutions of substrate, NaOH, $Hg(OAc)_2$, OsO_4 and the requisite volume of doubly distilled H_2O were placed in the reaction vessel, which was located in an electrically operated thermostatic waterbath maintained at the desired temperature within the $\pm 0.1^0$C range. When the mixture attained the bath temperature, reaction was initiated by adding the required vol. of $NaIO_4$ solution, which was also placed separately in the same bath in another vessel. The kinetics of the reaction was followed by estimating the quantity of unconsumed $NaIO_4$. An aliquot (5 ml) of

the reaction mixture was withdrawn at regular time intervals and was monitored by iodometric determination of the remaining $NaIO_4$ up to two half lives of the reaction. The rate of reaction (dc/dt) in each kinetic run was determined by the slope of the tangent drawn at fixed concentrations of $NaIO_4$ in the plots of unconsumed $NaIO_4$ versus time. The order of the reaction with respect to each reactant was determined with the help of (dc/dt) values calculated for various concentrations of each reactant. The moderately higher concentration of NaOH was used to maintain the OH^- concentration in the reaction. Hence, the effect of dissolved CO_2 on the rate was examined by carrying out the kinetics in the presence of CO_2 and N_2. It was found that there was no variation of rate constants which indicates that dissolved CO_2 had no effect on rate of reaction.

III. RESULTS

3.1. *Determination of stoichiometry and product analysis*

The stoichiometric analysis of oxidation reaction of proline with sodium periodate indicates that two moles of the oxidant react with one mole of substrate. This result showed 1:2 stoichiometry according to equation. Varying [$NaIO_4$]: [Proline] ratios were equilibrated at 40^0C for 72 hrs within the experimental conditions [$NaIO_4$] >> [Proline]. Estimation of unconsumed [$NaIO_4$] in different sets showed that two mole of $NaIO_4$ was consumed in order to oxidise one mole of Proline. Accordingly, the following stoichiometry equation can be formulated.

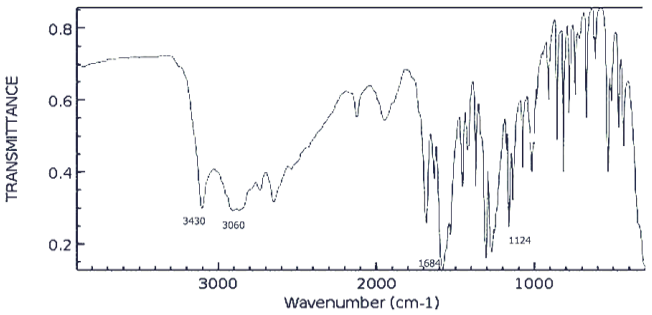


Figure 1. IR-spectrum of the main product

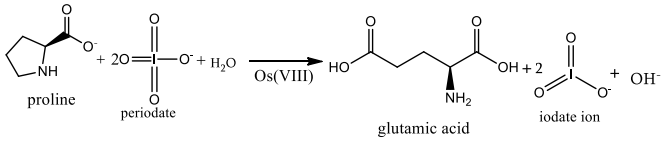
The main oxidative product of L-proline was identified as L-glutamic acid by its spot test in which the intense blue color was obtained by adding ninhydrin[16]. It supports the earlier work [17]. It is also estimated quantitatively as ninhydrin derivative by spectrophotometric methods [18]. It is found that L-proline was oxidized to L-glutamic acid. Other plausible products like glutamic semialdehyde and R-keto acid were not found.

Further, the L-glutamic acid was separated from reaction mixture by ether extract which was concentrated by evaporation and mixed with concentrated hydrochloric acid (2 ml). The residue was then evaporated several times with water (ca. 5 mL portions) to remove the excess of hydrochloric acid and finally with methanol (10 mL). The white needles produced were collected, dried, and analyzed for C, H, N, and Cl contents. The elemental analysis was consistent with that of L-glutamate hydrochloride ($C_{10}H_{17}N_2O_8Cl$). (Found: C, 40.5; H, 7.5; N, 8.6; Cl, 16.6. Calcd: C, 41.9; H, 7.3; N, 9.8; Cl, 17.2 %). Further it was subjected to IR scanning. It was observed that the stretching frequencies of -NH2, -COOH and carbonyl appeared to be 3430, 3060, and 1684 cm^{-1} respectively and C-N vibration frequencies at 1124 cm^{-1} were also observed. This clearly indicates that the oxidative product of L-proline was found to be L-glutamic acid which is formed by reacting with 2 moles of [$NaIO_4$] as shown in equation 1.

3.2 Reaction Orders

Reaction order and order with respect to each reactant was determined by varying the concentrations of oxidant, reductant, catalyst and alkali in turn, while keeping the others constant.

Equation 1



3.3 Effect of [L-Proline]

The dependence of reaction rate on L-proline concentration was examined over concentrations in the range (0.13-2.00) $\times 10^{-3}$ mol dm^{-3} at different temperatures in the range 30-45^0C. The results in (Table 1) showed that the rate constant increased with the increase in [L-proline]. Further the plot of dc/dt versus [L-proline] was linear (Figure1), passing through the origin according to equation 2. The zero intercept revealed that the self decomposition of $NaIO_4$ did not take place under the experimental conditions employed in this study.

$k_{obs} = k_2[proline]$ (2)

3.4 Effect *of Concentration of Alkali*

At a fixed ionic strength of 0.5 mol dm^{-3} and other conditions remaining constant, $[OH^-]$ was varied from 0.083 to 0.50 mol dm^{-3}. It was noticed that as $[OH^-]$ decreases the rate of reaction was increased (Table 1). The plot of log dc/dt versus log $[OH^-]$ was linear (Figure2). Its decreasing effect on rate is due to the variation of concentration of hydroxide species of Os(VIII) at different $[OH^-]$. The various forms of hydroxide complexes in alkaline medium such as $[OsO_3(OH)_3]^-$, $[OsO_4(OH)_2]^{2-}$, and $[OsO_5(OH)]^{3-}$ are in equilibrium with each other.

3.4 Effect of Temperature

The effect of temperatures on the reaction rate were studied over the range 30–45^0C and keeping all the other parameters at constant values. The dc/dt values increased with increase in the temperature. Plots of 1/T versus [4+log K] at different temperatures were linear (Figure 3). Thermodynamic activation parameters, associated with k_2K_1, were calculated using a least-squares fit to the transition state theory equation as, ΔH^* = 69.0 kJ mol^{-1} and, ΔS^* = -21.42JK^{-1} mol^{-1}. Both ΔH^* and ΔS^* are composite values that include formation of the precursor intermediate complex and the intramolecular electron transfer step. The reaction was endothermic as indicated from the positive value of ΔH^*, and the intermediate was rigid as indicated from the negative value of the entropy of activation (ΔS^*).

IV. Discussion

The variation of concentration of Os(VIII) with alkali as shown in Figure 2 indicates that $[OsO_4(OH)_2]^{2-}$ is the reactive species; its concentration was varied linearly with [OH-]. The concentrations of the other two species, $[OsO_5(OH)]^{3-}$ and $[OsO_3(OH)_3]^-$ are either decreased or increased drastically with various $[OH^-]$ and are not varied parallel to the variation of dc/dt for different $[OH^-]$. Hence, they are not considered as reactive species. The formation of $[OsO_4(OH)_2]^{2-}$ is important in this study as reported earlier[19].Each fractional order in [OH-] and [L-proline] is an implicit fact to support the expectation of the pre-equilibrium before rate determining step. First-order in oxidant and catalyst can also be accommodated in the mechanism as shown in Scheme 1. Hence, the scheme is written in accordance with the above facts and the consideration of active species of Os(VIII) in alkali as $[OsO_4(OH)_2]^{2-}$ in the first equilibrium step.

L-Proline has two donor atoms namely, N from imino moiety and O from the carboxylic group having a lone pair of electrons. It is a known [20] fact that N is a small potent atom and can donate a pair of electrons to the central metal ion of Os(VIII) to form an adducts. The presence of two $-CH_2$ groups on either side of the N atom favours the positive charge on the N atom and makes it easy to form the complex. Thus, formation of a complex between Os(VIII) and an O atom of carboxylic group can be ruled out. The adduct formed in this way with N might be very reactive and undergoes oxidation easily by $NaIO_4$. This is evidenced by the fact that in the absence of Os(VIII), the reaction between L-proline and $NaIO_4$ was not observed. Therefore, the intermediate as shown in the second step of Scheme 1 reacts with $NaIO_4$ in the rate- determining step to give an intermediate from L-proline. This justifies the unit order each in oxidant and catalyst. The mechanism as in Scheme 1 and rate law are verified by plotting the graphs of dc/dt versus 1/ [OH-] and 1/ [L-proline] which should be linear (Figure1, 2). From the slopes and intercepts of such plots, the values of *k, K*1, and *K*2 are calculated. The K_1 found in this study is in close agreement with the reported value [19]. This justifies the formation of $[OsO_4(OH)_2]^{2-}$.

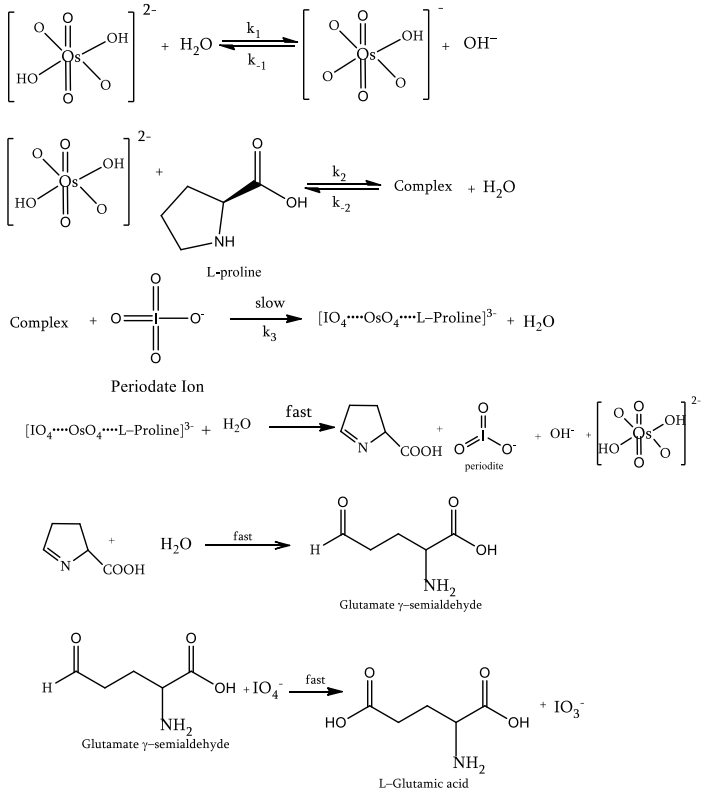
A negative value of ΔS^* (-21.42 J K^{-1} mol^{-1}) suggests that the two ionic species combine in rate determining step to give a single intermediate complex which is more ordered than the reactants [21,22]. The smaller rate constant of the slow step of the mechanism indicates that the oxidation presumably occurs through an inner-sphere mechanism. This conclusion was supported by earlier reports [23-25].

V. CONCLUSION

Thus, in the oxidation of L-proline by $NaIO_4$ in alkaline media, it has been found that $NaIO_4$ itself is the main oxidizing species, and the conjugate base of L-proline is the main reducing species and the reaction was first-order dependent on both [proline] and [$NaIO_4$]. L-glutamic acid was identified as the final oxidation product. Oxidation of L-proline was set-up to mimic the biological path. The reaction product was found to be L-

glutamic acid. However, earlier studies reveal that the products were 4-amino butyric acid [3], 4-amino butaraldehyde [26], and keto acids [27]. The 4-amino butaraldehyde is the most unpredictable product, as L-proline oxidizes through a pyrrolidine ring cleavage without decarboxylation. If aldehyde is formed at all, it would be glutamic semialdehyde. In the absence of Os(VIII), the reaction between L-proline and $NaIO_4$ is almost imperceptible, whereas the addition of a small amount of Os(VIII) favours the spontaneity of the reaction. This might be the reactive species of adduct, which is formed by interacting L-proline with Os(VIII).Though Os(VIII) is used as a catalyst it did not undergo reduction to Os(VI), but it catalyzes through the formation of active adduct and regenerates in the rate determining step by reacting with NaOH.

Scheme–1



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Appendix: Derivation of Rate Law for Scheme 1

$[\mathrm{Os(VIII)}_T]$ is equal to sum of concentration of,

$$\frac{d[IO_4^-]}{dt} = rate = k_3[IO_4^-][Complex] \quad \cdots(1)$$

$$\mathrm{Os(VIII)}_T = [C_1] + [C_2] + [Complex] \quad \cdots(2)$$

$$\frac{d[C_1]}{dt} = -k_1\,[C_1][OH^-] + k_{-1}[C_2] - k_2[C_1][L-Proline] + k_{-2}[Complex] \quad \cdots(3)$$

On applying steady state approximation to equation (3) we get,

$-k_1\,C_1[OH^-] + k_{-1}[C_2] - k_2[C_1][L-Proline] + k_{-2}[Complex] = 0 \quad \cdots(4)$ Similarly we have rate of formation of $[C_2]$,

$$\frac{d[C_2]}{dt} = k_1\,[C_1][OH^-] - k_{-1}[C_2] \quad \cdots(5)$$

On applying steady state approximation to the above equation we get,

$$k_1\,[C_1][OH^-] - k_{-1}[C_2] = 0 \quad \cdots(6)$$

$$[C_2] = \frac{k_1[C_1][OH^-]}{k_{-1}} \quad \cdots(7)$$

From equation (4) and (6) we get,

$$[C_1] = \frac{k_{-2}[Complex]}{k_2[L-Proline]} \quad \cdots(8)$$

Putting the value of $[C_1]$ in equation (7) we get,

$$[C_2] = \frac{k_1 k_{-2}[OH^-][Complex]}{k_{-1}\,k_2[L-Proline]}$$

$$[C_2] = \frac{K_1[OH^-][Complex]}{K_2[L-Proline]} \quad \left\{\because K_1 = \frac{k_1}{k_{-1}}\,;\, K_2 = \frac{k_2}{k_{-2}}\right\} \quad \cdots(9)$$

Therefore from eq. (2),(8) and (9), we get total concentration of catalyst i.e,

$$\mathrm{Os(VIII)}_T = \frac{[Complex]}{K_2[L-Proline]} + \frac{K_1[OH^-][Complex]}{K_2[L-Proline]} + [Complex]$$

$$= \frac{[Complex]}{K_2[L-Proline]} + \frac{K_1[OH^-][Complex]}{K_2[L-Proline]} + [Complex]$$

$$= [Complex]\{\frac{1 + \ K_1[OH^-] + K_2[L - Proline]}{K_2[L - Proline]}\}$$

$$[Complex] = \left\{\frac{K_2[L-Proline][\ \mathrm{Os(VIII)}_T\ ]}{1+ K_1[OH^-] + K_2[L-Proline]}\right\} \quad \cdots (10)$$

Therefore, from eq. (1) and (10) we get,

$$Rate = \left\{\frac{k_3\ K_2[HIO_4^-][\ \mathrm{Os(VIII)}_T]\ [L-Proline]}{1+ K_1[OH^-] + K_2[L-Proline]}\right\} \quad \cdots (11)$$

The rate law is in agreement with all observed kinetics.

Table 1. Effect of [$NaIO_4$], [L-Proline], [$Hg(OAc)_2$] [NaOH] and Os(VIII) on Oxidation of L-Proline by $NaIO_4$Catalyzed by Osmium(VIII) in Alkaline Medium at 30 ^{0}C

$[NaIO_4] \times 10^3$ (mol dm^{-3})	$[S]\times10^2$ (mol dm^{-3})	$[Hg(OAc)_2]\times10^3$ (mol dm^{-3})	$[NaOH]\times10^3$ (mol dm^{-3})	(-dc/dt) (mol $dm^{-3}s^{-1}$) Leucine	$K_1\times10^2$
0.83	1.00	1.25	1.00	0.40	1.87
1.00	1.00	1.25	1.00	0.48	2.10
1.25	1.00	1.25	1.00	0.53	2.91
1.67	1.00	1.25	1.00	0.78	3.64
2.50	1.00	1.25	1.00	1.00	3.30
5.00	1.00	1.25	1.00	1.84	6.10
1.00	0.13	1.25	1.00	0.20	1.04
1.00	0.17	1.25	1.00	0.21	1.08
1.00	0.25	1.25	1.00	0.23	1.26
1.00	0.50	1.25	1.00	0.24	1.40
1.00	2.00	1.25	1.00	0.26	1.69
1.00	1.00	0.83	1.00	0.33	1.85
1.00	1.00	1.00	1.00	0.29	1.73
1.00	1.00	1.67	1.00	0.27	1.86
1.00	1.00	2.50	1.00	0.28	1.10
1.00	1.00	5.00	1.00	0.30	1.03
1.00	1.00	1.25	0.83	0.28	1.42
1.00	1.00	1.25	1.25	0.23	1.34
1.00	1.00	1.25	1.67	0.21	1.19
1.00	1.00	1.25	2.50	0.20	1.03
1.00	1.00	1.25	5.00	0.19	0.84

Table 2

Activation parameters for Os(VIII) catalyzed oxidation of L-Proline by $NaIO_4$ in alkaline medium at 30-45^{0}C

Parameters	Temperature(^{0}C)	L-Proline
$k_1 \times 10^4 s^{-1}$	30^0	1.96
$k_1 \times 10^4 s^{-1}$	35^0	2.44
$k_1 \times 10^4 s^{-1}$	40^0	3.90
$k_1 \times 10^4 s^{-1}$	45^0	3.56
Log A	...	14.45
Ea* (k J mol^{-1})	35	82.93
Δ G* (k J mol^{-1})	35	71.83
Δ H * (k J mol^{-1})	35	80.35
Δ S* ($JK^{-1}mol^{-1}$)	35	-6.61

Solution Condition: Os(VIII)=2.63x10^{-6}M, [$NaIO_4$]=1.00x10^{-3}M, L-Proline=1.00 x 10^{-2}M, [$Hg(OAc)_2$]=1.25x10^{-3}M, [NaOH]=1.00×10^{-3}M.

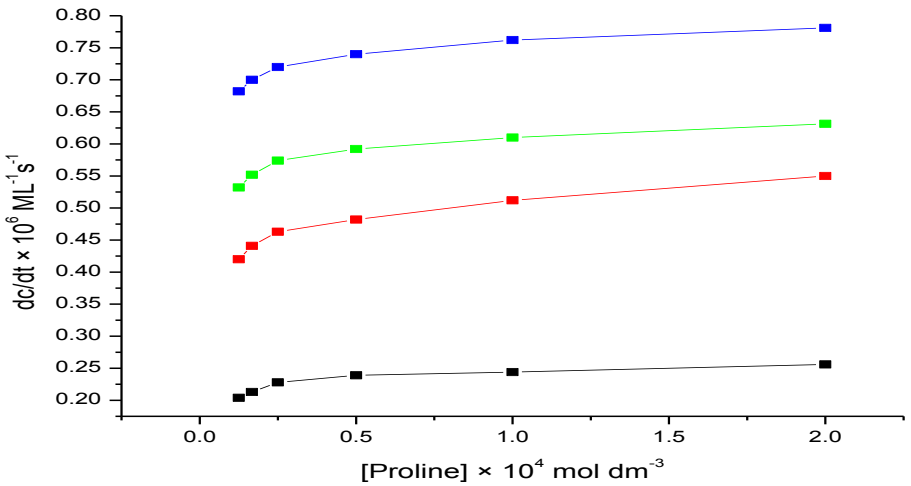

Figure 1. Plot between rate of reaction (-dc/dt) × 10^6 vs [L-Proline] × 10^4 on the reaction rate at different temperature (^{0}C). [Os(VIII)] = 26.25 X 10^{-5} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3} M, [Oxidant ($NaIO_4$)] = 1.00 X 10^{-3} M, [NaOH] = 1.00 X 10^3 M

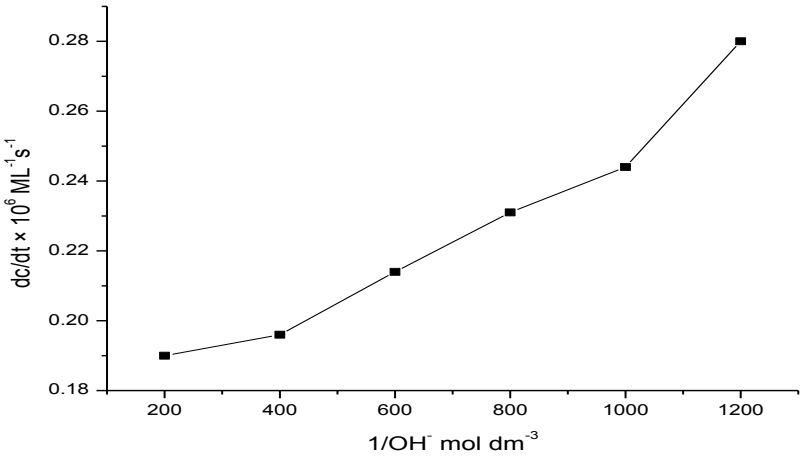

Figure 2. Plot between rate of reaction (-dc/dt) × 10^6 vs [1/OH^-] for the oxidation of L-Proline at 35^0C. [Os(VIII)] = 26.25 X 10^{-5} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3} M, [Oxidant ($NaIO_4$)] = 1.00 X 10^{-3} M, [L-Proline] = 1.00 X 10^2 M

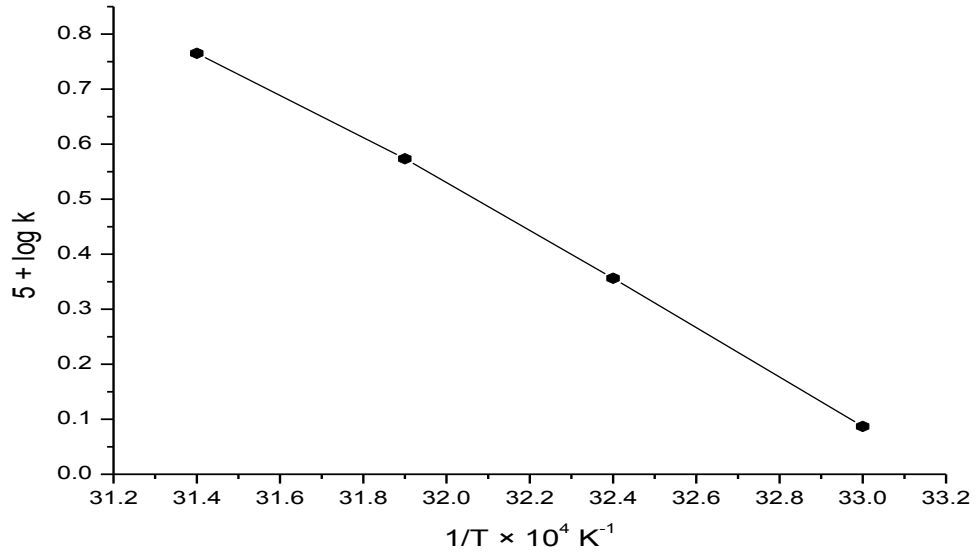

Figure 3. Plot between 5+log K vs 1/T for the oxidation of L-Proline at 35^0C. [Os(VIII)] = 26.25 X 10^{-5} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3} M, [Oxidant ($NaIO_4$)] = 1.00 X 10^{-3} M, [L-Proline] = 1.00 X 10^2 M, [NaOH] = 1.00 X 10^3 M

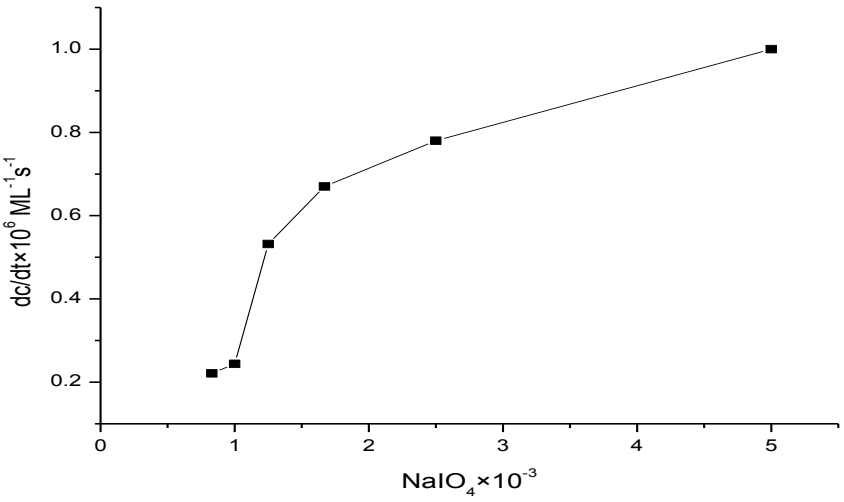

Figure 4. Plot between rate of reaction (-dc/dt) vs [$NaIO_4$] for the oxidation of L-Proline at 35^0C. [Os(VIII)] = 26.25 X 10^{-5} M, [$Hg(OAc)_2$] = 1.25 X 10^{-3} M, [L-Proline] = 1.00 X 10^2 M, [NaOH] = 1.00 X 10^3 M

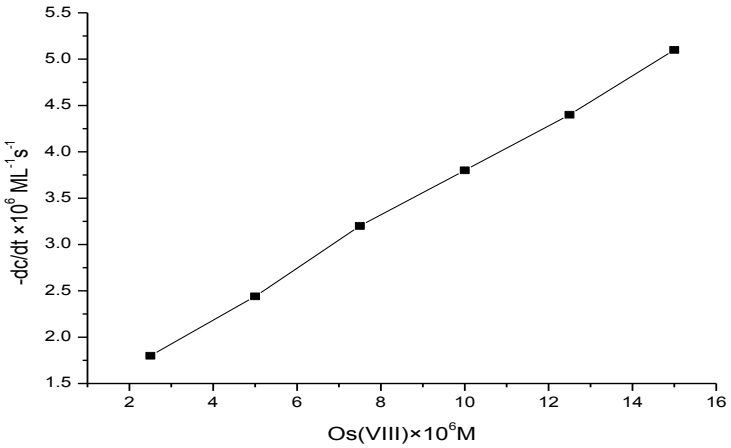

Figure 5. Plot between rate of reaction (-dc/dt) vs [Os(VIII)] on the reaction rate at 35^0C. $Hg(OAc)_2$] = 1.25 X 10^{-3} M, [Oxidant ($NaIO_4$)] = 1.00 X 10^{-3} M, [L-Proline] = 1.00 X 10^2 M, [NaOH] = 1.00 X 10^3 M