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OS (VIII) Catalysed Oxidation of L- Arginine by ferrate (VI) in Alkaline Medium: A Kinetic Study

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Abstract

Os (VIII) promoted oxidation of L-arginine by Fe(VI) has been studied spectrophotometrically in alkaline medium at 885 nm. Reaction is found to be pH dependent; faster rate are observed at lower pH. Fe(VI) shows excellent oxidant properties and first order kinetics is observed with respect to it. Oxidation rate is also found to be first order with respect to catalyst, Os (VIII). Rate of reaction increases with increase in concentration of arginine but order is fractional, i.e., increase of [S] shows positive effect. Oxidation product of the reaction was found to be 1-(4-oxobutyl) guanidine along with NH_3 and carbon dioxide. A plausible mechanism conforming to the results of kinetic studies, reaction stoichiometry and product analysis has been proposed. The energy of activation, Ea^* and entropy of activation, $\Delta S^\#$ were computed and were found to be 64.62 $kJmol^{-1}$ and -33.92 JK^{-1} respectvely.

Keywords: Oxidation, L-Arginine, Ferrate (VI), Os (VIII).

Introduction

Recently considerable attention has been focused on diverse nature of the chemistry of Fe^{VI+}. Oxidative properties of ferrate (VI) has been found to be strong but selective. The reduction potential for Fe(VI)/(III) are +2.2 V to +0.7 V in acidic and basic solutions, respectively[1]. It is employed for the oxidation of many functional groups and found that it oxidised primary alcohol to aldehyde, secondary alcohol to ketone, primary amine to aldehyde and amino acid oxidised by degrading to carbonyl compound [2-5]. It also attracted interest in "green chemistry" because side product of its redox reaction are rust like iron oxides which are environmentally innocuous and for this reason K_2FeO_4 has been described as a "green oxidant.". The ferrate ion is a stronger oxidising agent than permanganate[6] and will oxidise chromium (III) to chromate[7] and ammonia to molecular nitrogen[8]. Ferrate are excellent disinfectants and are capable of removing and destroying viruses[9].

L- arginine is an ɑ-amino acid that is used in the biosynthesis of proteins. Arginine is classified as a semiessential or conditionally essential amino acid, depending on the developmental stage and health status of the individual [9]. Arginine plays an important role in cell division, the healing of wounds, removing ammonia from the body, immune function, and the release of hormones [10-12].

The uncatalyzed oxidation of arginine by alkaline ferrate has been carried out at 303K. Because the direct reaction between alkaline ferrate and arginine was very slow and Os(VIII) was found to catalyse the reaction considerably, we have undertaken detailed kinetic and mechanistic study of the title reaction in alkaline medium.

Experimental Details

Materials:

Potassium ferrate (K_2FeO_4) of high purity was prepared by the method of Thampson et al. using ferric chloride, potassium hydroxide and sodium hypochlorite. Volumetric titration analysis has been used to determine the ferrate concentration accurately.

$$2FeCl_3 + 3NaClO + 10KOH \longrightarrow 2K_2FeO_4 + 3NaCl + 5H_2O + 6KCl$$

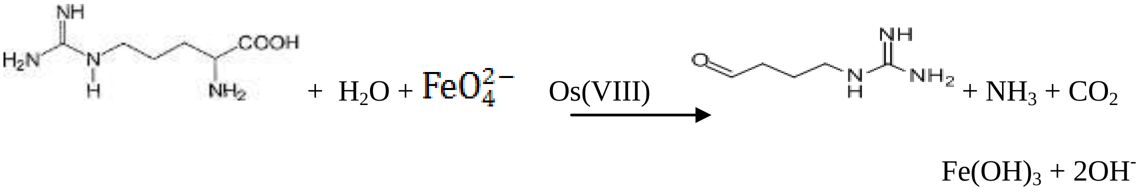
Other chemicals KCl, L- Arginine, KNO_3 used in this investigation were of A.R. grade and solution were prepared by dissolving weighed amount of samples in triple distilled water. KOH (S.D. fine) was used as a source of OH^- ions. A stock solution of OsO_4 (Johnson Matthey) was prepared by dissolving the sample in known strength of NaOH. Absorbance of the reaction mixture was recorded on systronics double beam spectrophotometer 2203 at 885 λ_{max} using water as standard.

Kinetic Procedure

Experimental task has been done by using spectrophotometer at room temperature. Requisite volumes of all reagents, including substrate, were taken in reaction vessel, then adding oxidant [K_2FeO_4] rapidly and transferring it in quartz cuvette having volume capacity 3.5ml of path length 10mm. There after fitted it in the spectrophotometer for the observation of absorbance of the reaction mixture. Absorbance of the reaction mixture was observed by varying the concentration of one reactant (0.2 g/l to 1.2 g/l oxidant, $0.2x10^{-3}$M to $1.2x10^{-3}$M substrate, $4.7x10^{-6}$ M to $28.8x10^{-6}$M catalyst and $0.4x10^{-3}$M to $2.4x10^{-3}$M for KCl, KNO_3 and KOH) and keeping concentration of other reactants constant.

Stoichiometry

Known amount of L-arginine were allowed to react with excess of ferrate in presence of Os(VIII) at 30 ^{0}C and at an ionic strength of 0.002M. The remaining amount of ferrate was analysed photospectrometrically. As per these results the stoichiometry was found to correspond to the equation.

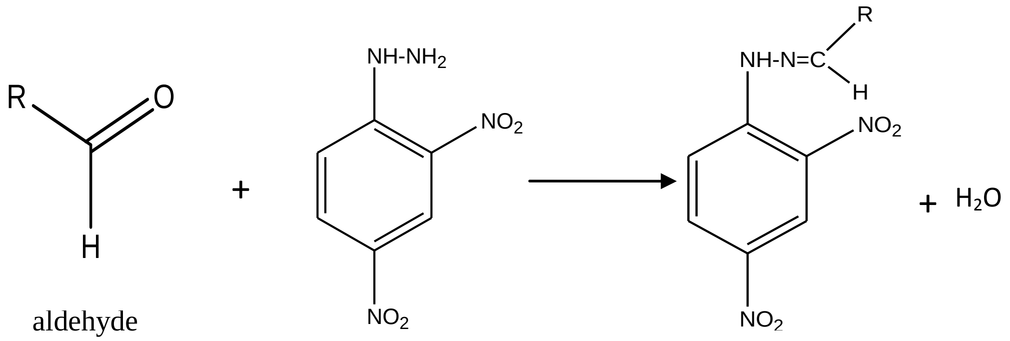


Results and Discussion

The kinetic results were collected at several set of reactant concentrations (Table 1). First order kinetics is observed with respect to the oxidant (K_2FeO_4) fig.-1; and catalyst Os (VIII) fig.-2. Positive effect is observed with respect to [S] fig.-3; and negative effect is observed with respect to [OH^-] fig.-4. Insignificant effect of increase in concentration of KCl and KNO_3 was observed, i.e., oxidation of Arginine catalysed by Os(VIII) by ferrate is not affected by Cl^- and NO_3^- radicals (Table 2).

The product formed was identified as 1-(4-oxobutyl) guanidine, Iron (III) hydroxide, ammonia and CO_2. 1-(4-oxobutyl) guanidine, was confirmed by IR spectrum of corresponding hydra zone. The reaction mixture was treated with acidified 2,4-dinitrophenyl hydrazine solution which yielded hydrazone (scheme: 1). The functional group CHO was also confirmed by Tollen's reagent and Schiff's reagent.

Similarly, ammonia was identified with the help of Nesseler's reagent and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing lime water. The separated products (yields 75-85%) were filtered and re-crystallised from alcohol. Iron (III) hydroxide was found to have no effect on the rate of the reaction.



aldehyde

2,4-dinitrophenyl hydrazine

2,4-dinitrophenyl hydrazone [2, 4-DNP derivative of RCHO]

Scheme 1: Formation of 2,4- DNP Derivatives.

[Oxidant] (Pot.ferrate) g/l	[Substrate]x 10^2 M (Arginine)	[Os(VIII)]x10^6M	(-dc/dt)x10^5ML^{-1}s^{-1}
0.20	1.00	23.50	0.40
0.40	1.00	23.50	0.55
0.60	1.00	23.50	0.82
0.80	1.00	23.50	0.96
1.00	1.00	23.50	1.20
1.20	1.00	23.50	1.50
1.00	0.20	23.50	0.60
1.00	0.40	23.50	0.78
1.00	0.60	23.50	0.90
1.00	0.80	23.50	1.10
1.00	1.00	23.50	1.20
1.00	1.20	23.50	1.30
1.00	1.00	4.70	0.35
1.00	1.00	9.40	0.65
1.00	1.00	14.10	0.80
1.00	1.00	18.80	1.05
1.00	1.00	23.50	1.21
1.00	1.00	28.20	1.60

Solution condition : [KOH]=1x10^{-3}M, [KCl]=1x10^{-3} M, & [KNO_3]=1x10^{-3}M.

Table 1: Effect of Oxidant, Substrate and Catalyst towards oxidation of arginine by Ferrate.

[KOH]x10^{3}M	**[KCl]x10^{3}M**	**[KNO_3]x 10^{3}M**	**(-dc/dt)x10^{5}ML^{-1}s^{-1}**
0.40	1.00	1.00	1.38
0.80	1.00	1.00	1.32
1.00	1.00	1.00	1.20
1.20	1.00	1.00	1.10
1.60	1.00	1.00	0.90
2.00	1.00	1.00	0.76
2.40	1.00	1.00	0.65
1.00	0.40	1.00	1.15
1.00	0.80	1.00	1.08
1.00	1.00	1.00	1.20
1.00	1.20	1.00	1.20
1.00	1.60	1.00	1.40
1.00	2.00	1.00	1.10
1.00	2.40	1.00	1.20
1.00	1.00	0.40	0.89
1.00	1.00	0.80	1.20
1.00	1.00	1.00	1.20
1.00	1.00	1.20	1.00
1.00	1.00	1.60	1.00
1.00	1.00	2.00	1.20
1.00	1.00	2.40	1.14

Solution Condition: [FeO_4^{-2}] = 1g/l, [S] = 1x10^{-2}M and [Os(VIII)] = 23.5x10^{-6}M

Table 2: Effect of KOH, KCl and KNO_3 towards oxidation of arginine by ferrate

The rate measurements were done at 30- 45 ^{o}C and specific rate constants were used to draw a plot of logk versus 1/ T,which was linear (fig-5).A thermostate water bath has been used to maintain the desired temperature. The values of activation energy (Ea*), the Arrhenius factor (A), Entropy of activation (ΔS*), free energy of activation (ΔG*) and enthalpy of activation (ΔH*) were calculated from the rate measurement at 30, 35, 40 and 45^{o}C and these values have been recorded in (Table-3).

Rate constant = log(-dc/dt)+ 5	**Temperature / ^{O}C**	**-dc/dt x10^{5}mol L^{-1}s^{-1}**
0.0792	30	1.2
0.2041	35	1.6
0.3424	40	2.2
0.4771	45	3.0
Arrhenius Parameters		
logA	35	11.04
Ea* (kJmol^{-1})	35	64.62
ΔS*(kJmol^{-1})	35	-37.41
ΔG*(kJmol^{-1})	35	76.14
ΔH* (kJmol^{-1})	35	86.43

Table 3: Activation Parameters for the oxidation of Arginine

On the basis of above discussion for the Os(VIII)-catalyzed oxidation arginine by K_2FeO_4 in alkaline medium, the following reaction steps are suggested.

Considering the negative effect of $[OH^-]$ on the rate of reaction, $[OsO_4(H_2O)_2]$ has been earlier reported as the reactive species in alkaline medium[14-16] for Os(VIII) and, the following equilibrium can be assumed to exist.

$$\underset{[C_1]}{[OsO_4(H_2O)_2]} + OH^- \underset{k_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{[C_2]}{[OsO_4\,(OH)(H_2O)]^-} + H_2O$$

$$\underset{[C_1]}{[OsO_4(H_2O)_2]} + \{S\} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{[C_3]}{[OsO_4(H_2O)\ldots.\{S\}]} + H_2O$$

$$\underset{[C_3]}{[OsO_4(H_2O)\ldots.\ \{S\}]} + [FeO_4]^{2-} \xrightarrow[k_3]{slow} [FeO_4..OsO_4...\{S\}]^{2-} + H_2O$$

$$[FeO_4..OsO_4...\{S\}]^{2-} + 4H_2O \xrightarrow{fast} Fe(OH)_3 + RCHO + NH_3 + CO_2$$
$$+ [OsO_4(H_2O)_2] + 2OH^-$$

$$Rate = \frac{-d[FeO_4^{2-}]}{dt} = k_3[FeO_4^{2-}][C_3]$$

$$Os(VIII)_T = [C_1] + [C_2] + [C_3]$$

$$\frac{d[C_1]}{dt} = -k_1[C_1][OH^-] + k_{-1}[C_2] - k_2[C_1][S] + k_{-2}[C_3] \qquad \ldots\ldots(1)$$

On applying steady state approximation to equation (1) we get,

$$-k_1[C_1][OH^-] + k_{-1}[C_2] - k_2[C_1][S] + k_{-2}[C_3] = 0 \qquad \textbf{\ldots\ \ldots\ldots\ldots(2)}$$

Similarly we have rate of formation of $[C_2]$,

$$\frac{d[C_2]}{dt} = k_1[C_1][OH^-] - k_{-1}[C_2] \qquad \textbf{\ldots\ldots\ldots\ldots\ldots(3)}$$

On applying s.s.a. to the above equation we get,

$$k_1[C_1][OH^-] - k_{-1}[C_2] = 0 \qquad \textbf{\ldots\ldots\ldots\ldots\ldots(4)}$$

$$[C_2] = \frac{k_1[C_1][OH^-]}{k_{-1}} \qquad \text{……………..….(5)}$$

From equation (2) and (4) we get,

$$[C_1] = \frac{k_{-2}[C_3]}{k_2[S]}$$

Putting the value of $[C_1]$ in equation (5) we get,

$$[C_2] = \frac{k_1 k_{-2}[OH^-][C_3]}{k_{-1}\, k_2[S]}$$

$$[C_2] = \frac{K_1[OH^-][C_3]}{K_2[S]}$$

$$\{\frac{k_2}{k_{-2}} = K_2 \; and \; \frac{k_1}{k_{-1}} = K_1\}$$

Therefore total concentration of catalyst,

$$\mathrm{Os(VIII)}_T = [C_1] + [C_2] + [C_3]$$

$$= \frac{[C_3]}{K_2[S]} + \frac{K_1[OH^-][C_3]}{K_2[S]} + [C_3]$$

$$= [C_3]\{\frac{1 + K_1[OH^-] + K_2[S]}{K_2[S]}\}$$

$$[C_3] = \left\{\frac{K_2[S][\,\mathrm{Os(VIII)}_T\,]}{1 + K_1[OH^-] + K_2[S]}\right\} \qquad \text{………… (6)}$$

Therefore,

$$Rate = \left\{\frac{k_3\; K_2[FeO_4^{-2}][\,\mathrm{Os(VIII)}_T]\,[S]}{1 + K_1[OH^-] + K_1[S]}\right\} \text{……….(7)}$$

The rate law is in agreement with all observed kinetics.

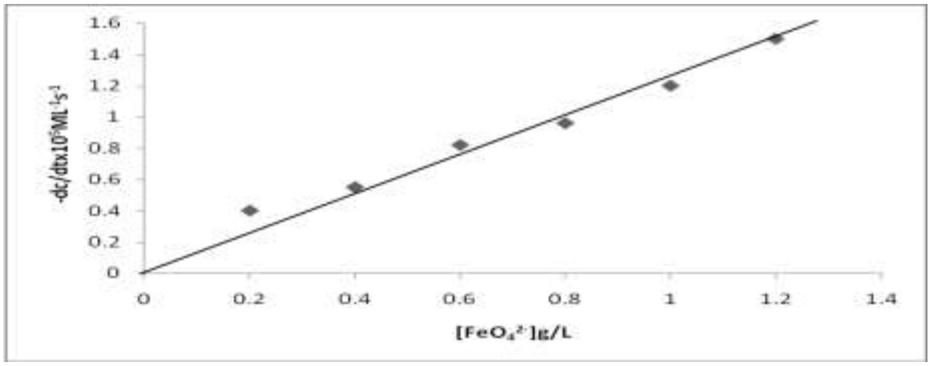


Fig.-1: Plot between (–dc/dt) x $10^5 ML^{-1}s^{-1}$ and $[FeO_4]^{2-}$g/L

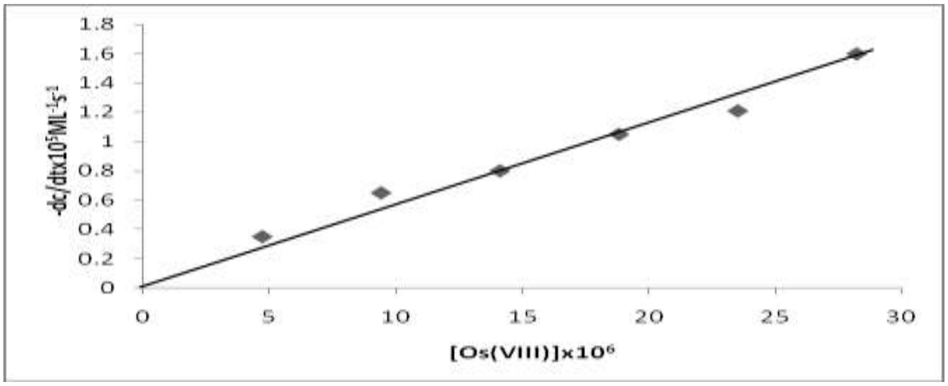


Fig.-2: Plot between (–dc/dt) x $10^5 ML^{-1}s^{-1}$ and [Os(VIII)] $x10^6$M.

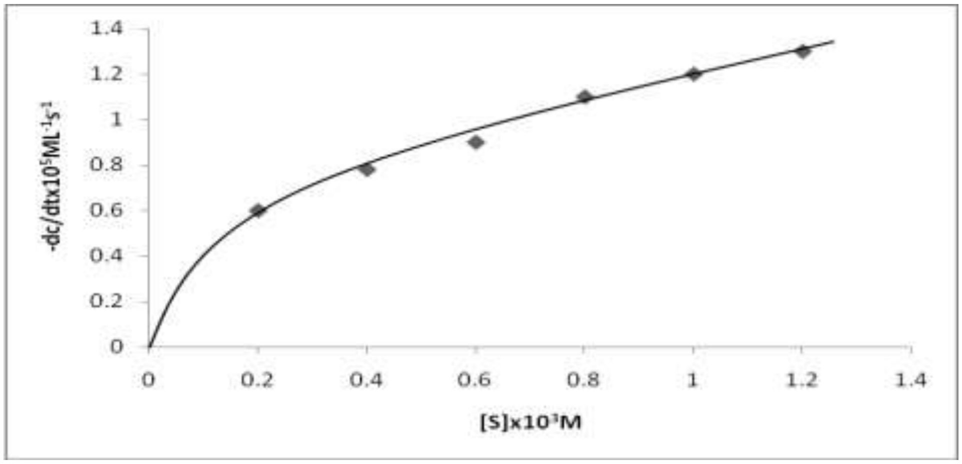


Fig.-3: Plot between (–dc/dt) x $10^5 ML^{-1}s^{-1}$ and [arginine] $x10^2$M.

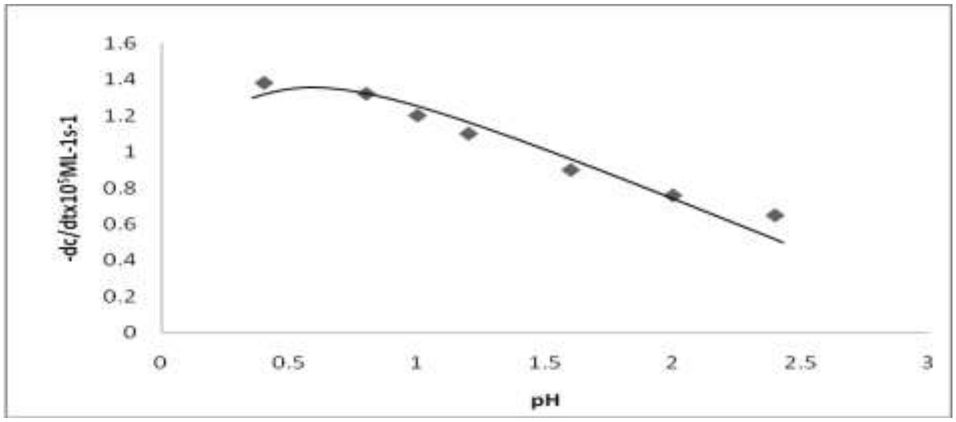


Fig.-4: Plot between (–dc/dt) x $10^5 ML^{-1}s^{-1}$ and pH.

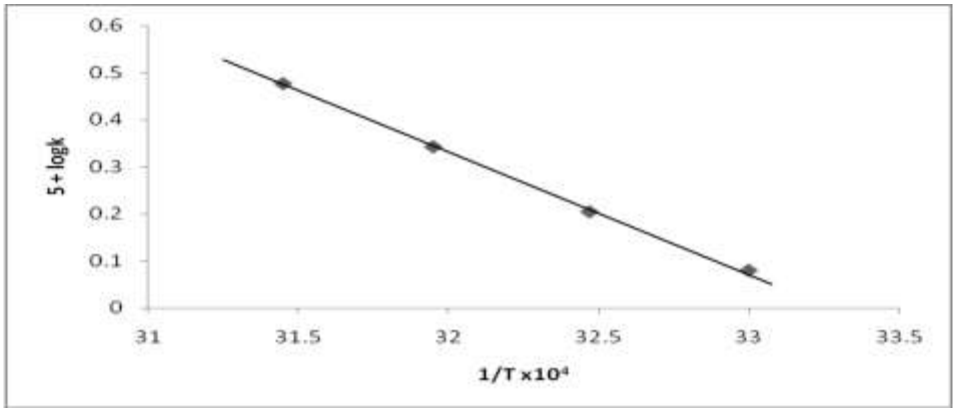


Fig.-5: Plot between logk and 1/ T

Conclusions

From the present spectrokinetic study of $[Os(VIII)]$ catalysed oxidation of arginine by $[FeO_4^{2-}]$ following points can be concluded-

- Ferrate is a dual-function chemical reagent and has great potential to oxidise amino acids throughout the entire pH range.
- $[FeO_4^{2-}]$ is found to be reactive species in present study.
- First order kinetics is observed in respect of ferrate (oxidant) and Os [VIII] (catalyst).
- $[OsO_4(H_2O)_2]$ is found to be reactive species in the present study.
- Negative effect is observed with respect to $[OH^-]$ and positive effect with respect to [arginine].
- Zero order kinetics is observed with respect to ionic species such as [KCl] & $[KNO_3]$
- $[FeO_4 ...OsO_4(OH)...\{S\}]^{2-}$ is the complex that has been reported to be formed in slow and rate determining step and produces product.

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