

Mechanism of Osmium(VIII) Catalysed Oxidation of *L*-Arginine by Periodate in Alkaline Medium - A Kinetic Study

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Abstract: The kinetics of the osmium(VIII) catalyzed oxidation of *L*-arginine by periodate has been studied spectrophotometrically in alkaline medium at 280 nm. The reaction is first order with respect to [catalyst]. The reaction showed second order dependence on [periodate], fractional order dependence on [alkali] and is independent of substrate. The oxidation product of the reaction was found to be α - keto acid. A plausible mechanism has been proposed. The energy of activation, E_a and entropy of activation, ΔS^\ddagger were computed and are found to be $53.00 \pm 1.78 \text{ kJ mol}^{-1}$ and $-46.30 \pm 5.34 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

Keywords: Oxidation of *L*-arginine, Periodate, Osmium(VIII)

Introduction

L-Arginine is one of the essential amino acid and is an important constituent of proteins. Since it is an essential amino acid it can not be synthesized by human body. The kinetics and mechanism of oxidation of arginine were studied previously using various oxidants¹⁻¹⁴. In continuation of our studies on the oxidation of *L*-arginine¹⁵⁻¹⁶, we now report the mechanism of its oxidation in alkaline medium by periodate in presence of osmium(VIII). Osmium(VIII) acts as a catalyst in several redox reactions in alkaline solution. The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of osmium.

The uncatalysed oxidation of arginine by alkaline periodate¹⁶ was studied at 323 K. Since there is no direct reaction between *L*-arginine and periodate at 303 K and since osmium(VIII) was found to catalyse the reaction considerably, we have undertaken a detailed kinetic and mechanistic study of the title reaction in 0.4 mol dm^{-3} alkaline medium.

The standard solution of *L*-arginine was prepared by using double distilled water. The other chemicals used were periodate, sodium hydroxide, osmium(VIII) and NaClO₄. All chemicals used were of AR grade. A 0.01 mol dm⁻³ solution of osmium(VIII) is prepared in 0.25 mol dm⁻³ sodium hydroxide from osmium tetroxide. Its strength is determined by taking an aliquot volume of the solution into 0.5 mol dm⁻³ hydrochloric acid, adding 10 mL of 10% KI and titrating the liberated iodine with sodium thiosulfate solution using starch as indicator. Solutions of desired concentration are prepared from this stock by suitable dilution. The reaction was initiated by mixing a calculated amount of periodate to a mixture of *L*-arginine, sodium hydroxide, osmium(VIII) and sodium perchlorate at a constant temperature of 30±0.1 °C. The progress of the reaction was followed by measuring the absorbance of periodate at 280 nm using Milton Roy 1201 UV-Visible spectrophotometer with 1 cm glass cells. The temperature is kept constant using a SISKIN JULABO V constant temperature liquid circulatory bath. Plots of 1/absorbance versus time are found to be linear even beyond 85% completion of the reaction indicating that the reaction is second order with respect to [periodate].

Results and Discussion

Known amounts of *L*-arginine were allowed to react completely with a known excess of periodate in presence of osmium(VIII) at 30 °C in 0.4 mol dm⁻³ NaOH at an ionic strength of 0.5 mol dm⁻³. The remaining periodate was then analyzed spectrophotometrically. As per these results the stoichiometry was found to correspond to the equation.

The test for free radicals was carried out by taking *L*-arginine, NaOH, Osmium(VIII) in a thumborg tube and acrylonitrile and periodate in a bent tube. After evacuating the system the solutions were mixed by tilting the tube. The reaction mixture was kept aside and even after 24 h no precipitate was observed, indicating the absence of free radicals. The main oxidation product was identified by FeCl₃ solution that gave a reddish brown precipitate indicating the presence of a keto acid. Similarly ammonia was identified by Nessler's reagent.

The [arginine] was varied in the range of 2.0-7.0x10⁻² mol dm⁻³ at 30 °C by keeping all other reactant concentrations and conditions constant. The rate constant values remain constant with increase in [arginine] (Table 1) and the order with respect to [arginine] was found to be zero.

Table 1. Effect of [periodate], [Arg], [OH⁻],[Os(VIII)] and ionic strength, on the pseudo second order rate constant (k''), at 30±0.1 °C

[periodate]x10 ³ mol dm ⁻³	[Arg]x10 ² mol dm ⁻³	Os(VIII)x10 ⁵ mol dm ⁻³	[OH ⁻] mol dm ⁻³	μ mol dm ⁻³	k'' x10 ⁶ , mol ⁻¹ dm ³ s ⁻¹
0.1	4.0	1.0	0.4	0.5	46.3
0.5	4.0	1.0	0.4	0.5	46.2
1.0	4.0	1.0	0.4	0.5	46.9
1.5	4.0	1.0	0.4	0.5	46.8
2.0	4.0	1.0	0.4	0.5	46.5
2.5	4.0	1.0	0.4	0.5	46.7
1.0	2.0	1.0	0.4	0.5	46.8
1.0	3.0	1.0	0.4	0.5	46.5
1.0	4.0	1.0	0.4	0.5	46.9
1.0	5.0	1.0	0.4	0.5	46.6
1.0	6.0	1.0	0.4	0.5	46.4
1.0	7.0	1.0	0.4	0.5	46.9
1.0	4.0	0.5	0.4	0.5	23.4

Contd....

1.0	4.0	1.0	0.4	0.5	46.9
1.0	4.0	1.5	0.4	0.5	66.5
1.0	4.0	2.0	0.4	0.5	89.9
1.0	4.0	2.5	0.4	0.5	113.4
1.0	4.0	3.0	0.4	0.5	136.9
1.0	4.0	1.0	0.20	0.8	35.2
1.0	4.0	1.0	0.25	0.8	37.1
1.0	4.0	1.0	0.30	0.8	39.1
1.0	4.0	1.0	0.35	0.8	43.0
1.0	4.0	1.0	0.40	0.8	46.9
1.0	4.0	1.0	0.50	0.8	50.8
1.0	4.0	1.0	0.60	0.8	54.7

The effect of alkali on the rate of the reaction was studied at constant concentrations of arginine and periodate and at a constant ionic strength of 0.8 mol dm^{-3} at 30°C . The rate constants obtained were found to increase with the increase in [alkali] (Table 1). Further, the plot $\log k''$ versus $\log[\text{OH}^-]$ (Figure 1) is found to be a straight line with a slope of 0.43 indicating fractional order dependence on $[\text{OH}^-]$.

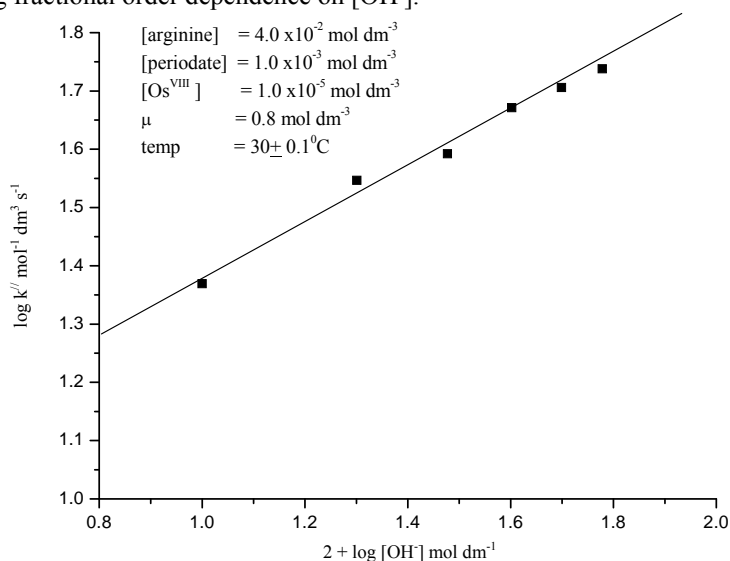


Figure 1. Plot of $\log k''$ versus $\log[\text{OH}^-]$ (order with respect to $[\text{OH}^-]$)

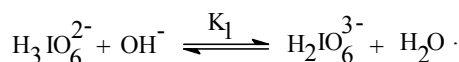
The effect of [periodate] was studied by varying the [periodate] in the reaction medium from $0.1 - 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ at constant arginine, alkali and osmium(VIII) concentrations. The rate constants obtained were presented in Table 1.

The catalyst, [osmium(VIII)] was varied in the range $0.5 - 3.0 \times 10^{-5} \text{ mol dm}^{-3}$ keeping the concentration of all other reactants constant. When the pseudo second order rate constants, k'' obtained at different [Osmium(VIII)] are plotted against [osmium(VIII)], a straight line passing through origin is noticed indicating unit order dependence on [osmium(VIII)].

The effect of ionic strength was studied by varying the $[\text{NaClO}_4]$ in the reaction medium from $0.5 - 1.0 \text{ mol dm}^{-3}$ at constant [periodate], [arginine], [alkali] and [osmium(VIII)]. The rate constants were found to remain constant (Table 1) indicating negligible effect of ionic strength on reaction rate.

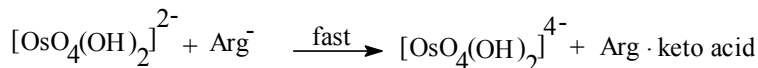
The effect of temperature on the rate is studied by carrying out the reaction at 25, 30, 35 and 40 °C and the rate constants thus obtained were found to be 35.2, 46.9, 66.9 and 93.9 mol⁻¹ dm³ s⁻¹ respectively. The plot of log k'' against $1/T$ is linear indicating that the reaction obeys Arrhenius temperature dependence. The energy of activation E_a and the entropy of activation ΔS^\ddagger are calculated using linear least squares method and found to be 53.04 ± 1.78 kJ mol⁻¹ and -46.342 ± 5.34 JK⁻¹mol⁻¹ respectively.

Under the present experimental conditions, at a $[\text{OH}^-] = 0.4$ mol dm⁻³ arginine exists in the form of anionic species, Arg⁻ (NH=C(NH₂)-NH-(CH₂)₃-CH(NH₂)-COOH). Since the rate of the reaction is independent of arginine concentration, the observed increase in rate with increase in alkali concentration is attributed to change in concentration of active periodate species according to the equation.

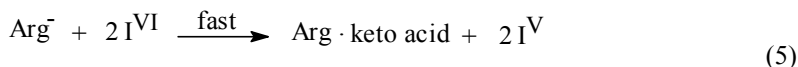
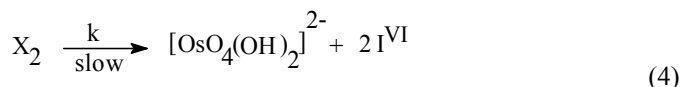
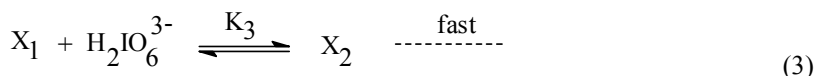
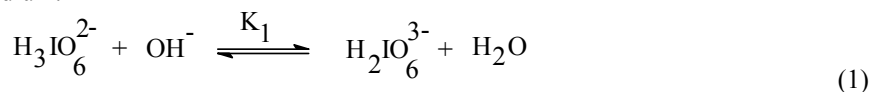


In strongly basic medium the active form of osmium(VIII) can be considered as $[\text{OsO}_4(\text{OH})_2]^{2-}$. Based on these observations the following mechanism is proposed for the osmium(VIII) catalysed oxidation of arginine by periodate.

Mechanism



Formation of osmium(VI) as intermediate in a fast step was also proposed earlier by Dikshitulu *et al.*¹⁷ in the osmium(VIII) catalysed oxidation of selenium(IV) by periodate in alkaline medium.



This mechanism leads to the rate equation,

$$\text{Rate} = \frac{-d[\text{periodate}]}{dt} = k[\text{X}_2] \quad (6)$$

Substituting for $[\text{X}_2]$ from equation(3) in equation (6) gives

$$= k K_3 [\text{X}_1] [\text{H}_2\text{IO}_6^{3-}]_e \quad (7)$$

$$k K_2 K_3 [\text{OsO}_4(\text{OH})_2]^{4-} [\text{H}_2\text{IO}_6^{3-}]_e^2 \quad (8)$$

$$[\text{per}]_t = [\text{H}_3\text{IO}_6^{2-}]_e + [\text{H}_2\text{IO}_6^{3-}]_e \quad (9)$$

$$= \frac{[\text{H}_2\text{IO}_6^{3-}] + K_1[\text{OH}^-][\text{H}_2\text{IO}_6^{3-}]}{K_1[\text{OH}^-]}$$

$$\text{Therefore, } [\text{H}_2\text{IO}_6^{3-}]_e = \frac{K_1[\text{OH}^-][\text{per}]_t}{1 + K_1[\text{OH}^-]} \quad (10)$$

Substituting for $[\text{H}_2\text{IO}_6^{3-}]$ from equation (10) in equation (8) leads to

$$\text{Rate} = \frac{k K_1^2 K_2 K_3 [\text{OsO}_4(\text{OH})_2^{2-}][\text{OH}^-]^2 [\text{per}]_t^2}{1 + K_1^2 [\text{OH}^-]^2} \quad (11)$$

The above equation explains second order dependence on [periodate], unit order with respect to [osmium(VIII)] and fractional order with respect to [alkali].

Since, $[\text{OsO}_4(\text{OH})_2^{2-}] = [\text{Os}^{\text{VIII}}]_t$, equation (11) may be written as

$$\frac{\text{Rate}}{[\text{per}]_t^2} = k'' = \frac{k K_1^2 K_2 K_3 [\text{Os}^{\text{VIII}}]_t [\text{OH}^-]^2}{1 + K_1^2 [\text{OH}^-]^2} \quad (12)$$

Taking reciprocals on both sides of equation (12) gives

$$\frac{1}{k''} = \frac{1}{k K_1^2 K_2 K_3 [\text{Os}^{\text{VIII}}]_t [\text{OH}^-]^2} + \frac{1}{k K_2 K_3 [\text{Os}^{\text{VIII}}]_t} \quad (13)$$

Equation(13) predicts the plot of $1/k''$ versus $1/[\text{OH}^-]^2$ should be a straight line with a positive intercept on Y-axis. Similar plot (Figure 2) was obtained experimentally at higher $[\text{OH}^-]$, but at lower $[\text{OH}^-]$ the deviation of points from the straight line indicates that $\text{H}_2\text{IO}_6^{3-}$ may be getting converted to $[\text{H}_3\text{IO}_6]^{2-}$, thus supporting the proposed mechanism.

Further, it is also possible to calculate the value of K_1 from the ratio of intercept to slope of the plot of $1/k''$ versus $1/[\text{OH}^-]^2$ and it was found to be $4.05 \text{ mol}^{-1}\text{dm}^3$. This value is found to be reasonably in good agreement with a value of $3.10 \text{ mol}^{-1}\text{dm}^3$ reported by Nandibewoor *et al.*¹⁸ in the ruthenium(III) / osmium(VIII) catalysed oxidation of allyl alcohol by periodate in aqueous alkaline medium, which further substantiates the proposed mechanism.

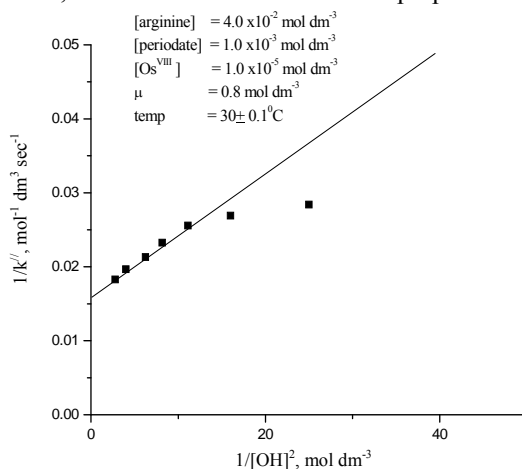
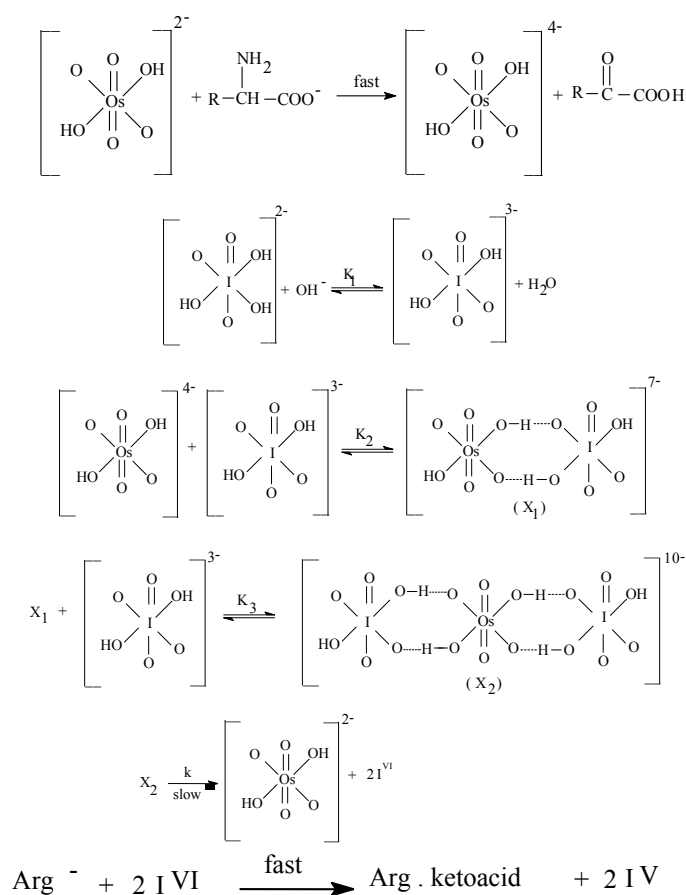


Figure 2. Plot of $1/k''$ versus $1/[\text{OH}^-]^2$

The following arguments are in support of the proposed intimate mechanism.

- Osmium(VIII) reacts with arginine to form osmium(VI) and 5-guanidino-2-oxo pentanoic acid (arginine keto acid) in a fast step.
- $\text{H}_3\text{IO}_6^{2-}$ is known to undergo dissociation in presence of alkali (>12.5 pH) to form $\text{H}_2\text{IO}_6^{3-}$.
- Osmium(VI) reacts with $\text{H}_2\text{IO}_6^{3-}$ to form an adduct(X_1)
- This adduct further reacts with another molecule of $\text{H}_2\text{IO}_6^{3-}$ in a fast step to form X_2 .
- Subsequently X_2 decomposes in a slow step to give osmium(VIII) and I(VI).
- I(VI) then reacts with arginine in a fast step to form arginine ketoacid and I(V).

Intimate mechanism



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