

Kinetics & Mechanism of Osmium Tetroxide Catalysed Oxidation of Pyridinium & Quinolinium Methiodides by Hexacyanoferrate (III) in Aqueous Alkaline Medium

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The rates of the title reactions at constant ionic strength are found to be first order in [substrate], [alkali] and [catalyst] but zero order in [hexacyanoferrate(III)]. The rates of reactions decrease with the decrease in the dielectric constant and increase with the increase in ionic strength of the medium. The entropy of activation is found to be negative. A suitable mechanism has been proposed in the light of results and product (1-methyl-2-pyridone, in the case of pyridinium salt, isolated.

IN continuation of our earlier work¹ on the kinetics of oxidation of aromatic ketones by alkaline hexacyanoferrate (III), we report in this note the results of the osmium tetroxide catalysed oxidation of pyridine and quinoline methiodides by hexacyanoferrate (III) in aqueous alkaline medium. In the absence of the catalyst, the oxidation is either extremely slow or does not proceed at all.

The methiodides of pyridine and quinoline were prepared by the reaction of the corresponding bases with the methyl iodide in 1:2 molar ratio in dry benzene: pyridine methiodide, m.p. 118° and quinoline methiodide, m.p. 133°. Potassium hexacyanoferrate (III), methanol, potassium hydroxide, and potassium chloride were of AR (BDH) grade. The solution of osmium tetroxide (0.004 M) was prepared by dissolving a known weight of the sample (Johnson Mathey, London) in aq. potassium hydroxide (0.05 M). Solutions were prepared in deionised water. Ionic strength was adjusted by adding potassium chloride.

The progress of the reaction at the desired temperature was followed by withdrawing aliquots of the reaction mixture at regular time intervals, quenching the reaction by adding ice and then estimating the amount of hexacyanoferrate (II) formed by titrating against standard ceric sulphate solution using ferroin as indicator. The standard zero order rate constants (k_0) reported are the average of duplicate runs. Diffused light did not affect the rate constants. In the stoichiometric runs the reaction mixtures ([oxidant] \gg [substrate]) were kept for 3-4 days at 30°C. It was found that one mol of substrate consumed 2 mol of oxidant. The reaction product was isolated by saturating the reaction mixture with sodium chloride followed by repeated extraction with chloroform. The product obtained after removing the solvent was purified by TLC over silica gel G using toluene-isopropyl alcohol-acetic acid-water (10 : 5 : 5 : 1) as the mobile phase. 1-Methyl-2-pyridone was detected and identified by direct com-

parison (CO-IR) with an authentic sample prepared as described by Bradlow and Vanderwerf².

Since both the substrates showed identical trends, the salient results and discussion given in the sequel refer to either of the substrate.

- (i) The rate is zero order in [hexacyanoferrate(III)] as shown by the constancy of the rate constants ($k_0 \times 10^5 \text{ M}^{-1} \text{ min}^{-1} = 14.90$ to 15.50 at 40°C , $\mu = 0.5\text{M}$, $[\text{OsO}_4] = 3 \times 10^{-6} \text{ M}$ and $[\text{pyridine methiodide}] = 0.05\text{M}$) over a ten fold variation of [hexacyanoferrate(III)] from 5 to $50 \times 10^{-3} \text{ M}$. The rate of the reaction is not affected by the added hexacyanoferrate(II).
- (ii) The rate of the reaction increases with increase in [reductant] (Table 1). The rate of the reaction is first order with respect to the concentration of pyridine and quinoline methiodides.
- (iii) The oxidation of pyridine and quinoline methiodides is directly proportional to [alkali] (Table 2) and hence the order in latter is unity.
- (iv) The rate constant increases with the increase in [catalyst]. The values of $k_0 / [\text{OsO}_4]$ show fairly concordant values at all concentrations of the catalyst (Table 3).
- (v) The rate of the reaction increases with the increase in ionic strength of the medium (Table 4) and a plot of $\log k_0$ versus $\sqrt{\mu}$ is linear, the slope corresponding to the charge of the ions produced in the rate-determining step and is equal to $4A$, indicating an ion-ion reaction.
- (vi) The decrease in the dielectric constant of the medium decreases the rate constant (Table 5). The plot of $\log k_0$ versus reciprocal of the dielectric constant of the medium is linear which provides an additional evidence in favour of ion-ion reaction.
- (vii) The plot of $\log k_0$ versus $\frac{1}{\epsilon}$ is linear. The energies and entropies of activations are found to be $7.6 \text{ kcal mol}^{-1}$ and -53.5 e. u. (pyridine methiodide) and $9.2 \text{ kcal mol}^{-1}$ and -49.00 e. u. (quinoline methiodide).

TABLE 1 — DEPENDENCE OF RATE ON [PYRIDINE METHIODIDE]
[HEXACYANOFERRATE(III)] = 0.01M ; $[\text{OH}^-] = 0.15\text{M}$;
 $[\text{OsO}_4] = 3.0 \times 10^{-6}\text{M}$; $\mu = 0.5\text{M}$; TEMP. = 40°C

[Pyridine methiodide] $\times 10^2 \text{ M}$	$k_0 \times 10^5$ mol litre^{-1} min^{-1}	$k_0 \times 10^5 \text{ min}^{-1}$ [Pyridine methiodide]
2.5	7.5	3.0
5.0	15.0	3.0
7.5	22.26	2.96
10.0	32.24	3.22
12.5	39.90	3.19
15.0	45.22	3.01
17.5	53.10	3.03
20.0	59.80	2.99
22.5	67.50	3.00
25.0	75.25	3.01

TABLE 2 — DEPENDENCE OF RATE ON $[\text{OH}^-]$
 [Hexacyanoferrate(III)] = 0.01 M; μ = 0.4M; $[\text{OsO}_4]$ = 3.0×10^{-5} M; [Quinoline methiodide] = 0.05M; Temp. = 30°C

$[\text{OH}^-] \times 10^2$ M	$k_0 \times 10^5$ (mol litre ⁻¹ min ⁻¹)	$k_0 \times 10^{-3}$ [OH ⁻] min ⁻¹
1.0	3.06	3.06
2.0	6.14	3.04
3.0	9.21	3.07
4.0	12.29	3.07
5.0	15.15	3.05
6.0	18.42	3.07
7.0	21.49	3.07
8.0	25.14	3.05
9.0	28.05	3.11
10.0	31.15	3.11

TABLE 3 — DEPENDENCE OF RATE ON $[\text{OsO}_4]$
 [Hexacyanoferrate(III)] = 0.01 M; $[\text{OH}^-]$ = 0.15 M; [Pyridine methiodide] = 0.05 M; μ = 0.5 M Temp. = 90°C.

$[\text{OsO}_4] \times 10^5$ M	$k_0 \times 10^5$ (mol litre ⁻¹ min ⁻¹)	k_0 min ⁻¹ [OsO ₄]
1.0	5.20	5.20
2.0	10.20	5.14
3.0	15.00	5.00
5.0	25.45	5.01
7.0	36.01	5.14
9.0	46.05	5.11
10.0	50.02	5.00

Based on the fact that the oxidation of pyridine and quinoline methiodides by hexacyanoferrate(III) in alkaline medium is first order in [catalyst], [pyridinium salts] and $[\text{OH}^-]$ but zero order in [oxidant], a mechanism shown in scheme 1, is proposed. Thus under these conditions a probable rate law is given by Eq. (1)

$$-\frac{d[\text{Fe}(\text{CN})_6]}{dt} = k[\text{Pyridinium salt}][\text{OH}^-][\text{OsO}_4] \dots (1)$$

Since the uncatalysed oxidation does not proceed at all and hexacyanoferrate (III) is consumed without taking part in rate law, it is assumed that the hexacyanoferrate(III) does not react directly until after the rate determining step. It has been observed that if only the pyridine methiodide or quinoline methiodide and OsO_4 are taken in alkaline medium the colour of the OsO_4 immediately disappears and if the reaction mixture is acidified and titrated against a standard solution of ceric sulphate, it is found that 2 mol of ceric sulphate are consumed for one mol of OsO_4 . This leads to the conclusion that it is the reduced osmium which is oxidised in a fast step to its original octavalent state by alkaline hexacyanoferrate (III). The same argument has been advanced by Singh and co-workers³ in the oxidation of acetone and ethyl methyl ketone and Meghani and co-workers⁴ in the oxidation of glycollic acid by alkaline hexacyanoferrate (III).

The mechanism shown in Scheme I suggests one-electron transfer. It implies possible existence of free radical intermediate. But the experimental results rule out the formation of free radical intermediate and favour the formation of an ionic inter-

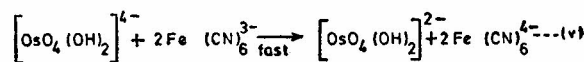
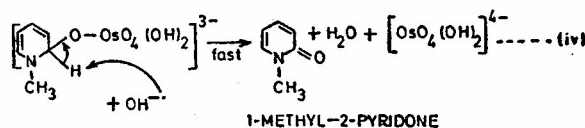
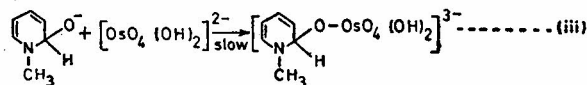
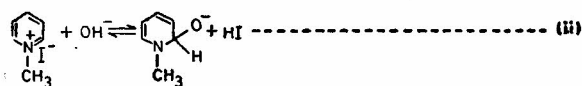
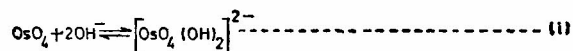
TABLE 4 — DEPENDENCE OF RATE ON IONIC STRENGTH :
 [Hexacyanoferrate(III)] = 0.01M; $[\text{OH}^-]$ = 0.04 M; [Quinoline methiodide] = 0.05M; $[\text{OsO}_4]$ = 3.0×10^{-5} M; Temp. = 30°C.

Ionic strength M	$k_0 \times 10^{-5}$ mol litre ⁻¹ min ⁻¹
0.1	8.00
0.2	10.0
0.4	12.29
0.6	14.20
0.8	16.12
1.0	18.04

TABLE 5 — EFFECT OF SOLVENT COMPOSITION ON RATE :
 [Hexacyanoferrate(III)] = 0.01M; $[\text{OH}^-]$ = 0.15 M; $[\text{OsO}_4]$ = 3.0×10^{-5} M; μ = 0.5 M.

Methanol % v/v	D			$k_0 \times 10^5$ mol litre ⁻¹ min ⁻¹			E_a - ΔS_{\ddagger} k cal/ mol e.u/ mol	
	35°C	40°C	45°C	35°C	40°C	45°C		
Nil	74.83	73.12	72.52	12.28	15.0	21.15	7.6	53.50
10	70.68	68.90	67.12	9.21	11.14	13.81	9.21	49.20
20	66.52	64.13	62.52	6.90	8.44	11.52	10.21	46.40
30	62.38	59.53	57.8	4.60	6.52	8.52	11.52	43.00

mediate. Since the reaction is influenced by the dielectric constant of the solvent and shows positive salt effect, a mechanism based on formation of a soluble complex between oxyanion and $\text{Os}(\text{VIII})$ is suggested. Further, according to the above rate law, the rate determining step involves interaction between negatively charged ions or between a negatively charged ion and a polar molecule and thus should correspond to a negative entropy change. This has been found true in many ionic reactions^{5,6}. For the reactions involving the interaction between similarly charged ions, the plots of $\log k_0$ versus reciprocal of dielectric constant would be linear having negative slope. In the present investigation, similar results have also been obtained and 1-methyl-2-pyridone has been isolated as the product



Scheme 1

of oxidation. These observations conclusively prove the existence of an ionic intermediate.

In the alkaline medium Os(VIII) exists in equilibrium with $[\text{OsO}_4(\text{OH})_2]^{2-}$. The mechanism proposed involves the formation of oxyanion of pyridine methiodide with alkali and then the formation of a complex between the oxyanion and $[\text{OsO}_4(\text{OH})_2]^{2-}$. This complex then rapidly decomposes to give 1-methyl-2-pyridone and Os(VI) ion which is oxidised in a fast step by hexacyanoferrate (III) to regenerate Os(VIII).

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Silver Ion Catalysed Oxidation of Co(II)-NTA Chelate (1:1) by Peroxydisulphate Ion

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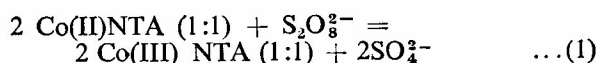
The oxidation of Co(II)NTA(1:1) by the peroxydisulphate ion shows zero order dependence on [Co(II)NTA], but first order dependence on each peroxydisulphate and silver ions (catalyst). The reaction stoichiometry shows that two mol of Co(II) NTA (1:1) consume one mol of the peroxydisulphate ion. Activation parameters have been calculated and a probable mechanism proposed.

THE peroxydisulphate oxidation of metal complexes have been studied by a number of investigators¹⁻⁷. In general, the oxidation of positively charged metal complexes is first order each in the oxidant and substrate. However the peroxydisulphate oxidation of negatively charged metal complexes exhibits a different behaviour. Ohashi and coworkers⁸ have suggested that oxidation of cobalt (II) nitrilopolyacetate with HCrO_4 in acidic media follows an inner sphere mechanism. We have presently investigated the silver ion catalysed peroxydisulphate oxidation reaction of cobalt(II) nitrilotriacetate (1:1) [Co(II)NTA(1:1)].

Co(II)NTA (1:1) was prepared by the standard method⁹. Stock solution of Co(II) NTA (1:1) was prepared by dissolving a known amount in doubly distilled water and stored in the dark. Potassium peroxydisulphate solution was prepared just before use and standardized by standard method¹⁰. The pH of the solutions was adjusted by the addition of requisite amount of acetate buffer solution. Ionic strength of the reaction mixture was maintained constant by the addition of sodium perchlorate. All the chemicals used were of AR grade.

The solutions of potassium peroxydisulphate, silver nitrate, acetate buffer and Co(II)NTA were equilibrated. For each kinetic run requisite volumes of these solutions were taken and mixed the oxidant solution being the last to be added. Aliquot of reaction mixture (2 ml) was taken at definite time intervals and diluted to 6 ml by ice cold water to quench the reaction, transferred into an optical cell (1 cm) and the absorbance of the solution measured on a Beckman model 26 spectrophotometer at 540 nm to monitor the concentration of the amount of Co(III) NTA formed in the reaction. In all the kinetic experiments [peroxydisulphate] \gg [Co(II)-NTA].

The change in absorbance with time of the Co(II) NTA(1:1) reaction solution was measured at pH 3.42 and 50°C. The results of the stoichiometric run indicated that 1 mol of the oxidant consumed 2 mol of the substrate in accordance with the Eq. (1)



At constant [substrate] ($5.0 \times 10^{-3} M$), $[\text{S}_2\text{O}_8^{2-}]$ ($5.0 \times 10^{-2} M$), $[\text{Ag}^+]$ ($1.0 \times 10^{-1} M$), pH = 3.42, ionic strength = 0.30 M and 40°C the plot of absorbance versus time was linear for 90% of the reaction indicating zero order dependence on [substrate]. There was negligible variation in the rate (from 4.5 to $4.8 \times 10^{-7} M \text{ sec}^{-1}$) at different initial [substrate] from (4.0 to $10.0 \times 10^{-3} M$) and constant [Oxidant] ($5.0 \times 10^{-2} M$), pH = 3.42, $\mu = 0.30 M$ and 50°C.

The reaction was studied at different initial [peroxydisulphate] and the ratios of rate constant upon concentration were fairly constant showing unit dependence in $\text{S}_2\text{O}_8^{2-}$.

In order to find out the order with respect to silver ion, the reaction was carried out at different initial $[\text{Ag}^+]$ and the plot of the zero order rate constant versus $[\text{Ag}^+]$ was linear indicating first order dependence on $[\text{Ag}^+]$. The rate expression for the silver catalysed oxidation of Co(II)NTA with $\text{S}_2\text{O}_8^{2-}$ is represented by Eq. (2)

$$\frac{d[\text{Co(III)NTA(1:1)}]}{dt} = k_{\text{cat}} [\text{S}_2\text{O}_8^{2-}] [\text{Ag}^+] \dots(2)$$

where k_{cat} is the rate constant for the silver ion catalysed oxidation reaction.

The rate constants for this reaction were determined at various temperatures (from 30° to 50°C). The Arrhenius plot was found to be linear. The values of activation parameters calculated from the linear Arrhenius plot at pH 3.42, $\mu = 0.30 M$ and