

Kinetics and Mechanism of Osmium(VIII) Catalysed Oxidation of 2-Aminoethanol and 3-Aminopropanol by Hexacyanoferrate(III) in Alkaline medium

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The kinetics of the osmium(VIII) catalysed oxidation of 2-aminoethanol and 3-aminopropanol by hexacyanoferrate(III) in alkaline medium have been studied spectrophotometrically. The reaction is first order each in oxidant, alkali and catalyst. The effect of substrate on rate of reaction is negligible in each case. A retarding effect of hexacyanoferrate(II) on the rate of reaction is observed. A suitable mechanism has been proposed for the oxidation process.

INTRODUCTION

The studies on oxidation of aminoalcohols by various oxidants^{1,2} in presence as well as in absence of the catalysts *viz.* osmium(VIII), ruthenium(III) etc. have shown a complex kinetics. However, the oxidation of primary aminoalcohols by hexacyanoferrate(III) does not proceed in absence of the catalyst. Therefore, in this communication the kinetics of Os(VIII) catalysed oxidation primary aminoalcohols *viz.* 2-aminoethanol and 3-aminopropanol by hexacyanoferrate(III) in alkaline medium are reported and a mechanism consistent with kinetic data is proposed.

EXPERIMENTAL

The reagents employed were ethanolamine, 3-aminopropanol (both AR grade), $K_3[Fe(CN)_6]$ and NaOH (both BDH, AR grade) and OsO_4 (Johnson-Matthey). Other reagents used were of AR grade. All the solutions were prepared in doubly distilled water. The solution of OsO_4 was prepared by dissolving the sample in very dilute NaOH. The final strength of osmium tetroxide and NaOH were kept at 15.7×10^{-3} M and 0.05 M respectively.

A thermostated water bath was used to maintain the desired temperature within $\pm 0.1^\circ C$. The rates were measured spectrophotometrically by monitoring the absorbance due to hexacyanoferrate(III) as a function of time at 420 nm on a Baush and Lomb spectronic-20 spectrophotometer. The absorbance due to hexacyanoferrate(II) and the catalyst were negligible at the chosen wavelength. The concentration of hexacyanoferrate(III) was kept below 5.0×10^{-4} M in order to comply with Beer's law.

Stoichiometry of the reaction shows that each molecule of aminoalcohol

(2-aminoethanol or 3-aminopropanol) consumes two molecules of hexacyanoferrate(III) in presence of catalyst Os(VIII).

The formic acid and acetic acid as the end products were detected by spot tests³. The carbon-carbon and carbon-nitrogen cleavage products resulting from the oxidation of aminoalcohols by other oxidants have also been reported previously^{4,5}. The osmium(VIII) catalysed oxidation of aldehydes by hexacyanoferrate(III) in alkaline medium is also reported⁶. Therefore, it is likely that aminoalcohols first give the aldehydes as the intermediate products which are further oxidised to give corresponding acids as the end products.

RESULTS AND DISCUSSION

The reactions were studied at different initial concentrations of the reactants. The log (absorbance) versus time plots in hexacyanoferrate(III) were found to be good straight lines and therefore the pseudo-first-order rate constants in hexacyanoferrate(III) (k_{obs}) were evaluated from their slopes. The observed rate constants (k_{obs}) remained nearly same on changing hexacyanoferrate(III) concentrations (Table 1) which further confirmed first order dependence of rate with respect to hexacyanoferrate(III). The pseudo-first order rate constants in hexacyanoferrate(III) at various initial concentrations of the aminoalcohols are also given in Table 1, which clearly indicate an independent nature of rate on substrate.

TABLE 1

EFFECT OF REACTANTS ON RATE CONSTANTS AT 35°C

[K ₃ Fe(CN) ₆] × 10 ⁴ M	[Aminoalcohols] × 10 ³ M	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$	
		2-amino-ethanol	3-amino-propanol
3.0	5.0	11.05	11.70
3.5	5.0	11.81	11.32
4.0	5.0	11.05	11.13
4.5	5.0	12.28	10.36
5.0	5.0	10.74	10.36
5.0	3.0	10.36	10.93
5.0	7.5	10.74	9.97
5.0	10.0	10.36	10.17
5.0	15.0	10.36	9.97

[OH⁻] = 1.0×10^{-2} M and [Os(VIII)] = 3.14×10^{-4} M.

The effect of $[\text{OH}^-]$ was studied at a fixed ionic strength ($\mu = 0.02 \text{ mol dm}^{-3}$) maintained by sodium perchlorate. The amount of NaOH already present in the catalyst was taken into account. The plots of k_{obs} versus $[\text{OH}^-]$ and $[\text{Os(VIII)}]$ are linear passing through the origin (Figure 1) showing first order dependence of rate in both $[\text{OH}^-]$ and $[\text{Os(VIII)}]$.

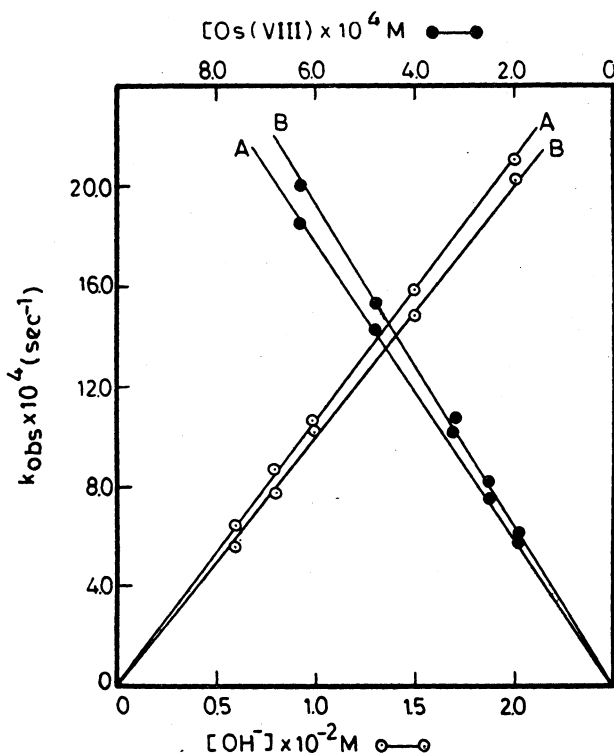


Fig.1

Fig. 1. Plots of k_{obs} versus $[\text{Os(VIII)}]$ or $[\text{OH}^-]$ at 35°C . A, 2-aminoethanol, B, 3-aminopropanol, $[\text{hexacyanoferrate(III)}] = 5.0 \times 10^{-4} \text{ M}$ and $[\text{Aminoalcohols}] = 5.0 \times 10^{-3} \text{ M}$. $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$ in case of k_{obs} vs $[\text{Os(VIII)}]$ plots, $[\text{Os(VIII)}] = 3.14 \times 10^{-4} \text{ M}$ in case of k_{obs} vs $[\text{OH}^-]$ plots.

Addition of a neutral salt ($[\text{NaClO}_4] = 0.05$ to 2.0 M) resulted in a slight increase in rate constant (Table 2). The values of observed rate constants (k_{obs}) were decreased on addition of hexacyanoferrate(II) (Table 2) in the reaction mixture. The rates were also measured at 35 , 40 , 45 and 50°C and the energies of activation calculated from Arrhenius plots for 2-aminoethanol and 3-aminopropanol were as 49.78 ± 0.05 and $80.41 \pm 0.05 \text{ kJ mol}^{-1}$ respectively.

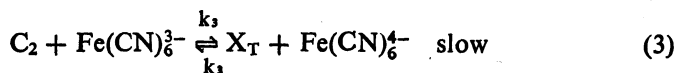
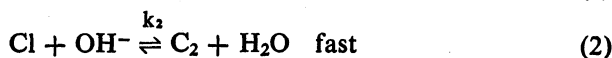
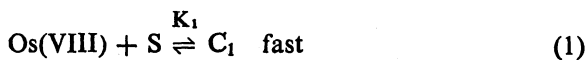
TABLE 2
EFFECT OF ADDITION OF HEXACYANOFERRATE(II)
AND NaClO₄ ON RATE CONSTANTS AT 35°C

[K ₄ Fe(CN) ₆] × 10 ⁴ M	[NaClO ₄] M	k _{obs} × 10 ⁴ sec ⁻¹	
		2-amino ethanol	3-amino propanol
Nil	—	10.74	10.36
2.0	—	8.82	9.02
3.0	—	7.10	8.84
4.0	—	5.56	7.67
5.0	—	4.60	6.90
—	Nil	10.74	10.36
—	.05	12.28	11.89
—	.10	13.62	13.43
—	.15	14.96	14.77
—	.20	16.50	16.12

[Hexacyanoferrate(III)] = 5.0 × 10⁻⁴ M, [Substrate] = 5.0 × 10⁻³ M
[OH⁻] = 1.0 × 10⁻² M and [Os(VIII)] = 3.14 × 10⁻⁴ M.

The oxidation of 2-aminoethanol and 3-aminopropanol by hexacyanoferrate(III) do not proceed in absence of the catalyst. However, in presence of catalyst a first order dependence of the rate on [oxidant], [catalyst] and [OH⁻] is observed.

The formation of an intermediate complex between the aminoalcohol and catalyst has been reported during the oxidation of aminoalcohols by other oxidants^{1,2} in presence of catalyst *viz.* ruthenium(III) or osmium(VIII). On the basis of these facts and experimental results the mechanism for the oxidation of 2-aminoethanol and 3-aminopropanol may be represented as follows:



(where S represents aminoalcohol).

According to above scheme the rate of disappearance of hexacyanoferrate(III) is given by

$$-\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = k_4[\text{X}_T] \quad (5)$$

where

$$[X_T] = \frac{k_3[C_2][Fe(CN)_6^{3-}]}{[k_3[Fe(CN)_6^{4-}] + k_4]} \quad (6)$$

Also, from steps (1) and (2)

$$[C_2] = K_2[C_1][OH^-]$$

or

$$[C_2] = K_1K_2[OH^-][Os(VIII)][S] \quad (7)$$

Now the total concentrations of osmium(VIII) are given by

$$[Os(VIII)]_T = [Os(VIII)] + [C_1] \quad (8)$$

By determining the concentration of Os(VIII) in terms of total concentration *i.e.* $[Os(VIII)]_T$, the rate law equation may be represented as

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{k_4k_3k_1k_2[S][OH^-][Os(VIII)]_T[Fe(CN)_6^{3-}]}{\{1 + K_1[S]\}\{k_4 + k_3[Fe(CN)_6^{4-}]\}} \quad (9)$$

Since step (1) is very fast, $K_1[S] \gg 1$ may be taken as a suitable approximation and the rate law equation (9) reduces to (10)

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{k_4k_3k_2[OH^-][Os(VIII)]_T[Fe(CN)_6^{3-}]}{k_4 + k_3[Fe(CN)_6^{4-}]} \quad (10)$$

The experimental results, *i.e.* a first order dependence of rate with respect to hexacyanoferrate(III), catalyst and alkali and zero order dependence with respect to substrate, retarding effect of hexacyanoferrate(II), are in agreement with rate law equation (10). The involvement of similarly charged species in step (3) is supported by observed slight positive salt effect.

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