Research Paper

Kinetics and Mechanism of Osmium (VIII) Catalysed Oxidation of L-Cystine by Alkaline Hexacyanoferrate (III)

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The kinetics of osmium (VIII) catalysed oxidation of L-cystine by hexacyanoferrate(III) in alkaline medium was studied spectrophotometrically at 30^0C. The reaction showed zero order dependence with [cystine]. The reaction was first order each in [hexacyanoferrate (III)], [OH^-] and [osmium(VIII)]. The energy of activation, E_a and the entropy of activation, $\Delta S^{\#}$ were found to be 60.0±1.5kJmol^{-1} and -28.3 ± 4.9JK^{-1}mol^{-1} respectively. A plausible mechanism in which formation of an intermediate complex between $OsO_4(OH)_2^{2-}$ and hexacyanoferrate(III) in a slow step was proposed.

Key Words: Kinetics; Mechanism; Oxidation of L-cystine; Hexacyanoferrate (III); Osmium (VIII)

1. Introduction

Redox potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple in alkaline medium is +0.45V. Despite of its high redox potential, the oxidations by hexacyanoferrate (III) (HCF(III)) surprisingly do not proceed in absence of a catalyst in alkaline medium. Such behaviour of this oxidant was observed in a large number of kinetic studies of organic [1-6] as well as inorganic [7-9] substrates. Osmium (VIII), is known to act as a catalyst in hexacyanoferrate (III) oxidations by the formation of an intermediate complex and is itself converted into a lower state. Very few kinetic studies were reported on the oxidation of L-cystine, a sulfur containing dimeric non essential amino acid using oxidants like iodine [10], alkaline permanganate [11], potassium ferrate [12], chlorite and chlorine dioxide [13] and hypochlorous acid [14]. In continuation to our earlier work [15] and to have a further insight into the mechanism of its oxidation, we now carried out kinetic investigations on the oxidation of L-cystine by alkaline hexacyanoferrate (III) in the presence of osmium (VIII) as catalyst.

2. Experimental

A 0.05 mol dm^{-3} solution of L-cystine (Himedia) in 0.125 mol dm^{-3} NaOH was prepared afresh by dissolving in required volume of sodium hydroxide.

A 0.01 mol dm^{-3} solution of hexacyanoferrate (III) (E. Merck) was prepared by dissolving the requisite amount of the salt in double distilled water. The solution was standardized by measuring the absorbance using Milton Roy UV-Visible 1201 spectrophotometer at 420 nm (ε = 1060 ± 50dm^3 mol^{-1}cm^{-1}). A 0.01 mol dm^{-3} solution of osmium (VIII) was prepared in 0.25 mol dm^{-3} sodium hydroxide from osmium tetraoxide (Johnson Matthey, London). 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 thiosulphate using starch as indicator. Solution of desired concentration was prepared from this stock by suitable dilution.

An approximately 8.0 mol dm^{-3} solution of sodium perchlorate is prepared by taking 424g of

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anhydrous sodium carbonate (Analar BDH) in a tall beaker of one litre capacity and sufficient water is added to cover the solid completely. Then 690mL of 70% perchloric acid is added little by little, while stirring the mass constantly with a glass rod. After the entire solid has dissolved, the contents of the beaker are heated to boiling to expel the carbon dioxide, cooled and filtered. The pH of the solution is adjusted to 7 with dilute perchloric acid using a pH meter and the solution is finally made up to one litre. The strength of sodium perchlorate solution thus prepared is determined gravimetrically by precipitating and weighing it as potassium perchlorate.

Kinetic measurements were carried out at 30±0.1°C in 0.1 mol dm^{-3} alkaline medium under the conditions $[OH^-]$ >> [cystine] > [HCF(III)] > [Os(VIII)]. The progress of the reaction was followed by measuring the absorbance of [HCF(III)] at 420nm (Fig. 1) at which no other species except

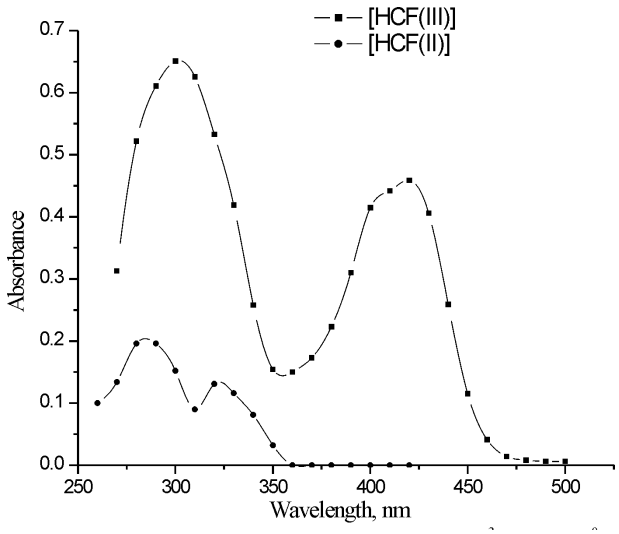


Fig. 1. Spectrum of HCF(III) and HCF(II) in 0.1 mol dm^{-3} NaOH at 30°C

hexacyanoferrate (III) has any significant absorption. Milton Roy 1201 UV-Visible Spectrophotometer with 1cm glass cells was used for the spectral work. The temperature is kept constant using a Siskin Julabo-V constant temperature liquid circulatory bath. The rate constants were found to be reproducible within ± 4%.

3. Product Analysis

The test for free radicals was carried out taking cystine, osmium (VIII) and NaOH in a thumberg tube and acrylonitrile and hexacyanoferrate (III) solution 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 24hours no precipitate was observed indicating the absence of free radical formation.

The product analysis was carried out chromatographically [16]. A slurry of the adsorbent (silica gel and cellulose powder) is spread uniformly over the plate to get a thickness of 200μm. The chromatographic plate was spotted with the reaction product and it was saturated with vapours of phenol and then run in water-saturated phenol. Development is allowed to proceed until the solvent front has travelled the required distance. After the development of the chromatogram, the plate was removed from the tank and dried. It was then sprayed with 1% solution of ninhydrin in n-butanol and heated in an oven for five minutes at 100°C. The r.f value was found to be 0.16 which was in good agreement with the value reported by Dixit and Srivastava [16].

The product was further confirmed by carrying out the microscopic study by transferring the reaction product to a dish and evaporated on a water bath at 60°C. On condensation of the solution, almost colourless mass was obtained. The mass was dissolved in 40% dilute alcohol and was re-crystallized. The crystals obtained were viewed under microscope and compared with those reported earlier by Shinohara [10] in the oxidation of cystine by iodine. In Fig. 2 the needle shaped crystals represent cysteic acid. The decomposition point was found to be 269°C which was in good agreement with those reported earlier.

Fig. 2. Needle shaped crystals of Cysteic acid

4. Results

(a) Stoichiometry of the Reaction

The reaction mixture containing an excess [HCF(III)] over [cystine] at 0.1 mol dm^{-3} NaOH at constant ionic strength in presence of osmium (VIII) is allowed to react and after completion of the reaction, the amount of ferrate (II) formed (which is equal to the amount of ferrate (III) consumed) is determined by measuring the absorbance of the reaction mixture spectrophotometrically at 420nm. It was observed that 10 moles of HCF(III) react with one mole of cystine as given by the equation

$$\text{cystine} + 10\text{HCF(III)} \xrightarrow{\text{osmium(VIII)}} 2\ \text{cysteic acid} + 10\text{HCF(II)}$$

Ionic strength effect was studied by varying the ionic strength in the range 0.10-0.40 mol dm^{-3} using sodium perchlorate and ionic strength was found to have negligible effect on the rate of the reaction. Hexacyanoferrate (II), one of the products was found to have no effect on the rate of the reaction.

(b) Reaction Orders

To determine the order with respect to hexacyanoferrate (III), kinetic runs are carried out at 30°C varying the concentrations of hexacyanoferrate (III) from 3.0-8.0x10^{-4} mol dm^{-3}, keeping the concentrations of all other ions constant. The pseudo-first order rate constants thus obtained are incorporated in Table 1. The pseudo first order rate constant, k′, obtained from the plots of log (absorbance) versus time, are fairly constant, indicating that the rate of reaction is first order with respect to [hexacyanoferrate(III)]. To find out the dependence of rate on [cystine], kinetic runs are performed varying the initial concentration of cystine and keeping the concentrations of all other species in the reaction mixture constant. The pseudo first order rate constants calculated from the slopes of these plots are recorded in Table 1 and the rate of the reaction was found to be independent of [cystine].

To study the effect of [OH^-] on the rate of the reaction, kinetic runs are carried out keeping the concentrations of all other reactants constant and varying the [OH^-] with sodium hydroxide. The pseudo first order rate constants obtained from the slopes of $\log A_t$ *versus* time plots are presented in Table 1.

Table 1. Effect of [HCF(III)], [cystine], [OH^-], [Os^{VIII}] on the pseudo first order rate constant, k′ at 30±0.1^{0}C

[HCF(III)] x10^4 (mol dm^{-3})	[cystine] x10^3 (mol dm^{-3})	[OH^-] (mol dm^{-3})	[Os^{VIII}]x10^6 (mol dm^{-3})	k′ x10^4 (sec^{-1})
3.00	4.00	0.10	8.00	1.28
4.00	4.00	0.10	8.00	1.15
5.00	4.00	0.10	8.00	1.16
6.00	4.00	0.10	8.00	1.15
7.00	4.00	0.10	8.00	1.15
8.00	4.00	0.10	8.00	1.14
4.00	2.00	0.10	8.00	1.10
4.00	4.00	0.10	8.00	1.15
4.00	6.00	0.10	8.00	1.18
4.00	8.00	0.10	8.00	1.14
4.00	10.00	0.10	8.00	1.16
4.00	12.00	0.10	8.00	1.15
4.00	4.00	0.10	2.00	3.19
4.00	4.00	0.10	4.00	6.39
4.00	4.00	0.10	6.00	9.59
4.00	4.00	0.10	8.00	11.51
4.00	4.00	0.10	10.00	14.39
4.00	4.00	0.10	12.00	19.19
4.00	4.00	0.050	8.00	0.57
4.00	4.00	0.075	8.00	0.64
4.00	4.00	0.100	8.00	1.15
4.00	4.00	0.125	8.00	1.34
4.00	4.00	0.150	8.00	1.44
4.00	4.00	0.175	8.00	1.54
4.00	4.00	0.200	8.00	1.91

Further, the plot of k′ versus [OH^-] was found to be a straight line passing through origin indicating unit order dependence on [OH^-] (Fig. 3).

To find out the dependence of rate on [osmium(VIII)], kinetic runs were carried out by varying the concentration of osmium (VIII) and keeping the concentrations of all other reactants constant and the pseudo first order rate constants

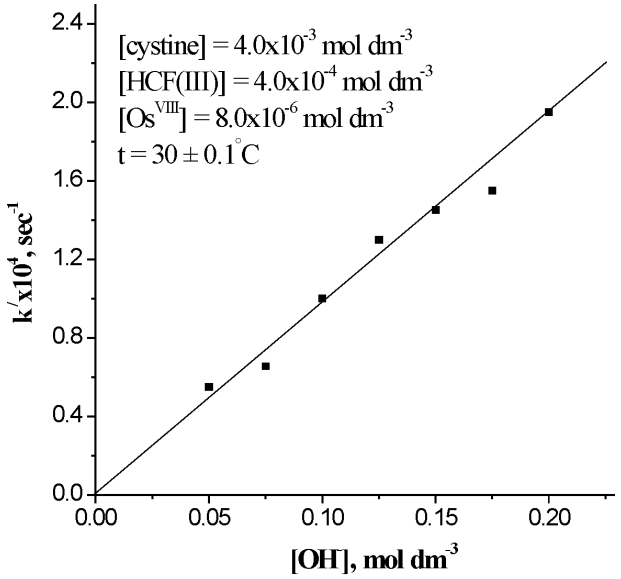


Fig. 3. Plot of k′ *versus* [OH⁻] (order with respect to [OH⁻])

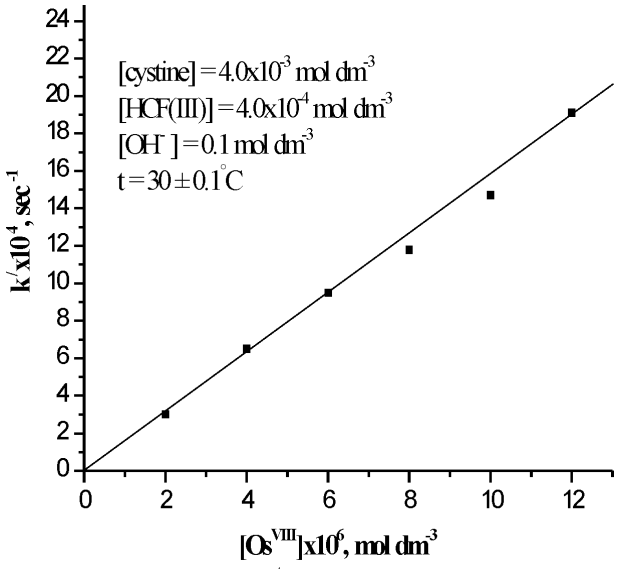


Fig. 4. Plot of k′ *versus* [osmium (VIII)] (order with respect to [osmium (VIII)]

calculated from the slopes of the log (absorbance) versus time plots are recorded in Table 1, the plot of k′ versus [osmium(VIII)] (Fig. 4) is found to be a straight line passing through origin indicating unit order dependence on [osmium(VIII)].

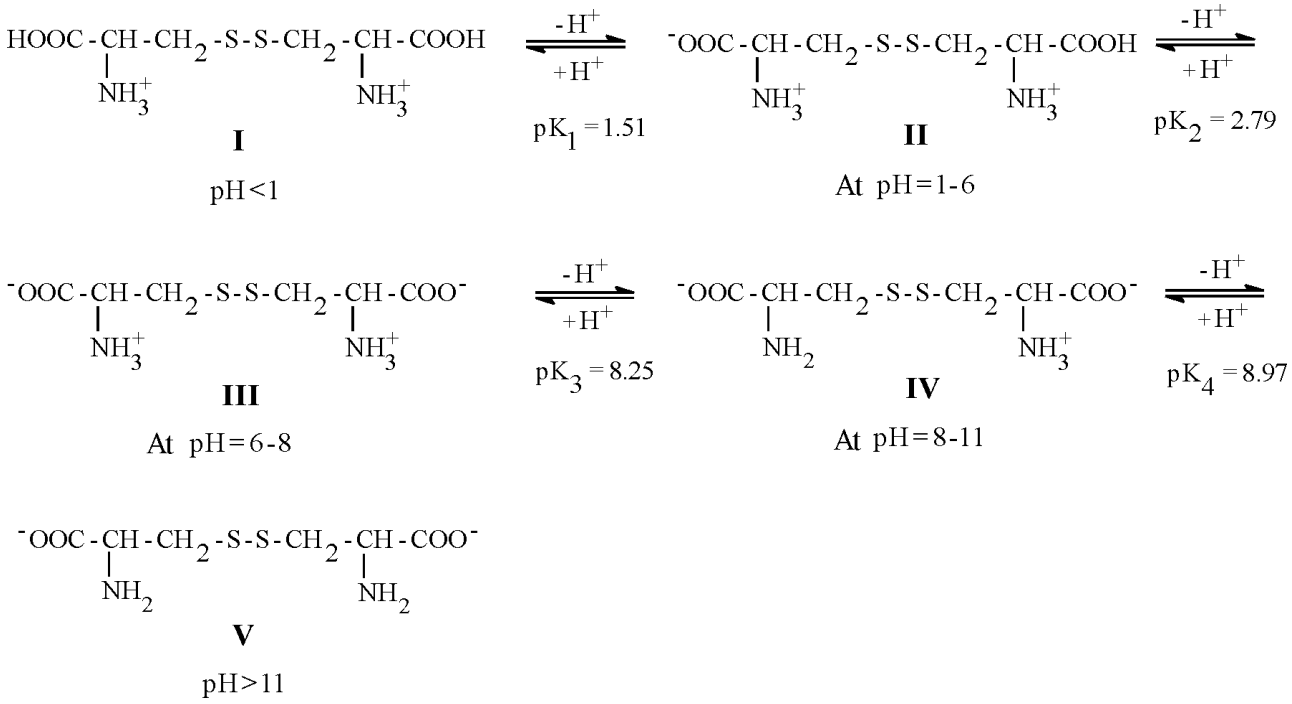
(c) Effect of Temperature

The effect of temperature on the rate of the reaction is studied by carrying out the reaction at 25, 30, 35 and 40°C. 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, $\Delta S^{\#}$ are calculated using linear least squares method and found to be $60.0 \pm 1.5 kJmol^{-1}$ and $-28.3 \pm 4.9 JK^{-1}mol^{-1}$ respectively.

5. Discussion and Conclusions

L-cystine, $[-SCH_2CH(NH_2)COOH]_2$ is a sulfur containing amino acid and it has four pK_a values. Two corresponding to the carboxylic groups $[(COOH)_1 = 1.51, (COOH)_2 = 2.79]$ and the other two for amino groups $[(NH_3^+)_1 = 8.25, (NH_3^+)_2 = 8.97]$.

Protonic Equilbria of L-Cystine



Only the predominant species existing in the respective pH ranges are shown in the above equilibria. It is obvious that cystine exists predominantly as cationic species (I & II) in acidic, as a zwitterion (III) under neutral, and as anionic species (IV & V) in alkaline conditions.

Hexacyanoferrate (III) is a one electron oxidant which is an octahedral inner orbital complex. Osmium (VIII) is known to form different complexes with OH^- and species such as OsO_4, $[OsO_4(H_2O)_2]$, $[OsO_4(H_2O)(OH)]^-$ and $[OsO_4(OH)_2]^{2-}$ coexist in fast equilibria with each other in basic medium [17]. Since the present reaction medium is strongly basic, the active form of osmium (VIII) can be assumed to be $[OsO_4(OH)_2]^{2-}$. In the present case, it was observed that there is no reaction between osmium (VIII) and cystine under the present experimental conditions. Hence, it is clear that osmium (VIII) is not involved in any redox step in the mechanism. However, osmium (VIII) is found to substantially catalyse the reaction and the order with respect to [cystine] is found to be zero. Hence it may be presumed that osmium (VIII) assists the redox reaction between hexacyanoferrate (III) and cystine. This is only possible if a complex intermediate between hexacyanoferrate (III) and osmium (VIII) species is assumed prior to its reaction with cystine. The following mechanism is proposed based on these observations.

$$OsO_3(OH)_3^- + OH^- \underset{}{\overset{K}{\rightleftharpoons}} OsO_4(OH)_2^{2-} + H_2O \qquad \text{... (1)}$$

$$OsO_4(OH)_2^{2-} + [Fe(CN)_6]^{3-} \xrightarrow[\text{slow}]{k} \text{(I)} + CN^- \qquad \text{... (2)}$$

(I)

$$I + \begin{matrix} R-S \\ | \\ R-S \end{matrix} \xrightarrow[\text{fast}]{} RS^+ + RS^{\bullet} + OSO_4(OH)_2^{2-} + Fe(CN)_5^{3-} \qquad \text{... (3)}$$

$$[Fe(CN)_5]^{3-} + CN^- \xrightarrow[\text{fast}]{} [Fe(CN)_6]^{4-} \qquad \text{... (4)}$$

$$RS^{\bullet} + [Fe(CN)_6]^{3-} \xrightarrow[\text{fast}]{} RS^+ + [Fe(CN)_6]^{4-} \qquad \text{... (5)}$$

$$2RS^+ \xrightarrow[\text{fast}]{H_2O} 2RSOH \qquad \text{... (6)}$$

$$2RSOH \xrightarrow[\text{fast}]{H_2O} 2RSO_3H \qquad \text{... (7)}$$

where R= $^-OOC\text{-}CH(NH_2)\text{-}CH_2$- .

The above scheme leads to the rate equation

$$\text{Rate} = k[OsO_4(OH)_2^{2-}][Fe(CN)_6^{3-}] \qquad \text{... (8)}$$

$$= kK[OsO_3(OH)_3^-]_e[OH^-][Fe(CN)_6^{3-}] \qquad \text{... (9)}$$

Since $[Os^{VIII}]_t = [OsO_3(OH)_3^-]_e$ under the present experimental conditions of $[OH^-]$ = 0.1mol dm^{-3}, the above equation now becomes

$$\text{Rate} = \frac{-d\,[Fe(CN)_6^{3-}]}{dt}$$

$$= kK[Os^{VIII}]_t[OH^-][Fe(CN)_6^{3-}]. \quad \ldots (10)$$

The above rate equation better explains the first order dependence with respect to [hexacyanoferrate (III)], [osmium(VIII)] and $[OH^-]$ and zero order dependence with respect to [cystine].

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