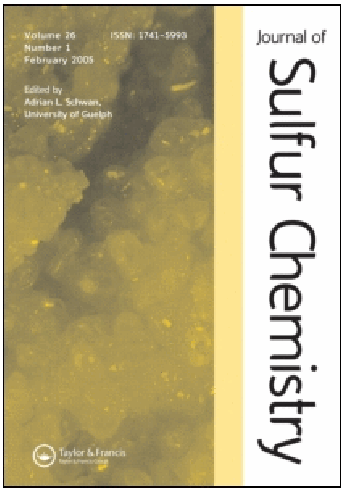

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# Osmium(VIII) catalyzed oxidation of a sulfur containing amino acid—a kinetics and mechanistic approach

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RESEARCH ARTICLE

# Osmium(VIII) catalyzed oxidation of a sulfur containing amino acid – a kinetics and mechanistic approach

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The kinetics of osmium (VIII) catalyzed oxidation of DL-methionine by hexacyanoferrate(III) (HCF) in aqueous alkaline medium at a constant ionic strength of 0.50 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between hexacyanoferrate(III) and DL-methionine in alkaline medium exhibits 2:1 stoichiometry (2HCF:DL-methionine). The reaction is of first order each in [HCF] and [Os(VIII)], less than unit order in [alkali] and zero order for [DL-methionine]. The decrease in dielectric constant of the medium increases the rate of the reaction. The added products have no effect on the rate of reaction. The main products were identified by spot test. A free radical mechanism has been proposed. In a prior equilibrium step Os(VIII) binds to OH$^-$ species to form a hydroxide species and reacts with $[Fe(CN)_6]^{3-}$ in slow step to form an intermediate species($C_1$). This reacts with a molecule of DL-methionine in a fast step to give the sulfur radical cation of methionine and yields the sulfoxide product by reacting with another molecule of $[Fe(CN)_6]^{3-}$. The rate constant of the slow step of the mechanism is calculated. The activation parameters with respect to slow step of the mechanism are evaluated and discussed.

*Keywords*: Hexacyanoferrate(III); DL-methionine; Kinetics and mechanism; Kinetics; Oxidation

## 1. Introduction

Hexacyanoferrate(III), (HCF(III)) has been widely used to oxidize numerous organic and inorganic compounds in alkaline media. The authors [1, 2] have suggested that alkaline HCF(III) ion supply acts as an electron abstracting reagent in redox reactions. However, Speakman and Water [3] have suggested different paths of oxidation of aldehydes, ketones and nitroparaffins. Singh and co-workers [4, 5], while discussing the oxidations of formaldehyde, acetone and ethyl methyl ketone have suggested that the oxidation takes place *via* an electron transfer process resulting in the formation of a free radical intermediate.

Methionine, is a sulfur containing essential amino acid which is not synthesized in the body and must be obtained from food. It contributes to supply mineral sulfur improving the tone and pliability of the skin, conditioning the hair and strengthens nails and protecting the cells from airborne pollutants. It contributes to other compounds including S-adenosyl-methionine

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(SAM), which transfers labile methyl group and sulfur to over 100 biochemical reactions for normal brain function, and L-cysteine, which is a component of glutathione, an important antioxidant molecule in the body.

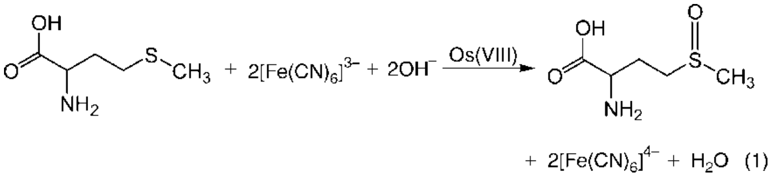
Earlier reports [6] reveal that the kinetics of osmium (VIII) catalysed oxidation of $\alpha$-amino acids by HCF(III) under first order reaction condition, the plots of log (concentration) *versus* time were not linear due to strong catalytic influence of HCF(II). As the HCF(II) is a reduction product of HCF(III), its accelerating influence was encountered in every kinetic run which showed curves with increasing slopes. However, such ambiguity was not observed in the present study. As reported by Solymosis [6], osmium tetroxide acts as a catalyst in the oxidation of many organic and inorganic substances by HCF(III). Therefore, in the present study the kinetics of osmium (VIII) catalyzed oxidation of DL-methionine by HCF(III) were investigated.

Several studies have been reported on the oxidation of DL-methionine by other oxidants such as $KMnO_4$ [7], Ce(IV) [8], and Cr(VI) [9] and pyridinium fluorochromate [10]. Different workers have identified different products by different oxidants for DL-methionine. Thus, the study of DL-methionine becomes important because of its biological significance and selectivity towards the oxidants. In view of the lack of literature on the oxidation of DL-methionine by HCF(III) and in order to explore the mechanistic aspects of HCF(III) oxidation in alkaline medium, we have chosen DL-methionine as a substrate and it is an interesting aspect to note that the uncatalyzed reaction is very very slow. However, with a trace amount of Os(VIII), reaction rate increases by nearly thousand folds. The present study deals with the title reaction to investigate the redox chemistry of HCF(III) in such media and to arrive at a suitable mechanism for the osmium(VIII) catalyzed oxidation of DL-methionine by alkaline HCF(III) ions on the basis of kinetic results.

## 2. Results and discussion

### 2.1 *Stoichiometry*

Different sets of reaction mixtures containing different concentrations of DL-methionine and HCF(III) with at constant ionic strength, osmium (VIII) and alkali were kept for *ca.* 6 h. at 26 ± 0.2 °C in an inert atmosphere in a closed vessel. When [HCF(III)] was higher than [DL-methionine], the unreacted [HCF(III)] was found by measuring the absorbance at 420 nm spectrophotometrically. The results indicated that two moles of HCF(III) consumed by one mole of DL-methionine as in equation (1).



(1)

The main reaction product was identified as DL-methionine sulphoxide, by spot test [11] and it is also confirmed as below. The reaction mixture was allowed to stand for a few hours. Then sodium bicarbonate was added and stirred vigorously, followed by a drop wise addition of benzoyl chloride solution. The precipitate *N*-benzoyl methionine sulfoxide was confirmed by its m.p. 183 °C [12]. The procedure is similar to the one employed in the oxidation of L-methionine by aqueous Cr(VI) [13]. The product is separated [14] by adding acetone–ethanol mixture (1:1) to the reaction mixture at pH 4 resulted in the precipitate. The yield was found to be of about 90% for most the different sets of reaction mixtures. This also confirmed by its m.p. (238 °C). The spectra of I.R. showed that the stretching for $-NH_2$ and $-COOH$ were remained same. However, the new band for $>S=O$ is appeared at $1032\,cm^{-1}$ for the product. No change in the NMR signals was observed. The reaction products do not undergo further oxidation to sulfone under the present kinetic conditions. This was confirmed by the test for sulfone [11].

### 2.2 *Reaction order*

The order with respect to [DL-methionine], [HCF(III)] and [alkali] were found by $\log k_{obs}$ *versus* log concentration plots and the obtained orders were also confirmed by differential method by the plot of log (rate) *versus* log concentration using the equation $\log(\text{rate}) = \log k + n \log c$; these orders were obtained by varying the concentration of DL-methionine, HCF(III), Os(VIII) and alkali in turn while keeping others constant.

### 2.3 *Effect of varying oxidant concentration*

The concentration of HCF(III) was varied in the range, $8.0 \times 10^{-5}$ to $8.0 \times 10^{-4}\,mol\,dm^{-3}$ at fixed [DL-methionine], [$OH^-$] and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of HCF(III) indicates the order in [HCF(III)] as unity (table 1). This was also confirmed from the linearity of plots of log[HCF(III)] *versus* time ($r > 0.9994$, $S \leq 0.026$) up to 85% completion of the reaction.

### 2.4 *Effect of varying substrate concentration*

The substrate, DL-methionine was varied in the range of $1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}\,mol\,dm^{-3}$ at $26 \pm 0.2$ °C keeping all other reactants concentrations constant (table 1). The $k_{obs}$ values were constant with increase in concentration of DL-methionine indicating a zero order dependence on [DL-methionine] (table 1).

### 2.5 *Effect alkali concentration*

The effect of [alkali] on the rate of reaction was studied at constant concentrations of DL-methionine, HCF(III) and ionic strength at $0.5\,mol\,dm^{-3}$. The rate constants increased with increase in [alkali] and the order was found to be $\approx 0.4$ (table 1).

### 2.6 *Effect of varying catalyst concentration*

The concentration of Osmium(VIII) was varied in the range, $5.0 \times 10^{-7}$ to $5.0 \times 10^{-6}\,mol\,dm^{-3}$ at fixed HCF(III), [DL-methionine], [$OH^-$] and ionic strength (table 1) and order was found to be unity.

### 2.7 *Effect of ionic strength and solvent polarity*

The effect of ionic strength was studied by varying the $NaClO_4$ concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.5 to $1.5\,mol\,dm^{-3}$ at constant [HCF(III)], [DL-methionine], [Os(VIII)] and [alkali]. It was found that the rate constants increased with increase in concentration of $NaClO_4$ and the plot of $\log k_{obs}$ versus

Table 1. Effect of variation of $[Fe(CN)_6]^{3-}$, [DL-Methionine], [Os(VIII)] and $[OH^-]$ on Osmium(VIII) catalyzed oxidation of DL-methionine by $[Fe(CN)_6]^{3-}$ at 26 °C, I = 0.50 mol dm$^{-3}$.

| $[Fe(CN)_6]^{3-} \times 10^4$ (mol dm$^{-3}$) | [DLM] $\times 10^3$ (mol dm$^{-3}$) | [OS(VIII)] $\times 10^6$ (mol dm$^{-3}$) | $[OH^-]$ (mol dm$^{-3}$) | $k_{obs} \times 10^3$ (s$^{-1}$) Found | Calculated |
|---|---|---|---|---|---|
| 0.8 | 5.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 1.0 | 5.0 | 1.0 | 0.20 | 1.38 | 1.39 |
| 2.0 | 5.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 4.0 | 5.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 6.0 | 5.0 | 1.0 | 0.20 | 1.38 | 1.39 |
| 8.0 | 5.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 4.0 | 1.0 | 1.0 | 0.20 | 1.38 | 1.39 |
| 4.0 | 2.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 4.0 | 4.0 | 1.0 | 0.20 | 1.37 | 1.39 |
| 4.0 | 6.0 | 1.0 | 0.20 | 1.38 | 1.39 |
| 4.0 | 8.0 | 1.0 | 0.20 | 1.36 | 1.39 |
| 4.0 | 10 | 1.0 | 0.20 | 1.35 | 1.39 |
| 4.0 | 5.0 | 0.5 | 0.20 | 0.66 | 0.69 |
| 4.0 | 5.0 | 0.8 | 0.20 | 1.07 | 1.11 |
| 4.0 | 5.0 | 1.0 | 0.20 | 1.36 | 1.40 |
| 4.0 | 5.0 | 2.0 | 0.20 | 2.25 | 2.80 |
| 4.0 | 5.0 | 4.0 | 0.20 | 5.62 | 5.60 |
| 4.0 | 5.0 | 5.0 | 0.20 | 6.91 | 6.99 |
| 4.0 | 5.0 | 1.0 | 0.05 | 0.70 | 0.69 |
| 4.0 | 5.0 | 1.0 | 0.08 | 0.91 | 0.93 |
| 4.0 | 5.0 | 1.0 | 0.10 | 1.02 | 1.04 |
| 4.0 | 5.0 | 1.0 | 0.20 | 1.37 | 1.40 |
| 4.0 | 5.0 | 1.0 | 0.40 | 1.72 | 1.69 |
| 4.0 | 5.0 | 1.0 | 0.50 | 1.82 | 1.76 |

$I^{1/2}$ was linear with positive slope. (figure 1, r = 0.9989, S = 0.031). The relative permittivity ($\varepsilon_T$) effect was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities of the mixture of t-butyl alcohol–water were not successful. However, they were computed from the

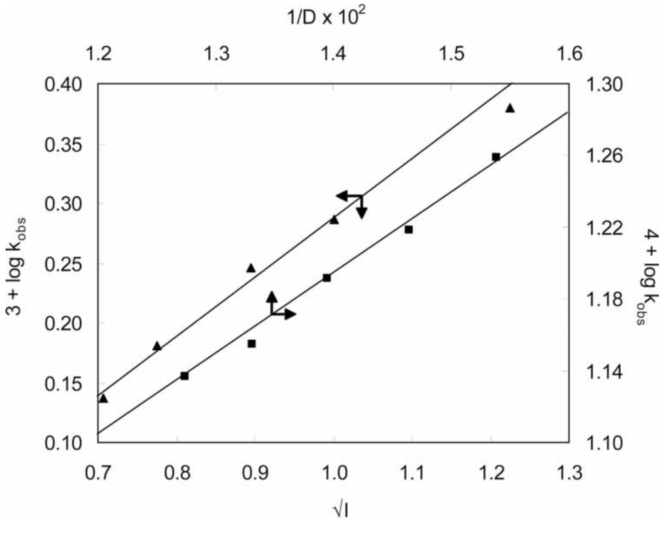


Figure 1. Effect of ionic strength and dielectric constant of the medium on osmium(VIII) catalyzed oxidation of DL-methionine by hexacyanoferrate(III) at 26 °C.

values of pure liquids [15]. It was also found that there was no reaction of the solvent with the oxidant or catalyst under the experimental conditions used. The $K_{obs}$ values increase with the decrease in the dielectric constant of the medium (figure 1). Hence, the graph of log $k_{obs}$ *versus* $1/\varepsilon_T$ was found to be linear with positive slope.

## 2.8 *Effect of initially added products*

The initially added products such as $[Fe(CN)_6]^{4-}$ and sulphoxide did not show any significant effect on the rate of the reaction.

## 2.9 *Polymerization study*

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of intervention of free radicals in the reaction. The blank experiment of either HCF(III), DL-methionine alone or mixture of catalyst and oxidant with acrylonitrile did not induce polymerization under the same condition as those induce with reaction mixture. Initially added acrylonitrile decreases the rate also indicating the free radical intervention, which is the case as in earlier work [16, 17].

## 2.10 *Effect of temperature*

The rate of reaction was measured at different temperatures under varying $[OH^-]$ concentrations. The rate constants, k of slow step of scheme 1 were obtained from intercepts of the plots of $1/k_{obs}$ *versus* $1/[OH^-]$ (figure 2) ($r > 0.9998$, $S \leq 0.0152$) and used to calculate the thermodynamic parameters. The values of k ($dm^3\ mol^{-1}\ s^{-1}$) are given in table 2. The rate of reaction increased with the increase in temperature. The activation parameters corresponding to these constants for a slow step of reaction (scheme 1) were evaluated from the plot of log k *versus* $1/T$ ($r > 0.9989$, $S \leq 0.0135$) (table 2).

Osmium (VIII) is known to form different complexes with $OH^-$ in basic media as shown in equation (2) and (3) with equilibrium constants of $K_1$ and $K_2$ having the values of 24 and

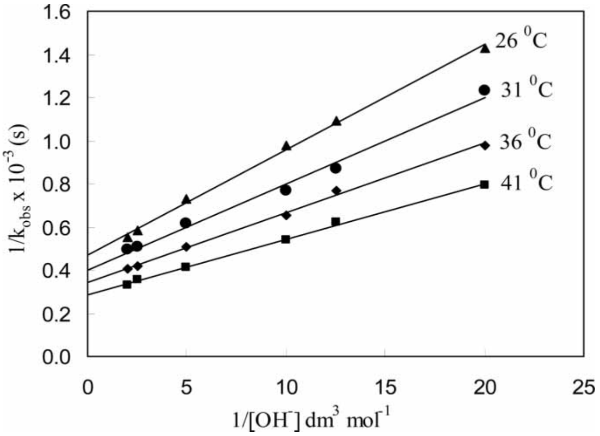


Figure 2. Verification of rate law of osmium(VIII) catalyzed oxidation of DL-methionine by hexacyanoferrate(III) at different temperatures.

Table 2. Activation and thermodynamic parameters for the OS(VIII) catalyzed oxidation of DL-methionine by hexacyanoferrate(III) in aqueous alkaline medium.

(a) Effect of temperature:*

| Temp. (K) | $k \times 10^3$ ($dm^3\ mol^{-1}\ s^{-1}$) |
|---|---|
| 299 | 2.12 |
| 304 | 2.49 |
| 309 | 2.91 |
| 314 | 3.48 |

(b) Activation parameters:*

| Log A | Ea ($kJ\ mol^{-1}$) | $\Delta H^{\#}$ ($kJ\ mol^{-1}$) | $\Delta S^{\#}$ ($JK^{-1}\ mol^{-1}$) | $\Delta G^{\#}$ ($kJ\ mol^{-1}$) |
|---|---|---|---|---|
| $2.66 \pm 0.2$ | $31.6 \pm 0.2$ | $29.2 \pm 0.2$ | $-201 \pm 10$ | $89 \pm 4$ |

(c) Thermodynamic Parameters of step 1 of scheme 1 at 299 K

| $\Delta H$ ($kJ\ mol^{-1}$) | $\Delta S$ ($JK^{-1}\ mol^{-1}$) | $\Delta G$ ($kJ\ mol^{-1}$) |
|---|---|---|
| $8.7 \pm 0.3$ | $47.8 \pm 2$ | $-5.6 \pm 0.2$ |

*With respect to slow step of scheme 1.

6.8 $dm^3\ mol^{-1}$, respectively [18–20].

$$OsO_3(OH)_3^- + OH^- \rightleftharpoons OsO_4(OH)_2^{2-} + H_2O\ K_1 \quad (2)$$

$$OsO_4(OH)_2^{2-} + OH^- \rightleftharpoons OsO_5(OH)^{3-} + H_2O\ K_2 \quad (3)$$

Hence, the total [osmium (VIII)] in alkaline medium is sum of [$OsO_3(OH)_3^-$], [$OsO_4(OH)_2^{2-}$] and [$OsO_5(OH)^{3-}$]. However, the [$OsO_3(OH)_3^-$] is existed in lower [$OH^-$] and at [$OH^-$] used in the present study, virtually all Os(VIII) is present as $OsO_4(OH)_2^{2-}$ and $OsO_5(OH)^{3-}$. The fractions of total [Os(VIII)] species, [$OsO_4(OH)_2^{2-}$] and [$OsO_5(OH)^{3-}$] calculated using $K_1$ and $K_2$ reveal that the [$OsO_5(OH)^{3-}$] with different [$OH^-$] are parallelism with [$OH^-$] (table 3 and figure 3). Because of this reason and the fact that the $k_{obs}$ is a function of [$OH^-$], the main active species of catalysis is likely to be [$OsO_5(OH)^{3-}$] and its formation in the equilibrium (3) is of importance in this study.

The first order each in catalyst and oxidant, fractional order in alkali and zero order in DL-methionine accommodate the mechanism as given in scheme 1, where osmium (VIII) forms its hydroxide species in prior equilibrium step, interact with HCF(III) in a slow step to yield a complex. This complex reacts with DL-methionine in a fast step to give sulfur radical

Table 3. Variation of concentration of Os(VIII) species at different [$OH^-$] at 26 °C.

| [$OH^-$] ($mol\ dm^{-3}$) | $\alpha_0$ | $\alpha_1$ | $\alpha_0$ | $k_{obs} \times 10^3$ ($s^{-1}$) |
|---|---|---|---|---|
| 0.05 | 0.3834 | 0.4601 | 0.1564 | 0.70 |
| 0.08 | 0.2522 | 0.4843 | 0.2635 | 0.91 |
| 0.10 | 0.1987 | 0.4769 | 0.3243 | 1.02 |
| 0.20 | 0.0811 | 0.3893 | 0.5295 | 1.37 |
| 0.40 | 0.0272 | 0.2615 | 0.7112 | 1.72 |
| 0.50 | 0.01859 | 0.2230 | 0.7584 | 1.82 |

*Note*: $\alpha_0$, $\alpha_1$ and $\alpha_2$ are the fractions of concentrations of $OsO_3(OH)_3^-$, $OsO_4(OH)_2^{2-}$ and $OsO_5(OH)^{3-}$ to $[OS(VIII)]_T$ respectively.

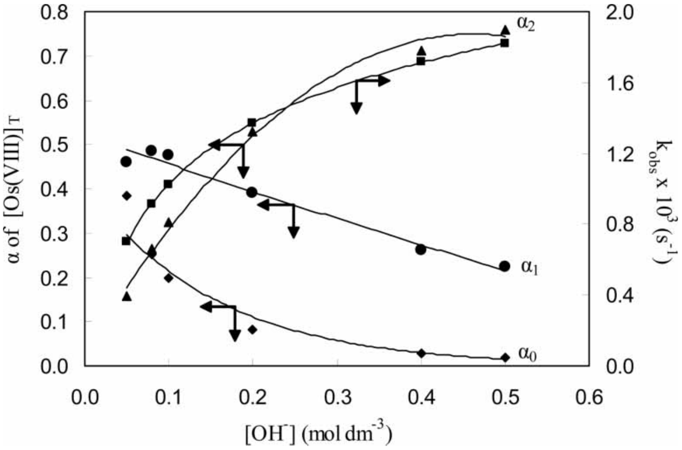
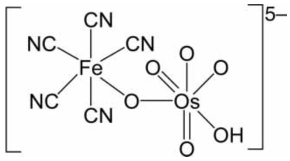


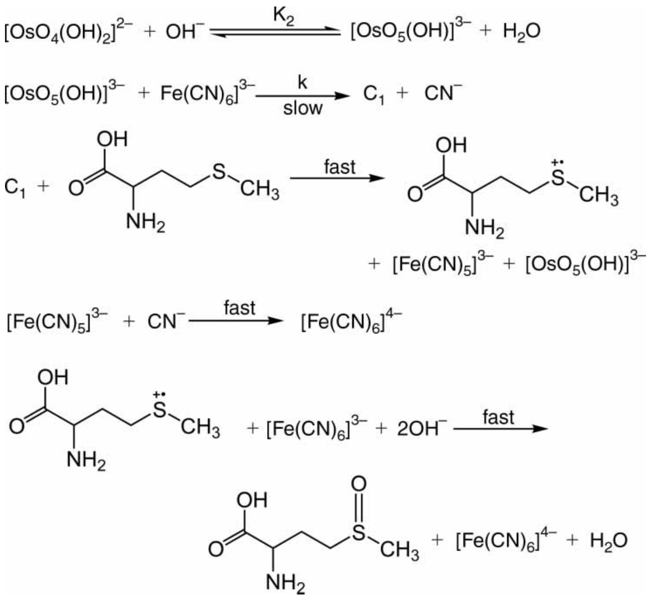
Figure 3. Effect of variation of [$OH^-$] on different species of catalyst with $k_{obs}$ at 26 °C.

cation of DL-methionine followed by formation of DL-methionine sulfoxide in the subsequent fast step.

The complex($C_1$) might have the structure



Though the DL-methionine contains the coordinating centers nitrogen and oxygen of $NH_2$ and COOH group as the coordinating centers and sulphur as the sites of attacking by the oxidant or a catalyst, the 'S' is oxidized to sulfoxide as per the sequence [21] of the reaction



SCHEME 1

taking place in sulfoxides is R−S−R > R−SO−R > R−SO$_2$−R. The sulfide to sulfoxide step is fast as observed in the present study compared to the sulfoxide to sulfone step.

In the present study, the sulfoxide was found to be the main oxidation product which supports the above facts. Thus, the oxidation at the sites of nitrogen and oxygen is ruled out.

The intermediate complex($C_1$) due to interaction between osmium (VIII) and HCF(III) in the rate determining step is written as reported [22–24] by earlier workers which justifies the unit order each in oxidant and catalyst and zero order in substrate. The formation of DL-methionine free radical in the fast step is in accordance with the experimental result of retardation of rates in the added radical scavenger like acrylonitrile and formation of copious precipitate on diluting with methanol. The scheme 1 is written in accordance with experimentally observed facts. Generally, in Os(VIII) catalyzed reactions Os(VIII) oxidizes the substrate followed by reoxidation of Os(VI) with oxidant in alkali. If that is the case, the order with respect to substrate would be unity or fraction and there could not be an intervention of free radicals. However, in the present study the above facts could be ruled out as order with respect to substrate is zero and reaction occurring through intervention of free radical. The another factor of reoxidation of Os(VI) by $[Fe(CN)_6]^{3-}$ can be ruled out as their redox potentials do not permit the reaction. This is also confirmed from their direct reaction. The another factor of noncatalytic influence of $[Fe(CN)_6]^{4-}$ in the present study supports the mechanism written in scheme 1. Scheme 1, leads to the rate equation (4).

$$\text{Rate} = \frac{kK_2[Fe(CN)_6^{3-}][Os(VII)]_T[OH^-]_T}{1 + K_2[OH^-]} \tag{4}$$

The rate law (4) can be derived as below

$$\begin{aligned}-\frac{d[Fe(CN)_6^{3-}]_T}{dt} &= \text{Rate} = k[Fe(CN)_6^{3-}][OsO_5(OH)^{3-}]\\ &= K_2k[Fe(CN)_6^{3-}][OsO_4(OH)_2^{2-}]_f[OH^-]_f\end{aligned} \tag{5}$$

$[Os(VIII)]_T$ is equal to the sum of the concentrations of $OsO_4(OH)_2^{2-}$ and $OsO_5(OH)^{3-}$.
i.e.

$$\begin{aligned}[Os(VIII)]_T &= [OsO_4(OH)_2^{2-}]_f + [OsO_5(OH)^{3-}]\\ &= [OsO_4(OH)_2^{2-}]_f + K_2[OsO_4(OH)_2^{2-}][OH^-]_f\\ &= [OsO_4(OH)_2^{2-}]_f\{1 + K_2[OH^-]_f\}\end{aligned}$$

Therefore,

$$[OsO_4(OH)_2^{2-}]_f = \frac{[Os(VIII)_T]}{1 + K_2[OH^-]_f} \tag{6}$$

Similarly,

$$\begin{aligned}[OH^-]_T &= [OH^-]_f + [OsO_5(OH)^{3-}]\\ &= [OH^-]_f + K_2[OsO_4(OH)_2^{2-}][OH^-]_f\\ &= [OH^-]_f\{1 + K_2[OsO_4(OH)_2^{2-}]\}\\ [OH^-]_f &= \frac{[OH^-]_T}{1 + K_2[OsO_4(OH)_2^{2-}]}\end{aligned} \tag{7}$$

Therefore, from equations (6) and (7), the equation (5) becomes,

$$\text{Rate} = \frac{K_2k[Fe(CN)_6^{3-}][Os(VIII)]_T[OH^-]_T}{(1 + K_2[OH^-]_f)(1 + K_2[OsO_4(OH)_2^{2-}])}$$

In view of low concentration of Os(VIII) used, the term $(1 + K_2[OsO_4(OH)_2^{2-}])$ tends to unity in the denominator. Therefore, the above equation becomes,

$$\text{Rate} = \frac{K_2k[Fe(CN)_6^{3-}][Os(VIII)]_T[OH^-]_T}{1 + K_2[OH^-]_f} \tag{8}$$

For the verification of rate law the subscripts "T" and "f" are omitted and hence, equation (8) becomes,

$$\text{Rate} = \frac{K_2k[Fe(CN)_6^{3-}][Os(VIII)][OH^-]}{1 + K_2[OH^-]}$$

or

$$\frac{\text{Rate}}{[Fe(CN)_6^{3-}]} = k_{obs} = \frac{K_2k[Os(VIII)][OH^-]}{1 + K_2[OH^-]} \tag{9}$$

The mechanism shown in scheme 1 and rate law (9) are verified by a plot of $1/k_{obs}$ *versus* $1/[OH^-]$ which should be linear and slope and intercept should lead to the values of $K_2$ and k. Such a plot is shown in figure 3 with $K_2 = 9.6 \pm 0.4\,dm^3\,mol^{-1}$ ($K = 6.8\,dm^3\,mol^{-1}$ at 50 °C from earlier work [25]) and $k = 2.12 \times 10^3\,dm^3\,mol^{-1}\,s^{-1}$. The values of k and $K_2$ were further used to calculate rates for several experimental situations. Rate constants calculated in this way have been found to be comparable with experimentally measured rate constants (table 1) and there is generally a good agreement.

The effect of increasing ionic strength on the rate is also in the expected direction on the basis of the reaction between the negatively charged $OsO_5(OH)^{3-}$ and $[Fe(CN)_6]^{3-}$ in the rate determining step. Ion pairing between $[Fe(CN)_6^{3-}]$ and $K^+$ is well known [26–28]. Thus, ion pairing between $Na^+$ and $[Fe(CN)_6]^{3-}$ may be expected in the presence of NaOH and $NaClO_4$ which were used to maintain [alkali] and ionic strength respectively. Thus, the overall increase of $k_{obs}$ with increase in ionic strength (figure 1).

The increase in rate with decreasing the relative permittivity of the media is contrary to the expected direction [29] as the ionic species involved in the slow step. This may be due to the more solvation of activated complex at low relative permittivity media than at higher one where the reactants are more solvated.

The hydroxyl ion concentration (as in table 1) was varied at four different temperatures; and from the slopes and intercepts of plots of $1/k_{obs}$ *versus* $1/[OH^-]$ the $K_2$ values were determined as 9.6, 10.1, 10.7, 11.3 $dm^3\,mol^{-1}$ at 26, 31, 36 and 41 °C, respectively. The van't Hoff's plot was made for the variation of $K_2$ with temperature (i.e. log $K_2$ versus 1/T) (figure 4). The thermodynamic parameters like enthalpy change (ΔH) of the first equilibrium step ($K_2$) of the reaction, entropy of the reaction (ΔS) and free energy of reaction (ΔG) were calculated (table 2) as $8.7 \pm 0.3$, $47.8 \pm 2$ and $-5.62 \pm 0.2\,kJ\,mol^{-1}$, respectively. And these values are compared with the values obtained for slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step are fairly slow and involves high activation energy [30, 31].

A high negative value of $\Delta S^{\#}$ (−201 kJ) suggests that the two ionic species combine in rate determining step to give one intermediate complex which is more ordered than the reactants [29, 32]. The higher rate constants of the slow step of the mechanism indicated that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion

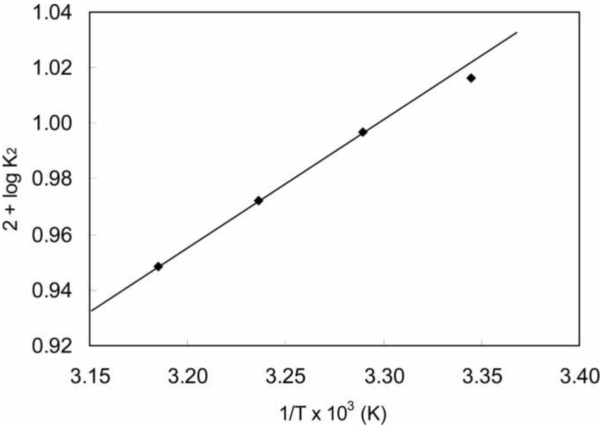


Figure 4. Van't Hoff's plot for the calculation of thermodynamic parameters for step 1 of scheme 1.

was supported by earlier work [33–35]. The unexpected low value of frequency factor (log A $= 2.66$) clearly indicates that the similar charged ions are interacting rather than DL-methionine with Os(VIII) or $[Fe(CN)_6]^{3-}$ in a slow step which supports the mechanism as in scheme 1.

## 3. Conclusion

Unanalyzed alkaline hexacyanoferrate(III) oxidation of DL-methionine occurs with a little rate, however, the same in presence of about 0.1 μ mole of osmium(VIII) under the identical condition, the rate of reaction multiplies in the order of more than a million times (half life period of unanalyzed reaction is 1,20,000 minutes where as osmium (VIII) catalyzed under the same reaction condition is 5 minutes). This may be due to formation of intermediate compound of a mixture of hexacyanoferrate(III) facilitates the transfer of electron from reductant to oxidant through a common bridging ligand 'O' of osmium (VIII) (vide probable structure of complex $C_1$). The oxidation product of DL-methionine was found to be DL-methionine sulfoxide which is unlike to the formation of L-methionine from D-methionine in the metabolism *via* the formation of keto-acid followed by amination. The role of $[Fe(CN)_6]^{4-}$ is not observed as its catalytic effect might be masked in presence of a strong catalyst like Os(VIII). Thermodynamic parameters of step of scheme 1 supports the increase in concentration of $OsO_5(OH)^{3-}$ with increase of $[OH^-]$ as ΔG has a very small negative value.

## 4. Experimental

All chemicals used were of reagent grade. Double distilled water was used throughout the work. A solution of $[Fe(CN)_6]^{3-}$ was prepared by dissolving $K_3Fe(CN)_6$ (BDH) in $H_2O$ and was standardized iodometrically [36]. The solution was again standardized by measuring the absorbance using Hitachi 150–20 Spectrophotometer with a 1 cm cell at 420 nm ($\varepsilon = 1060 \pm 50\,dm^3\,mol^{-1}\,cm^{-1}$). DL-methionine is colorless or white lustrous plates, or a white crystalline powder and has a slight characteristic odour. Soluble in water, alkali and mineral acids, and partially soluble in alcohol but insoluble in ether. Stock solution of DL-methionine (S. D. Fine) was prepared by dissolving the appropriate amount of purified sample of DL-methionine sample in water. The purity of the sample was checked by TLC and its m.p. (279 °C). The stock solution of Osmium(VIII) was obtained by dissolving osmium tetroxide(Johnson Matthey) in 0.50 mol dm$^{-3}$ sodium hydroxide solution and its concentration was ascertained [37] by standardizing it with standard cerium ammonium sulphate solution. NaOH(Merk) and $NaClO_4$(BDH) were used to provide the required alkalinity and to maintain the ionic strength, respectively in reaction solutions.

## 4.1 *Kinetics measurements*

All kinetic measurements were performed under pseudo-first order conditions with [DL-methionine] in excess over [HCF(III)] at constant ionic strength of 0.5 mol dm$^{-3}$. The reaction was initiated by mixing previously thermostated solutions of [HCF(III)] and DL-methionine which also contained the necessary quantities of osmium(VIII) a catalyst, NaOH and $NaClO_4$ to maintain the required alkalinity and ionic strength, respectively. The temperature was maintained at $26 \pm 0.2$ °C. The course of reaction was followed by monitoring the decrease in absorbance of HCF(III) in a 1 cm quartz cell of a Hitachi 150–20 spectrophotometer at its absorption maximum of 420 nm as a function of time. The application of Beer's law to [HCF(III)] at 420 nm had earlier been verified, giving $\varepsilon = 1060 \pm 50\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$. The first order rate constants, $k_{obs}$ were evaluated by the plots of log[HCF(III)] versus time and were linear in almost all cases up to 85% completion of the reaction and the $k_{obs}$ values were reproducibility to within ±5%.

The effect of dissolved oxygen on the rate of the reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of $N_2$. No significant difference between the results obtained under $N_2$ and in presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used when conducting the experiment.

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