

Kinetics and Mechanism of Osmium(VIII)-Catalyzed Oxidation of Thiomorpholine by Alkaline Hexacyanoferrate(III)

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Abstract: Thiomorpholine (tetrahydro-1,4-thiazine), in the presence of Os(VIII) as catalyst, is oxidized by alkaline hexacyanoferrate(III) to 2-hydroxythiomorpholine. There is a first-order dependence in $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{Os}(\text{VIII})]$ and zero-order dependence in $[\text{thiomorpholine}]$ and $[\text{OH}^-]$. The observed rate constant was dependent on $[\text{Fe}(\text{CN})_6^{4-}]$ the type of electrolyte and the permittivity of the reaction medium (10-40% ethanol). The proposed mechanism includes the formation of a transient $[\text{OsO}_4(\text{OH})_2]^{2-}$ -thiomorpholine complex prior to the rate-determining regeneration of Os^{VIII} by $[\text{Fe}(\text{CN})_6^{3-}]$. The values of the enthalpy and entropy of activation are calculated from rate constant values measured at different temperatures (20-40 °C)

Key Words: Alicyclic, Catalysis, Hexacyanoferrate(III), Kinetics, Mechanism, Organosulfur, Os^{VIII} , Oxidation, Tetrahydro-1,4-thiazine, Thioethers, Thiomorpholine

Introduction

Hexacyanoferrate(III), a one-electron oxidant, has been reported to react with a large number of different organic compounds where the oxidizing species is a complex electron-abstracting ion (Rosenblatt *et al.*, 1967; Jarrar, 1977; Al subu *et al.*, 1991; 1990 and 1990). Radicals are produced from the oxidation of some substrates (Meehan *et al.*, 1962), though oxidation of others does not involve the production of such radicals (Speakman and Waters, 1955).

Because some reactions with hexacyanoferrate(III) are slow or not feasible, $\text{Os}(\text{VIII})$ and other metal ions have been frequently employed to speed up such reactions. $\text{Os}(\text{VIII})$ acts, *via* an intermediate complex, either to oxidize the substrate and gets itself converted to a lower oxidation state (Upadhyay and Agrawal, 1977; 1978; 1979; Nyilasi and Orsos, 1973; Nyilasi and Somogyi, 1964; Mehrota and Kapoor, 1984 and Acharya *et al.*, 1982) or catalyze the reaction without being reduced to any lower oxidation state (Upadhyay, 1983). In the former case, hexacyanoferrate(III) functions to regenerate $\text{Os}(\text{VIII})$, where In the latter $\text{Fe}(\text{CN})_6^{3-}$ acts as the actual oxidizing agent.

The oxidations of both tertiary and secondary amines by alkaline hexacyanoferrate(III) are well documented. In most cases four intermediate species are involved in the course of oxidation; aminium radical cation, α -amino-radical, an iminium ion and carbinol amine (Audeh and Lindsay, 1970; Lindsay *et al.*, 1973; Audeh and Lindsay, 1971 and Lindsay and Mead, 1976).

In a previous work (Al Subu, 2001 and 1965), the oxidation of two organosulfur compounds, namely 1,4-thioxane and pentamethylenesulfide, by alkaline Os^{VIII} - hexacyanoferrate(III) has been reported. The mechanisms proposed for the oxidation of these organosulfur substrates assumed the reaction to occur on the carbon alpha to the sulfur atom to produce the corresponding α -hydroxy derivative.

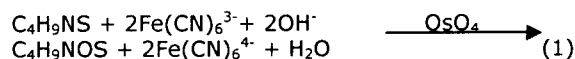
The goal of the present work was to investigate the oxidation of thiomorpholine, as an example of alicyclic bases that contain both secondary amine and sulfide groups in the same ring. This study aimed to

investigate whether oxidation occurs on the carbon alpha to the nitrogen atom, as in the case of secondary and tertiary amines, or follows the same path as was noticed in the case of the two previously reported thioethers. The study was motivated by the lack of enough work on the oxidation of organosulfur compounds by hexacyanoferrate(III).

Materials and Methods

OsO_4 (Johnson-Matthey) and all other reagents were AR grade and used as such. Doubly distilled water was used for preparing solutions. Stock solutions of OsO_4 were prepared by dissolving the required amount in dilute NaOH (0.01 mol.dm⁻³) and the reaction vessels were coated with aluminum foil. Temperature of the reaction was maintained constant. Ferricyanide was mixed with the reagents in a reaction vessel to initiate the reaction. The progress of reaction was followed spectrophotometrically by determining the absorbance due to unreacted ferricyanide as a function of time at 414 nm ($\epsilon = 1.00 \times 10^3$) using a Sp 8-100 Spectrophotometer. The reproducibility of the rate constant values was within $\pm 5\%$ in replicate runs.

Stoichiometry: A reaction mixture, containing known excess of hexacyanoferrate(III) over thiomorpholine, was allowed to stand in the presence of NaOH and $\text{Os}(\text{VIII})$ at 30 °C. After completion of the reaction, the unreacted hexacyanoferrate(III) was estimated. The results showed that one mole of thiomorpholine consumed two moles of $\text{Fe}(\text{CN})_6^{3-}$ according to the stoichiometric equation (1):



The formation of 2-hydroxythiomorpholine as an end product was detected from the i.r spectrum of the product.

Results and Discussion

The reaction was studied at various initial concentrations of ferricyanide, $\text{Os}(\text{VIII})$, thiomorpholine and hydroxyl ion. Log $[\text{Fe}(\text{CN})_6^{3-}]$ versus time plots were linear ($r > 0.998$) and values of pseudo-first order

rate constant (k_1) in hexacyanoferrate(III) at various concentrations of the reactants were evaluated from the slopes of these plots.

The rate constant (k_1) remained nearly unchanged with varying the concentration of hexacyanoferrate(III) (Table 1) and thus confirms first order dependence of rate in $[\text{Fe}(\text{CN})_6^{3-}]$.

The plot of k_1 versus $[\text{Os}(\text{VIII})]$ is linear ($r > 0.96$) (Table 1 and Fig. 1) and the plot of $\log [k_1]$ versus $\log [\text{Os}(\text{VIII})]$

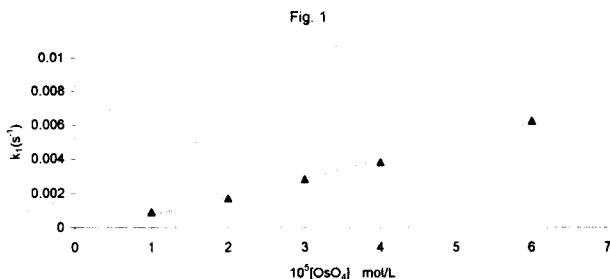


Fig. 1: Effect of varying $[\text{Os}(\text{VIII})]$ at 20°C. $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{C}_4\text{H}_9\text{NS}] = 0.01 \text{ M}$, $[\text{NaOH}] = 0.01 \text{ M}$, $\mu = 0.1 \text{ M}$.

Table 1: Effect of Concentration of Ferricyanide and Os(VIII) on the Rate of Oxidation of Thiomorpholine at 20°C

$10^3 [\text{Fe}(\text{CN})_6^{3-}]$ (mol dm ⁻³)	10^5 $[\text{Os}(\text{VIII})]$ (mol dm ⁻³)	$10^3 k_1$ (s ⁻¹)	$10^2 k_2$ (s ⁻¹ dm ³ mol ⁻¹)
0.60	1.00	0.90	0.90
0.80	1.00	0.90	0.90
1.00	1.00	0.90	0.90
1.20	1.00	0.90	0.90
1.00	2.00	1.70	0.85
1.00	3.00	2.80	0.93
1.00	4.00	3.80	0.95
1.00	6.00	6.20	1.03

$[\text{C}_4\text{H}_9\text{NS}] = 0.01 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$, $\mu = 0.1 \text{ M}$

versus $\log k_1$ is also linear ($r > 0.998$) with a slope of 1.08. More over, the $1/k_1$ versus $1/[\text{Os}(\text{VIII})]$ plot was linear also and nearly passing through the origin. Thus the reaction is first order in Os(VIII) and will, if it does, proceed very slowly in the absence of the catalyst.

The effect of $[\text{OH}^-]$ on the reaction rate was studied at fixed ionic strength ($\mu=0.1 \text{ mol.dm}^{-3}$) maintained with KCl (Table 2). No effect on rate constant values was found upon increasing $[\text{OH}^-]$. The rate was found independent also with respect to the concentration of thiomorpholine (Table 2).

Addition of ferrocyanide (up to $4 \times 10^{-3} \text{ mol.dm}^{-3}$) to the reaction mixture retarded the reaction rate remarkably (Table 3 and Fig. 3). No change in rate constant value was noticed upon increasing the concentration of KCl in the reaction solution (Table 3). Adding salts of different anions KX (X=F⁻, Cl⁻, Br⁻, I⁻) resulted in a small change in rate constant value (Table 4 and Fig. 3). However, changing the type of cation MX (M= Na⁺, K⁺, NH₄⁺) decreased the rate in the order

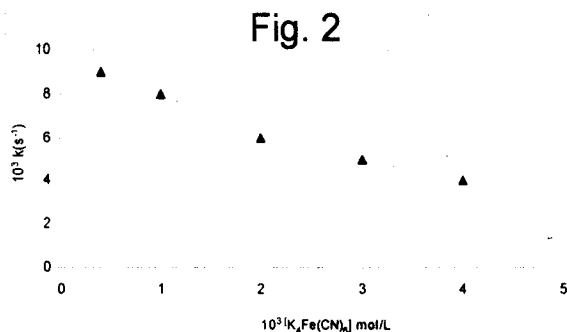


Fig. 2: Effect of varying $[\text{Fe}(\text{CN})_6^{4-}]$ at 20°C $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5} \text{ M}$, $[\text{C}_4\text{H}_9\text{NS}] = 0.01 \text{ M}$, $[\text{NaOH}] = 0.1 \text{ M}$

Table 2: Effect of Concentration of Thiomorpholine and Sodium Hydroxide on the Rate of Oxidation of Thiomorpholine at 20°C

$[\text{C}_4\text{H}_9\text{NS}]$ mol dm ⁻³	$[\text{NaOH}]$ mol dm ⁻³	$10^3 k_1$ (s ⁻¹)
0.01	0.01	0.90
0.02	0.01	1.00
0.03	0.01	1.00
0.04	0.01	1.00
0.06	0.01	0.90
0.01	0.02	1.10
0.01	0.03	1.10
0.01	0.05	1.00
0.01	0.10	0.90

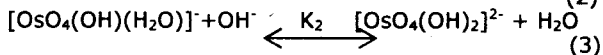
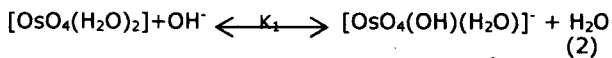
$[\text{Fe}(\text{CN})_6^{3-}] = 1 \times 10^{-3} \text{ M}$; $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5} \text{ M}$

$\text{NH}_4^+ \gg \text{Na}^+ > \text{K}^+$ (Table 4 and Fig. 4).

Using aqueous ethanol up to 40% as a reaction medium resulted in a moderate decrease in the rate constant values (Table 4 and Fig. 4).

Rates were also studied at different temperatures. ΔS^\ddagger and ΔH^\ddagger values were calculated as $-11.3 \text{ JK}^{-1}\text{mol}^{-1}$ and 15.5 kJ mol^{-1} respectively, using Arrhenius Equation.

The stock solution of Os(VIII) was prepared in 0.01M NaOH. Osmium tetroxide is known to exist in alkaline solutions as $[\text{OsO}_4(\text{OH})_2]^-$ according to the following equilibria (Griffith, 1965):



where ($K_1 = 5.5 \times 10^{13}$ and $K_2 = 28$).

Oxidation of amines and amino acids by Os(VIII) is known to proceed by the formation of 1:1 complex between Os(VIII) and the amine followed by the formation of imine. This takes place either by direct generation of Os(VIII) or through metal hydride intermediate and a subsequent decomposition (Mehrotra and Kapoor, 1984).

The experimental data suggest the following rate law:

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k[\text{Fe}(\text{CN})_6^{3-}][\text{Os}(\text{VIII})] \quad (4)$$

Based on these results, the following mechanism has been proposed (Eq. 5-9).

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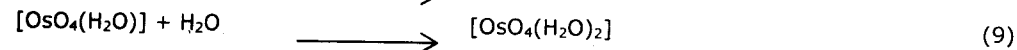
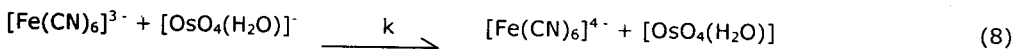
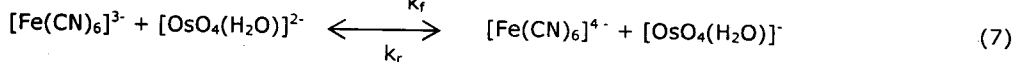
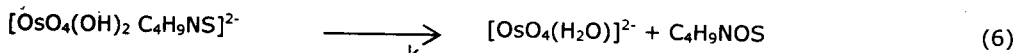
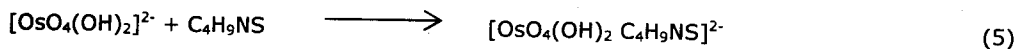


Fig. 3

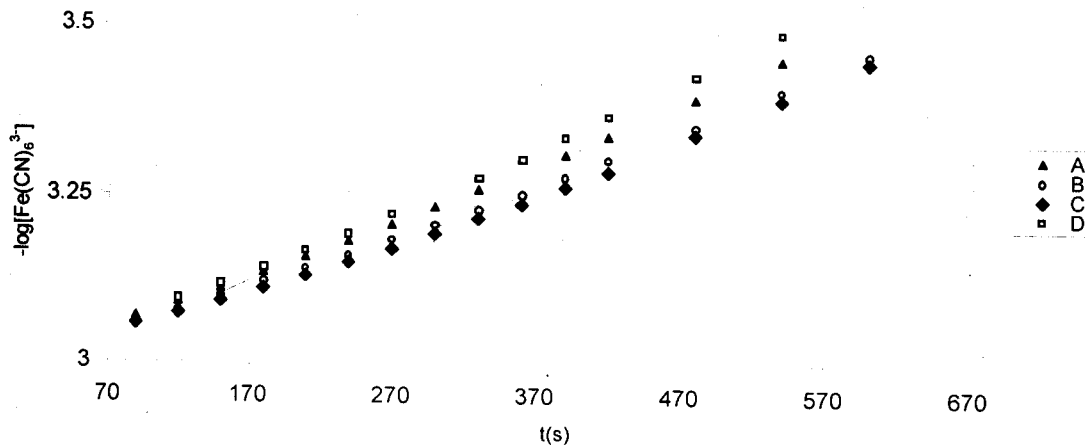


Fig. 3: Effect of varying anion at 20°C. $[\text{C}_4\text{H}_9\text{NS}] = 0.01\text{M}$, $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5}\text{ M}$, $[\text{NaOH}] = 0.01\text{M}$. A = KBr; B = KCl; C = KF; D = KI

Fig. 4

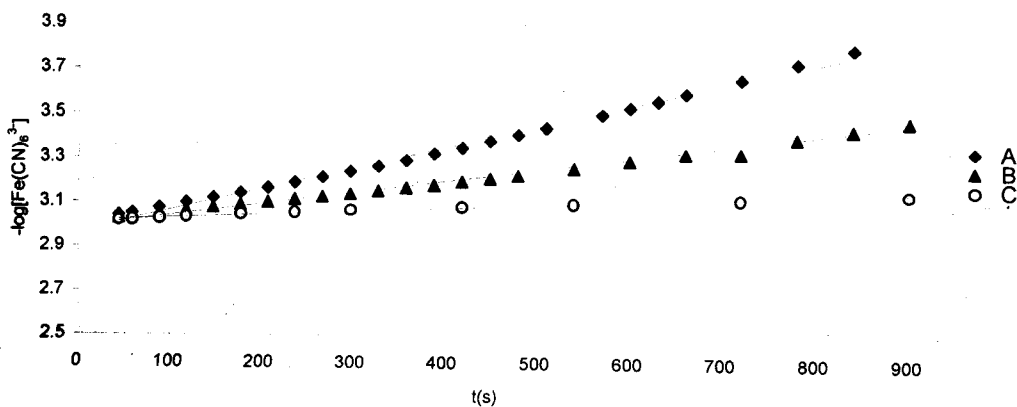


Fig. 4: Effect of Varying Cation at 20°C. $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3}\text{ M}$, $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5}\text{ M}$, $[\text{C}_4\text{H}_9\text{NS}] = 0.01\text{M}$, $[\text{NaOH}] = 0.01\text{ M}$. A = KCl; B = NaCl; C = NH_4Cl

Table 3: Effect of $[\text{Fe}(\text{CN})_6^{4-}]$ and KCl on the Rate of Oxidation of Thiomorpholine at 20 °C

$10^3 [\text{Fe}(\text{CN})_6^{4-}]$ mol dm ⁻³	KCl Mol dm ⁻³	$10^3 k_1$ (s ⁻¹)
0.40	-	0.90
1.00	-	0.80
2.00	-	0.60
3.00	-	0.50
4.00	-	0.40
-	0.01	0.90
-	0.02	0.90
-	0.03	0.90
-	0.04	1.00

$[\text{Fe}(\text{CN})_6^{3-}] = 1 \times 10^{-3} \text{ M}$; $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5} \text{ M}$;
 $[\text{NaOH}] = 0.01 \text{ M}$; $[\text{C}_4\text{H}_9\text{NS}] = 0.01 \text{ M}$

Table 4: Effect of Type of Anion (KX) and Cation (MCl) and Percentage Ethanol on the Rate of Oxidation of Thiomorpholine at 20°C

KX	MX	% ethanol	$10^3 k_1$ (s ⁻¹)
KF	-	-	1.00
KCl	-	-	0.90
KBr	-	-	0.70
KI	-	-	0.80
-	NaCl	-	0.50
-	NH ₄ Cl	-	0.20
-	-	10	0.70
-	-	20	0.60
-	-	30	0.50
-	-	40	0.50

$[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{C}_4\text{H}_9\text{NS}] = 0.01\text{M}$; $[\text{NaOH}] = 0.010 \text{ M}$; $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5} \text{ M}$.

Oxidation of thiomorpholine by hexacyanoferrate(III) does not proceed in the absence of Os(VIII). Besides, a zero-order dependence of rate in thiomorpholine is observed. These indicate a fast interaction between the dominant form of the catalyst, namely $[\text{OsO}_4(\text{OH})_2]^{2-}$ and the substrate to give a transient complex in a fast step [Eq. 5]. In this complex, two electrons are transferred successively from Os^{VIII} to the substrate before being reduced to Os^{VI} . The first electron results in the formation of the aminium radical cation. Because the rate is zero-order in $[\text{OH}^-]$, it is inferred that one of the two hydroxyl groups available in the complex abstracts a proton from the carbon alpha to the amine, intramolecular H-abstraction, to produce the α -amino-radical. Then, the transfer of the second electron takes place to give the iminium ion followed by the attack of the second hydroxyl ion on the carbo cation to produce the carbinol amine. All are assumed to occur in a fast step before the transient complex splits to give the oxidation product [Eq. 6]. The presence of -NH group in the substrate supports this assumption (Bahr, 1954). The oxidation of thiomorpholine followed first-order dependence in both the catalyst and hexacyanoferrate(III) with two moles of $\text{Fe}(\text{CN})_6^{3-}$ being consumed by each mole of thiomorpholine, in the

presence of alkali and Os(VIII). It is therefore likely that Os^{VI} reacts successively with two molecules of $\text{Fe}(\text{CN})_6^{3-}$ to regenerate Os^{VIII} in relatively slow steps [Eq. 7 & 8]. Therefore, under the present experimental conditions, the possibility of reducing Os(VIII) into a lower oxidation state appears feasible in the case of thiomorpholine. In this respect, the oxidation of thiomorpholine is different from the previously reported oxidation of 1,4-thioxane and pentamethylenesulfide that lack the presence of NH groups. The observed retardation of rate by added $[\text{Fe}(\text{CN})_6^{4-}]$ indicates that equations 7 is slow and reversible. The sulfur atom, in the ring, is assumed intact as the one electron oxidation potential of alkyl sulfides is much larger than that of secondary amines (Watanabe *et al.*, 1980).

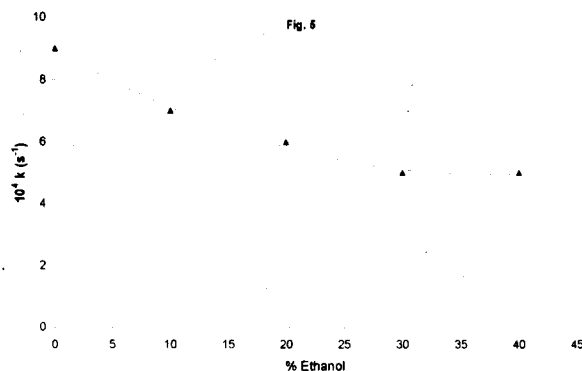


Fig. 5: Effect of Varying Percentage Ethanol at 20°C. $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{Os}(\text{VIII})] = 1.0 \times 10^{-5} \text{ M}$, $[\text{NaOH}] = 0.01\text{M}$ $[\text{C}_4\text{H}_9\text{NS}] = 0.01$. A = KCl; B = NaCl; C = NH₄Cl.

The effects of introduced electrolytes, which agree with their relative acid - base strength, and the relative permittivity of the reaction medium support that step 7 is involved in the rate-determining step. The zero-order rate dependence in $[\text{OH}^-]$ is explained by its relative high concentration compared to $[\text{Os}^{\text{VIII}}]$ and the assumption that OH^- acts as part of the Os^{VIII} complex. The calculated values of the reaction entropy and enthalpy are comparable to similar oxidation reactions (Lindsay and Mead, 1973; Audeh and Lindsay, 1971 and 1976)

The formation the hydroxy product for the oxidation of organic sulfur compounds by alkaline hexacyanoferrate(III) has been reported in literature (Srinivassan and Subramaniam, 1990).

The above mechanism enables us to derive the following rate law

$$-d [\text{Fe}(\text{CN})_6^{3-}] / dt = k_f [\text{Os}(\text{VIII})][[\text{Fe}(\text{CN})_6^{3-}] \{1 - k_r / [[\text{Fe}(\text{CN})_6^{4-}] / k[\text{Fe}(\text{CN})_6^{3-}]] \} \quad (10)$$

The derived rate law explains the obtained experimental results especially the retardation effect of $[\text{Fe}(\text{CN})_6^{4-}]$ observed at later stages of the reaction.

Acknowledgement

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