

Kinetics and mechanism of osmium(VIII)-catalyzed oxidation of 1,4-thioxane by alkaline hexacyanoferrate(III)

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Abstract

The kinetics of oxidation of 1,4-thioxane (1,4-oxathiane) by alkaline $K_3Fe(CN)_6$ have been studied in the presence of Os^{VIII} as catalyst. The reaction is first order in hexacyanoferrate(III) and Os^{VIII} . The order in thioxane and OH^- is zero. While added salts and ethanol have a negligible effect on the oxidation rate, $K_4Fe(CN)_6$ retards it. On the basis of kinetic evidence, a mechanism has been proposed.

Introduction

Potassium hexacyanoferrate(III), a one-electron oxidant with a redox potential of +0.36 V, has been successfully used to oxidize several substrates. The reactions of organic sulfur compounds with this oxidant are not facile and require the presence of a removable proton on the α -carbon atom [1–3].

Osmium(VIII), is known to act as a catalyst in hexacyanoferrate(III) oxidations, and to enhance the rate of the reaction. Osmium(VIII) generally acts by effectively oxidizing the substrate *via* an intermediate complex and is itself converted into a lower state, with $Fe(CN)_6^{3-}$ being used to regenerate osmium(VIII) [4, 5]. There are few kinetic studies of the reactions of organic sulfur compounds with metal ion oxidants. The present paper deals with the kinetics of oxidation of 1,4-thioxane by alkaline hexacyanoferrate(III) in the presence of Os^{VIII} as a catalyst.

Experimental

Solutions of 1,4-thioxane (Aldrich, A.R.) and $K_3Fe(CN)_6$ (Riedel–de Haen, A.R.) were freshly prepared from samples which were used as received. A standard OsO_4 (Sigma, A.R.) solution was diluted with aqueous NaOH, which was freshly prepared and standardized against potassium hydrogen phthalate solution. KCl was used throughout to adjust the ionic strength. Doubly distilled H_2O was used for preparing solutions. All other reagents were analytical grade chemicals.

Kinetic procedure

The required quantities of 1,4-thioxane, KCl, Os^{VIII} and other reagents were thermostatted in a reaction vessel. Hexacyanoferrate(III), separately equilibrated, was added to the mixture in order to initiate the reaction.

The kinetics were followed spectrophotometrically by measuring the absorbance of hexacyanoferrate(III) at 414 nm using a Sp 8-100 spectrophotometer.

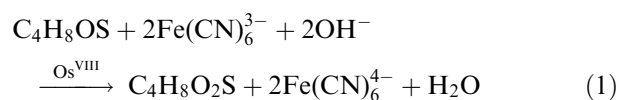
Rate of reaction

All kinetics was carried out under pseudo-first-order conditions with 1,4-thioxane in at least tenfold excess, unless stated otherwise. The pseudo-first-order rate constant (k_1) was calculated from the slope of the linear plot of $\log[Fe(CN)_6^{3-}]$ versus time. The rate of loss of hexacyanoferrate(III) was followed to more than 70% conversion. The reproducibility of the rate constant values was *ca.* $\pm 5\%$.

Stoichiometry

A mixture containing a known excess of hexacyanoferrate(III) over 1,4-thioxane was allowed to stand in the presence of 0.1 M NaOH and 1.0×10^{-5} M Os^{VIII} until completion of the reaction. The remaining hexacyanoferrate(III) was estimated and corresponds to the consumption of two moles of ferricyanide per mole of 1,4-thioxane. The formation of 3-hydroxy-1,4-thioxane as an end product was indicated by the presence of the hydroxyl group in the i.r. spectrum of the product.

The experimental results are consistent with the following stoichiometric equation:



Results and discussion

The oxidation of 1,4-thioxane by alkaline hexacyanoferrate(III) in the presence of osmium(VIII) is first order

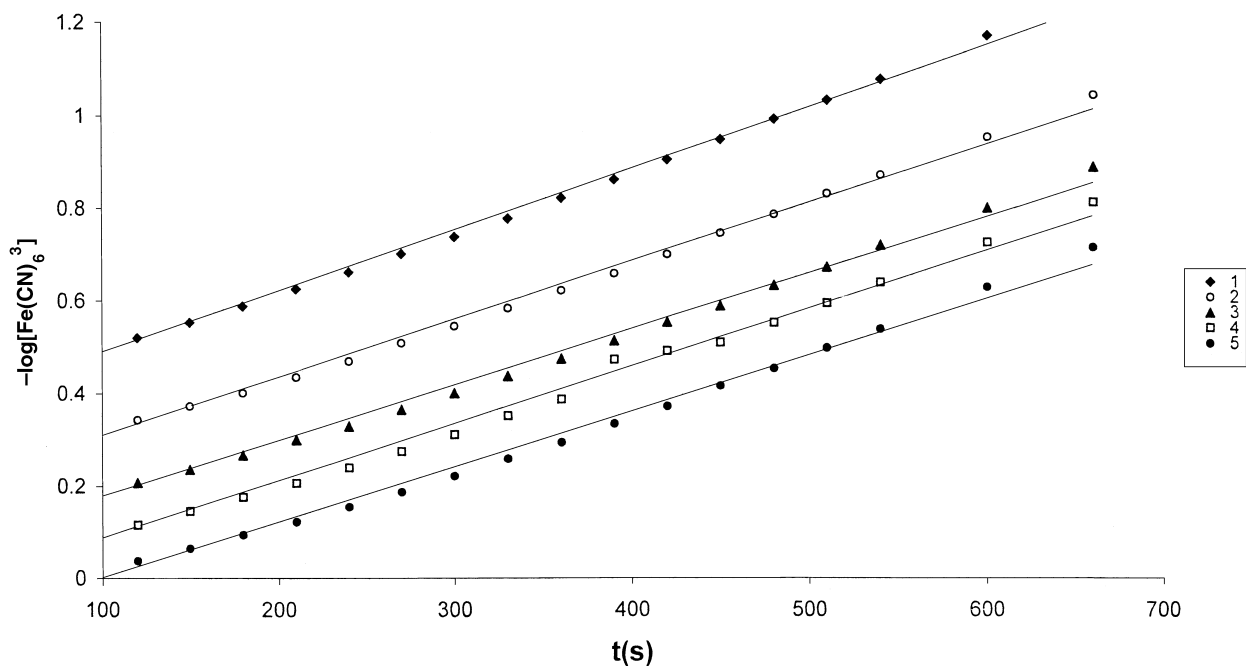


Fig. 1. Effect of varying $[\text{Fe}(\text{CN})_6^{3-}]$ in the catalyzed oxidation of 1,4-thioxane at 20 °C. $[\text{1,4-thioxane}] = 0.01 \text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5} \text{ M}$, $[\text{NaOH}] = 0.01 \text{ M}$. $[\text{Fe}(\text{CN})_6^{3-}]$: 1 = $0.4 \times 10^{-3} \text{ M}$; 2 = $0.6 \times 10^{-3} \text{ M}$; 3 = $0.8 \times 10^{-3} \text{ M}$; 4 = 10^{-3} M ; 5 = $1.2 \times 10^{-3} \text{ M}$.

in $[\text{Fe}(\text{CN})_6^{3-}]$ as shown by the good linear plots ($r > 0.990$) of $\log[\text{Fe}(\text{CN})_6^{3-}]$ versus time (Figure 1) and also by constant pseudo-first-order rate constants at different initial concentration of hexacyanoferrate(III) (Table 1).

The constant second-order-rate constant at different initial $[\text{Os}^{\text{VIII}}]$ concentrations (Table 1) and the excellent linear plot of $\log k_1$ versus $\log[\text{Os}^{\text{VIII}}]$ ($r = 0.999$) with a slope of 0.99, indicate the first-order dependence of $[\text{Os}^{\text{VIII}}]$. The good linear plot of k_1 versus $[\text{Os}^{\text{VIII}}]$ ($r = 0.999$) (Figure 2) and of $1/k_1$ versus $1/[\text{Os}^{\text{VIII}}]$ ($r = 0.999$), passing through the origin, implies that alkaline hexacyanoferrate(III) does not oxidize 1,4-thioxane to any appreciable extent in the absence of osmium(VIII).

The rate of oxidation was found to be independent of $[\text{1,4-thioxane}]$ and $[\text{OH}^-]$ (Table 2). The rate also does not change with increase in the ionic strength of the

medium (maintained by addition of KCl) (Table 3). This indicates that the rate-determining step might involve ions of like charge [6].

Table 4 indicates that changing the added anions (F^- , Cl^- , Br^- and I^-) has no effect on the reaction rate, however, changing the cation (Na^+ , K^+ and NH_4^+) resulted in a decrease in rate in the order: $\text{NH}_4^+ > \text{Na}^+ > \text{K}^+$. These results support the assumption that the slow step could involve negatively charged reactants [7–9]. Changing percentage ethanol in the reaction medium (up to 40%) had a negligible effect on rate of oxidation (Table 3).

Added hexacyanoferrate(II) retards the rate (Table 3 and Figure 3), indicating that $\text{Fe}(\text{CN})_6^{4-}$ is involved in a slow reversible step and suggesting that the reaction proceeds through a radical intermediate.

Table 1. Rate dependence on the concentration of ferricyanide and Os^{VIII} 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)	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
0.4	1.0	1.30	1.30
0.6	1.0	1.30	1.30
0.8	1.0	1.20	1.20
1.0	1.0	1.20	1.20
1.2	1.0	1.20	1.20
1.0	2.0	2.40	1.20
1.0	3.0	3.60	1.20
1.0	4.0	4.70	1.18
1.0	6.0	7.10	1.18

$[\text{NaOH}] = 10^{-2} \text{ M}$, $[\text{1,4-thioxane}] = 10^{-2} \text{ M}$, $\mu = 0.01 \text{ M}$.

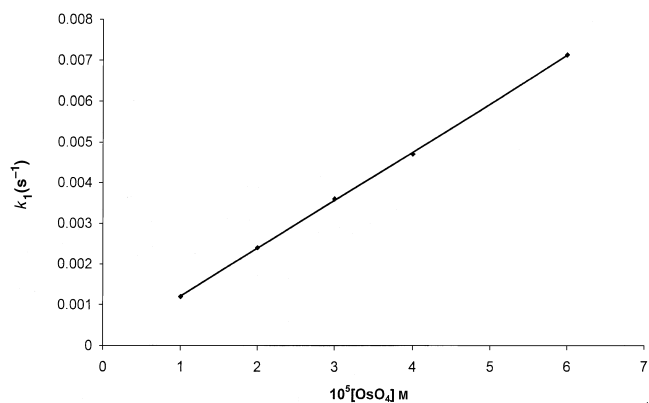


Fig. 2. Effect of varying $[\text{Os}^{\text{VIII}}]$ at 20 °C. $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{1,4-thioxane}] = 0.01 \text{ M}$, $[\text{NaOH}] = 0.01 \text{ M}$.

Table 2. Rate dependence on concentration of NaOH and 1,4-thioxane at 20 °C

$10^2 [\text{C}_4\text{H}_8\text{OS}] \text{ (mol dm}^{-3}\text{)}$	$10^2 [\text{NaOH}] \text{ (mol dm}^{-3}\text{)}$	$10^3 k_1 \text{ (s}^{-1}\text{)}$
1.0	1.0	1.20
2.0	1.0	1.10
3.0	1.0	1.10
4.0	1.0	1.10
6.0	1.0	1.00
1.0	2.0	1.30
1.0	3.0	1.20
1.0	5.0	1.20
1.0	10.0	1.20

$[\text{Fe}(\text{CN})_6^{3-}] = 10^{-3} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5} \text{ M}$.

Table 3. Rate dependence on added $[\text{Fe}(\text{CN})_6^{4-}]$, $[\text{KCl}]$ and EtOH (%) at 20 °C

$10^3 [\text{Fe}(\text{CN})_6^{4-}] \text{ (mol dm}^{-3}\text{)}$	$10^2 [\text{KCl}] \text{ (mol dm}^{-3}\text{)}$	$\text{EtOH} \text{ (%)}$	$10^3 k_1 \text{ (s}^{-1}\text{)}$
0.1	1.0	–	0.90
0.4	1.0	–	0.70
0.7	1.0	–	0.70
1.0	1.0	–	0.60
2.0	1.0	–	0.40
3.0	1.0	–	0.30
4.0	1.0	–	0.30
–	2.0	–	1.20
–	3.0	–	1.30
–	4.0	–	1.30
–	1.0	10	1.10
–	1.0	20	1.10
–	1.0	30	1.10
–	1.0	40	1.2

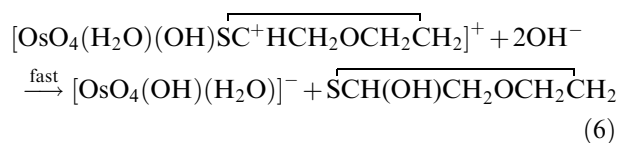
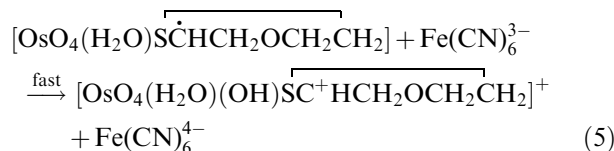
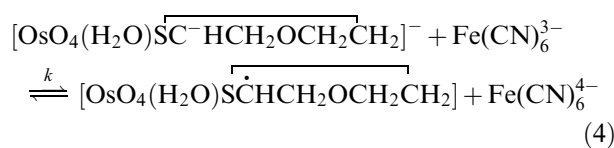
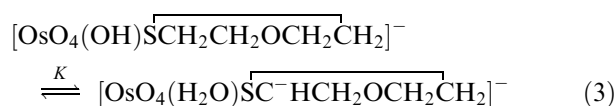
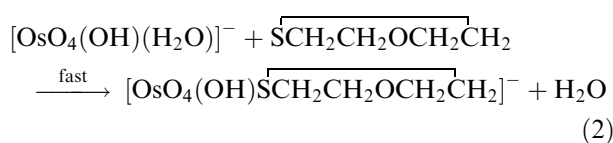
$[\text{Fe}(\text{CN})_6^{3-}] = 10^{-3} \text{ M}$, $[\text{1,4-thioxane}] = 10^{-2} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5} \text{ M}$, $[\text{NaOH}] = 10^2 \text{ M}$.

Table 4. Rate dependence on type of anion (KX) and cation (MCl) at 20 °C

KX	MCl	$10^3 k_1 \text{ (s}^{-1}\text{)}$
KF	–	1.20
KCl	–	1.20
KBr	–	1.20
KI	–	1.20
–	NaCl	1.05
–	NH_4Cl	0.15

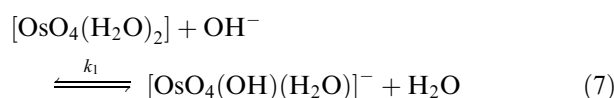
$[\text{Fe}(\text{CN})_6^{3-}] = 10^{-3} \text{ M}$, $[\text{1,4-thioxane}] = 10^{-2} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5} \text{ M}$, $[\text{NaOH}] = 10^{-2} \text{ M}$, $[\text{KX}] = 10^{-2} \text{ M}$, $[\text{MCl}] = 10^2 \text{ M}$.

Taking into account all the above experimental results, the mechanism shown in Equations (2)–(6) is proposed.



Mechanism and rate law

Osmic acid in KOH solution at 25 °C has the first (K_{1a}) and second (K_{2a}) dissociation constants, 1×10^{-2} and $3 \times 10^{-5} \text{ mol dm}^{-3}$ respectively [10]. Further, osmium tetroxide gives, with alkalis, the possible equilibrium [11].



with $K_1 = K_{1a}[\text{H}_2\text{O}]/K_w = 5.55 \times 10^{13}$ which means that almost all of the $[\text{OsO}_4(\text{H}_2\text{O})_2]$ exists as $[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^-$, even in dilute alkaline solution.

The first step in the mechanism [Equation (2)] is fast. Abstraction of hydrogen from the α -carbon atom in a reversible step [Equation (3)] has been proposed because only substrates with acidic protons have been reported to undergo oxidation by alkaline $\text{Fe}(\text{CN})_6^{3-}$ [1]. The

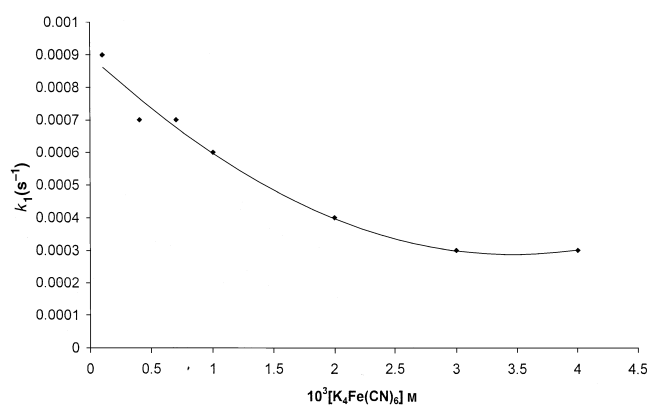


Fig. 3. Effect of varying $[\text{Fe}(\text{CN})_6^{4-}]$ at 20 °C. $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 1.0 \times 10^{-5} \text{ M}$, $[\text{1,4-thioxane}] = 0.01 \text{ M}$, $[\text{NaOH}] = 0.01 \text{ M}$.

Table 5. Rate constants and thermodynamic parameters for oxidation of 1,4-thioxane

Temp. (°C)	$10^3 k_1$ (s ⁻¹)
20	1.20
29	1.50
33	1.7
43	2.20

$\Delta H^\ddagger = 18.0 \text{ kJ mol}^{-1}$
 $\Delta S^\ddagger = -2.5 \text{ J K}^{-1} \text{ mol}^{-1}$

$[\text{Fe}(\text{CN})_6^{3-}] = 10^{-3} \text{ M}$, $[\text{1,4-thioxane}] = 10^{-2} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5} \text{ M}$, $[\text{NaOH}] = 10^{-2} \text{ M}$, $\mu = 0.01 \text{ M}$.

removal of an acidic proton has been reported also in a variety of hexacyanoferrate(III) oxidations [12–14].

The anion formed [Equation (3)] and also the subsequent formation of a radical [Equation (4)] in the reaction are stabilized by the adjacent sulfur atom due to $d\pi-p\pi$ bonding, resulting in the expansion of the sulfur valence shell [15, 16].

Since the overall process is a two-electron transfer, the clean first-order kinetics in $[\text{Fe}(\text{CN})_6^{3-}]$ implies that a free radical is formed in the slow step. The second molecule of hexacyanoferrate(III) has to react only in a fast step [Equation (5)].

The reversible nature of Equation (4) stems from the rate retardation by added $\text{Fe}(\text{CN})_6^{4-}$. This retardation is due to the shifting of the equilibrium towards the left in the presence of an excess of hexacyanoferrate(II).

The invariant first-order rate constants at different initial $[\text{Fe}(\text{CN})_6^{3-}]$ (Table 1) and good linear first-order plots of the reaction without any retardation indicate that the backward reaction is slow compared to the forward reaction.

The plot of logarithms rate constants versus $1/T$ at different temperatures gives an excellent straight-line (r 0.999) from which ΔH^\ddagger and ΔS^\ddagger were calculated as 18.0 kJ mol^{-1} and $-2.5 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively (Table 5).

The formation of the α -hydroxy product agrees with reported studies on the oxidation of organosulfur compounds [1, 17]. The rate expression, shown in

Equation (8), is derived and accounts for the experimental observations.

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k_{\text{obs}}[\text{Os}^{\text{VIII}}][\text{Fe}(\text{CN})_6^{3-}] \quad (8)$$

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