

Osmium(VIII)-catalyzed oxidation of pentamethylene sulfide

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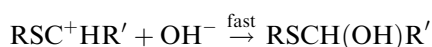
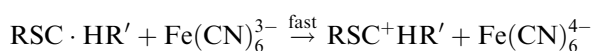
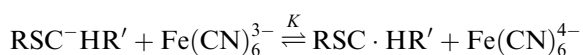
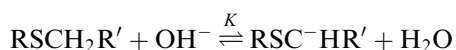
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Abstract

Although pentamethylene sulfide (tetrahydrothiopyran) lacks acidic hydrogen, Os^{VIII} has been found to catalyze its oxidation by alkaline K₃Fe(CN)₆ to produce 3-hydroxypentamethylene sulfide as the only product. The kinetics reveal first-order dependence on ferricyanide and Os^{VIII}, and zero order on pentamethylene sulfide and OH⁻. The effects of introduced electrolytes, K₄Fe(CN)₆, relative permittivity and temperature have also been studied. On the basis of kinetic evidence, a mechanism that involves anation of the osmium catalyst (sulfide/water interchange) followed by intramolecular proton abstraction, followed by an electron transfer step has been proposed and discussed.

Introduction

Although potassium hexacyanoferrate(III) has been found to be suitable for the oxidation of a wide variety of substrates [1–8], the oxidation of phenylmercaptoacetates has indicated the inertness of several sulfides toward this oxidant unless the sulfide has at least one acidic hydrogen [2].



where R = Ar and R' = CH₂COOH.

Organosulfur compounds are known to form stable complexes with metal ions, and some of these ions, *viz.* Ag^I, Cu^{II}, Os^{VIII}, have a marked catalytic effect on the reaction rate [9, 10]. Os^{VIII}, being able to form complexes with electron-pair donors, is known to enhance the rate of oxidation of various organic compounds by alkaline hexacyanoferrate(III) through different mechanistic pathways [1, 2, 11–14]. The present work reports a systematic kinetics study of oxidation of the cyclic thioether, *pentamethylene sulfide* (C₅H₁₀S), to demonstrate the possible oxidation of such organosulfur compounds that lack the presence of both acidic hydrogen and electronegative atoms (O or N) in the thioether skeleton. The oxidation of pentamethylene sulfide is an interesting redox reaction as this substrate is a widely used additive for several polymerizations.

Experimental

Materials

A standard OsO₄ solution (Sigma, AR) was diluted with NaOH solution, which was freshly prepared and standardized against potassium hydrogen phthalate. Solutions of pentamethylene sulfide (Aldrich, AR) and K₃Fe(CN)₆ (Riedel-de Haen, AR) were freshly prepared from samples which were used as received. KCl was used throughout for adjusting the ionic strength. All other reagents used for the experiment were analytical grade chemicals and were used as such. Doubly distilled H₂O was used for preparing solutions.

Kinetic procedure

The required concentration of Os^{VIII}, KCl, pentamethylene sulfide, and other reagents were thermostatted in a reaction vessel. K₃Fe(CN)₆, separately equilibrated, was added to the mixture to initiate the reaction. The reactions were followed spectrophotometrically by measuring the change in absorption of K₃Fe(CN)₆ at 414 nm against a standard solution of ferricyanide in aqueous alkaline. The absorption of K₄Fe(CN)₆ at this wavelength is negligible. The linearity of the relationship between the absorbance at 414 nm and K₃Fe(CN)₆ concentration in the aqueous alkaline medium was confirmed using a Sp 8-100 spectrophotometer.

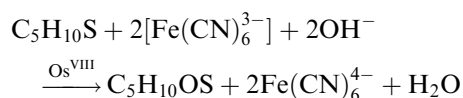
Rate of reaction

All kinetics was carried out under pseudo-first-order conditions with the sulfide being in excess (10-fold), unless stated otherwise. The pseudo-first-order rate

constant (k_1) was calculated from the slope of the linear plots of $\log[\text{Fe}(\text{CN})_6^{3-}]$ versus time. The rate of loss of ferricyanide was followed to more than 90% conversion. The reproducibility of the rate constant values was about $\pm 3\%$.

Stoichiometry

A reaction mixture containing a known excess of $\text{K}_3\text{Fe}(\text{CN})_6$ over the sulfide was allowed to stand in 0.1 M NaOH in the presence of the catalyst until completion of the reaction. The stoichiometry of the net reaction was determined spectrophotometrically by measuring, at $\lambda = 414$ nm, the concentration of $\text{K}_3\text{Fe}(\text{CN})_6$ remaining after completion. The results of three experiments reveal the same ratio of ferricyanide to sulfide (2:1):



Product analysis

A stoichiometric mixture of the sulfide and hexacyanoferrate(III) in the presence of the catalyst was kept in NaOH until completion of the reaction, then extracted with CHCl_3 . On removal of CHCl_3 the product was found to be 3-hydroxypentamethylene sulfide (tetrahydrothiopyran-3-ol). The i.r. spectrum of the product, measured on a FT-IR Shimadzu 8201 spectrophotometer, indicated the presence of a C—O bond (1030 cm^{-1}) and a secondary hydroxyl group (3450 cm^{-1}), but no indication of any band corresponding to the S=O frequency. Reaction of the product with Lucas' reagent (anhydrous ZnCl_2 in concentrated HCl) gave further support for the formation of a secondary alcohol.

Results and discussion

Effect of varying reactants

The Os^{VIII} catalyzed hexacyanoferrate(III) oxidation of pentamethylene sulfide has been investigated for several initial concentrations of the reactants. The plots of $\log[\text{Fe}(\text{CN})_6^{3-}]$ versus time were found to be linear ($r > 0.99$) (Figure 1) and the rate constant, k_1 , at varying $[\text{Fe}(\text{CN})_6^{3-}]$ is constant, indicating first-order dependence of rate with respect to the concentration of ferricyanide (Table 1). The effect of concentration of catalyst is incorporated in Table 1. The plot of k_1 versus $[\text{Os}^{\text{VIII}}]$ shows a linear relationship ($r > 0.96$) (Figure 2) with negligible intercept, suggesting that the rate of uncatalyzed oxidation of pentamethylene sulfide is negligible. The linear plot of $\log k_1$ versus $\log[\text{Os}^{\text{VIII}}]$ ($r > 0.98$) with a slope of 1.1 supports a first-order dependence of the rate on the concentration of osmium(VIII). This was also apparent from the constant

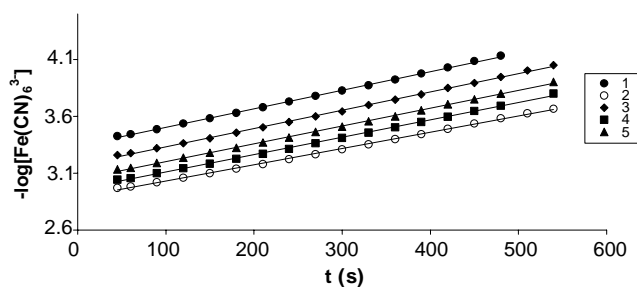


Fig. 1. Effect of varying $[\text{Fe}(\text{CN})_6^{3-}]$ in the catalyzed oxidation of pentamethylene sulfide at 20°C . $[\text{C}_5\text{H}_{10}\text{S}] = 0.01\text{ M}$, $[\text{Os}^{\text{VIII}}] = 10^{-5}\text{ M}$, $[\text{NaOH}] = 0.01\text{ M}$, $[\text{Fe}(\text{CN})_6^{3-}]$: 1 = $0.4 \times 10^{-3}\text{ M}$; 2 = $0.6 \times 10^{-3}\text{ M}$; 3 = $0.8 \times 10^{-3}\text{ M}$; 4 = 10^{-3} M ; 5 = $1.2 \times 10^{-3}\text{ M}$.

Table 1. Rate dependence on the concentration ferricyanide and Os^{VIII} at 20°C

$10^3 [\text{Fe}(\text{CN})_6^{3-}]\text{ M}$	$10^5 [\text{Os}^{\text{VIII}}]\text{ M}$	$10^3 k_1 (\text{s}^{-1})$	$10^3 k_2 (\text{M s}^{-1})$
0.40	1.00	1.60	1.60
0.60	1.00	1.40	1.40
0.80	1.00	1.60	1.60
1.00	1.00	1.50	1.50
1.20	1.00	1.40	1.40
1.00	2.00	3.10	1.55
1.00	3.00	4.60	1.53
1.00	4.00	6.00	1.50
1.00	6.00	7.80	1.30

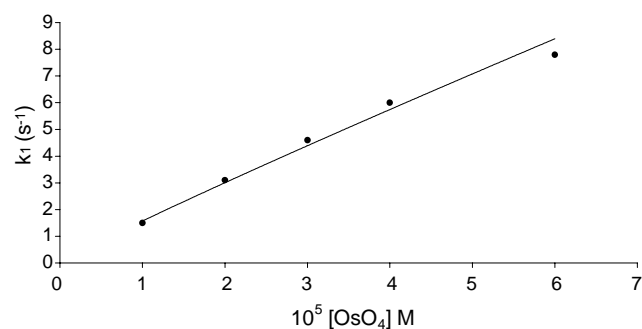


Fig. 2. Effect of varying $[\text{OsO}_4]$ at 20°C . $[\text{Fe}(\text{CN})_6^{3-}] = 10^{-3}\text{ M}$, $[\text{C}_5\text{H}_{10}\text{S}] = 0.01\text{ M}$, $[\text{NaOH}] = 0.01\text{ M}$.

values of k_2 , $k_2 = k_1/[\text{Os}(\text{VIII})]$. The results of changing the concentration of pentamethylene sulfide (Figure 3) and hydroxyl ion are noted in Table 2. The pseudo-first-order rate constant, k_1 , does not vary with changing concentrations of the sulfide or the hydroxyl ion, indicating a zero-order dependence of the rate on $[\text{sulfide}]$ and $[\text{OH}^-]$.

Thus the experimental data suggests the following rate law:

$$\text{Rate} = k[\text{Os}^{\text{VIII}}][\text{Fe}(\text{CN})_6^{3-}]$$

Influence of introduced electrolytes

Tables 3 and 4 indicate that changing either the ionic strength of the medium (maintained by the addition of

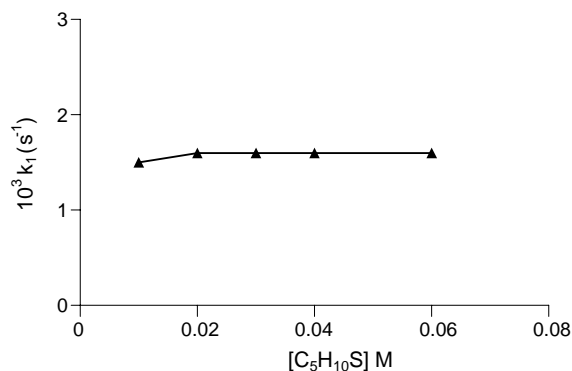


Fig. 3. Effect of varying $[C_5H_{10}S]$ at 20 °C. $[Fe(CN)_6^{3-}] = 10^{-3}$ M, $[Os^{VIII}] = 10^{-5}$ M, $[NaOH] = 0.01$ M.

Table 2. Rate dependence on the concentration of pentamethylene sulfide and NaOH at 20 °C

$[C_5H_{10}S]$ M	$[NaOH]$ M	$10^3 k_1$ (s^{-1})
0.01	0.01	1.50
0.02	0.01	1.60
0.03	0.01	1.60
0.04	0.01	1.60
0.06	0.01	1.60
0.01	0.02	1.50
0.01	0.05	1.60
0.01	0.10	1.60

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

KCl) or the type of added anion (F^- , Cl^- , Br^- , I^-) does not affect the oxidation rate. These results suggest the involvement of ions of like charges in the rate-controlling step [15–17]. In this case the rate will not depend on ionic strength, but rather on the concentration and character of salt ions having signs opposite to that of the reactants. To test this hypothesis, other electrolytes (at the same concentrations) were introduced into the reaction mixture (Table 4). The results clearly reveal the existence of specific salt effect of cations; the rate constant (k_1) increased in the order NH_4^+ ($0.6 \times 10^{-3} s^{-1}$) < Na^+ ($1.2 \times 10^{-3} s^{-1}$) < K^+ ($1.5 \times 10^{-3} s^{-1}$). For Na^+ and K^+ , this catalytic effect follows the polarizability trend of the cations. The relatively low k_1 value observed for ammonium ion supports the assumed catalytic effect of alkali metals; the introduced

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

$10^3 [Fe(CN)_6^{4-}]$ M	$[KCl]$ M	$10^3 k_1$ (s^{-1})
0.40	–	1.45
1.00	–	1.40
2.00	–	1.40
3.00	–	1.35
4.00	–	1.45
–	0.01	1.50
–	0.02	1.55
–	0.03	1.45
–	0.04	1.50

$[Fe(CN)_6^{3-}] = 10^{-3}$ M, $[Os^{VIII}] = 10^{-5}$ M, $[C_5H_{10}S] = 0.01$ M, $[NaOH] = 0.01$ M.

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

KX	MCl	EtOH (%)	$10^3 k_1$ (s^{-1})
KF	–	–	1.60
KCl	–	–	1.50
KBr	–	–	1.50
KI	–	–	1.40
–	NaCl	–	1.20
–	NH_4Cl	–	0.60
–	–	10	1.20
–	–	20	1.00
–	–	30	0.90
–	–	40	0.90

$[Fe(CN)_6^{3-}] = 10^{-3}$ M, $[Os^{VIII}] = 10^{-5}$ M, $[C_5H_{10}S] = 0.01$ M, $[NaOH] = 0.01$ M, $[KX] = 10^{-2}$ M, $[MCl] = 10^{-2}$ M.

NH_4^+ will react instantly with the hydroxyl ion in the medium to produce ammonia and hence the specific salt effect of a cation no longer exists. Relevant contributions to the role played by cations like alkali-metal ions has been reported for several ferricyanide oxidation processes [3, 18–22] and becomes a common feature of several chemical reactions between two charged species or an uncharged and a charged species. The role of the cation is assumed to reduce the repulsion between the charged ions [3, 22–26].

Influence of potassium hexacyanoferrate(II)

In the pseudo-first-order plots, no deviation was observed even near completion of the reaction, whereas the concentration of hexacyanoferrate(II) will increase during the course of reaction. To confirm this assumption, the initial amount of potassium hexacyanoferrate(II) was added to the reaction mixtures that results in no change in the rate constant (k_1) values (Table 3). This implies that if hexacyanoferrate(II) ion is involved in the rate-determining step, this step is irreversible and may proceed through a radical intermediate [27–29].

Influence of relative permittivity

Table 4 lists the variation of the rate constant (k_1) with solvent composition using ethanol–water mixtures. Decreasing the relative permittivity of the solvent, by increasing the percentage of ethanol, results in a noticeable decrease in the rate constant values. This trend is attributed to a chemical reaction between two negatively charged reactants where a medium of relatively higher permittivity is expected to enhance the overall reaction rate [30]. This also confirms the conclusions reached above for the influence of introduced electrolytes.

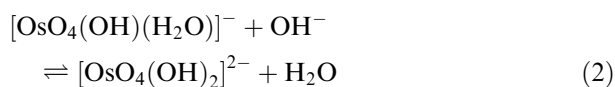
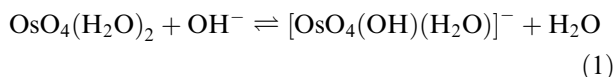
Thermodynamic parameters

The kinetics were obtained at 22, 29, 33 and 43 °C by applying the Arrhenius Law. The results are incorpo-

rated in Table 5 along with ΔH^\ddagger and ΔS^\ddagger values that have been calculated using the Wynne–James and Eyring equations [30]. The relatively small negative value of the entropy of activation in the present oxidation suggests that the rate-determining step involves a radical intermediate formation.

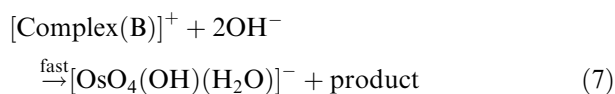
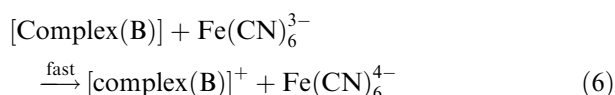
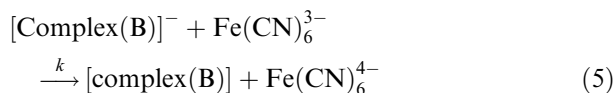
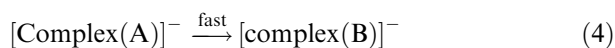
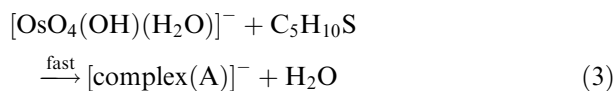
Rate law and mechanism

Osmium tetroxide exists in different forms depending on the medium [31–33]. In alkali, the following two equilibria exist (Equations 1 and 2):



The corresponding equilibrium constants (at 25 °C) are 5.55×10^{13} and 16.6, respectively. Thus, $[\text{OsO}_4(\text{H}_2\text{O})_2]$ is assumed to exist as $[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^-$ under the experimental conditions (dilute alkali) and is presumed to be the effective catalyst for oxidation.

Based on experimental findings, the following mechanism is proposed:



The first step (Equation 3) is the anation of $[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^-$ and involves a fast interchange of the sulfide molecule (entering group) with the coordinated H_2O molecule (leaving group) to give $[\text{complex(A)}]^-$, ($k > 10^4$) [34]. Formation of a metal–sulfur linkage in a step

preceding oxidation has been observed in several instances [35, 36]. Because the employed concentration of the sulfide was 1000-fold that of Os^{VIII} , the oxidation of the sulfide by Os^{VIII} is considered to be negligible and Os^{VIII} merely acts as a catalyst for proton abstraction from the sulfide at the α -carbon atom to produce a carbanion intermediate, $[\text{complex(B)}]^-$ (Equation (4)). This step is also fast (intramolecular H-abstraction by the coordinated OH ligand) and has been suggested in an initial step in several hexacyanoferrate(III) oxidations [2]. The adjacent sulfur atom is expected to stabilize the formation of the carbanion intermediate $\{[\text{complex(B)}]^- \}$ and the subsequent formation of the carbon radical intermediate $\{[\text{complex(B)}] \}$ (Equation 5) due to the d_π – p_π bonding results from utilizing the vacant sulfur d-orbital [37]. The first-order dependence of rate on $[\text{Fe}(\text{CN})_6^{3-}]$ indicates its involvement in a slow one-electron transfer to form the radical intermediate $\{[\text{complex(B)}] \}$ (Equation 5). Performing the reaction in the presence of the radical scavenger, acryl amid, supported the formation of this radical. The rate of oxidation increased upon adding the acryl amide. The scavenger attacks the carbon atom carrying the odd electron (Equation 5) and thus enhances the consumption of $\text{Fe}(\text{CN})_6^{3-}$. The irreversible nature of the slow step stems from the absence of any rate retardation by added hexacyanoferrate(II) (Table 3). The good linear first-order plots with respect to $[\text{Fe}(\text{CN})_6^{3-}]$ up to near completion of the reaction without any retardation (Figure 1) support this assumption. In the next step (Equation 6), The second ferricyanide molecule abstracts a second electron from the carbon radical $\{[\text{complex(B)}] \}$ to produce the primary carbocation intermediate $\{[\text{complex(B)}]^+ \}$. The primary carbocation rearranges to the secondary carbocation (β -carbon) before being hydrolyzed to give 3-hydroxypentamethylene sulfide.

The above mechanism enables us to derive the following rate law:

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k[\text{complex(B)}]^-[\text{Fe}(\text{CN})_6^{3-}] \quad (8)$$

Due to the fast nature of steps 3 and 4, and the fact that $[\text{Os}^{\text{VIII}}]/[\text{sulfide}] = 1/1000$, it is safe to assume that the concentration of $[\text{complex(B)}]^-$ equals that of Os^{VIII} . Thus the derived rate law could be written as

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k[\text{Os}^{\text{VIII}}][\text{Fe}(\text{CN})_6^{3-}] \quad (9)$$

Equation (9) accounts satisfactorily for all the experimental observations, *i.e.* the effect of concentrations of $\text{Fe}(\text{CN})_6^{3-}$, sulfide, Os^{VIII} and OH^- , on the reaction rate. The nature of the slow step (6) also explains the effect of electrolytes and permittivity of the solvent as mentioned earlier.

3-Hydroxypentamethylene sulfide was the sole product of the oxidation of pentamethylene sulfide. The formation of sulfoxide, which could occur if the sulfur atom was attacked, is not expected as the one electron

Table 5. Rate constants and thermodynamic parameters for oxidation of pentamethylene sulfide

Temp. (°C)	22	29	33	43
$10^3 k_1$ (s ⁻¹)	1.8	2.1	2.4	2.7
$\Delta H^\ddagger = 12.3$ kJ mol ⁻¹				
$\Delta S^\ddagger = -20.7$ J K ⁻¹ mol ⁻¹				
[Fe(CN) ₆ ³⁻] = 10 ⁻³ M, [C ₅ H ₁₀ S] = 10 ⁻² M, [Os ^{VIII}] = 10 ⁻⁵ M, [NaOH] = 10 ⁻² M, $\mu = 0.01$ M.				

oxidation potential of alky sulfides is much higher than that of hexacyanoferrate(III) [32, 33]. The proposed mechanism also explains the role of Os^{VIII} in the oxidation of an organosulfur compound, even if the latter lacks an acidic hydrogen.

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