Bull. Chem. Soc. Jpn., 55, 587—593 (1982)

Electron Transfer between Hexacyanoferrate(III) and Thiosulfate. Kinetic Studies in the *trans*-Dihydroxotetraoxoosmate(VIII) Oxidation and the *trans*-Dihydroxotetraoxoosmate(VIII)-catalyzed Hexacyanoferrate(III) Oxidation of Thiosulfate in Aqueous Alkaline Media

Rama Krushna Panda,* Gautam Neogi, and Dorai Ramaswamy†
Department of Chemistry, Berhampur University, Berhampur-760007, India
† *Chemical Laboratories, Central Leather Research Institute, Madras-600020, India*

(Received November 17, 1980)

Kinetics of oxidation of thiosulfate to tetrathionate by *trans*-dihydroxotetraoxoosmate(VIII) (Os(VIII)) and by hexacyanoferrate(III) in the catalytic presence of Os(VIII) have been studied in aqueous alkaline media. The observed pseudo-first-order rate constants for disappearance of Os(VIII) in the Os(VIII)–$S_2O_3^{2-}$ system (k_{obsd}), and those for disappearance of hexacyanoferrate(III) in the Os(VIII)-catalysed $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ system (k_{cat}) conform, respectively, to Eqs. A and B:

$$k_{obsd}=k_3K_{Os}K_2[S_2O_3^{2-}](1+K_{Os}[OH^-]+K_{Os}K_2[S_2O_3^{2-}])^{-1}, \tag{A}$$

$$k_{cat}=k_6K_{Os}K_2[Os(VIII)][OH^-][S_2O_3^{2-}](1+K_{Os}K_2[S_2O_3^{2-}])^{-1}, \tag{B}$$

where K_{Os} is the stability constant of *trans*-dihydroxotetraoxoosmate(VIII) in aqueous alkaline media, K_2 and k_3 are the formation and decomposition constant of the intermediate complex **1**, and k_6 refers to the rate constant of electron-transfer from **1** to hexacyanoferrate(III). The values of K_{Os} and K_2, as obtained from spectrophotometric titrations and stopped-flow spectrophotometry, respectively, are 19.5±3 dm³ mol⁻¹ and 5.58±0.13; the computed values from kinetic data of K_{Os}, K_2, and k_3 at 30 °C and $\mu=0.32$ mol dm^{-3}, and that of k_6 at 35 °C and $\mu=0.32$ mol dm^{-3} are 22.5±2 dm^3 mol^{-1}, 6.12±0.5, $(3.32\pm0.3)\times10^{-1}$ dm^3 mol^{-1} s^{-1}, and $(3.31\pm0.3)\times10^{-2}$ dm^6 mol^{-2} s^{-1}, respectively. Possible mechanisms for electron-transfer are discussed in terms of an initial equilibrium interaction between Os(VIII) and $S_2O_3^{2-}$ forming an intermediate complex $[OsO_4(OH)(S_2O_3)^{3-}]$ (**1**) followed by (a) a rate-determining decomposition of **1**, with concomitant electron-transfer, in the Os(VIII)–$S_2O_3^{2-}$ system, and (b) a rate-determining outersphere electron-transfer from **1** to hexacyanoferrate(III) in the Os(VIII)-catalyzed $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ system.

The oxidation of thiosulfate by various metallic oxidants has been shown to proceed either through the intermediacy of metal-thiosulfato complexes[1–5)] formed prior to electron-transfer or without a change in the inner co-ordination sphere of the metal.[6–9)] We have observed[7)] that the oxidation of thiosulfate is zero-order in hexacyanoferrate(III) over a pH range 6.03—12.3, the main reaction being the spontaneous decomposition of thiosulfate. Similar observations were made by Howlett and Wedzicha[6)] who reported that the initial 5% reaction of hexacyanoferrate(III) with thiosulfate in the presence of H_2(edta) and acetate was of zero-order in hexacyanoferrate(III). In the presence of 'Osmium Tetraoxide' and an 8—10% aqueous solution of potassium hydroxide, hexacyanoferrate(III) was found to oxidise thiosulfate to sulfate,[10)] but the details of the reaction were not presented. In the present study, we are reporting the *trans*-dihydroxotetraoxoosmate(VIII)-catalyzed hexacyanoferrate(III) oxidation of thiosulfate to tetrathionate. Unlike earlier reports on the Os(VIII)-catalyzed electron-transfer reactions, the present kinetics exhibit a first-order dependence in hexacyanoferrate(III).

An understanding of the extent to which Os(VIII) can function as an electron-transfer agent is crucial to the interpretation of kinetics and mechanism of Os(VIII)-catalyzed electron-transfer reactions. Quite a few organic functions have been directly oxidized by Os(VIII); however, no study appears to have been carried out on the direct oxidation of inorganic compounds by Os(VIII). Keeping this in view, the electron-transfer in the Os(VIII)–$S_2O_3^{2-}$ system has been studied as an extension by stopped-flow spectrophotometry.

Experimental

Materials and Methods. All the chemicals used were of Analar grade, and the solutions were prepared using doubly distilled water exclusively. A requisite amount of Os(VIII) solution from the stock (prepared by dissolving 'OsO_4' of Johnson-Matthey in a weakly aqueous alkaline solution, estimated by iodometry[11)] and stored in a cool dark place) was taken (as such for the direct oxidation by Os(VIII) or along with hexacyanoferrate(III) solution in the case of catalyzed reactions), made up, thermostated and mixed with the thiosulfate solution at appropriate pH and ionic strength. The ionic strength (μ) of the medium was adjusted by the addition of a required amount of the supporting electrolyte, sodium sulfate. The pH of the medium (±0.01), maintained by the addition of suitable amounts of standard aqueous buffers or carbonate-free hydroxide, as the case may be, was recorded by a Systronics 335 digital pH meter both before and after the reaction; the hydroxide concentrations were calculated from the mean recorded pH after correcting for the ionic strength effect of the medium. The Os(VIII)-catalyzed hexacyanoferrate(III) oxidation reactions were performed by mixing 1 ml aliquots of reactant solutions in a 1 cm-quartz cell by means of semimicro syringes. The course of the reactions was monitored for the decrease in absorbance of hexacyanoferrate(III), continuously as a function of time, at 420 nm (ε_{420} 9.8×10^2 dm^3 mol^{-1} cm^{-1}), in a Pye Unicam SP 1800 spectrophotometer maintained at a desired temperature (±0.1 °C). An extended absorbance scale was used for experiments in which lower concentration of the oxidant was taken.

The electronic spectrum of an aqueous alkaline solution of *trans*-$OsO_4(OH)_2^{2-}$, abbreviated as Os(VIII), showed characteristic bands at 316 nm (ε_{316} 500 $dm^3 mol^{-1} cm^{-1}$) and 247 nm (ε_{247} 690 $dm^3 mol^{-1} cm^{-1}$); earlier workers[11] did not report this observation. In visible region, the solution absorbed strongly around 390 nm, the absorption decreasing with increasing wavelength but without any characteristic maximum in the 390—750 nm region. Tetrathionate, the oxidation product of thiosulfate, absorbed significantly around 247 nm. The kinetic runs for the Os(VIII)-$S_2O_3^{2-}$ system were, therefore, followed by monitoring the disappearance of $OsO_4(OH)_2^{2-}$ at 316 nm in an Aminco stopped-flow spectrophotometer with quartz windows and a 1 cm-light path coupled to a Beckman D. U. monochromator. The nominal mixing time for this spectrophotometer is 0.2 ms. For every entry, at least five replicate runs were performed.

The pseudo-first-order rate constants were computed by least-squares analysis of the expression: $-\ln[(A_t-A_\infty)/(A_0-A_\infty)]=k_{obsd}t$, where A_t, A_0, and A_∞, respectively, represent the absorbance of the reactant at time 't', the initial absorbance and the absorbance at effective infinite time.

For experiments where $[\text{Substrate}]_0$—$[\text{Oxidant}]_0$, the second-order rate constants (k') were calculated by the usual method; for these experiments the first-order rate constants were calculated from the expression: First-order-rate constant$=k'$ $[\text{Substrate}]_0$.

Computations were done by a D. C. M. Data Products minicomputer Microsystem 1121. The self-decomposition of thiosulfate in air was found to be negligible in the conditions employed.

Stoichiometry. The stoichiometric experiments were performed in the presence of 7.8×10^{-7} $mol\ dm^{-3}$ of Os(VIII) and in the absence of sodium sulfate. The experiments for the stoichiometric runs were carried out at 35 °C under the conditions of $[S_2O_3^{2-}]_0 \gtrsim [Fe(CN)_6^{3-}]_0$; for higher concentrations of hexacyanoferrate(III), under the conditions of $[S_2O_3^{2-}]_0 \gtrsim [Fe(CN)_6^{3-}]_0$, the runs were carried out at 35 °C and at pH 11.3 till the reaction, with respect to hexacyanoferrate(III), was complete (Table 1). The unconsumed $[S_2O_3^{2-}]_\infty$ was determined iodimetrically. Tests for tetrathionate were done following an earlier procedure.[12] The observed stoichiometric ratio $(\Delta[Fe(CN)_6^{3-}]/\Delta[S_2O_3^{2-}])$ of 0.98 ± 0.02 is in accord with the overall Eq. 1:

$$2Fe(CN)_6^{3-} + 2S_2O_3^{2-} \longrightarrow 2Fe(CN)_6^{4-} + S_4O_6^{2-}. \quad (1)$$

In the oxidation of thiosulfate in aqueous medium at pH 11.3 and 35 °C, 1 mol of Os(VIII) consumed 1.96 ± 0.03 mol of thiosulfate (Table 1) conforming to the formation of tetrathionate.

$$OsO_4(OH)_2^{2-} + 2S_2O_3^{2-} + 2H_2O \longrightarrow OsO_2(OH)_4^{2-} + S_4O_6^{2-} + 2OH^-. \quad (2)$$

On allowing the final reaction solution to stand for 24 h at room temperature (≈35 °C), it was observed that about 80% of the originally consumed thiosulfate was being reformed. Back-formation of thiosulfate in reaction mixtures of completed thiosulfate oxidation has been reported earlier and explained[1a] to be due to the hydrolysis of tetrathionate. The reformation is, however, very slow and does not complicate the kinetics studied.

TABLE 1. STOICHIOMETRIC DATA[a] FOR THE OXIDATION OF $S_2O_3^{2-}$ (AQUEOUS MEDIUM, pH 11.3, 35°C)

$Fe(CN)_6^{3-}$-$S_2O_3^{2-}$ system (Os(VIII)[b]-catalyzed)

10^2 $[Fe(CN)_6^{3-}]_o$[c]	10^2 $[S_2O_3^{2-}]_o$	10^2 $[S_2O_3^{2-}]_\infty$[d]
0.01	0.1	—[f]
0.01	0.05	0.039[f,g]
0.1	0.2	0.1[g]
0.2	1.0	0.79[g]
0.4	0.5	0.098[g]
0.5	1.0	0.49[g]
5.0	10.0	4.95[g]
5.0	10.02	8.1[h]
5.0	10.0	9.1[i]
5.01	5.95	4.9[i]

Os(VIII)-$S_2O_3^{2-}$ system

10^3 $[Os(VIII)]_o$[e]	10^3 $[S_2O_3^{2-}]_o$	10^3 $[Os(VIII)]_\infty$[e]	10^3 $[S_2O_3^{2-}]_\infty$[d]
2.0	1.0	1.48	
2.5	1.1	1.94	
3.2	1.2	2.58	
4.1	1.0	3.58	
5.0	1.0	4.49	
0.93	2.1		0.3[g]
0.94	3.0		1.2[g]
0.92	4.0		2.2[g]
0.98	5.2		4.3[g]
5.0	16.7		14.8[h]
10.1	22.0		18.0[i]

a) All concentration units are in $mol\ dm^{-3}$. b) In the presence of 7.8×10^{-7} $mol\ dm^{-3}$ of Os(VIII). c) *Key*: o; initial concentration, ∞; final concentration when the reaction is effectively over. d) Analysis by iodimetry in the presence of zinc sulfate solution just after the reaction is effectively complete. e) Analysis by spectrophotometry at 316 nm. f) At 45 °C. g) Analysis just after the reaction is complete. h) Analysis after keeping the final reaction solution at 35 °C for 24 h. i) Analysis after keeping the final reaction at 60 °C for 5 h (after h).

Results and Discussion

Electron-transfer in the Os(VIII)-$S_2O_3^{2-}$ System. In weakly alkaline solutions, OsO_4 appears to exist in the form of $OsO_3(OH)_3^-$ which combines with OH^- to yield the reactive form of Os(VIII), *trans*-$OsO_4(OH)_2^{2-}$. This is in accord with the findings of Sauerbrum and Sandell[13] on the dissociation of osmic acid.

$$OsO_3(OH)_3^- + OH^- \overset{K}{\rightleftharpoons} OsO_4(OH)_2^{2-} + H_2O,\ K/[H_2O] = K_{Os}. \quad (3)$$

($K_{Os}=24\pm4$ $dm^3 mol^{-1}$ at 25 °C and $\mu=1.0$ $mol\ dm^{-3}$, ΔH and ΔS associated with this equilibrium are 24 ± 1 $kJ\ mol^{-1}$ and $-146+6$ $J\ K^{-1} mol^{-1}$).[11]

Applying Benesi-Hildebrand equation[14] for the determination of equilibrium constant and ε,

$$[Os(VIII)]_0A^{-1} = (K\varepsilon[OH^-])^{-1} + \varepsilon^{-1} \text{ at } [Os(VIII)]_0 < [OH^-], \quad (4)$$

where $[Os(VIII)]_0$ is the total analytical concentration of Os(VIII) fixed by iodometry, and A and ε respectively refer to the absorbance and molar absorptivity of the complex at 316 nm, the values of K_{Os} and ε_{316} at 30 °C and $\mu=0.32$ mol dm^{-3} have been obtained by a weighted non-linear least-squares programme of the absorbance data at various $[Os(VIII)]_0$ and $[OH^-]$ ($[Os(VIII)]_0$ 0.6×10^{-4}—20.4×10^{-4} mol dm^{-3}, $[OH^-]$ 1×10^{-3}—40.1×10^{-3} mol dm^{-3}) as 19.5 ± 3 dm^3 mol^{-1} and 500 ± 20 dm^3 mol^{-1} cm^{-1}, respectively; these values should be independent of the concentrations of Os(VIII) and OH^- employed. The K_{Os} value of this work is in good agreement with that obtained earlier.[11)]

The Os(VIII)–$S_2O_3^{2-}$ reaction exhibits a first-order dependence on [Os(VIII)] in the range 0.45×10^{-4}—9.06×10^{-4} mol dm^{-3}. At 316 nm, first there is an abrupt increase in the absorbance ($t_{1/2}\approx125$ ms) followed by a subsequent slower step where the absorbance decreases. The first step probably represents a fast formation of an intermediate complex and is followed by a slower decay. The k_{obsd} value (corresponding to the decrease in absorbance) at a constant $[S_2O_3^{2-}]_0$ ($=5.0\times10^{-2}$ mol dm^{-3}) registers a marginal increase with the increase in $[OH^-]$ from 6.18×10^{-3} mol dm^{-3} to 1.0×10^{-2} mol dm^{-3}, remains almost unchanged till $[OH^-]=3.06\times10^{-2}$ mol dm^{-3}, and decreases significantly at much higher $[OH^-]$. The k_{obsd} is found to increase almost linearly with increasing $[S_2O_3^{2-}]$ for $[S_2O_3^{2-}]_0=1.0\times10^{-4}$—$10\times10^{-3}$ mol dm^{-3}; however, beyond $[S_2O_3^{2-}]$ of 50×10^{-3} mol dm^{-3}, the k_{obsd} varies only slightly by about 5% for an almost two-fold increase in $[S_2O_3^{2-}]$. The rate expression for the reduction of Os(VIII) should, therefore, include a distinct $[S_2O_3^{2-}]$- dependent term, getting saturated at higher $[S_2O_3^{2-}]$.

The k_{obsd} increases with an increase in ionic strength of the medium. It does not appreciably change in the range 25—45 °C. Added acrylonitrile retards the rate, but no polymerisation could be observed.

Rate Law and Mechanism: The preliminary kinetic results suggest that the mechanism of reduction of Os(VIII) by $S_2O_3^{2-}$ involves incorporation of a thiosulfato-ligand into the inner-coordination sphere of Os(VIII) prior to an electron-transfer step.

$$OsO_4(OH)_2^{2-} + S_2O_3^{2-} \overset{K_2}{\rightleftharpoons} [OsO_4(OH)(S_2O_3)^{3-}] + OH^-, \tag{5}$$

$$[OsO_4(OH)(S_2O_3)^{3-}] + H_2O \xrightarrow{k_3} OsO_4(OH)(H_2O)^{2-} + S_2O_3^-, \tag{6}$$

$$OsO_4(OH)(H_2O)^{2-} + S_2O_3^{2-} + H_2O \xrightarrow[\text{fast}]{k_4} OsO_2(OH)_4^{2-} + OH^- + S_2O_3^-, \tag{7}$$

$$2S_2O_3^- \xrightarrow[\text{fast}]{k_5} S_4O_6^{2-}. \tag{8}$$

Since $S_2O_3^{2-}$ is an effective one-electron reducing agent, an Os(VII) species will probably be produced which will further get reduced rapidly to Os(VI) with another $S_2O_3^{2-}$. Os(VII) is known in solution[16)] and has been prepared in solid state.[17)] Such a one-electron change can take place only with a high activation enthalpy because two very unstable species are formed (Eq. 6) and that the subsequent step, Os(VII) + e$^-$ → Os(VI), can proceed without obstacle.

Consequently, the mechanism of the reaction would result in the rate law (Eq. 9), on the basis of Eqs. 3, 5—8, and on applying a steady-state treatment to the intermediate complex $[OsO_4(OH)(S_2O_3)^{3-}]$ (**1**)

$$-\frac{d[Os(VIII)]}{dt} = \frac{k_3K_{Os}K_2[Os(VIII)]_T[S_2O_3^{2-}]}{1+K_{Os}[OH^-]+K_{Os}K_2[S_2O_3^{2-}]}, \tag{9}$$

where the total analytical $[Os(VIII)]_T=[OsO_3(OH)_3^-]+[OsO_4(OH)_2^{2-}]+[OsO_4(OH)(S_2O_3)^{3-}]$. If as a first approximation, a reasonable assumption is made that at the low $[OH^-]$ employed, $K_{Os}[OH^-]\ll(1+K_{Os}\times K_2[S_2O_3^{2-}])$, Eq. 10 is obtained.

$$-\frac{d[Os(VIII)]}{dt} = \frac{k_3K_{Os}K_2[Os(VIII)]_T[S_2O_3^{2-}]}{1+K_{Os}K_2[S_2O_3^{2-}]}, \tag{10}$$

$$k_{obsd} = k_3K_{Os}K_2[S_2O_3^{2-}](1+K_{Os}K_2[S_2O_3^{2-}])^{-1}, \tag{11}$$

which on rearrangement becomes

$$(k_{obsd})^{-1} = (k_3)^{-1} + (k_3K_{Os}K_2)^{-1}([S_2O_3^{2-}])^{-1}. \tag{12}$$

Eq. 12 predicts that $(k_{obsd})^{-1}$ should be a linear function of $([S_2O_3^{2-}])^{-1}$. From the intercept and slope of this least-squares plot (Fig. 1), using the experimentally determined K_{Os} value, the k_3 and K_2 values have been computed respectively as $(3.32\pm0.3)\times10^{-1}$ dm^3 mol^{-1} s^{-1} and 6.12 ± 0.5 at 30 °C and 0.32 mol dm^{-3} of ionic strength. The computed K_2 is very close to the average value (5.58) of the observed constant pertaining to the first abrupt increase in the absorbance at 316 nm. Also the agreement of the k_{calcd} (Eq. 12) values obtained (employing the estimated values of k_3, K_2, and the experimental value of K_{Os}) with the experimentally determined k_{obsd} is in support of the postulated mechanism.

Eq. 9 can be rearranged to Eq. 13:

$$(k_{obsd})^{-1} = (1+K_2[S_2O_3^{2-}]K_{Os})(k_3K_2[S_2O_3^{2-}]K_{Os})^{-1} + [OH^-](k_3K_2[S_2O_3^{2-}])^{-1}. \tag{13}$$

At $[S_2O_3^{2-}]_0=5.0\times10^{-2}$ mol dm^{-3}, employing the value of k_3 computed earlier, K_{Os} has been calculated from the least-squares slope and intercept of the $(k_{obsd})^{-1}$ *vs.* $[OH^-]$ plot as 22.5 ± 2 at 30 °C and $\mu=0.32$ mol dm^{-3}. This value is quite close to that experimentally determined. There is also agreement of the k_{calcd} (Eq. 13) values with the k_{obsd} values (Table 2).

Supporting evidences from kinetics or otherwise,

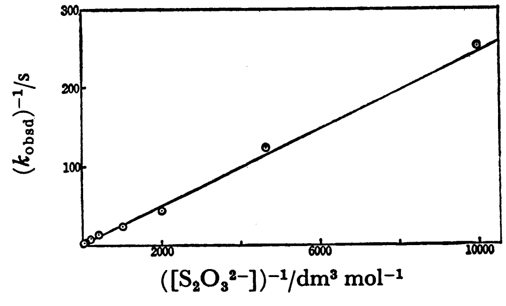

Fig. 1. $1/k_{obsd}$ *vs.* $1/[S_2O_3^{2-}]$ (The Os(VIII)–$S_2O_3^{2-}$ reaction) $[Os(VIII)]=6\times10^{-4}$, $[OH^-]=1\times10^{-2}$; Aqueous medium, 30 °C, $\mu=0.32$ (All concentrations are in mol dm^{-3}).

TABLE 2. TYPICAL AVERAGE[a)] RATE CONSTANTS FOR THE REACTION BETWEEN Os(VIII) AND $S_2O_3^{2-}$
(Aqueous medium, 30 °C, $\mu=0.32$[b)])

10^4 $[\mathrm{Os(VIII)}]_0$	10^3 $[S_2O_3^{2-}]_0$	10^2 $[\mathrm{OH}^-]$	$k_{\mathrm{obsd}}/\mathrm{s}^{-1}$ [c)]	$k_{\mathrm{calcd}}/\mathrm{s}^{-1}$
9.00	52	1.10	0.42[d)]	
9.00	50	1.10	0.50[e)]	
9.01	51	(6.18×10^{-8})[m)]	0.23	0.29[l)]
9.04	110	(6.18×10^{-8})[m)]	0.24	0.29[l)]
9.02	50	(4.28×10^{-6})[m)]	0.24	0.29[l)]
9.06	51	1.00	0.33	0.282[l)]
9.03	50	2.12	0.32	0.274[l)]
9.05	51	3.06	0.315	0.27[l)]
9.13	50	50.6	0.12	0.12[l)]
9.10	50	110	0.07	0.07[l)]
9.00	51	1.10	0.32[f)]	
9.06	51	1.00	0.33[g)]	
9.03	51	1.08	0.33[h)]	
3.00	53	1.03	0.32	
3.10	53	1.30	0.33[i)]	
3.05	50.5	1.20	0.32[i)]	
1.70	49	1.15	0.33	
9.04	51	1.02	0.19[j)]	
1.51	5.01	1.03	5.52*	
3.01	5.01	1.02	5.57*	
5.06	5.02	1.00	5.53*	
6.00	5.03	1.00	5.74*	
6.05	5.0	1.05	5.01*[f)]	
6.05	5.01	1.06	5.38*[g)]	
6.03	5.01	1.01	6.48*[h,k)]	
9.03	5.0	1.07	5.71*	
3.02	7.0	1.04	5.50*	
3.02	10.1	1.03	5.46*	
3.02	50.1	1.05	5.61*	

a) Standard deviations range from ±0.02 to 0.1 (at least five experiments for each entry). b) All concentration units in mol dm^{-3}. c) Average first-order rate constants with respect to the disappearance of Os(VIII) at 316 nm. d,e) Respectively at 0.42 and 0.52 mol dm^{-3} of ionic strength. f,g,h) Respectively at 25, 40, and 45 °C. i) For the appearance of $OsO_2(OH)_4^{2-}$ at 500 nm ($\Delta A/\Delta t>0$). j) In the presence of 1×10^{-4} mol dm^{-3} of acrylonitrile. k) Average ΔH^* and ΔS^* respectively 7.1 kJ mol^{-1} and -207 J K^{-1} mol^{-1}. l) Average k_{calcd} from Eq. 13 (representative). m) Calculated from measured pH. * Calculated for the first abrupt increase in absorbance of Os(VIII) at 316 nm.

have been well presented for the formation of intermediate complexes between metal ions and thiosulfate.[1–5)] In the Os(VIII)–$S_2O_3^{2-}$ system also, the kinetic evidences and the abrupt increase in absorbance at 316 nm, as soon as Os(VIII) and thiosulfate are mixed, are suggestive of the inner-sphere substitution of a hydroxo-ligand by a thiosulfato-ligand in the *trans*-$OsO_4(OH)_2^{2-}$.

The attack by the sulfur-end rather than by the oxygen-end of thiosulfate is consistent[18,4)] with the value of the formation constant of the intermediate complex $[OsO_4(OH)(S_2O_3)^{3-}]$. Spectrophotometric titrations could not be performed because of the rapidity of the change in absorbance of Os(VIII) and also due to the considerable absorption of tetrathionate between 240—290 nm. However, we got indications for the formation of a 1:1 intermediate complex involving Os(VIII) and thiosulfate by the following method. Zero-time absorbance at 316 nm were obtained by extrapolation for different $[\mathrm{Os(VIII)}]:[S_2O_3^{2-}]$ ratios in isomolar and non-isomolar mixtures. When the increase in the absorbance difference, $+\Delta A$, was plotted against the mole-fraction of Os(VIII), a maximum in ΔA was observed at the mole-fraction of Os(VIII)=0.5.

It is more rational to assume that an electron-transfer from thiosulfate to Os(VIII) has taken place during the substitution. The activated complex could then offer, at the same time, the lowest energy barrier to substitution and also to electron-transfer (Eq. 5), since the orbitals of the central osmium are disturbed (Table 2, foot note for activation parameters pertaining to the first abrupt increase in absorbance at 316 nm); the process starts as a substitution and continues with a one-electron transfer. Since *trans*-dihydroxotetraoxoosmate(VIII) ends up finally as *trans*-dioxotetrahydroxoosmate(VI), an equatorial attack by the outer-sulfur of thiosulfate on osmium is likely,[15b)] leading to a fair degree of displacement of the axial hydroxo-ligand.

Os(VIII)-catalyzed $Fe(CN)_6^{3-}$*–*$S_2O_3^{2-}$ *Electron-transfer.* Studies on Os(VIII)-catalysed oxidation reactions of various inorganic[11)] and organic substrates[19)] by hexacyanoferrate(III) are increasingly becoming useful probes in the elucidation of the nature of oscillatory catalysis of Os(VIII). In these studies and in numerous other studies of Os(VIII)-catalyzed oxidations by other oxidants,[20,21)] Os(VIII) is involved in an initial equilibrium formation of an intermediate Os(VIII)-substrate complex which breaks down rate-determingly to the products and Os(VI); the Os(VI) formed is oxidised rapidly to Os(VIII) by the main oxidant, resulting in zero-order kinetics with respect to the main oxidant.

In contrast to the earlier observations, the Os(VIII)-catalysed hexacyanoferrate(III) oxidation of thiosulfate is first-order in hexacyanoferrate(III) over the $[Fe(CN)_6^{3-}]_0$ range 0.1×10^{-4}—20.1×10^{-4} mol dm^{-3}. The observation is interesting as it is probably the first report of a main oxidant exhibiting first-order kinetics in the presence of an oscillatory catalyst.

At constant ionic strength and constant $[\mathrm{Na}^+]$ ($[\mathrm{Na}^+]\gg[\mathrm{K}^+]$), the k_{cat} value linearly increases with the increase in $[S_2O_3^{2-}]$, [Os(VIII)], or $[\mathrm{OH}^-]$ for their respective ranges of concentration: 1.0×10^{-5}—2.46×10^{-3}, 3.9×10^{-7}—97.3×10^{-7}, and 1.0×10^{-5}—50.5×10^{-3} mol dm^{-3} (Fig. 2). Also the good reproducibility of the k_{cat} value obtained by following the first-order disappearance of thiosulfate at 217 nm (in a representative run) with that obtained by monitoring the disappearance of hexacyanoferrate(III), shows that the rate of disappearance of thiosulfate is the same as that of hexacyanoferrate(III). There is a retardation in the rate in the presence of added mannitol, acrylonitrile or hexacyanoferrate(II) in this system (Table 3).

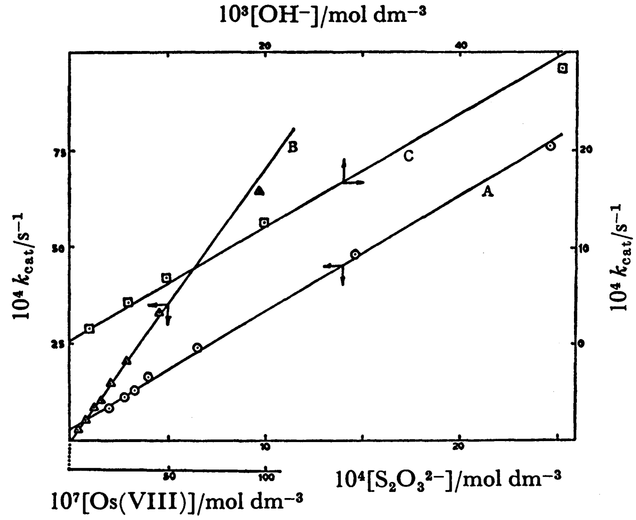

Fig. 2. k_{cat} *vs.* $[S_2O_3^{2-}]$, $[OH^-]$ or $[Os(VIII)]$ (The Os(VIII)-catalyzed $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ reaction). A: $[OH^-]=1\times10^{-2}$, $[Os(VIII)]=7.8\times10^{-7}$; B: $[S_2O_3^{2-}]=1.2\times10^{-4}$, $[OH^-]=1\times10^{-2}$; C: $[S_2O_3^{2-}]=1.6\times10^{-4}$, $[Os(VIII)]=7.8\times10^{-7}$; $[Fe(CN)_6^{3-}]=1\times10^{-4}$, aqueous medium, 35 °C, $\mu=0.32$ (All concentrations are in mol dm^{-3}).

The k_{cat} value increases linearly with μ. Considerable ion-pairing has been reported in oxidations by alkaline hexacyanoferrate(III), but in the present case as the rate is independent of the $[Fe(CN)_6^{3-}]_0$, any ion-pairing between K^+ or Na^+ and hexacyanoferrate(III) will have no significant effect[22] on the rate. A plot of oxidation rate (k_{cat}) against μ yields a straight line with no zero-rate at zero-electrolyte concentration. This, therefore, appears to be a mere ionic strength effect.[15a] A plot of $\log k_{cat}$ *vs.* $\mu^{1/2}$ is also linear, but no meaningful inference regarding the charge of the reacting ions could be drawn[23a] from the slope of the straight line, as the oxidation process is a multi-step one.

Rate Law and Mechanism: In the absence of Os(VIII), the oxidation of thiosulfate by hexacyanoferrate(III) does not virtually proceed[7] under the conditions employed for the catalysed oxidation, demonstrating that the presence of catalytic amounts of Os(VIII) accelerates the reaction tremendously. The observed kinetic data for the catalyzed system can be presented in terms of a reaction scheme consisting of Eqs. 3, 5, and 14.

$$[OsO_4(OH)(S_2O_3)^{3-}] + Fe(CN)_6^{3-} \xrightarrow[k_6]{OH^-} OsO_4(OH)_2^{2-} + Fe(CN)_6^{4-} + S_2O_3^-. \quad (14)$$

Since in the catalysed system, $[S_2O_3^{2-}] \gg [Os(VIII)] \ll [Fe(CN)_6^{3-}]$, the contribution of the catalytic $[Os(VIII)]$ to the direct oxidation of thiosulfate is negligible. Applying steady-state treatment to $[OsO_4(OH)(S_2O_3)^{3-}]$, a rate expression can be derived as in Eq. 15.

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{k_6K_{Os}K_2[Os(VIII)][Fe(CN)_6^{3-}][OH^-][S_2O_3^{2-}]}{1+K_{Os}K_2[S_2O_3^{2-}]}, \quad (15)$$

Table 3. Typical average[a] rate constants for Os(VIII)-catalyzed $Fe(CN)_6^{3-}$ oxidation of $S_2O_3^{2-}$

(Aqueous medium, 35 °C, $\mu=0.32$,[b] $[Fe(CN)_6^{3-}]_0=(1.0-1.05)\times10^{-4}$, $[Os(VIII)]=7.8\times10^{-7}$, $[OH^-]=(10.0-10.2)\times10^{-3}$)

$10^4\,[S_2O_3^{2-}]_0$	$10^4\,k_{cat}/s^{-1}$ [c]	$10^4\,k_{cat}(calcd)/s^{-1}$ [d]
1.23	5.00	4.79
1.25	5.17	4.87
1.61	6.70	6.24
2.00	7.78	7.72
2.17	8.84	8.36
2.80	11.15	10.70
3.28	13.20	12.50
4.00	16.40	15.10
6.45	24.00	23.70
14.6	48.0	49.1
24.6	76.0	75.2
2.10	7.53[e]	
0.1	0.4[f]	0.40
1.25	5.20[e]	4.87
2.80	12.20[g]	
2.80	17.74[h]	
2.81	11.26[i]	
2.82	11.25[j]	
2.80	11.22[k]	
2.80	11.10[l]	
3.00	0.07[m]	
2.03	1.36[n]	
2.78	0.35[o]	

a) Standard deviations range from ±0.002 to 0.05. b) All concentration units in mol dm^{-3}. c) Average first-order rate constants with respect to the disappearance of $Fe(CN)_6^{3-}$ at 420 nm. d) Average $k_{cat(calcd)}$ calculated from Eq. 16 (representative). e) Under an atmosphere of nitrogen gas; $[Fe(CN)_6^{3-}]_0=1.0\times10^{-3}$. f) For the disappearance of $S_2O_3^{2-}$ at 217 nm; $[Fe(CN)_6^{3-}]_0=1\times10^{-5}$. g, h) Respectively at 0.42 and 0.52 mol dm^{-3} of ionic strength. i,j,k,l) Respectively at 30, 40, 45, and 60 °C. m,n,o) Respectively in the presence of 1.0×10^{-4} mol dm^{-3} of added mannitol, acrylonitrile or $Fe(CN)_6^{4-}$.

or

$$k_{cat}(1+K_{Os}K_2(S_2O_3^{2-}]) = k_6K_{Os}K_2[Os(VIII)][OH^-][S_2O_3^{2-}]. \quad (16)$$

A plot of k_{cat} $(1+K_{Os}K_2[S_2O_3^{2-}])$ *vs.* $[S_2O_3^{2-}]$ should be a straight-line. At constant [Os(VIII)] and $[OH^-]$, employing the experimental value of K_{Os} and the computed value of K_2, the k_6 value for this system at 35 °C and $\mu=0.32$ mol dm^{-3} can be calculated from the least-squares slope of the above straight-line (neglecting the small value of the intercept) as $(3.31\pm0.3)\times10^{-2}$ dm^6 mol^{-2} s^{-1}. The $k_{cat(calcd)}$ values, calculated with the above values of k_6, K_{Os}, and K_2, agree with those obtained experimentally lending credence to the proposed rate expression.

Inasmuch as the redox potentials[24] for the couples $S_2O_3^{2-}/S_4O_6^{2-}$ and $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, are thermodynamically favourable for electron-transfer from thiosulfate to $Fe(CN)_6^{3-}$, it is expected that the oxidation of thiosulfate to tetrathionate should proceed by a direct interaction between thiosulfate and hexacyanoferrate(III). In fact, in numerous oxidation studies of thiosulfate by metallic oxidants like complexes of Cu(II),[1)] Co(III),[2)] Au(III),[3)] Cr(VI),[4)] and Fe(III),[5)] kinetic and other evidences suggest that intermediate metal-thiosulfato complexes (where the metal has lost one formal oxidation state and thiosulfate has gained one) are formed prior to the rate-determining electron-transfer step. Even though hexacyanoferrate(III) oxidations mostly involve outer-sphere electron change, in an analogous system[25)] involving hexacyanoferrate(III) and SO_3^{2-}, intermediate complexes of $Fe(CN)_5(CNSO_3)^{5-}$ and $Fe(CN)_5(CNSO_3)^{4-}$ have been evidenced in aqueous alkaline solution and definitely identified. Lancaster and Murray[25)] have suggested that many oxidations by transitional-metal complexes which are weak oxidants may proceed *via* intermediate complexes as described in the case of $Fe(CN)_6^{3-}$–SO_3^{2-} system. Legros[26)] has also reported that the hydrolysis of $Fe(CN)_5(S_2O_3)^{5-}$ in aqueous medium is accompanied by a high activation energy and positive activation entropy.

In the present system, however, no indication of any intermediate complex could be obtained from repeated and continuous scanning of the reaction solutions (from 250 nm to 650 nm). Also if the experiment is conducted in the presence of $^{14}CN^-$, there is no labelled cyano-ligand in the $Fe(CN)_6^{4-}$ product ensuring the absence of cyano exchange. Any direct interaction between hexacyanoferrate(III) and thiosulfate to form an intermediate complex necessiates a thiosulfato-ligand of very low Lewis-basicity to substitute or attach itself to, a cyano-ligand in a non-labile low-spin d^5-octahedral complex $Fe(CN)_6^{3-}$, and this is inherently not allowed in all probability. A comparison of the divergent pK of CN^- and SO_3^{2-} with that of $S_2O_3^{2-}$ (respectively 9.1, 9.1, and 1.9)[15c)] would show that even if any analogous complexes of $[Fe(CN)_5(CNS_2O_3)^{5-}]$ and $[Fe(CN)_5(CNS_2O_3)^{4-}]$ are thought of, they would not be stable enough in aqueous alkaline medium to be experimentally distinguishable.

However, in view of the expected higher redox potential of the couple Os(VIII)/Os(VI), the d^0-configuration of Os(VIII) and the decreased $10Dq$ value of Os(VIII) in the substitution of an octahedral complex, as compared to that in a substitution-inert $Fe(CN)_6^{3-}$, the substitution of a hydroxo-ligand by a thiosulfato-ligand in *trans*-dihydroxotetraoxoosmate(VIII) is possible. The intermediate complex thus formed, between Os(VIII) and $S_2O_3^{2-}$, undergoes hydrolysis (in the direct oxidation reaction by Os(VIII)) with concomitant electron transfer, or is involved in an outer-sphere electron-transfer in the presence of alkaline hexacyanoferrate(III) in a termolecular rate-determining step.

Evidences for the presence of $S_2O_3^-$, thiosulfate(1−), have been well presented.[5)] In the present system radical-trapping agents retard the rate; polymerisation, however, is not detected. This may be because $k(S_2O_3^- + S_2O_3^-) \gg k$ (induced polymerisation) so that the induced change is too insignificant to be practically detectable. Moreover, absence of polymerisation does not necessarily mean absence of radical formation; in acidic medium, in the presence of dissolved oxygen, acrylonitrile does not polymerise even if the process is initiated by γ-radiolysis or by thermal decomposition of peroxodisulfate.

A reprisal of the data in Table 3 shows that there is a near-linear-k_{cat} *vs.* $[S_2O_3^{2-}]$-relationship. To verify the validity of Eq. 16, experiments at higher $[S_2O_3^{2-}]_0$ appear necessary; such an investigation is precluded as the $[S_2O_3^{2-}]$-dependence beyond $[S_2O_3^{2-}]_0 = 24.6 \times 10^{-4}$ mol dm^{-3} tends to be somewhat different from that observed in the concentration range employed suggesting that another reaction path[27)] probably becomes important at higher $[S_2O_3^{2-}]_0$.

The reactions are accompanied by an imperceptible temperature co-efficient in the range 30—60 °C as there is no appreciable change in the rate. This is probably due to the fact that the reaction has been studied at or very near the isokinetic temperature. We cannot offer at this stage any other reasonable explanation for this than that the large negative activation entropy created in the substitution step is probably counterbalanced by the more positive activation enthalpy in the electron-transfer step so that the net $\Delta G^{*} \approx 0$, thus causing no appreciable rate constant variation.[23b)]

Grateful acknowledgements are due to the UGC, New Delhi for the grant of a National Associateship Scheme, and to the Director, CLRI for providing some of the facilities. We thank Prof. P. S. Radhakrishnamurti for helpful discussions. The CSIR, New Delhi for providing a Junior Research Fellowship to G. Neogi, and Mrs. H. Ranganathan, C. K. Ranganathan and D. Rajendra Prasad of CLRI for some technical assistance are acknowledged.

References

1) a) J. J. Beyerley, S. A. Fouda, and G. L. Rampel, *J. Chem. Soc., Dalton Trans.*, **1973**, 889, and references cited therein; b) J. J. Beyerley, S. A. Fouda, and G. L. Rampel, *ibid.*, **1975**, 1329.

2) H. Yoneda, *Bull. Chem. Soc. Jpn.*, **28**, 125 (1955); M. A. Thacker and W. C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, **1975**, 704.

3) G. Nord, L. H. Skibsted, and A. S. Khalonin, *Acta Chem. Scand., Ser. A*, **29**, 505 (1975).

4) I. Baldea and G. Niac, *Inorg. Chem.*, **9**, 110 (1970), and references cited therein.

5) F. M. Page, *Trans. Faraday Soc.*, **56**, 398 (1960); **49**, 1953 (1953).

6) K. E. Howlett and B. L. Wedzicha, *Inorg. Chim. Acta*, **18**, 133 (1976), and references cited therein.

7) R. K. Panda, G. Neogi, and D. Ramaswamy, (Communicated).

8) Y. A. Komkov, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, **12**, 692 (1970).

9) R. I. Novoselov and Z. A. Muzykantora, *Zh. Neorg. Khim.*, **15**, 3084 (1970).

10) G. S. Deshmukh and M. G. Bapat, *Z. Anal. Chem.*, **156**, 105 (1957).

11) D. Mohan and Y. K. Gupta, *J. Chem. Soc., Dalton*

Trans., **1977**, 1085, and references cited therein.

12) J. H. Karchmer, "The Analytical Chemistry of Sulfur and its Compounds," Wiley Interscience, New York (1970), Chemical Analysis Series, Vol. 29, Part 1, pp. 237—247.

13) R. D. Sauerbrum and E. E. Sandell, *J. Am. Chem. Soc.*, **75**, 4170 (1953).

14) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

15) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley, New York (1967), (a) p. 35, (b) Chap. 4, (c) p. 140.

16) S. E. Livingstone, "Comprehensive Inorganic Chemistry," ed by J. C. Bailar *et al.*, Pergamon, New York (1973), Vol. 3, pp. 1230—1232.

17) R. Scholder and G. Schatz, *Angew. Chem.*, **2**, 264 (1963).

18) G. P. Haight, P. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1977 (1964).

19) P. S. Radhakrishnamurti and B. Sahu, *Indian J. Chem.*, **17A**, 93 (1979), and references cited therein.

20) G. P. Panigrahi, S. N. Mohapatro, and P. K. Misro, *Indian J. Chem.*, **16A**, 1095 (1978), and references cited therein.

21) P. S. Radhakrishnamurti and B. Sahu, *Indian J. Chem.*, **16A**, 259 (1978), and references cited therein.

22) C. W. Davis, "Ion Association," Butterworths, London, (1962), Chap. 13.

23) J. Lewis and R. G. Wilkins, "Modern-Coordination Chemistry-Principles and Methods," Interscience, New York (1960), (a) D. R. Stranks, Chap. 2, p. 103, (b) F. J. C. Rossotti, Chap. 1, pp. 20—33.

24) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall Inc., Englewood Cliffs, N. J. (1952), p. 75.

25) J. M. Lancaster and R. S. Murray, *J. Chem. Soc., A*, **1971**, 2755, and references cited therein.

26) J. C. R. Legros, *Acad. Sci., Paris*, **242**, 1605 (1956).

27) At higher $[S_2O_3^{2-}]_0$, there is probably a further interaction involving the product $S_4O_6^{2-}$, in addition to the involvement of one more $S_2O_3^{2-}$ molecule; this should, we feel, provide the basis for further fruitful study.