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Mechanistic Studies of Osmium(VIII) Catalysed Oxidation of Sulfanilic Acid by Hexacyanoferrate (III) in Alkaline Medium

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Abstract The kinetics of osmium(VIII) catalyzed oxidation of sulfanilic acid (*p*-aminobenzenesulfonic acid) by hexacyanoferrate(III) (HCF(III)) in alkaline medium was studied spectrophotometrically. The reaction showed first order kinetics in hexacyanoferrate(III) and osmium concentrations and an order of less than unity in sulfanilic acid (SAA) and alkali concentrations. The rate of reaction increased with increase in alkali concentration. Increasing ionic strength and dielectric constant of the medium increased the rate of the reaction. A retarding effect was observed by one of the products i.e. hexacyanoferrate(II) (HCF(II)). A mechanism involving the formation of a complex between sulfanilic acid and osmium(VIII) species, $[(OsO_5(OH)]^{3-}$ (in presence of high OH^- concentrations), has been proposed. The main products were identified by spectral studies. The reaction constants involved in the mechanism are evaluated.

Keywords Sulfanilic acid · Os(VIII) catalysis · Hexacyanoferrate(III) · Oxidation · Kinetics

1 Introduction

Hexacyanoferrate(III), (HCF(III)) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. The authors [1, 2] have suggested that alkaline hexacyanoferrate(III) ion simply acts as an electron abstracting reagent in redox reactions. However, Speakman and Waters [3] have suggested different paths of oxidation of aldehydes, ketones and nitroparaffins. Singh and coworkers [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.

Sulfanilic acid (*p*-aminobenzenesulfonic acid) (SAA) is an important and interesting compound, which finds a number of applications in the syntheses of organic dyes [6]. The amide of sulfanilic acid (sulfanilamide) and certain related substituted amides are of considerable medical importance as the sulfa drugs [7]. Several studies have been reported on the oxidation of sulfanilic acid by other oxidants such as peroxomonophosphoric acid [8], periodiate [9], H_2O_2 [10], Ce(IV) [11], persulfate [12] and peroxy disulfate [13].

Different workers have identified different products by different oxidants for sulfanilic acid [8–13]. Thus the study of sulfanilic acid becomes important because of its biological significance and selectivity towards the oxidants.

Osmium(VIII) is reported to be an efficient catalyst for such oxidations in alkaline medium [14, 15]. The uncatalysed reaction between sulfanilic acid and HCF(III) in alkaline medium has also been studied previously [16]. In view of the lack of literature on the oxidation of sulfanilic acid by HCF(III) in presence of micro amounts of osmium(VIII) catalyst, and in order to explore the mechanistic aspects of HCF(III) oxidation in alkaline medium, we have chosen sulfanilic acid as a substrate. 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 sulfanilic acid by alkaline hexacyanoferrate(III) on the basis of kinetic results.

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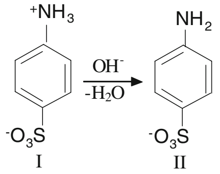
2 Experimental

Kinetic measurements were performed on a Shimadzu model-1700, UV-VIS spectrophotometer at its absorption maximum, 420 nm as a function of time where the other constituents of the reaction mixture do not absorb significantly.

2.1 Materials and Method

Reagent grade chemicals and doubly distilled water were used throughout. A solution of $Fe(CN)_6{}^{3-}$ was prepared by dissolving $K_3Fe(CN)_6$ (BDH) in H_2O and was standardized iodometrically[17]. Sulfanilic acid is not only insoluble in organic solvents, but also nearly insoluble in water and in aqueous acids. Sulfanilic acid is soluble in aqueous bases. These properties of sulfanilic acid are understandable when we realize that sulfanilic acid actually has the structure I which contains the $-NH_3{}^+$ and $-SO_3{}^-$ groups, sulfanilic acid being a zwitterionic [7].

In alkaline solution, the strongly basic hydroxide ion pulls hydrogen ion away from the weakly basic $–NH_2$ group to yield the *p*-aminobenzenesulfonate ion (II), which like most sodium salts, is soluble in water. Therefore the solution of sulfanilic acid (Merck) was prepared by dissolving appropriate amount of sample in warm very dilute alkaline solution.



Hexacyanoferrate(II) solution was prepared by dissolving a known amount of $K_4Fe(CN)_6$ (BDH), in water. A stock standard solution of Os(VIII) was prepared by dissolving OsO_4(Johnson Matthey) in 0.50 mol dm^{-3} NaOH. The concentration of Os(VIII) was ascertained [18] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce(IV) solution in acid medium. Sodium hydroxide (Merck) and sodium perchlorate (BDH) were used to provide the required alkalinity and to maintain the ionic strength, respectively.

2.2 Techniques Used

Shimadzu model-1700, UV-VIS spectrophotometer, FT-IR, ^1H NMR by Gemini-200MHZ spectrometer with operating procedure (DOP-13) (in CF_3COOD), Electron Impact Mass spectrometer and Elementar Vario EL.

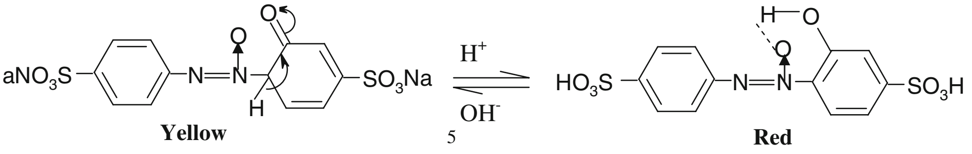
2.3 Kinetic Measurement

All kinetic measurements were performed under pseudo first-order conditions where [sulfanilic acid] in excess over [HCF(III)] at a constant ionic strength of 1.0 mol dm^{-3} in alkaline medium in presence of micro amounts of Os(VIII) catalyst at a constant temperature of 30.0 ± 0.1 °C. The progress of the reaction was followed by measuring the absorbance of hexacyanoferrate(III) in the reaction solution in a 1 cm quartz cell of a thermos tatted compartment of a Shimadzu model-1700, UV-VIS spectrophotometer at its absorption maximum, 420 nm as a function of time where the other constituents of the reaction mixture do not absorb significantly. The application of Beer's law for hexacyanoferrate(III) at 420 nm, under the reaction conditions had earlier been verified giving $\varepsilon = 1{,}060 \pm 20$ dm^3 mol^{-1} cm^{-1}. Pseudo first-order rate constants were obtained from the plots of log [HCF(III)] versus time, the plots were linear up to 75% completion of the reaction in alkaline medium and the k_C values were reproducible within ±5% and deviation from linearity was also observed due to the retarding effect of one of the products.

In view of the modest concentrations of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessels on the kinetics. Use of polythene/acrylic ware and quartz or polyacrylate cells gave the same results as glass vessels and cells, indicating that the surfaces play no important role in the reaction rate.

2.4 Identification of Keto Azoxy Dye from its uv/vis Spectrum

When the uv/vis spectrum was observed at different pH i.e. from pH = 4 to pH = 7, no absorption was observed in the visible region but in the uv region at $\lambda_{max} = 278$ nm, the extinction coefficient was found to be $\varepsilon = 174.1$ dm^3 mol^{-1} cm^{-1} indicating $\pi \rightarrow \pi^*$ transition due to carbonyl chromophore (>C=O). At high H^+ ion concentration absorption is observed in the visible region at $\lambda_{max} = 601.6$ nm, with $\varepsilon = 13.1$ dm^3 mol^{-1} cm^{-1} indicating $n \rightarrow \pi^*$ transitions [19, 20]. When we compare the uv/vis spectrum of azobenzene and azoxybenzene with that of the product keto azoxydye, it has been found that for azodye at $\lambda_{max} = 433$ nm, $\varepsilon = 727$ for azoxybenzene at $\lambda_{max} = 322$ nm, $\varepsilon = 14{,}700$, in MeOH, where as for keto azoxybenzene, at $\lambda_{max} = 601.6$ nm, $\varepsilon = 13.1$ in HCl, indicating forbidden transition. The shift in λ_{max} value of the product towards longer wavelength may be due to increase in conjugation. Carbonyl group (>C=O) extends the conjugation of a chromophore $–N{=}N{\rightarrow}O$ by resulting in a different absorption maximum with very low extinction coefficient. The disodium salt of keto azoxy dye in acid medium exist in an enolic form, which is more stable than its keto tautomer due to change from nonaromatic to aromatic and also due to the formation of intramolecular hydrogen bonding, as shown below.



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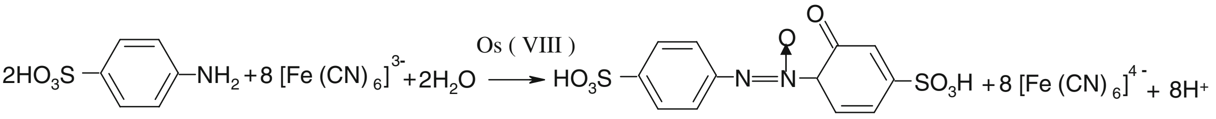
2.5 2-Hydroxy-azoxy-benzene-4,4′-disulfonic Acid (Compound 1)

A mixture of HCF(III) (395 mg, 1.2 mmol) and sulfanilic acid (34.64 mg, 0.2 mmol) in sodium hydroxide (12 g, 3 × 10^2 mmol) in presence of micro amounts of Os(VIII) (0.6 × 10^{-6} mol (0.6 µmol)) was stirred under nitrogen atmosphere at 30.0 °C for 4 h. the reaction mixture was acidified using dilute HCl and filtered using Buchner funnel. This was subjected to column chromatography (solvent methanol) to give purified form of title compound 1(28 mg, 75%) as a red solid, [found: C, 38.32; H, 2.52; S, 17.21 and N, 7.52. $C_{12}H_{10}O_8N_2S_2$ requires C, 38.5; H, 2.67; S, 17.1; and N, 7.48%]; υ_{max} (KBr) 1,128, 079, 1,727 and 1,375 cm^{-1}; δ_H (200 MHz CF_3COOD) 7.6–8.8 (10H, m, H, SO_3H, OH); m/z 374 (4), 372 (4) 183 (28), 91 (24), 86 (32), 69 (66), 58 (74), 43 (100%). Autospec EI: MH^+, found 374. $C_{12}H_{10}O_8N_2S_2$ requires 374.

3 Results

3.1 Stoichiometry and Product Analysis

The reaction mixture containing excess HCF(III) concentration over sulfanilic acid were mixed in presence of 0.30 mol dm^{-3} NaOH, 6.0 × 10^{-5} mol dm^{-3} Os(VIII) and adjusted to a constant ionic strength of 1.0 mol dm^{-3} and allowed to react for about 4 h. at 30 ± 0.1 °C. The remaining HCF(III) was then analysed spectrophotometrically. The results indicated that eight moles of HCF(III) were consumed by two moles of sulfanilic acid according to Eq. 1.



(1)

The reaction product, disodium salt of 2-keto-azoxybenzene-4,4′-disulfonic acid was eluted with ether, and submitted to spot test [21] which revealed the presence of an azo, nitroso and keto groups. The presence of dye was also confirmed by measuring its uv/vis spectrum [22] and by its IR [23] spectrum. IR (KBr) showed bands at (υ) 1,128 cm^{-1} and 1,079 cm^{-1} for ($-C_6H_4SO_3Na$), 1,727 cm^{-1} (for carbonyl, >C=O stretching) and 1,375 cm^{-1} (for N=N→O) stretching). The acidified product of disodium salt of ketoazoxy dye (2-hydroxy-azoxybenzene-4,4′-disulfonic acid) was further characterized by ^{1}H NMR, Electron Impact Mass spectrum and CHN and S analysis. The ^{1}H NMR showed a multiplet from 7.6 to 8.8 δ in CF_3COOD, (for the solvent, CF_3COOD at 11.5 δ). The mass spectrum of this compound displayed a peak at m/z 372 after the loss of two hydrogens from its molecular ion of 374. The elemental analysis was in agreement with a molecular formula $C_{12}H_{10}O_8N_2S_2$. The only organic product obtained in the oxidation is 2-hydroxy-azoxybenzene-4,4′-disulfonic acid, which is further confirmed by single spot in TLC and the yield obtained was found to be 75% from its acetyl derivative. However, the other product, in alkaline medium is hexacyanoferrate(II), $Fe(CN)_6^{4-}$, identified by titration [24].

The product disodium salt of keto azoxydye in alkaline medium does not undergo further oxidation under the present kinetic conditions, since the test for probable oxidation product of ketone i.e. acid and nitrosobenzene was negative.

3.2 Reaction Order

In the presence of catalyst, the reaction is understood to occur in parallel paths with contribution from the uncatalysed and catalysed paths. Thus the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C and uncatalyzed (k_U) reactions.

$k_C = k_T - k_U$

The reaction orders were determined from the k_C versus concentration plots, by varying the concentration of the reductant, alkali and osmium(VIII) catalyst while keeping others constant.

3.3 Effect of [oxidant], [substrate], [alkali] and [osmium (VIII)]

The oxidant, HCF(III) concentration was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} and the linearity of the plot of log [HCF(III)] versus time ($r > 0.9930$, $s \leq 0.01745$) indicates the order in [HCF(III)] as unity. This was also confirmed by varying [HCF(III)]$_0$, which did not show any change in pseudo first order rate constants k_C (Table 1). The substrate, sulfanilic acid, concentration was varied in the range of 2.0×10^{-3} to 2.0×10^{-2} mol dm^{-3} at 30.0 °C keeping all other reactant concentration and conditions constant (Table 1). The apparent order in [SAA] was found to be less than unity (0.835) ($r > 0.9991$, $s \leq 0.0427$). The effect of increasing the concentration of alkali was studied on the reaction rate at constant concentrations of sulfanilic acid, Os(VIII), HCF(III) and ionic strength of 1.0 mol dm^{-3} at 30.0 °C and the order was found to be less than unity (Table 1, order = 0.628, ($r > 0.9932$, $s \leq 0.0611$). Similarly the effect of increasing the concentration of Os(VIII) was studied on the reaction rate at constant concentrations of sulfanilic acid OH$^-$, HCF(III) and constant ionic strength at 30.0 °C and the order was found to be equal to unity (Table 1, order = 1.077, ($r > 0.9824$, $s \leq 0.0436$)). The oxidation of sulfanilic acid by osmium(VIII) is negligibly small under the experimental conditions.

3.4 Effect of Initially Added Reaction Product

Initially adding the product, i.e. HCF(II), in the range of (1.0–15) $\times 10^{-4}$ mol dm^{-3} keeping other conditions constants had a retarding effect on the rate of the reaction. As the initial concentration of HCF(II) is increased, the rate progressively decreased. This illustrates the retarding nature of the product.

3.5 Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of the reaction medium was varied from 0.1 to 1.0 mol dm^{-3} at constant concentrations of HCF(III), sulfanilic acid alkali and Os(VIII). It was found that the rate constant increased

Table 1 Effect of [SAA], [HCF(III)] [OH$^-$] and [Os(VIII)] on the Os(VIII) catalysed oxidation of sulfanilic acid by alkaline hexacyanoferrate(III) at 30.0 °C, $I = 1.0$ mol dm^{-3}

[SAA] $\times 10^3$ (mol dm^{-3})	[HCF(III)] $\times 10^4$ (mol dm^{-3})	[OH$^-$] $\times$ 10 (mol dm^{-3})	[Os(VIII)] $\times 10^5$ (mol dm^{-3})	$k_U \times 10^4$ (s^{-1})	$k_T \times 10^3$ (s^{-1})	$k_C \times 10^3$ (s^{-1})
2.0	5.0	3.0	6.0	2.45	0.99	0.75
6.0	5.0	3.0	6.0	5.88	2.58	1.99
10	5.0	3.0	6.0	7.83	3.97	3.18
15	5.0	3.0	6.0	11.5	5.29	4.14
20	5.0	3.0	6.0	32.0	9.28	6.08
10	1.0	3.0	6.0	7.78	3.99	3.21
10	3.0	3.0	6.0	7.80	3.97	3.19
10	5.0	3.0	6.0	7.83	3.97	3.18
10	7.0	3.0	6.0	7.85	3.95	3.16
10	10	3.0	6.0	7.84	3.97	3.18
10	5.0	0.8	6.0	1.93	1.42	1.23
10	5.0	1.6	6.0	4.01	2.69	2.29
10	5.0	3.0	6.0	7.83	3.97	3.18
10	5.0	6.0	6.0	9.46	6.04	5.10
10	5.0	8.0	6.0	12.80	7.37	6.09
10	5.0	3.0	0.8	7.83	1.07	0.28
10	5.0	3.0	2.0	7.83	1.98	1.19
10	5.0	3.0	4.0	7.83	2.46	1.67
10	5.0	3.0	6.0	7.83	3.97	3.18
10	5.0	3.0	8.0	7.83	4.32	3.53

Error ±5%

with increasing concentration of $NaClO_4$ and the plot of log K_C vs $I^{1/2}$ was linear with positive slope ($r > 0.9612$, $s \leq 00242$).

The relative permittivity (D) effect was studied by varying *t*-butyl alcohol–water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids [25]. There is no reaction of the solvent with the oxidant under the experimental conditions. It was found that the rate constant increased on decreasing the dielectric constant of the medium and the plot of log k_C vs 1/D was linear with positive slope ($r > 0.9762$, $s \leq 0.0401$).

3.6 Test for Free Radical

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been initially added, was kept for one hour in a nitrogen atmosphere. On diluting the reaction mixture with methanol, no precipitate resulted, indicating the absence of free radicals.

3.7 Effect of Temperature (T)

The rate of reaction was measured at four different temperatures. The rate of reaction increased with the increase of temperature. The Arrhenius plot was drawn for the variation of rate constant, k_C with temperature. The values of k_C (s^{-1}) are 3.18, 5.82, 8.39, $11.2 \times 10^{-3}\ s^{-1}$ at 30, 35, 40 and 45 °C, respectively. The activation parameters corresponding to these constants are $Ea = 39.5 \pm 1.8\ kJ\ mol^{-1}$ $\Delta H^{\#} = 41.6 \pm 2.0\ kJ\ mol^{-1}$, $\Delta S^{\#} = -82 \pm 4\ J\ K^{-1}\ mol^{-1}$, $\Delta G^{\#} = 66 \pm 3\ k\ J\ mol^{-1}$.

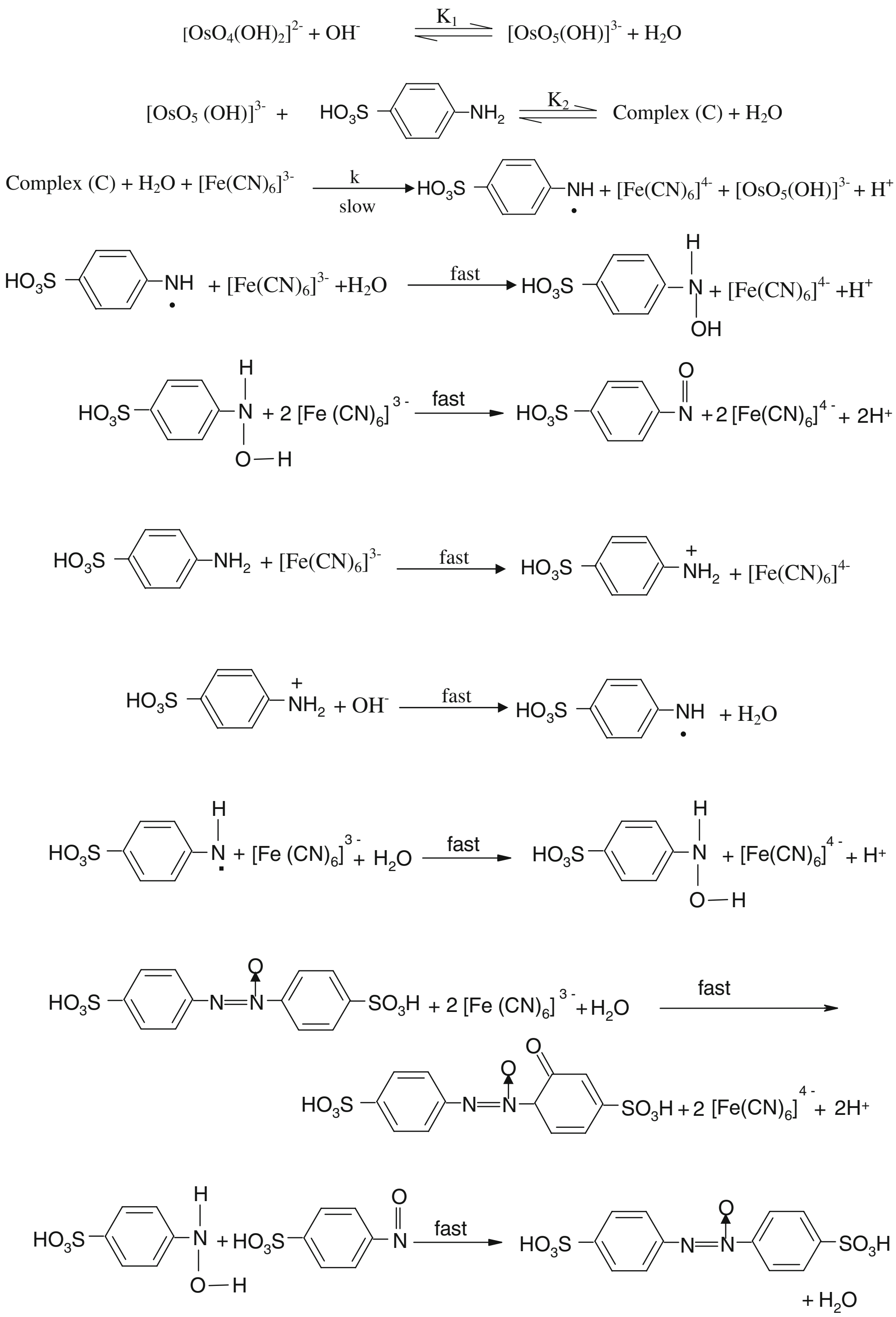
4 Discussion

Variation of the concentrations each of the oxidant (HCF(III)), substrate (SAA) alkali and Os(VIII), while keeping the others constant showed that the reaction is first-order in oxidant and osmium(VIII) and less than unit order in substrate and alkali concentrations (Table 1). The reaction between SAA and HCF(III) in NaOH in presence of osmium(VIII) catalyst has a stoichiometry of 1:4. It has been observed that the presence of ferrocyanide, $[Fe(CN)_6]^{4-}$ retards the rate of reduction of ferricyanide by SAA. However the retardation is small, increasing the initial concentration of the ferrocyanide produced only a 4% reduction in rate, and this has been attributed to a secondary salt effect [26]. Based on the experimental results, a mechanism can be proposed for which all the observed orders in each constituent such as [oxidant], [reductant] and $[OH^-]$ may be well accommodated. Oxidation of sulfanilic acid by hexacyanoferrate(III) in NaOH media in presence of Os(VIII) is a non-complementary reaction with oxidant undergoing eight equivalent changes. In most of the oxidation reactions, hexacyanoferrate(III) resembles Cu(II), which involves free radical formation and rapidly oxidizes it [27–31]. The hexacyanoferrate(III)–hexacyanoferrate(II) system, which has higher redox potential than Cu(II)–Cu(I), substantiates a better possibility for the rapid oxidation of the free radical with hexacyanoferrate(III) in the alkaline medium and the rapid oxidation of the free radicals might completely mask the polymerization. Sometimes the vinyl compounds themselves are oxidized under the experimental conditions used and the test for free radicals fails [32]. In view of less than unit order in $[OH^-]$ and also high alkali concentration, the active species of osmium(VIII) is considered as $[OsO_5(OH)]^{3-}$ [33], which is shown in prior equilibrium of Scheme 1. In the present study, the oxidation reaction proceeds via formation of a complex between substrate and Os(VIII), which decomposes in a slow step to a free radical derived from SAA and hexacyanoferrate(II) with regeneration of osmium catalyst. The free radical further reacts with one mole of HCF(III) in aqueous media in a fast step to give another intermediate product, hydroxylamine benzene sulfonic acid, and HCF(II). The hydroxylamine benzene sulfonic acid so formed further reacts with two moles of HCF(III) in a fast step to give nitrosobenzene sulfonic acid and HCF(II). Another molecule of SAA reacts with two moles of HCF(III) in fast steps to give hydroxylamine benzene sulfonic acid as intermediate product and HCF(II). The two intermediate products namely nitrosobenzene sulfonic acid and hydroxylamine benzene sulfonic acid rearrange themselves in a fast step to azoxybenzene-4,4′-disulfonic acid as another intermediate product, which in presence of two moles of HCF(III) undergoes further oxidation to the final products, 2-keto-azoxybenzene-4,4′-disulfonic acid and hexycyanoferrate(II) (HCF(II)), satisfying the stoichiometric observations. The results can be accommodated by Scheme 1.

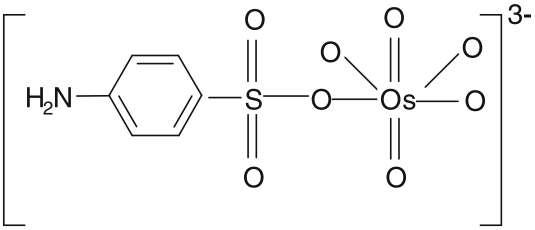
$$7H^+ + 7OH^- \rightarrow 7H_2O$$

The results of our study on the osmium(VIII)-catalyzed reaction suggest that the formation of complex between the catalyst and substrate followed by its reaction with $[Fe(CN)_6]^{3-}$ in the rate determining step to give the products. Attempts to obtain UV/Vis. Spectral evidence for the intermediate complex of the Os(VIII) and Os(VIII)-sulfanilic acid mixture were not successful. However, the

Scheme 1 Detailed scheme for the Os(VIII) catalyzed oxidation of sulfanilic acid by alkaline hexacynoferrate(III)



interaction may be weak, but such analogous effects upon complex formation between a substrate and an Os(VIII) have been observed in other investigations [34]. The evidence for complex formation is restricted to kinetic data which is proved kinetically by the non-zero intercept of the plot of [Os(VIII)]/k_C versus 1/[SAA] (Fig. 1). The probable structure of the complex (C) may be .



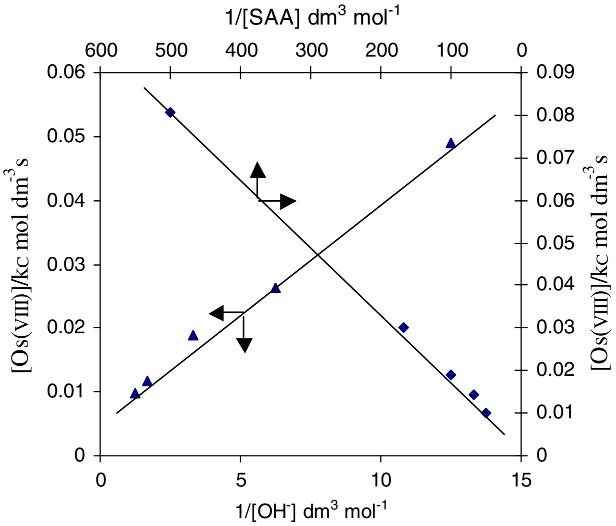


Fig. 1 Verification of rate law (3) in the form of (4) (conditions as given in Table 1)

The observed modest enthalpy of activation and a relatively low value of the entropy of activation, indicates that the oxidation presumably occurs *via an* inner-sphere mechanism. This conclusion is supported by earlier observations [35, 36].

Scheme 1 leads to the rate law (2)

$$\text{Rate} = -\frac{d\left[\text{Fe(CN)}_6{}^{3-}\right]}{dt} = \frac{kK_1K_2[\text{SAA}]_T\left[\text{Fe(CN)}_6{}^{3-}\right][\text{Os(VIII)}]_T[\text{OH}^-]_T}{\left\{1+K_1K_2[\text{Os(VIII)}]_T[\text{OH}^-]_T\right\}\left\{1+K_1[\text{Os(VIII)}]_T\right\}\left\{1+K_1[\text{OH}^-]_T+K_1K_2[\text{SAA}]_T[\text{OH}^-]_T\right\}} \quad (2)$$

where $[\text{SAA}]_T$, $[\text{Os(VIII)}]_T$ and $[\text{OH}^-]_T$ refer to total concentrations of sulfanilic acid, osmium and alkali, respectively.

The terms $(1 + K_1K_2[\text{Os(VIII)}]_T\ [\text{OH}^-]_T)$ and $\{1 + K_1[\text{Os(VIII)}]_T)$ in the denominator of Eq. 2 approximate to unity in view of low concentration of osmium(VIII) used. Therefore Eq. 2 becomes Eq. 3, (omitting the subscripts 'T'). Therefore Eq. 3 becomes

$$\frac{\text{Rate}}{[\text{Fe(CN)}_6{}^{3-}]} = k_C = k_T - k_U = \frac{kK_1K_2[\text{SAA}][\text{Os(VIII)}][\text{OH}^-]}{1+K_1[\text{OH}^-]+K_1K_2[\text{SAA}][\text{OH}^-]} \quad (3)$$

Further Eq. 3 can be rearranged to the following form, which is suitable for verification of the rate law.

$$\frac{[\text{Os(VIII)}]}{k_C} = \frac{1}{kK_1K_2[\text{OH}^-][\text{SAA}]} + \frac{1}{KK_2[\text{SAA}]} + \frac{1}{k} \quad (4)$$

According to Eq. 4, the plots of $[\text{Os(VIII)}]/k_C$ versus $1/[\text{SAA}]$ ($r > 0.9999$, $s \le 0.0236$) and $[\text{Os(VIII)}]/k_C$ versus $1/[\text{OH}^-]$ ($r > 0.9978$, $s \le 0.03536$) should be linear, with an intercept supporting the Os(VIII)-sulfanilic acid complex, and which is verified in Fig 1. The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. The negative value of the entropy of activation indicates that the complex is more ordered than the reactants [37]. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Amis [38] has shown that a plot of log k_C versus 1/D is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction. However, in the present study, an increase in the content of *t*-butanol in the reaction medium leads to the increase in the reaction rate, which is in agreement with Amis theory [38]. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

5 Conclusion

The osmium(VIII) catalyzed oxidation of SAA with HCF(III) in alkaline medium involves the retardation by one of the products and the overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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