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Kinetic, mechanistic and spectral studies for the oxidation of sulfanilic acid by alkaline hexacyanoferrate(III)

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Abstract—The kinetics of oxidation of sulfanilic acid (*p*-aminobenzenesulfonic acid) by hexacyanoferrate(III) in alkaline medium was studied spectrophotometrically. The reaction showed first order kinetics in hexacyanoferrate(III) and alkali concentrations and an order of less than unity in sulfanilic acid concentration (SAA). The rate of reaction increases with increase in alkali concentration. Increasing ionic strength increases the rate but the dielectric constant of the medium has no significant effect on 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 hexacyanoferrate(III) has been proposed. The reaction constants involved in the mechanism are evaluated. There is a good agreement between the observed and calculated rate constants under different experimental conditions. Investigations at different temperatures allowed the determination of the activation parameters with respect to the slow step of the proposed mechanism.

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 co-workers,[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. Although they have been supplanted to a wide extent by the antibiotics such as penicillin, terramycin, chloromycetin and aureomycin, the sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical industry.[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 SAA becomes important because of its biological significance and selectivity towards the oxidants. In view of the lack of literature on the oxidation of sulfanilic acid by HCF(III), 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 oxidation of sulfanilic acid by alkaline hexacyanoferrate(III) ions on the basis of kinetic results.

2. Results

2.1. Stoichiometry and product analysis

The reaction mixture containing excess HCF(III) concentration over sulfanilic acid were mixed in the presence of 0.9 mol dm^{-3} NaOH, adjusted to a constant ionic strength of 2.5 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 8 mol of HCF(III) were consumed by 2 mol of sulfanilic acid according to Eq. (1).

Keywords: hexacyanoferrate (III); sulfanilic acid; 2-keto-azoxybenzene-4,4′-disulfonic acid.

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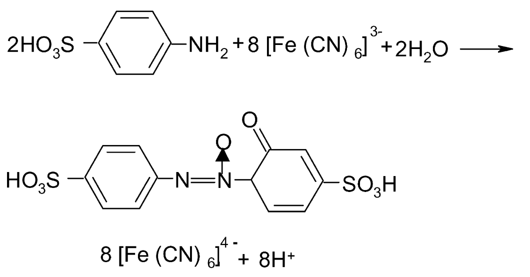


(1)

The reaction product, disodium salt of 2-keto-azoxybenzene-4,4′-disulfonic acid was eluted with ether, and submitted to spot test,[14] which revealed the presence of an azo, nitroso and keto groups. The presence of dye was also confirmed by measuring its UV/Vis spectrum[15] and by its IR[16] spectrum. IR (KBr) showed bands at (ν) 1128 and 1079 cm^{-1} for ($-C_6H_4SO_3Na$), 1727 cm^{-1} (for carbonyl, $>C{=}O$ stretching) and 1375 cm^{-1} (for $N{=}N{\rightarrow}O$ stretching). The acidified product of disodium salt of ketoazoxy dye (2-hydroxy-azoxybenzene-4,4′-disulfonic acid) was further characterized by ^1H NMR, electron impact mass spectrum and CHN and S analysis. ^1H NMR showed seven aromatic protons, two protons for SO_3H and one phenolic proton as 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 hydrogen 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.[17] The spectral changes during the reaction are shown in Figure 1. It is evident that [HCF(III)] decreases at 420 nm.

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.

2.2. Reaction orders

The reaction orders were determined from the slope of log k_{obs} versus log concentration plots, by varying the concentration of the reductant, and alkali while keeping others constant.

2.3. Effect of [oxidant], [substrate] and [alkali]

The oxidant, HCF(III) concentration was varied in the range of 1.0×10^{-4}–10×10^{-3} mol dm^{-3} and the linearity of the plot of log [HCF(III)] versus time (Fig. 2) ($r>0.9987$, $s\leq0.0255$) 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_{obs} (Table 1). The substrate, sulfanilic acid, concentration was varied in the range of 2.0×10^{-3}–2.0×10^{-2} mol dm^{-3} at 30°C keeping all other reactant concentration and conditions constant (Table 1). The apparent order in [SAA] was found to be less than unity (0.60) ($r>0.9949$, $s\leq0.03417$). The effect on the reaction rate of increasing the concentration of alkali was studied at constant concentration of sulfanilic acid and HCF(III) at constant ionic strength of 2.50 mol dm^{-3} at 30°C. The rate constants increased with

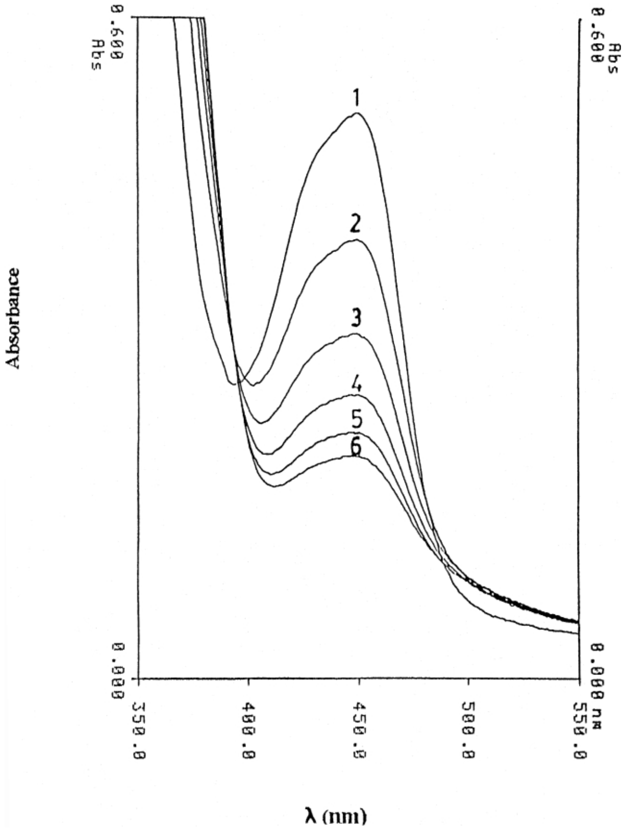


Figure 1. Spectroscopic changes occurring in the oxidation of sulfanilic acid by hexacyanoferrate(III) with $[HCF(III)]=5.0\times10^{-4}$, $[SAA]=10\times10^{-3}$, $[OH^-]=9.0\times10^{-1}$ and $I=2.5$/mol dm^{-3} at 30°C (scanning time interval: 1 min).

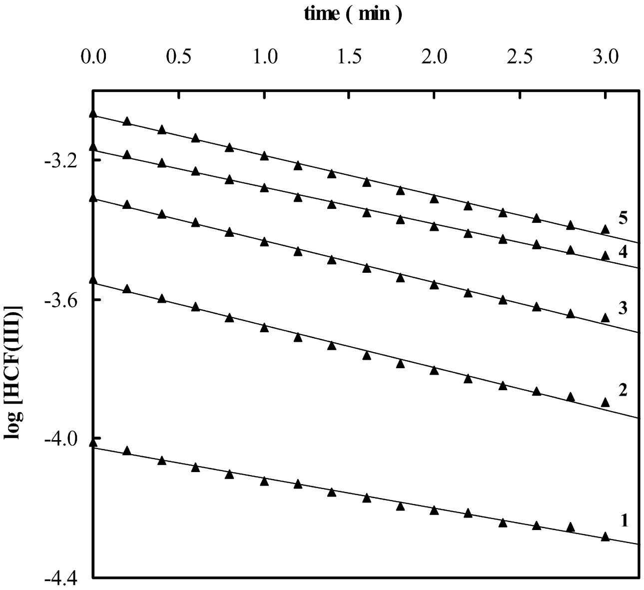


Figure 2. The plot of log [HCF(III)] versus time in alkaline medium, [HCF(III)] ($\times10^4$ mol dm^{-3}): (1) 1.0, (2) 3.0, (3) 5.0, (4) 7.0 and (5) 10.

Table 1. Effect of [sulfanilic acid], [HCF(III)] and [OH$^-$] on the oxidation of sulfanilic acid by alkaline hexacyanoferrate(III) at 30°C, I=2.5 mol dm^{-3}

[SAA] (×10^3 mol dm^{-3})	[HCF(III)] (×10^4 mol dm^{-3})	[OH$^-$] (×10^1 mol dm^{-3})	k_{obs} (×10^3 s^{-1})	k_{cal} (×10^3 s^{-1})	Initial rate (×10^7 mol dm^{-3} s^{-1})	
					obs.	cal.
2.0	5.0	9.0	1.76	1.75	7.14	7.01
6.0	5.0	9.0	3.76	3.78	11.9	13.2
10	5.0	9.0	4.74	4.90	15.5	16.2
15	5.0	9.0	5.62	5.77	17.5	18.2
20	5.0	9.0	6.85	6.33	24.5	19.3
10	1.0	9.0	4.72	4.90	3.91	3.23
10	3.0	9.0	4.75	4.90	9.29	9.71
10	5.0	9.0	4.72	4.90	15.5	16.2
10	7.0	9.0	4.76	4.90	26.3	22.7
10	10	9.0	4.71	4.90	30.2	32.3
10	5.0	1.5	8.52	0.82	2.72	2.70
10	5.0	5.0	2.39	2.72	8.63	8.98
10	5.0	9.0	4.79	4.90	15.5	16.1
10	5.0	12	6.61	6.54	19.7	21.6
10	5.0	15	8.07	8.17	23.5	26.9

Error±5%.

the increase in alkali concentration. (Table 1, order=unity) (r>0.9976, s≤0.0536).

2.4. Effect of initially added reaction products

Initially adding the product, i.e. HCF(II), in the range of (1.0–15)×10^{-4} mol dm^{-3} keeping other conditions constant 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 (Table 2).

2.5. 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 0.9 to 3.0 mol dm^{-3} at constant concentrations of HCF(III), sulfanilic acid and alkali. It was found that the rate constant increased with increasing concentration of NaClO$_4$ (Fig. 3) (r>0.9843, s≤0.0467).

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.[18] There is no reaction of the solvent with the oxidant under the experimental conditions. It was found that the rate constant did not change on decreasing the dielectric constant of the medium.

Table 2. Effect of product, HCF(II) on the oxidation of sulfanilic acid by alkaline hexacyanoferrate(III) at 303 K, [SAA]=10×10^{-3} mol dm^{-3}, [HCF(III)]=5.0×10^{-4} mol dm^{-3}, [OH$^-$]=9.0×10^{-1} mol dm^{-3} and I=2.5 mol dm^{-3}

[HCF(II)] (×10^4 mol dm^{-3})	k_{obs} (×10^3 s^{-1})
1.0	4.65
5.0	4.57
8.0	4.24
12	3.80
15	3.23

2.6. Test for free radicals

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 1 h in a nitrogen atmosphere. On diluting the reaction mixture with methanol, no precipitate resulted, indicating the absence of free radicals.

2.7. Effect of temperature

The rate of reaction was measured at different temperatures under varying [SAA]. The rate of reaction increased with the increase in temperature. The rate constants, k of the slow step of Scheme 1 were obtained from intercept and slope of [OH$^-$]/k_{obs} versus 1/[SAA] and used to calculate the activation parameters. The values of k (s^{-1}) are given in

Table 3. Thermodynamic activation parameters for the oxidation of sulfanilic acid by HCF(III) in aqueous sodium hydroxide medium, [OH$^-$]=9.0×10^{-1}mol dm^{-3} and I=2.5/mol dm^{-3}

(a) *Effect of temperature*

Temperature (°C)	k (×10^3 dm^3 mol^{-1} s^{-1})
30	9.90
35	15.8
40	23.7
45	33.2
50	43.2

(b) *Activation parameters with respect to the slow step of Scheme 1*

Activation parameters	±
E_a (kJ mol^{-1})	60±3
$\Delta H^\#$ (kJ mol^{-1})	58±3
log A	8.4±0.4
$\Delta S^\#$ (J K^{-1} mol^{-1})	−93±3
$\Delta G^\#$ (kJ mol^{-1})	86±4

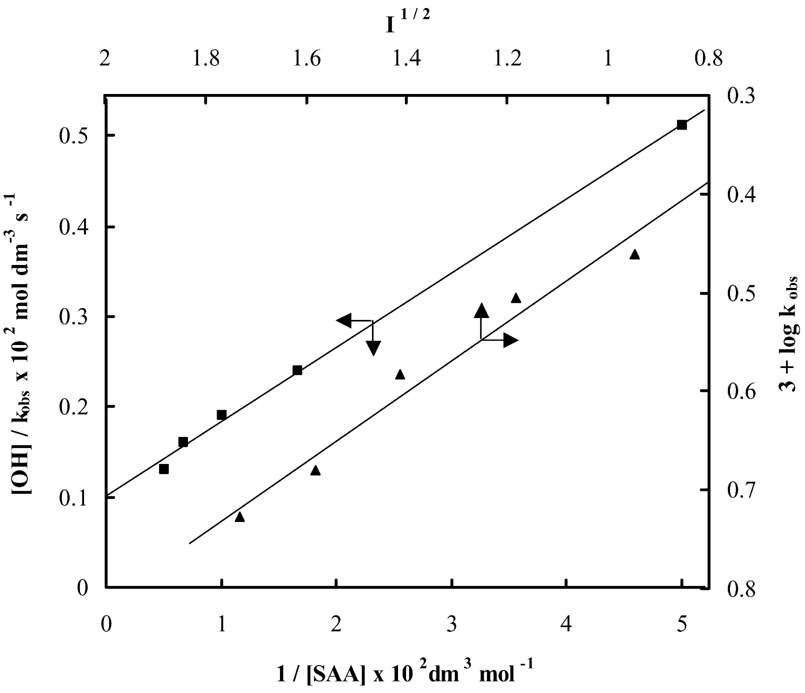


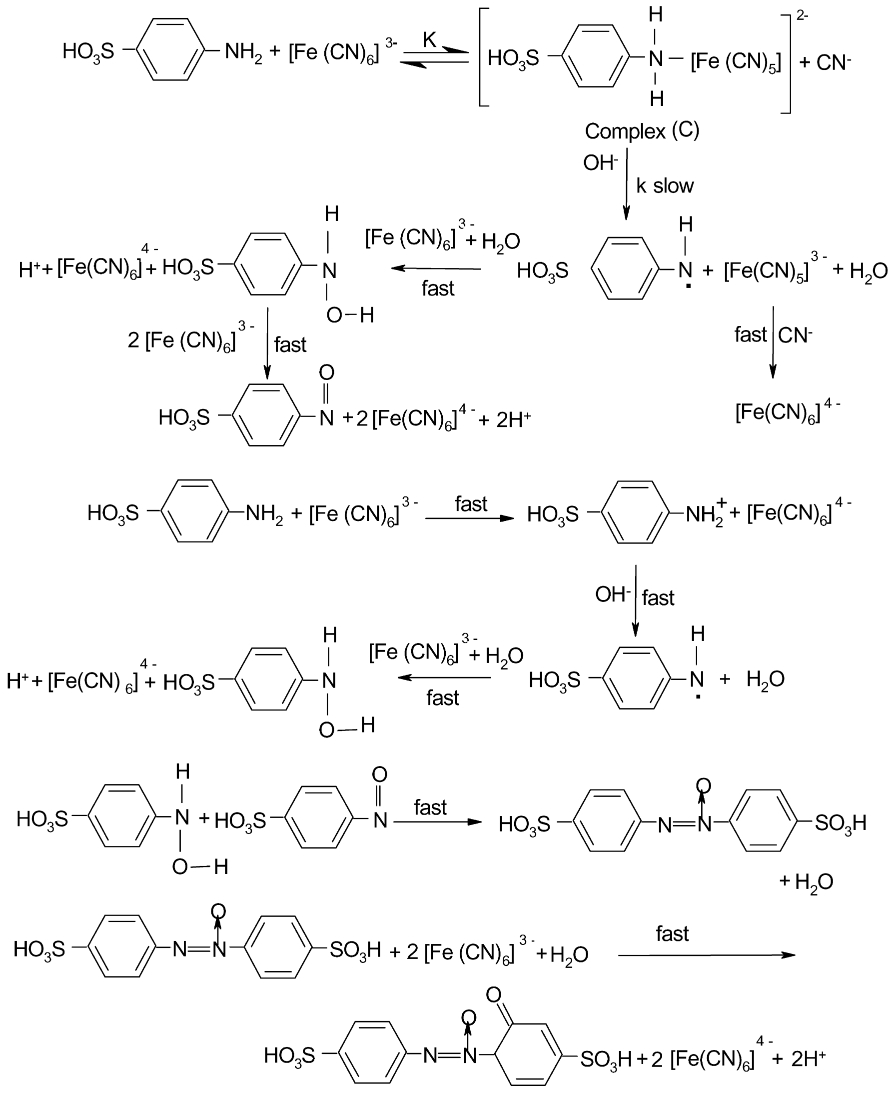
Figure 3. Plot of log k_{obs} versus $I^{1/2}$ (-▲-) and $[OH^-]/k_{obs}$ versus 1/[SAA] (-■-).

Table 3. The activation parameters corresponding to these constants were evaluated from the plot of log k versus $1/T$ ($r>0.9960$, $s\leq 0.08900$) (Table 3).

3. Discussion

Variation of the concentrations each of the oxidant (HCF (III)), substrate (SAA) and alkali, while keeping the others constant showed that the reaction is first-order in oxidant, alkali and less than unit order in substrate concentrations (Table 1). The reaction between SAA and HCF(III) in NaOH 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.[19] 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 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 oxidises it.[20–22] 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.[23] In the present study, the oxidation reaction proceeds via formation of a complex between substrate and oxidant, which decomposes in the presence of alkali in a slow step to a free radical derived from SAA and hexacyanoferrate(II). The free radical further reacts with 1 mol 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 2 mol of HCF (III) in a fast step to give nitrosobenzene sulfonic acid and HCF(II). Another molecule of SAA reacts with 2 mol 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 2 mol of HCF(III) undergoes further oxidation to the final products, 2-keto azoxybenzene-4,4′-disulfonic acid and hexacyanoferrate(II) (HCF(II)), satisfying the stoichiometric observations. The results can be accommodated by Scheme 1.

Spectroscopic evidence for complex formation between oxidant and substrate was obtained from UV/Vis spectra of the HCF(III) and HCF(III)–sulfanilic acid mixture. A hypsochromic shift of about 5 nm from 290 to 285 nm was observed, and hyperchromicity was observed at 285 nm. Analogous effects upon complex formation between a substrate and an oxidant have been observed in other investigations.[24] Further, the formation of complex is also proved kinetically by the non-zero intercept of the plot of $[OH^-]/k_{obs}$ versus 1/[SAA] (Fig. 3). The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step, indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.[25] Scheme 1 is in



Scheme 1.

accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequences of one electron steps.

Scheme 1 leads to the rate law (2):

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{Fe(CN)}_6^{3-}]}{\mathrm{d}t}$$

$$= \frac{kK[\mathrm{SAA}][\mathrm{Fe(CN)}_6^{3-}][\mathrm{OH}^-]}{(1+K[\mathrm{Fe(CN)}_6^{3-}])(1+K[\mathrm{SAA}])} \quad (2)$$

$$\text{Rate} =$$

$$= \frac{kK[\mathrm{SAA}][\mathrm{Fe(CN)}_6^{3-}][\mathrm{OH}^-]}{1+K[\mathrm{SAA}]+K[\mathrm{Fe(CN)}_6^{3-}]+K^2[\mathrm{SAA}][\mathrm{Fe(CN)}_6^{3-}]} \quad (3)$$

The terms ($K[\mathrm{Fe(CN)}_6^{3-}]$) and ($K^2[\mathrm{SAA}][\mathrm{Fe(CN)}_6^{3-}]$ in the denominator of Eq. (3) are negligibly small compared to unity in view of the low concentration of $\mathrm{Fe(CN)}_6^{3-}$ used and the observed first order with respect to $\mathrm{Fe(CN)}_6^{3-}$. Therefore Eq. (3) becomes:

$$\text{Rate} = \frac{kK[\mathrm{SAA}][\mathrm{Fe(CN)}_6^{3-}][\mathrm{OH}^-]}{1+K[\mathrm{SAA}]} \quad (4)$$

$$\frac{\text{Rate}}{[\mathrm{Fe(CN)}_6^{3-}]} = k_{\mathrm{obs}} = \frac{kK[\mathrm{SAA}][\mathrm{OH}^-]}{1+K[\mathrm{SAA}]} \quad (5)$$

Eq. (5) can be rearranged to the following form, which is used for verification of the rate law:

$$\frac{[\mathrm{OH}^-]}{k_{\mathrm{obs}}} = \frac{1}{kK[\mathrm{SAA}]} + \frac{1}{k} \quad (6)$$

According to Eq. (6), the plots of $[\mathrm{OH}^-]/k_{\mathrm{obs}}$ versus 1/[SAA] ($r>0.9990$, $s\leq0.0148$) should be linear, as verified in Figure 3. The slope and intercept of such a plot lead to the values of, K and k at 30°C as $(1.22\pm0.04)\times10^2$ dm^3 mol^{-1}, $(9.9\pm0.4)\times10^{-3}$ dm^3 mol^{-1} s^{-1}, respectively. Using these values rate constants under different experimental conditions were calculated and compared with experimental data (Table 1). There is a reasonable agreement between them. 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.[26] The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

4. Conclusion

The 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.

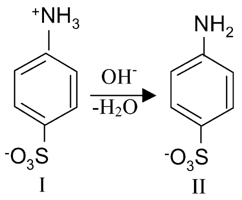
5. Experimental

Since the initial reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

5.1. Materials and methods

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.[27] 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 is a zwitterion.[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. Sodium hydroxide (Merck) and sodium perchlorate (BDH) were used to provide the required alkalinity and to maintain the ionic strength, respectively.

5.2. Instruments used

UV–Vis Spectrometer (Hitachi U-2001, Peltier temperature Control Varian 50 Bio) connected to a rapid kinetic accessory (HI-TECH SFA-12), thin layer chromatography, FT-IR, ^{1}H NMR by Gemini—200 MHz spectrometer with operating procedure (DOP-13) (in CF_3COOD), Autospec Electron Impact Mass spectrometer and Elementar Vario EL.

5.3. Kinetic measurements

All kinetic measurements were performed under pseudo first-order conditions where [sulfanilic acid] was always $\geq$10-fold in excess over [HCF(III)] at a constant ionic strength of 2.50 mol dm^{-3} in alkaline medium at a constant temperature of 30 ± 0.1°C, respectively. The reaction was initiated by mixing the thermostatted hexacyanoferrate(III) and sulfanilic acid solutions, which also contained the required amounts of sodium hydroxide and sodium perchlorate. 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 thermostatted compartment of a Hitachi model 150-20 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 $\varepsilon=1060\pm20$ 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_{obs} values were reproducible within ±5% and deviation from linearity was also observed due to the retarding effect of one of the products. The results are also interpreted in terms of the initial rate of the reaction to avoid the complexities, which may arise due to interference by the products. Initial rates were obtained from tangents at the initial stages of concentration versus time curves by the plane mirror method and were reproducible to within ±4%.

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.

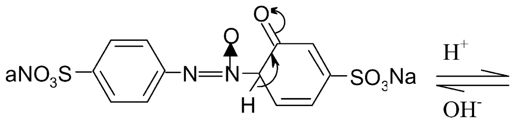
The effect of dissolved oxygen on the rate of the reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied. Added carbonate up to 1.0×10^{-3} mol dm^{-3} showed no effect on the reaction rate. However, fresh solutions were used while performing the experiments.

In alkaline medium during the progress of the reaction, the color of the solution changed from yellow to almost colorless, which is verified by titration for HCF(II).[17] A regression analysis of experimental data in order to obtain the regression coefficient, *r* and standard deviation, *s* of plots from the regression line was performed with a Pentium-III personal computer.

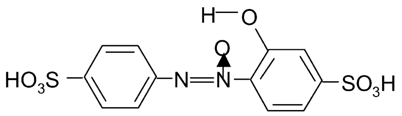
5.4. Identification of keto azoxy dye from its UV/vis spectrum

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 λ_{max}=278 nm. The extinction coefficient was found to be ε=174.1 dm^3 mol^{-1} cm^{-1} indicating $\pi\rightarrow\pi^*$ transition due to the carbonyl chromophore (>C=O). At high H$^+$ ion concentration absorption was observed in the visible region at λ_{max}=601.6 nm, with ε=13.1 dm^3 mol^{-1} cm^{-1} indicating $n\rightarrow\pi^*$ transitions.[28] 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 λ_{max}=433 nm, ε=727 for azoxybenzene at λ_{max}=322 nm, ε=14700 in MeOH, whereas for keto azoxybenzene, at λ_{max}=601.6 nm, ε=13.1 in HCl, indicating a forbidden transition. The shift in λ_{max} value of the product towards longer wavelength may be due to increase in conjugation. A carbonyl group (>C=O) extends the conjugation of a chromophore –N=N→O by resulting in a different absorption maximum with very low extinction coefficient. The disodium salt of a keto azoxy dye in acid medium exists in an enolic form, which is more stable then its keto tautomer due to the change from non-aromatic to aromatic and also due to the formation of intramolecular hydrogen bond, as shown below.



Yellow



Red

5.4.1. 2-Hydroxy-azoxybenzene-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 (36 g, 9×10^2 mmol) was stirred under nitrogen atmosphere at 30°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 the 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%]; ν_{max} (KBr) 1128, 1079, 1727, and 1375 cm^{-1}; δ_H (200 MHz CF$_3$-COOD) 7.6–8.8 (10H, m, Ar, *H*, SO$_3$*H*, O*H*); *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.

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