A kinetic and mechanistic study on the oxidation of sulfanilamide by hexacyanoferrate (III) in aqueous alkaline medium

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ABSTRACT

The kinetics of oxidation of sulfanilamide by hexacyanoferrate (abbreviated as HCF) (III) ions in aqueous alkaline medium at constant ionic strength $0.01 mol/dm^3$ and temperature $298°K$ has been studied spectrophotometrically. The reaction exhibit 1:3 stoichiometry and follows first order kinetics in [HCF (III)] and in [alkali]. The dependence of the rate on substrate concentration has been found to be of fractional order type. The ionic strength of the reaction mixture shows positive salt effect on the reaction rate. To calculate thermodynamic parameters the reaction has been studied at six different temperatures from $283°K$ to $333°K$. Mechanism involving formation of complex between hexacyanoferrate and sulfanilamide has been proposed. Azoxybenzene-4, 4'-disulfonamide have been identified chromatographically and spectroscopically as the final product of oxidation of sulfanilamide. Based on the kinetic data and product analysis a reaction mechanism is proposed.

Keywords: Oxidation, Mechanism, Hexacyanoferrate (III), Sulfanilamide

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INTRODUCTION

Iron (III) in the form of different complexes in oxidation of different compounds has acknowledged great interest due to cost-effective availability, less difficulty involved in the estimation and its capability to act in both acidic and alkaline medium. Iron (VI) is an environment friendly oxidant and also used as coagulant for water and waste water treatment[1,2]. It is possible to use hexacyanoferrate (III) as a moderate oxidant because of oxidation potential of the couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (0.36V). Hexacyanoferrate (III), (HCF) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. Researchers[3] have suggested that alkaline hexacyanoferrate (III) ion simply acts as an electron abstracting reagent in redox reactions. Though, Speakman

and Waters[4] have recommended different paths of oxidation of aldehydes, ketones and nitroparaffins. While, Singh and co-workers[5,6] during discussion of the oxidations of formaldehyde, acetone and ethyl methyl ketone have suggested that the oxidation takes place through an electron transfer process resulting in the formation of a free radical intermediate.

Extensive work on the oxidation of amines by hexacyanoferrate (III) was done by a number of researchers[7-13]. Majority of the oxidation work were carried on tertiary amines and less on the oxidation of primary and secondary amines Oxidation of anilines and substituted anilines using hexacyanoferrate (III) was reported by Dasgupta and

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Mahanti[14-15]suggests formation of an aminium radical cation and radical intermediate. Due to some synthetic utility ferricyanide oxidation has become known as Decker oxidation[16]

Sulfanilamide is a sulfonamide antibacterial. Chemically it is a molecule containing sulfonamide functional group attached to aniline. As a sulfonamide antibiotic it functions by competitively inhibiting enzymatic reactions involving para-amino benzoic acid (PABA)[17] PABA is needed in enzymatic reactions which produce folic acid that acts as a coenzyme in the synthesis of purine, pyrimidine and other amino acids. Acetazolamide, methazolamide, dichlorophenamide, ethoxolamide and dorzolamide, as carbonic anhydrase (CA-II) isozyme inhibitors, sulfonamide compounds are clinically used drugs for the treatment of glaucoma[18]. All the drugs used for the treatment of glaucoma have some systemic side effects[19]

A survey on earlier literature indicates that no attention was paid to the oxidation of sulfanilamide by this oxidant. The present work has been undertaken with a view at shedding some light on the influence of the nature of both the oxidant and the media on the kinetics and mechanistic of the redox reactions as well as on the nature of oxidation products. Moreover, the results obtained may gain some information on the chemistry of sulfanilamide in aqueous solutions.

Compound of sulfanilamide like sulfanilic acid (p-aminobenzenesulfonic acid) (SAA) is a significant and interesting compound, which is useful in a number of applications in the synthesis of organic dyes[20]. Sulfanilamide and some 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.[21] Literature survey reveals no study on oxidation of sulfanilamide by but several studies have been reported on the oxidation of sulfanilic acid by other oxidants such as Ce (IV)[22] H_2O_2[23] peroxomonophosphoric acid[24] persulfate[25] periodiate[26] peroxy disulfate[27] and HCF(III)[28]. Different workers have identified different products by different oxidants for sulfanilic acid[.22-27]. In view of the lack of literature on the oxidation of sulfanilamide by HCF (III), and in order to explore the mechanistic aspects of HCF(III) oxidation in alkaline medium, we have chosen sulfanilamide as a substrate. In continuation of our earlier work [29,30]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 sulfanilamide by alkaline hexacyanoferrate (III) ions on the basis of kinetic results
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EXPERIMENTAL SECTION

Reagent grade chemicals and doubly distilled water were used throughout. A solution of $Fe(CN)_6^{3-}$ was prepared by dissolving $K_3Fe(CN)_6$ (SD fine chem.) in H_2O and was standardized iodometrically. Sulfanilamide is soluble in aqueous bases. The solution of sulfanilamide (lobachemie) was prepared by dissolving appropriate amount of sample in very dilute alkaline solution. Sodium hydroxide (Merck) and sodium nitrate (SD fine chem.) were used to provide the required alkalinity and to maintain the ionic strength respectively.

Instruments used
A sophisticated double beam bio-spectrophotometer BL-198 was used is a microprocessor based scanning UV-visible spectrophotometer with PC compatabity and with RS232C interface; MS Windows based software used for data acquisition, processing, storage and interpretation of data. This spectrophotometer has automatic wavelength calibration system, Lamp selection; auto focusing, programmable wavelength and thermoelectrically temperature controller. Thermostat used was of 'Toshniwal' Instrument. The constancy of the temperature maintained was to an accuracy of ±0.5 ºC

Kinetic Procedure
Stoichiometry and Product Analysis:
Reaction mixture containing various ratios of hexacyanoferrate (III) to sulfanilamide in presence of 5×10^{-2} mol dm^{-3} at 307°K, under the condition [SNA]>>[HCF], were equilibrated for 24h. Determination of unreacted HCF showed 1:3 stoichiometry. Oxidation product Azoxybenzene-4, 4'-disulfonamide was detected by thin layer

chromatography. Further it was confirmed by its MP, IR and NMR spectra. Strong peak for —N=N— group was observed at 1315 cm^{-1}
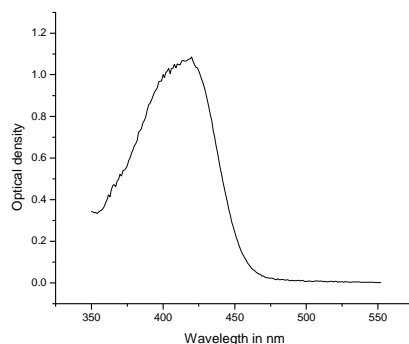
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RESULTS AND DISCUSSION

Figure.1 Determination max wavelength of potassium hexacyanoferrate (III) 1x10⁻⁴ M

Figure.1 λ_{max} for potassium hexacyanoferrate(1x10⁻⁴M) determined spectrophotometrically using bio-spectrophotometer BL-198 Elico make and found to be 420nm
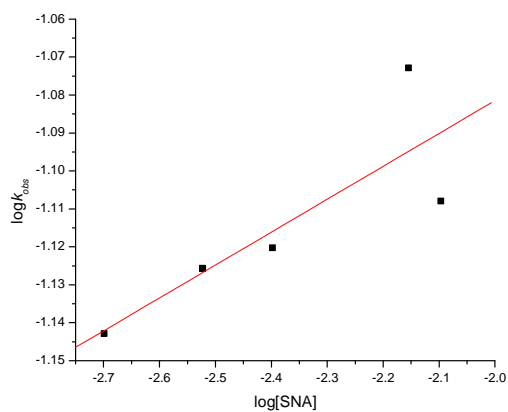
Figure.2 Plot of log[SNA] Vs logk_{obs}
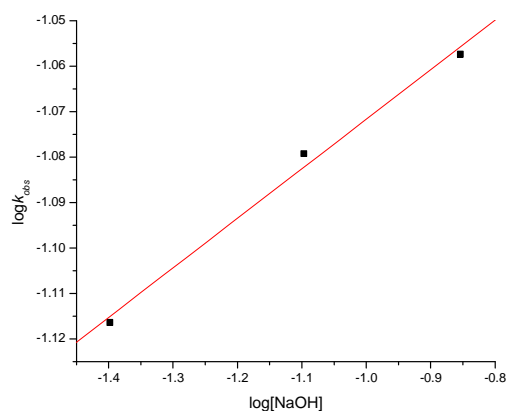
Figure.3 Plot of log[NaOH] Vs logk_{obs}

1. Effect of Reactants on the Reaction Rate

With substrate in excess, at constant [SNA], [OH⁻] and temperature, plots of log [HCF] Vs time were linear indicating first order dependence of rate on [HCF]. Rate constant k increases by with increase in [HCF] (Table.1) confirming first order dependence on [HCF]. Increase [SNA] lead to increase in rate of reaction (Table.1) at constant

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[HCF], [NaOH], [NaNO$_3$] and temperature. Plot of log[SNA] Vs logk_{obs} (Figure.2) was linear   with a slope of 0.50 indicating fractional order dependence on [SNA]. The rate increases with increase in [NaOH] (Table 1). Plot of log[NaOH] Vs logk_{obs} (Figure 3) was linear with slope of 0.994, showing first order dependence on [OH$^-$]

2. Effect of salts on the Rate

To study the effect of variation of salts, the concentration of salts were varied from 1 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration of other reaction ingredients such as [HCF]=7x10^{-4} M, [SNA]=5x10^{-3}M, [NaOH]=8x10^{-2}M and [NaNO$_3$]=8x10^{-2}M (Table.6). From the obtained results, it is clear that pseudo first order rate constant k_{obs} increased with increase in concentration for KBr, KI, KNO$_3$, NaHCO$_3$ and NH$_4$Br. A plot of log k_{obs} vs $\sqrt{\mu}$ according to extended Bronsted-Debye-Huckel equation was found to be linear with positive slopes indicating positive salt effect. On the other hand pseudo first order rate constant decreased with increase in concentration for KCl, K$_2$SO$_4$, NaCl, Na$_2$CO$_3$ and NH$_4$Cl. A plot of log k_{obs} vs $\sqrt{\mu}$ was found to be linear with negative slopes indicating negative salt effect.

Table.6 Effect of added Salt on first order rate constant
K$_3$[Fe(CN)$_6$]=7x10^{-4} M [SNA]= 5x10^{-3} M [NaOH]=8x10^{-2}M [NaNO$_3$]=8x10^{-2}M

Conc. of salts(M)	Rate constant (k), S^{-1}									
	KCl	KBr	KI	KNO$_3$	K$_2$SO$_4$	NaCl	NaHCO$_3$	Na$_2$CO$_3$	NH$_4$Cl	NH$_4$Br
0.01	0.07959	0.07131	0.07503	0.07523	0.07705	0.07856	0.07871	0.07893	0.08334	0.07137
0.02	0.08347	0.08121	0.07981	0.07781	0.08174	0.07986	0.07499	0.08556	0.07850	0.08121
0.03	0.07428	0.07576	0.07615	0.08301	0.08082	0.07931	0.07830	0.07244	0.08161	0.07576
0.04	0.07285	0.08068	0.08418	0.07729	0.08026	0.08214	0.08258	0.08421	0.08054	0.08068
0.05	0.07437	0.07857	0.08062	0.08334	0.07786	0.07947	0.08290	0.07805	0.07935	0.07857
0.06	0.07090	0.08050	0.07594	0.07904	0.07986	0.08410	0.08368	0.08297	0.07895	0.08050
0.07	0.07774	0.08283	0.08424	0.07744	0.08057	0.07912	0.08142	0.08174	0.08293	0.08283
0.08	0.08028	0.08171	0.08184	0.07786	0.07860	0.07930	0.08100	0.07915	0.08054	0.07666
0.09	0.08455	0.08020	0.07792	0.08398	0.08367	0.07947	0.07777	0.07868	0.07951	0.08020

3. Effect of Ionic Strength and Dielectric Constant on the Rate

Variation in ionic strength using NaNO$_3$ solution (1 x 10^{-3} mol dm^{-3} to 9 x 10^{-3} mol dm^{-3}) affect (Table.2) the rate of the reaction indicating that species are involved in the rate limiting step.

Dielectric constant (D) of the medium was varied by adding methanol, ethanol, DMSO, and acetonitrile (Table.3). It was found that rate constant increased on decreasing the dielectric constant of acetonitrile and DMSO, while rate constant decreased on decreasing the dielectric constant of methanol and ethanol. The relative permittivity (*D*) effect was studied by varying solvent-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[31]. Plot of (1/D) Vs logk_{obs} was found to be linear.

4. Effect of Temperature on the Reaction Rate

Reaction was studied over a range of temperature 283°K to 333°K by varying the concentration of sulfanilamide (Figure.4), keeping other experimental conditions constant.

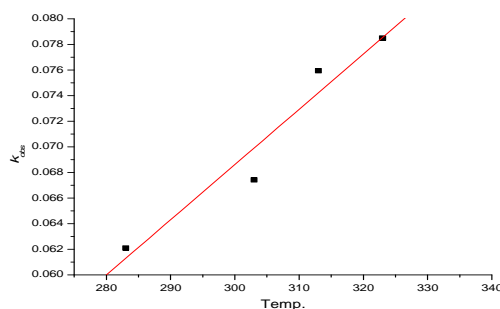It was found that the rate increased with increase in temperature (Table.5)

Figure.4 Plot of temp. Vs k_{obs}

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From the Arrhenius plot (Figure.5), activation parameters like energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), free energy of activation ($\Delta G^{\#}$), and logA were computed (Table.5).
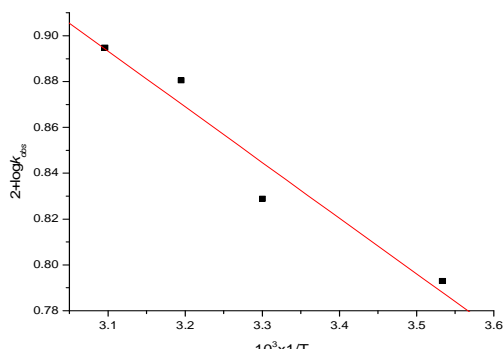

Figure.5 Arrhenius plot

5. Test of Free Radicals

Addition of reaction mixture to aqueous acrylonitrile solution did not initiate polymerization, showing absence of free radical species.

Table.1-Effect of Reactant Concentrations on the Reaction Rate at 307K

10^4[HCF]	10^3[SNA]	10^2[NaOH]	10^2[NaNO$_3$]	10^4 k
Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}
2.0	20	20	20	7.20
3.0	30	20	20	7.49
4.0	40	20	20	7.58
7.0	70	20	20	8.46
7.0	2	20	20	8.11
7.0	3	20	20	8.17
7.0	5	20	20	8.26
7.0	5	4	20	7.65
7.0	5	8	20	8.33
7.0	5	12	20	8.82

Table.2-Effect of Ionic strength on the Reaction Rate at 307K

10^4[HCF]	10^3[SNA]	10^2 [NaOH]	10^2 [NaNO$_3$]	10^4 k
Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}
7.0	5	8	2	6.82
7.0	5	8	6	7.49
7.0	5	8	12	7.89
7.0	5	8	14	8.09

Table.3-Effect of solvent on first order rate constant

$K_3[Fe(CN)_6]$ = 7×10^{-4} M [SNA]= 5×10^{-3} M [NaOH]= 8×10^{-2}M [NaNO$_3$]= 8×10^{-2}M

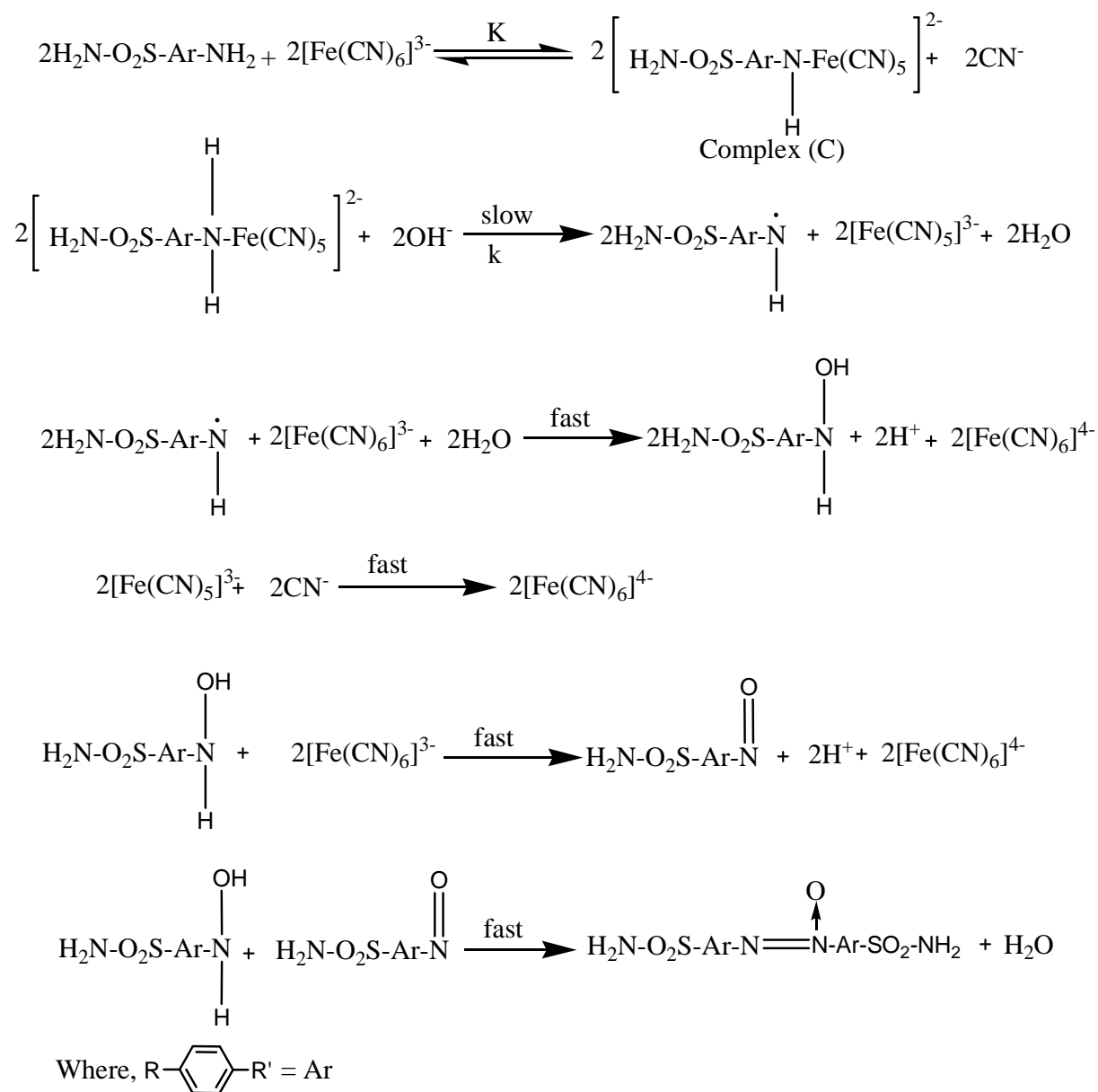| Sr. No.	Conc. of solvent %	Variation of solvents (k_{obs})			
		Methanol	Ethanol	Acetonitrile	DMSO
01	10	0.0816	0.0773	0.0774	0.0774
02	20	0.0764	0.0831	0.0764	0.0803
03	30	0.0895	0.0746	0.0800	0.0778
04	40	0.0834	0.0772	0.0750	0.0769
05	50	0.0805	0.0745	0.0764	0.0775
06	60	0.0791	0.0774	0.0806	0.0832

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Table.4-Effect of Temperature on Oxidation of sulfanilamide in basic media
$K_3[Fe(CN)_6] = 7 \times 10^{-4}$ M [SNA]= 5×10^{-3} M [NaOH]=8×10^{-2}M [NaNO$_3$]=8×10^{-2}M
Activation Energy = -4.6528 KJ/mole

Sr. No.	temp °K	$\Delta H^{\#}$ (KJ/mole)	$\Delta S^{\#}$ (KJ/mole)	$\Delta G^{\#}$ (KJ/mole)
01	283	-7.0056	-0.1269	28.9240
02	293	-7.0887	-0.1260	29.8544
03	303	-7.1718	-0.1264	31.1387
04	313	-7.2550	-0.1259	32.1555
05	323	-7.3381	-0.1257	33.2650
06	333	-7.4213	-0.1259	34.5264
Avg.		**-7.2134**	**-0.1261**	**31.6440**

Table.5- Effect of Temperature on the Reaction Rate & Activation parameters

Temperature(K)	10^4 k(s^{-1})	Activation parameters	
		Parameter	Value
283	0.0621	Ea(J mol^{-1})	4652.8
293	0.0765	$\Delta H^{\#}$(J mol^{-1})	-7213.4
303	0.0674	$\Delta G^{\#}$(J mol^{-1})	31644
313	0.0759	$\Delta S^{\#}$ (J K^{-1}mol^{-1})	-126.1
323	0.0785	logA	-243.0
333	0.0714		

Variation of the concentration of each of the oxidant HCF (III), substrate (SNA) base and ionic strength, while maintaining the others concentration constant showed that the reaction is first-order in oxidant, in base and with respect to ionic strength and fractional order in substrate. The stoichiometry of the reaction between SNA and HCF (III) is 1:3. Oxidation of sulfanilamide using hexacyanoferrate (III) in basic media is non-complementary reaction whereby oxidant undergoes six equivalent changes. Like Cu (II) in most oxidation reactions hexacyanoferrate (III) shows free radical formation and its rapid oxidation[32-36]. Due to higher oxidation potential of $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ (0.36V) in alkaline medium compared to Cu(II)/Cu(I) (0.159V) suggests better possibility of rapid oxidation of the free radical might completely mask the polymerization. In the present investigation the oxidation proceeds via formation of a complex with SNA and HCF (III), which decomposes in the presence of alkali in a slow step to a free radical derived from SNA and HCF (II). The free radical further reacts with 1 mole of HCF (III) in aqueous media in a fast step to give intermediate product hydroxylamine benzene sulfonamide and HCF (II). The hydroxylamine benzene sulfonamide so formed further reacts with 2 moles of HCF (III) in a fast step to give nitrosobenzene sulfonamide and HCF (II). Another molecule of SNA reacts with 2 moles of HCF (III) in the fast step to give hydroxylamine benzene sulfonamide and HCF (II). The two intermediate products products namely nitrosobenzene sulfonamide and hydroxylamine benzene sulfonamide rearrange themselves in a fast step to azoxybenzene-4, 4'-disulfonamide as the final product, satisfying the stoichiometric observations. Further, the formation of complex is also proved kinetically by non zero intercept of the plot of [OH-]/k_{obs} versus 1/[SNA]. The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as higher rate constant for slow step indicate that the oxidation most probably occurs via an inner-sphere mechanism. Scheme 1 is in accordance with the generally accepted principle of non- complementary oxidations taking place in sequences of one electron steps.

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$$2H_2N\text{-}O_2S\text{-}Ar\text{-}NH_2 + 2[Fe(CN)_6]^{3-} \overset{K}{\rightleftharpoons} 2\left[H_2N\text{-}O_2S\text{-}Ar\text{-}\underset{\underset{H}{|}}{N}\text{-}Fe(CN)_5\right]^{2-} + 2CN^-$$

Complex (C)

$$2\left[H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\text{-}Fe(CN)_5\right]^{2-} + 2OH^- \xrightarrow[k]{slow} 2H_2N\text{-}O_2S\text{-}Ar\text{-}\underset{\underset{H}{|}}{\dot{N}} + 2[Fe(CN)_5]^{3-} + 2H_2O$$

$$2H_2N\text{-}O_2S\text{-}Ar\text{-}\underset{\underset{H}{|}}{\dot{N}} + 2[Fe(CN)_6]^{3-} + 2H_2O \xrightarrow{fast} 2H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{N}} + 2H^+ + 2[Fe(CN)_6]^{4-}$$

$$2[Fe(CN)_5]^{3-} + 2CN^- \xrightarrow{fast} 2[Fe(CN)_6]^{4-}$$

$$H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{N}} + 2[Fe(CN)_6]^{3-} \xrightarrow{fast} H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{O}{||}}{N} + 2H^+ + 2[Fe(CN)_6]^{4-}$$

$$H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{N}} + H_2N\text{-}O_2S\text{-}Ar\text{-}\overset{\overset{O}{||}}{N} \xrightarrow{fast} H_2N\text{-}O_2S\text{-}Ar\text{-}N\overset{\overset{O}{\uparrow}}{=\!=}N\text{-}Ar\text{-}SO_2\text{-}NH_2 + H_2O$$

Where, R–⟨◯⟩–R' = Ar

Scheme.1

Scheme.1 suggests to the rate law (1)

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

$$Rate = \frac{kK[SNA][Fe(CN)_6^{3-}][OH^-]}{(1+K[Fe(CN)_6^{3-}])(1+K[SNA]} \tag{1}$$

$$Rate = \frac{kK[SNA][Fe(CN)_6^{3-}][OH^-]}{1+K[SNA]+K[Fe(CN)_6^{3-}]+K^2[SNA][Fe(CN)_6^{3-}]} \tag{2}$$

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

$$Rate = \frac{kK[SNA][Fe(CN)_6^{3-}][OH^-]}{1+K[SNA]} \qquad (3)$$

$$\frac{Rate}{[Fe(CN)_6^{3-}]} = k_{obs} = \frac{kK[SNA][OH^-]}{1+K[SNA]} \qquad (4)$$

Eq. (4) can be rearranged to the following form, which is used for verification of the rate law,

$$\frac{[OH^-]}{k_{obs}} = \frac{1}{kK[SNA]} + \frac{1}{k} \qquad (5)$$

According to Eq. (5), the plots of $\dfrac{[OH^-]}{k_{obs}}$ versus $\dfrac{1}{[SNA]}$ (r> 0.9751, s≤0.0158) should be linear as verified in Figure.6
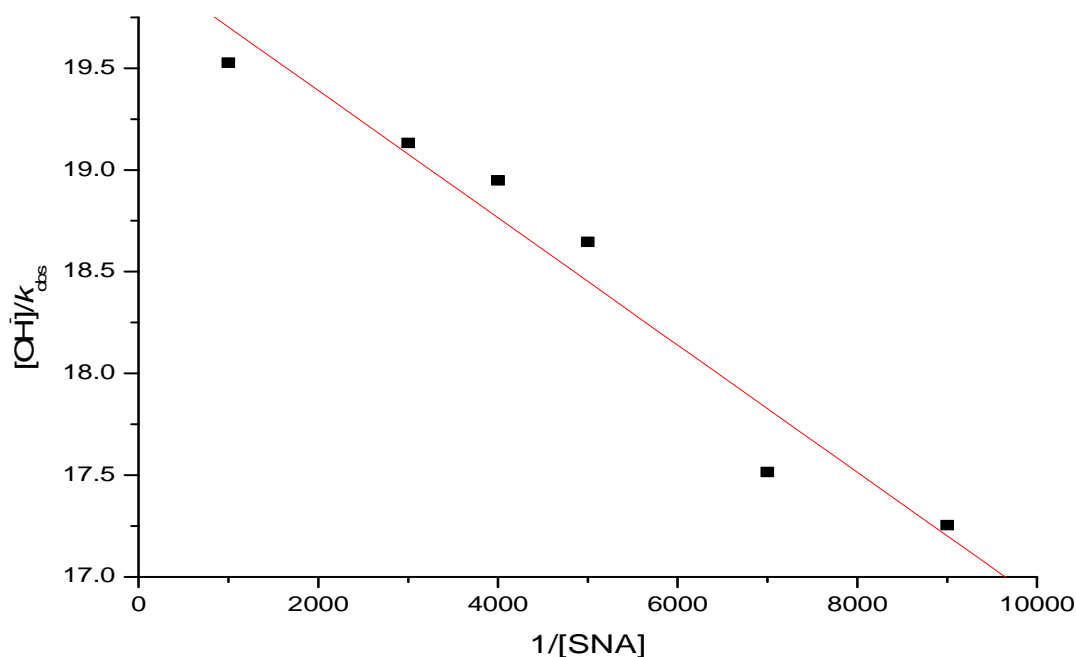

Figure.6 Plot of [OH⁻]/k_{obs} versus 1/[SNA]

CONCLUSION

The oxidation of SNA with HCF(III) in alkaline medium involves an inner-sphere mechanism and non-complementary oxidations taking place in sequences of one electron steps. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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