

Kinetics and Mechanism of Reduction of A Binuclear Complex Fe^{III}.L.Co^{III} by Hydroquinone

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Summary: Fully oxidized binuclear complex Fe^{III}.L.Co^{III} complex was synthesized by reaction of salicylato pentaammine cobalt (III) with ferric nitrate. Reduction kinetics of Fe^{III}.L.Co^{III} by hydroquinone i.e. (H₂Q) was followed spectrophotometrically. Fe^{III} was reduced rapidly but Co^{III} was not.

Reduction kinetics follows the rate law.

$$-d[\text{Fe}^{\text{III}}.\text{L}.\text{Co}^{\text{III}}] = k_{\text{obs}} [\text{Fe}^{\text{III}}.\text{L}.\text{Co}^{\text{III}}]$$

$$\text{where } k_{\text{obs}} = \left[\frac{k_1 k_3 [\text{H}^+][\text{H}_2\text{Q}]}{k_2 + k_3 [\text{H}_2\text{Q}]} \right]$$

Kinetic measurements have been carried out at four different temperatures and pH.

Temperature has no effect on the value of k_2 / k_3 . Redox Potential (E°) of the complex at different pH were determined by cyclic voltametry. The mechanism of this reaction is discussed in the context of Marcus cross relation for outer sphere process.

Introduction

Oxidation reduction reactions involving metal ions and their complexes are of two main types [1-2] called inner sphere and outer sphere reaction. Rates of electron transfer between metal centres in a complex depends on (a) nature of medium (b) distance between metal centers (c) differences of redox potential value i.e E° (d) work contribution to free energy. These factors are incorporated in Marcus equation [3]. In order to understand these, a number of researchers [4-12] have prepared stable binuclear complexes, in which two metal centers are joined at a fixed distance by an organic ligand. In a complex of fixed bridging ligand above factors (a) & (d) can not be studied but (b) & (c) and estimation of electronic coupling constants in the Marcus equation of adiabatic electron transfer may be possible.

In order to understand these, a stable binuclear complex was synthesized containing Fe^{III} and Co^{III}, joined by salicylate group. Where Fe^{III}, coordinated to salicylato in a bidentate mode, would be expected to reduce rapidly by hydroquinone. It was expected

that the Fe^{II} moiety thus formed would reduce the Co^{III}. However, the Co^{III} was not reduced by the Fe^{II} generated as evidenced by the persistence of the characteristic 502 nm d-d band of the (NH₃)₅Co^{III} salicylato complex.

The kinetics of reduction of Fe^{III}, coordinated to the OH of the salicylate which is coordinated to Co^{III} pentaammine moiety through its carboxylate group is reported here.

Results and Discussion

The reduction of Fe^{III}.L.Co^{III} complex by [H₂Q] was performed at four different temperatures and pH. The observed rate constants (k_{obs}) at different pH and temperatures with [H₂Q] are summarized in Tables 1-4 and are represented in Figures (2-5). k_{obs} vs [H₂Q] plots at a given pH and temperature show curvature and levelling off at high [H₂Q] indicating the expectation of saturation kinetics. The initial slopes of these plots are larger than the maximum

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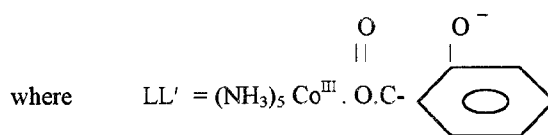
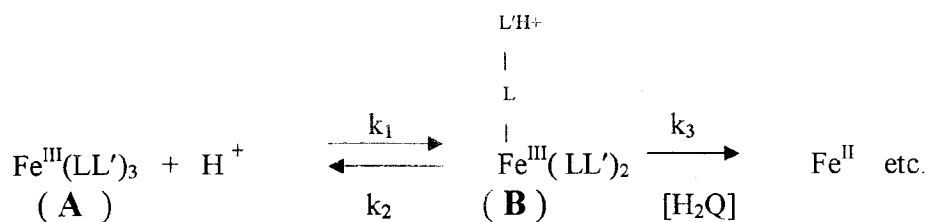
Table-1: Pseudo First Order Reduction Rate Constants of Fe^{III}co^{III}Salicylato Complex by Hydroquinone

[Fe ^{III}] [Co ^{III} Salicylato]	1x10 ⁻³ M 5x10 ⁻³ M	pH 2.28 512 nm			
[H ₂ Q] Mx10 ³	k _{obs} 20°C	k _{obs} 25°C	k _{obs} 30°C	k _{obs} 35°C	
5	0.047	0.054	0.062	0.085	
6	0.050	0.064	0.070	0.092	
8	0.054	0.068	0.087	0.101	
10	0.073	0.080	0.091	0.102	
30	0.090	0.095	0.102	0.107	
50	0.094	0.100	0.108	0.115	

value of k_{obs}. at each pH, remaining almost constant with increasing pH.

When different plots of k_{obs} vs [H₂Q] at different pH are compared, it is observed that rates increase with pH. For this, it is postulated that at high pH when there is no proton assisted dissociation of the phenolate group from the complex, the rate will keep on increasing with [H₂Q].

A possible mechanism and rate law consistent with the observation can be derived



Applying steady state approximation for the precursor complex i.e. [B], the rate of appearance and disappearance will be equal. On deriving these equation and substitution these values we get a final rate equation.

$$\text{Rate} = \left[\frac{k_1 k_3 [\text{H}^+][\text{H}_2\text{Q}]}{k_2 + k_3 [\text{H}_2\text{Q}]} \right] [\text{Fe}^{\text{III}}(\text{LL}')_3]$$

i.e. Rate = k_{obs} [complex]

$$k_{\text{obs}} = \left[\frac{k_1 k_3 [\text{H}^+][\text{H}_2\text{Q}]}{k_2 + k_3 [\text{H}_2\text{Q}]} \right]$$

At low [H₂Q] :- k₂ >> k₃ [H₂Q], so the

Table-2

[Fe ^{III}] [Co ^{III} Salicylato]	1x10 ⁻³ M 5x10 ⁻³ M	pH 2.64 510 nm			
[H ₂ Q] Mx10 ³	k _{obs} 20°C	k _{obs} 25°C	k _{obs} 30°C	k _{obs} 35°C	
5	0.034	0.040	0.047	0.054	
6	0.040	0.048	0.055	0.074	
8	0.050	0.055	0.065	0.082	
10	0.052	0.060	0.071	0.086	
30	0.080	0.088	0.104	0.108	
50	0.096	0.110	0.112	0.119	

Table-3:

[Fe ^{III}] [Co ^{III} Salicylato]	1x10 ⁻³ M 5x10 ⁻³ M	pH 3.0 506 nm			
[H ₂ Q] Mx10 ³	k _{obs} 20°C	k _{obs} 25°C	k _{obs} 30°C	k _{obs} 35°C	
5	0.0327	0.045	0.05	0.065	
6	0.045	0.051	0.06	0.084	
8	0.052	0.059	0.071	0.085	
10	0.055	0.069	0.078	0.092	
30	0.062	0.078	0.094	0.108	
50	0.073	0.092	0.116	0.122	

Table-4:

[Fe ^{III}] [Co ^{III} Salicylato]	1x10 ⁻³ M 5x10 ⁻³ M	pH 3.7 494 nm			
[H ₂ Q] Mx10 ³	k _{obs} 20°C	k _{obs} 25°C	k _{obs} 30°C	k _{obs} 35°C	
5	0.038	0.047	0.053	0.070	
6	0.046	0.051	0.064	0.085	
8	0.054	0.064	0.073	0.089	
10	0.058	0.070	0.080	0.093	
30	0.066	0.081	0.095	0.110	
50	0.075	0.093	0.117	0.123	

Therefore, k_{obs} appear to be linearly proportional to [H₂Q] i.e. initial slope and k_{obs} become

$$k_{\text{obs}} = \frac{k_1 k_3 [\text{H}^+][\text{H}_2\text{Q}]}{k_2}$$

i.e. k_{obs} appear to be linearly proportional to $[\text{H}_2\text{Q}]$ i.e. initial slope

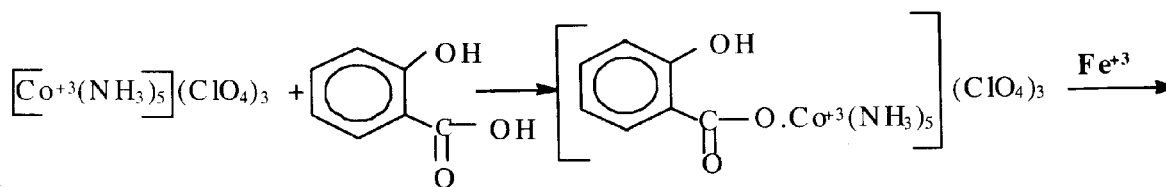
So in this condition the k_{obs} will increase with increasing concentration of $[\text{H}_2\text{Q}]$.

At high $[\text{H}_2\text{Q}]$: $k_3 [\text{H}_2\text{Q}] \gg k_2$

$$k_{\text{obs}} \approx k_1 [\text{H}^+]$$

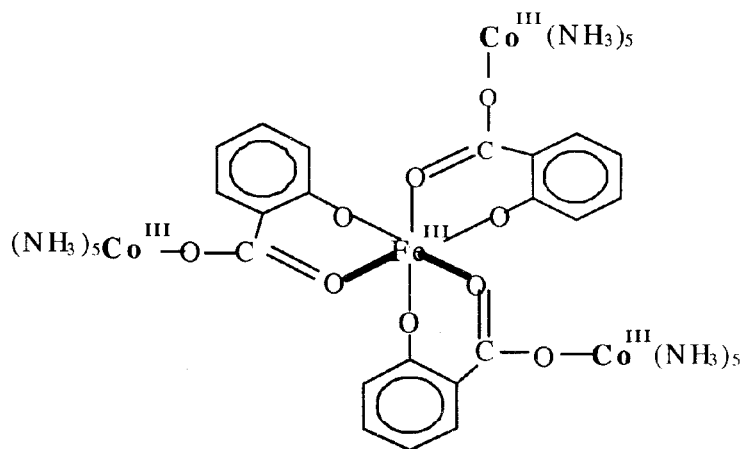
i.e. k_{obs} is independent of $[\text{H}_2\text{Q}]$ and now k_{obs} becomes constant at particular pH i.e. level off portion of plot is explained by this situation where saturation kinetics has been achieved. It is also observed from the constant values of higher slopes.

The reduction potential of Hydroquinone is pH dependent. It becomes more -ve at higher pH [13]. As such the outer sphere electron transfer at higher pH would be expected to be faster. However, the lower pH is likely to shift the equilibrium of the complex formation reaction towards a lower coordination of Fe^{III} . In such a state the reduction would be faster. Thus there are two opposite effects, i.e.,



$$\lambda_{\text{max}} = 494 \text{ nm}, \epsilon = 49 \text{ L. Mol.}^{-1} \text{ cm}^{-1}$$

$$\lambda_{\text{max}} = 502 \text{ nm}, \epsilon = 78 \text{ L. Mol.}^{-1} \text{ cm}^{-1}$$



$$\lambda_{\text{max}} = 510 \text{ nm}, \epsilon = 1000 \text{ L. Mol.}^{-1} \text{ cm}^{-1}$$

(Binuclear Complex)

Fig. 1: Synthesis of $\text{Fe}^{\text{III}} [\text{Co}^{\text{III}} (\text{NH}_3)_5 \text{Salicylato}]_3$ Complex.

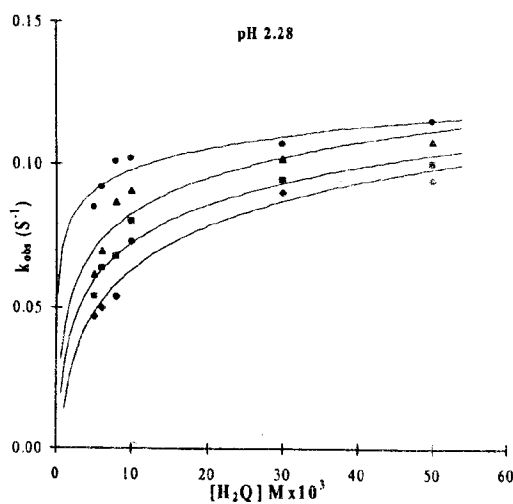


Fig. 2: Temperature Dependence of Reduction Rate Constants of Fe^{III} . L. Co^{III} Complex by Hydroquinone.

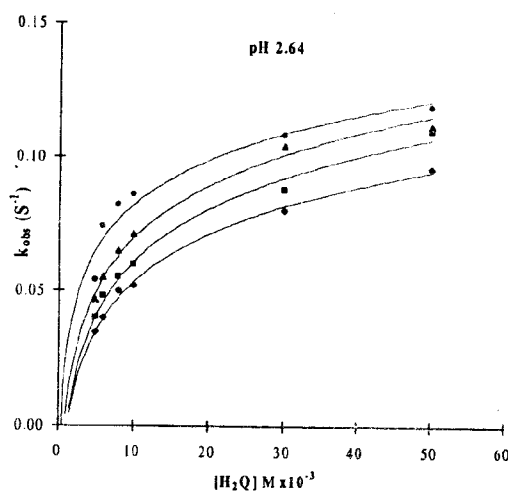


Fig. 3: Temperature Dependence of Reduction Rate Constants of Fe^{III} . L. Co^{III} Complex by Hydroquinone.

low pH favor faster reduction of the Fe^{III} centre due to reduced coordination while high pH, favor reduction by hydroquinone due to a more negative E° .

In the present study the proton assisted dissociated form of the Fe^{III} complex is the predominant oxidant and as such the $[\text{H}^+]$ term is in the numerator. However, as the pH is raised hydroquinone also becomes a stronger reductant. The

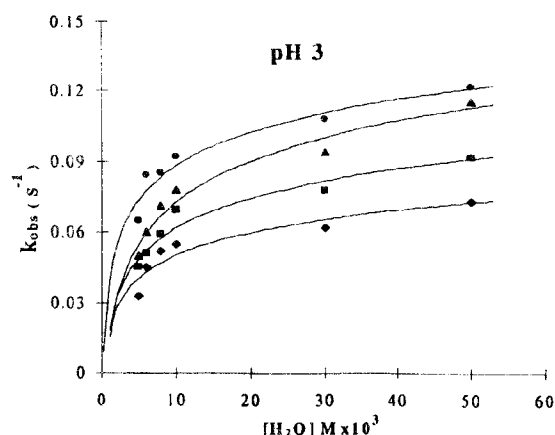


Fig. 4: Temperature Dependence of Reduction Rate Constants of Fe^{III} . L. Co^{III} Complex by Hydroquinone.

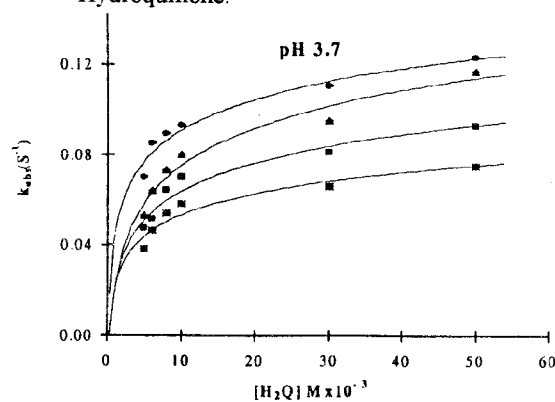


Fig. 5: Temperature Dependence of Reduction Rate Constants of Fe^{III} . L. Co^{III} Complex by Hydroquinone.

rate constant for reduction by hydroquinone is expected to be larger at higher pH. A careful examination of Figure 2-5 reveals that at the highest $[\text{H}_2\text{Q}]$, the leveling off is complete. It is postulated that at these high $[\text{H}_2\text{Q}]$, the k_3 path way i.e reduction of complex along with the intact coordinated ligand by hydroquinone becomes effective. The rate of disappearance of Fe^{III} species take place along the k_3 path.

The reciprocal plots of k_{obs}^{-1} vs $[\text{H}_2\text{Q}]^{-1}$ at different temperatures are shown in Figures 6-9. In these plots $1/k_1[\text{H}^+]$ is obtained as the intercept and $k_1k_3[\text{H}^+]/k_2$ as the slopes. Since k_1 (acid hydrolysis constant) obtained from $1/\text{intercept}[\text{H}^+]$ are given in Table 5.

Table-5: Ratio of Rate Constants at Different Temps. and pH by Hydroquinone

pH	$k_2/k_3 \times 10^3$			
	20°C	25°C	30°C	35°C
2.28	4.160	5.070	4.437	1.771
2.64	11.130	10.200	9.285	8.122
3.00	5.583	6.016	7.266	4.319
3.70	5.489	5.832	6.344	3.750

Table-6: Protonation Rate Constants (k_1) at Different Temps. and pH by Hydroquinone

pH	k_1			
	20°C	25°C	30°C	35°C
2.28	21.45	21.47	23.49	22.50
2.64	50.05	54.4	59.63	61.15
3.00	84.6	101.97	129.75	130.87
3.70	423.35	522.08	636.03	648.20

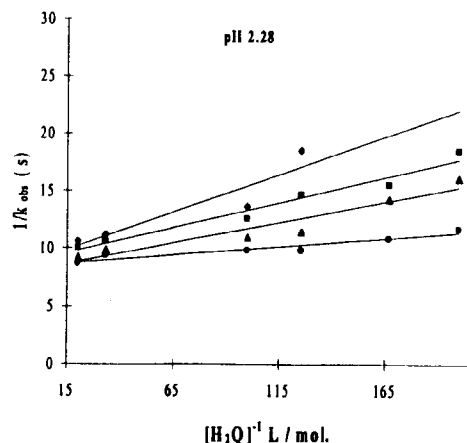
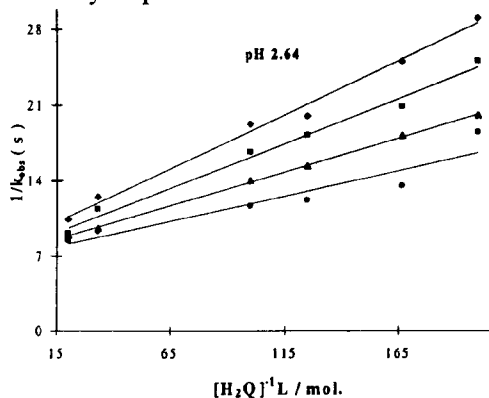
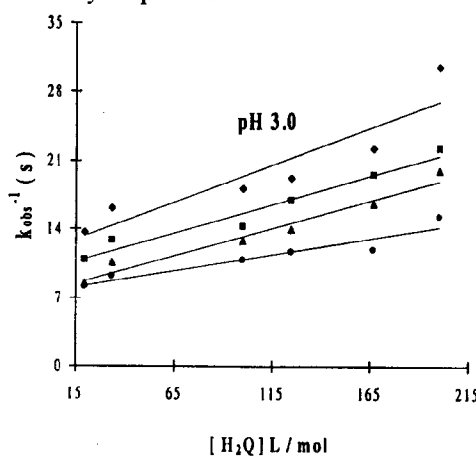
Table-7: Redox Potential of Fe^{III} Salicylate Co^{III} (NH_3)₅ Complex and Reductant at different pH

pH	E° (complex)	E° (complex)	E° (H_2Q)
	Vs. Ag / AgCl	Vs. N.H.E	
2.28	-0.375	-0.133	0.325
2.64	-0.357	-0.113	0.31
3.00	-0.344	-0.096	0.29
3.70	-0.320	-0.073	0.25

The ratios of k_2/k_3 obtained at different pH and temperatures are tabulated in Table 6. These values do not permit evaluation of activation parameters. However certain trends are noticeable. According to the proposed mechanism, the k_1 are found to increase with increase of pH and temperature where as k_2/k_3 decrease with the increase of pH but temperature has little effect on k_2/k_3 ratio. Redox potential E° of hydroquinone taken from literature [12] whereas E° of $[\text{Fe}^{\text{III}}(\text{Co}^{\text{III}}(\text{NH}_3)_5\text{salicylate})_3]$ complex at different pH obtained from a related study in our lab [14], are listed in Table 7 which shows that redox potential of both i.e. (complex & hydroquinone) are pH dependent. Using these redox potential values, reduction rate constants were rationalized in terms of Marcus theory.

As k_3 step is the reduction step at low $[\text{H}_2\text{Q}]$, it can be considered that initial slope of k_{obs} (up to low conc. of $[\text{H}_2\text{Q}]$) is a direct function of k_3 and may be used as k_{12} (cross reaction rate constant) in the Marcus equation [15].

$$\log k_{12} = 0.5 \log k_{11} + 0.5 \log k_{22} + 8.5 \Delta E^\circ$$

Fig. 6: Double Reciprocal Plots for Temp. Dependence Reduction of Fe^{III} . L. Co^{III} Complex by HydroquinoneFig. 7: Double Reciprocal Plots for Temp. Dependence Reduction of Fe^{III} . L. Co^{III} Complex by HydroquinoneFig. 8 Double Reciprocal Plots for Temp. Dependence Reduction of Fe^{III} . L. Co^{III} Complex by Hydroquinone

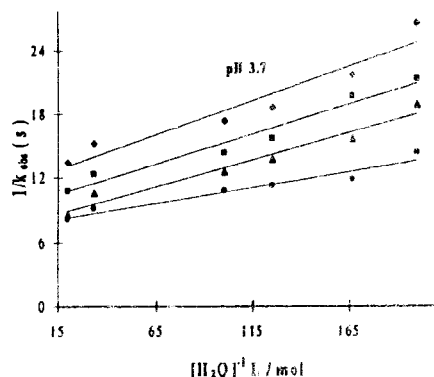


Fig. 9: Double Reciprocal Plots for Temp. Dependence Reduction of $\text{Fe}^{\text{III}} \cdot \text{L} \cdot \text{Co}^{\text{III}}$ Complex by Hydroquinone

By the application of this Marcus equation to ascorbate the results of driving force contribution towards k_{12} (assuming that k_{11} and k_{12} are pH independent) were calculated at different pH and they are compared with k_2/k_3 as given below.

pH	k_2/k_3 at 25°C	$3.45 \Delta E^\circ$ ($\log k_{12}$)
2.28	5.07×10^{-3}	-3.84
2.64	1.02×10^{-3}	-3.57
3.00	6.01×10^{-3}	-3.27
3.70	5.83×10^{-3}	-2.73

From the Marcus calculation, expected values k_{12} at different pH obtained for $[\text{H}_2\text{Q}]$ is 13.32 fold but experimentally the ratio of k_2/k_3 obtained is 2 fold. On this basis it can be concluded that our assumption of pH independent self-exchange rate constant is not true i.e. self-exchange rate constants are also pH dependent because the expected rate calculated by Marcus equation is greater than actual.

Taking the experimental k_{12} ($8.5 \text{ M}^{-1}\text{s}^{-1}$) from the initial slope and k_{11} for hydroquinone ($2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) from the literature [16] and ΔE° values of the system at pH 2.28 and 25°C we obtain the self-exchange rate constant of this complex k_{22} as $0.1733 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This value compares reasonably well with many other $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couples [16-19] under similar ligand environment. It is particularly encouraging since the k_{11} for H_2Q in literature is an approx. value. As predicted rate constant value obtained from Marcus theory and expected rate constant values are found to be an order of magnitude indicating the electron transfer is proceeding by an outer sphere mechanism.

Experimental

1. Salicylato pentaammine cobalt (III) complex was prepared by refluxing sodium salt of the salicylic acid with $[\text{Co}^{\text{III}}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}] (\text{ClO}_4)_3$ for 3 hrs at 60°C and was characterized spectrophotometrically.

2. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was obtained from E. Merck and its stock solution were maintained at 0.1M HNO_3 . Fe^{III} solutions were standardized spectrophotometrically with ortho-phenanthroline (o-phen)

3. $[\text{Fe}^{\text{III}} \{ \text{Co}^{\text{III}}(\text{NH}_3)_5 \text{ salicylato} \}_3]$

A fully oxidized violet color binuclear complex was prepared. In this complex, one Fe^{III} is coordinated to 3 $\text{Co}^{\text{III}}(\text{NH}_3)_5$ Salicylato ligands where the carbonyl O and the phenolic O are the two arms of the bidentate ligand. In the absence of coordinating metal the phenolic proton of salicylic acid would begin to dissociate at pH 10. However once the carboxylate group is coordinated to $\text{Co}^{\text{III}}(\text{NH}_3)_5$ moiety, this pKa of the phenolic will change somewhat. However, in presence of Fe^{III} this phenolic proton would be displaced by the metal because of the high formation constant (e.g., the $\log K_f$ between Fe^{III} and $\text{C}_6\text{H}_5\text{OH}$ is 7.81).

This complex is stable in the pH range 2.28 - 3.70. The λ_{max} and E° of the binuclear complex are pH dependent and the high ϵ value ($1000 \text{ L} \cdot \text{Mol}^{-1} \text{ cm}^{-1}$) at λ_{max} 512 nm is indicative of a phenolate $\rightarrow \text{Fe}^{\text{III}}$ charge transfer band.

Figure 1 summarizes the spectroscopic characteristics of the binuclear complex. Job plot method indicated 1:3 metal to ligand stoichiometry where salicylato cobalt complex acts as a bidentate ligand.

4. Hydroquinone (1,4 benzene diol) i.e. H_2Q (M.W.110.1):- Freshly prepared hydroquinone solution were used for reduction purpose.

All the solutions were prepared in deionised distilled water

Kinetic Measurement

Separate solutions of the $\text{Fe}^{\text{III}} \cdot \text{L} \cdot \text{Co}^{\text{III}}$ and $[\text{H}_2\text{Q}]$ were prepared at the desired concentration.

ionic strength and pH and then deaerated by flushing the solutions with pure N₂ gas. All kinetic experiments were performed under pseudo first order condition, with hydroquinone in excess over the complex. The temperature was controlled by circulating water from a thermostated water bath. The solutions were transferred anaerobically to the reservoir syringes of the Stopped-flow apparatus (Hi-Tech, SFA 11). Four replicate measurements were carried out for each pair of solution. The reactions were followed by monitoring a decrease in absorbance at 512 nm. Absorbance vs. time data collected in a computer interfaced to the stopped-flow apparatus, were fitted by a non-linear least-squares program to the equation

$$\ln (A_t - A_\alpha) = \ln (A_0 - A_\alpha) - k_{\text{obs}} \cdot t$$

Where A₀, A_t and A_α are the absorbances at time 0, t, and after 8-10 half lives respectively and k_{obs} is the first order rate constant for the decomposition of the complex.

Plots of ln (A_t - A_α) vs. time were linear for up to 85% of the reaction confirming first order behaviour in complex. The slopes of these plots give k_{obs}.

Conclusions

A binuclear complex has been synthesized in which Fe^{III} and Co^{III}(NH₃)₅ share a salicylato group. The Fe^{III} centre is reduced by hydroquinone rapidly enough but the reduced Fe^{II} fails to reduce the Co^{III}(NH₃)₅ center. This is probably so because ligand environment around the reduced Fe^{III} falls apart and the Fe^{II} is not a strong enough reducing agent to be able to reduce Co^{III}(NH₃)₅ centre in our experimental time frame. The rates of hydroquinone reduction increase with pH and are rate limited by a pre equilibrium step in which one arm of the ligand is dissociated. The species so formed is postulated to be more reactive. The aim was to attempt an approximation based on Marcus theory. The discrepancy between exchange rate constants themselves are pH dependent. This would appear to be a reasonable conclusion.

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