

# The Kinetics and Mechanism of Ruthenium(III)-Catalyzed Oxidation of Tris(2-amino ethyl)amine by Hexacyanoferrate(III) in Aqueous Alkaline Medium

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The kinetics of ruthenium(III)-catalyzed oxidation of TREN, i.e. tris(2-amino ethyl)amine(3-hydrochloride) by an outer sphere electron transfer oxidant, potassium hexacyanoferrate(III), was investigated spectrophotometrically in aqueous alkaline medium. The extent of the reaction was followed by registering a decrease in absorbance at 420 nm ( $\lambda_{\max}$  of  $\text{Fe}(\text{CN})_6^{3-}$ ) due to its consumption as a function of  $[\text{OH}^-]$ , ionic strength,  $[\text{Fe}(\text{CN})_6^{3-}]$ , [TREN], and temperature by varying only one variable at a time and keeping all other variables constant. The rate data indicate that the reaction exhibited first order dependence in [oxidant] and at a lower concentrations of reductant. The overall reaction follows second order kinetics at constant  $[\text{OH}^-]$  and proceeds via an associative  $\text{S}_\text{N}^2$  reaction path. The reaction was found to be first order at lower alkali concentrations, tending towards zero at higher concentrations. The rate of reaction increased linearly with increased ionic strength of the medium. A most probable mechanistic scheme explaining all the observed results has been proposed.

Activation parameters were computed using the Arrhenius and Eyring equations, which provided additional support to the proposed associative  $\text{S}_\text{N}^2$  pathway.

**Key Words:** Ru(III) catalyzed oxidation, oxidation of TREN, hexacyanoferrate (III)oxidation of TREN.

## Introduction

Interest in the oxidation of inorganic<sup>1</sup> and organic substrates<sup>2,3</sup> by hexacyanoferrate(III) has been growing. These studies revealed that oxidation by the hexacyanoferrate(III) ion proceeds through an outer-sphere electron transfer mechanism, which depends not only on the nature of the substrate, but also on the medium of reaction used for the study. In contrast, there are numerous reports on Ru(III)-catalyzed

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oxidation of several substrates, such as sulfoxides,<sup>4</sup> amides,<sup>5</sup> amines,<sup>6,7</sup> alcohols,<sup>8</sup> glycols,<sup>9</sup> and polyamine ocarboxylates,<sup>10</sup> by hexacyanoferrate(III). Ruthenium in its higher oxidation state, i.e. Ru(VI), is also known to act as a catalyst in the oxidation of several organic compounds.<sup>11,12</sup> The oxidation of organic compounds by hexacyanoferrate(III) in aqueous medium catalyzed by platinum,<sup>13,14</sup> osmium,<sup>15</sup> and iridium<sup>16</sup> has also been reported. It has been observed that among these metals Ru(III) acts as a comparatively more effective catalyst towards the oxidation of several substrates; however, no such oxidation of a tripodal tetraamine catalyzed by Ru(III) has as yet been reported.

As a result we considered it worthwhile to attempt to study the oxidation of a tripodal tetraamine ligand, tris(2-amino ethyl)amine(3-hydrochloride) (designated as TREN), by the hexacyanoferrate(III) ion in aqueous alkaline medium using Ru(III) chloride as an effective catalyst, so as order to strengthen our understanding of Ru(III)-catalyzed oxidation of substrates in general and the oxidation of TREN in particular.

## Experimental

All chemicals used were of analytical grade and solutions were prepared with double distilled water.  $K_3[Fe(CN)_6]$  (Glaxo, India),  $RuCl_3$  (Johnson and Matthey), TREN (Aldrich, USA), and  $KNO_3$  (Glaxo, India) were used in the present work. The solution of  $K_3[Fe(CN)_6]$  was prepared by weighing its desired amount, which was then placed in amber-colored bottles and kept in the dark to prevent photodecomposition. The appropriate dilutions were made accordingly from the above solution immediately before use. Tris(2-amino ethyl)amine(3-hydrochloride) was used in place of tris(2-amino ethyl)amine, as amine hydrochlorides are easily soluble in water. The stock solution of ruthenium trichloride was prepared in a  $0.5\text{-mol dm}^{-3}$  HCl solution, which was subsequently diluted to the desired concentration before its use.

Dilute solutions of sodium hydroxide and perchloric acid were used to adjust the pH of solutions before each kinetic run. Ionic strength of the reaction mixture was maintained at 0.1 M by using  $KNO_3$ .

All kinetic measurements and the recording of repetitive spectra of the reaction mixture were carried out with a Shimadzu UV-240 double beam UV-Vis spectrophotometer equipped with a thermostatted cell component. The temperature of the cell compartment was maintained at the desired temperature with a thermostat. Each solution was hung in the thermostat at the desired temperature for at least 30 min in order to maintain thermal equilibrium. The pH measurements were made with a Toshniwal CL-46 digital pH meter. The pH meter was standardized before its use using standard BDH buffers.

## Kinetic Measurements

The pH of the all reactants of appropriate concentrations was maintained at a desired value with the help of a digital pH meter, and dilute solutions of  $HClO_4$  and NaOH.

The requisite amount of each reactant was first placed in a test tube and thermostated at  $45\text{ }^\circ\text{C}$  to attain thermal equilibrium. The appropriate quantities of reactants were mixed in a 50-ml measuring flask in a sequence of TREN, NaOH, and then  $RuCl_3$ , at a fixed ionic strength. The reaction was finally initiated by injecting  $[Fe(CN)_6]^{3-}$  into the above mixture. The reaction mixture was properly shaken and quickly transferred to the spectrophotometer's cuvette, which had a path length of 10 mm, and was previously maintained at a constant temperature through circulatory arrangement of water from a thermostatic bath.

The extent of reaction was monitored by the decrease in absorbance at 420 nm corresponding to  $\lambda_{\max}$  of  $[\text{Fe}(\text{CN})_6]^{3-}$ .

The complexation of Ru(III) chloride with TREN or other reactants was ruled out because no change in color or absorbance was observed without adding  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The values of the initial rates ( $dc/dt$ ) were evaluated from the slopes of absorbance versus time plots by dividing  $dA/dt$  by the molar extinction coefficient of  $[\text{Fe}(\text{CN})_6]^{3-}$ , where A is the absorbance at any time (t).

## Results and Discussion

### Effect of $[\text{OH}^-]$ on the Initial Reaction Rate

The reaction was carried out by varying the concentration of  $[\text{OH}^-]$  from  $5.0 \times 10^{-3}$  M to  $10.0 \times 10^{-3}$  M at  $45 \pm 0.1$  °C, taking the fixed concentration of  $[\text{Fe}(\text{CN})_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[\text{TREN}] = 1.5 \times 10^{-3}$  M,  $[\text{Ru}(\text{III})] = 2.0 \times 10^{-6}$  M, and  $I = 0.1$  M ( $\text{KNO}_3$ ). In TREN, all primary amine groups get protonated around  $\text{pH} = 10$ , or  $\text{pOH} = 4$ . The central N atom will be protonated when all 3 neighboring amine groups are protonated. The  $\text{pK}_a$  values of TREN are reported in the literature<sup>17</sup> at 25 °C and  $I = 0.1$  M ( $\text{KNO}_3$ ) as  $\text{pK}_{a4} = 10.24$ ,  $\text{pK}_{a3} = 9.43$ ,  $\text{pK}_{a2} = 8.45$ , and  $\text{pK}_{a1} = 2.60$ . It is clear from the  $\text{pK}_a$  values of TREN that the predominant reacting species of TREN in the entire pOH or pH region selected for the present study are monoprotinated and deprotonated forms, i.e. HL and L only. The  $[\text{Fe}(\text{CN})_6]^{3-}$  exists in its deprotonated form in the whole  $[\text{OH}^-]$  taken in the present study; however, the rate due to protonated and deprotonated forms of TREN could not be resolved due to non-availability of its  $\text{pK}_a$  values in our experimental conditions. Thus, the initial rate increase that occurred with increased  $[\text{OH}^-]$  was attributed to conversion of the monoprotinated form of HL into deprotonated L. The leveling-off rate at  $[\text{OH}^-] > 1.5 \times 10^{-2}$  M is also justified as  $[\text{Fe}(\text{CN})_6]^{3-}$ , as well as  $[\text{TREN}]$ ; both exist in their deprotonated forms as shown in Figure 1.

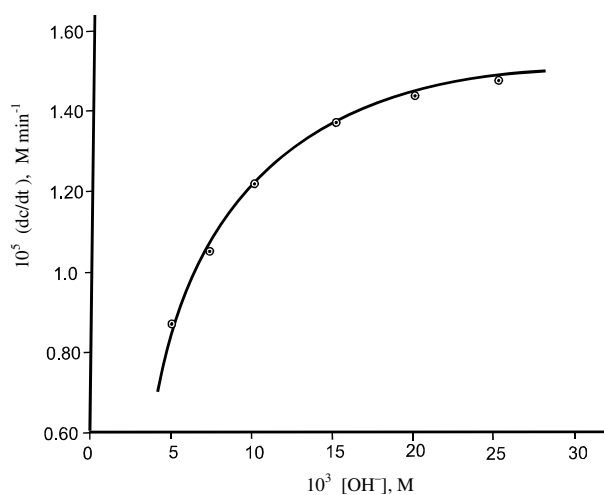
Similar behavior was observed in the Ru(III)-catalyzed oxidation of benzyl amine by hexacyanoferrate(III) in alkaline medium.<sup>6</sup>

### Effect of $[\text{TREN}]$ on Initial Rate

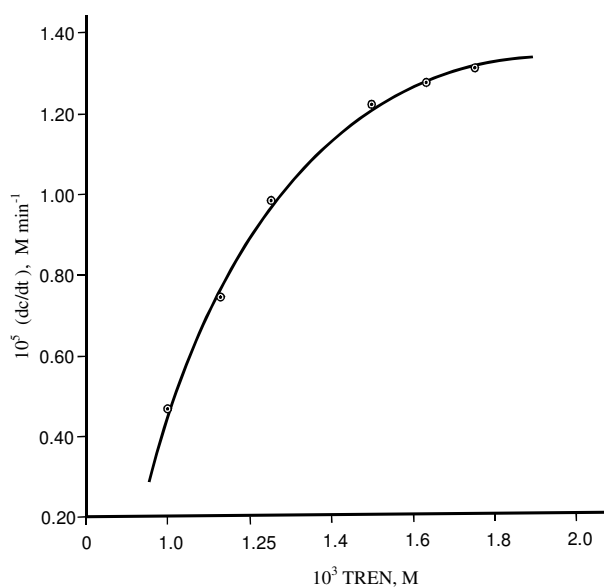
The rate of reaction was studied as a function of TREN in the concentration range of  $1.0 \times 10^{-3}$  M- $1.75 \times 10^{-3}$  M, keeping all other reactant concentrations fixed as:  $[\text{Fe}(\text{CN})_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[\text{OH}^-] = 1.0 \times 10^{-2}$  M, Ionic = 0.1 M ( $\text{KNO}_3$ ), and  $[\text{Ru}(\text{III})] = 2.0 \times 10^{-6}$  M at  $45 \pm 0.1$  °C. The plot of the initial rate versus  $[\text{TREN}]$  is given in Figure 2. This plot shows that the dependence of TREN on the initial rate follows first order kinetics at lower concentrations and tends toward zero order at its higher concentration.

### Effect of $[\text{Fe}(\text{CN})_6]^{3-}$ on the Initial Rate

The effect of  $[\text{Fe}(\text{CN})_6]^{3-}$  on the initial rate of reaction has been studied in the concentration range of  $2.0 \times 10^{-4}$  M- $6.25 \times 10^{-4}$  M, keeping all other reactant concentrations fixed. The rate data for variation of hexacyanoferrate(III) under the above specified conditions are compiled in Table 1.



**Figure 1.** The  $[\text{OH}^-]$  dependence on the initial rate at  $[\text{Fe}(\text{CN})_6^{3-}] = 3.75 \times 10^{-4} \text{ M}$ ,  $[\text{TREN}] = 1.5 \times 10^{-3} \text{ M}$ ,  $[\text{Ru}^{3+}] = 2.0 \times 10^{-6} \text{ M}$ , and  $I = 0.1 \text{ M}$  ( $\text{KNO}_3$ ) at  $45.0 \pm 0.1 \text{ }^\circ\text{C}$ .



**Figure 2.** The  $[\text{TREN}]$  dependence on the initial rate at  $[\text{Fe}(\text{CN})_6^{3-}] = 3.75 \times 10^{-4} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ru}^{3+}] = 2.0 \times 10^{-6} \text{ M}$ , and  $I = 0.1 \text{ M}$  ( $\text{KNO}_3$ ) at  $45.0 \pm 0.1 \text{ }^\circ\text{C}$ .

**Table 1.** Effect of  $10^4 [\text{Fe}(\text{CN})_6^{3-}] \text{ M}$  on the initial reaction rate of Ru(III)-catalyzed oxidation of TREN by  $[\text{Fe}(\text{CN})_6^{3-}]$ .  $[\text{TREN}] = 1.5 \times 10^{-3} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ru}^{3+}] = 2.0 \times 10^{-6} \text{ M}$ , and Ionic = 0.1 ( $\text{KNO}_3$ ) at  $45.0 \pm 0.1 \text{ }^\circ\text{C}$ .

$10^4 [\text{Fe}(\text{CN})_6^{3-}] \text{ M}$	2.00	2.25	3.00	3.75	4.50	5.00	6.25
$10^5 \left(\frac{dc}{dt}\right) \text{ M min}^{-1}$	1.10	1.13	1.16	1.21	1.25	1.28	1.36

### Effect of Ionic Strength (I) on the Initial Rate

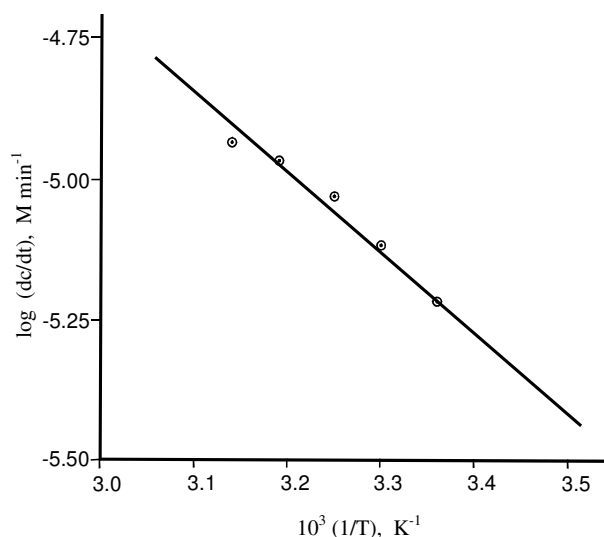
The influence of ionic strength was studied in the range of 0.05 M-0.40 M using  $\text{KNO}_3$  at  $[\text{Fe}(\text{CN})_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[\text{OH}^-] = 2.0 \times 10^{-2}$  M,  $[\text{TREN}] = 1.5 \times 10^{-3}$  M, and  $[\text{Ru}(\text{III})] = 2.0 \times 10^{-6}$  M at  $45 \pm 0.1$  °C. Higher ionic strength was not attempted due to the limited solubility of  $\text{KNO}_3$  in water. The data for dependence of the initial rate on ionic strength are given in Table 2, which shows that the reaction rate increased as the ionic strength of the medium increased.

**Table 2.** Effect of ionic strength on the initial reaction rate of Ru(III)-catalyzed oxidation of TREN by  $[\text{Fe}(\text{CN})_6]^{3-}$ .  $[\text{Fe}(\text{CN})_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[\text{TREN}] = 1.5 \times 10^{-3}$  M,  $[\text{Ru}^{3+}] = 2.0 \times 10^{-6}$  M, and  $[\text{OH}^-] = 1.0 \times 10^{-2}$  at  $45.0 \pm 0.1$  °C.

I [ $\text{KNO}_3$ ], (M)	0.05	0.01	0.15	0.20	0.30	0.40
$10^5 \left(\frac{dc}{dt}\right) \text{M min}^{-1}$	1.17	1.21	1.22	1.27	1.31	1.37

### Effect of Temperature Dependence on the Initial Rate

The kinetics of Ru(III)-catalyzed oxidation of TREN by the hexacyanoferrate(III) ion was studied between 25 and 45 °C. The Arrhenius plot of  $\log (dc/dt)$  versus  $(1/T)$  is given in Figure 3. Activation energy was calculated from the slope of the above plot to be  $18.50 \pm 0.03$   $\text{kJmol}^{-1}$ . The entropy of activation ( $\Delta S^\ddagger$ ) and enthalpy of activation ( $\Delta H^\ddagger$ ) were calculated using Eyring's equation as  $-289.74 \pm 0.06$   $\text{JK}^{-1} \text{mol}^{-1}$  and  $15.06 \pm 0.05$   $\text{kJmol}^{-1}$ , respectively.

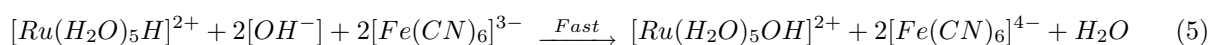
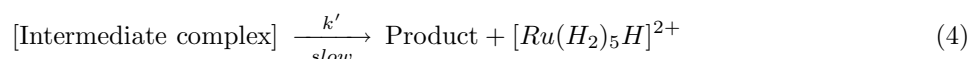
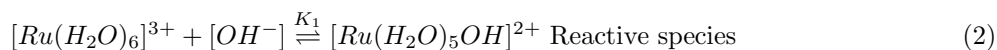


**Figure 3.** The temperature dependence on the initial rate at  $[\text{Fe}(\text{CN})_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[\text{OH}^-] = 1.0 \times 10^{-2}$  M,  $[\text{TREN}] = 1.5 \times 10^{-3}$  m,  $[\text{Ru}^{3+}] = 2.0 \times 10^{-6}$  M, and  $I = 0.1$  M ( $\text{KNO}_3$ ).

The ruthenium(III) chloride-catalyzed oxidation of TREN was studied in aqueous alkaline medium at 45 °C under the condition in which the unanalyzed reaction became negligible. On the basis of detailed experimental observations a most probable rate law for the oxidation of TREN may be expressed through the following equation:

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = k'[TREN][OH^-][Ru^{III}] \quad (1)$$

where  $k'$  is the rate constant for the oxidation of TREN. The oxidation of TREN by hexacyanoferrate(III) was found to proceed through a 4-step mechanistic pathway given by equations (2)-(5).



In order to determine the amount of  $[Fe(CN)_6]^{4-}$  produced each time, a known excess of  $[Fe(CN)_6]^{3-}$  was added to a known quantity of TREN in the presence of a fixed concentration of Ru(III) at  $pH \geq 11.0$  at  $45 \pm 0.1$  °C. The absorbance change at 420 nm was recorded until no appreciable changes were observed. The mole ratio of  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$  per mole of TREN was  $1.08 \pm 0.04$  (average of 5 values) at the end of the reaction.

In the first step a reactive aqua complex of ruthenium,  $[Ru(H_2O)_5OH]^{2+}$ , formed by replacing one molecule of water with a hydroxyl ion when  $RuCl_3$  was dissolved in water in alkaline medium. Now, this reactive species of ruthenium(III) in aqueous alkaline medium directly reacts with the substrate molecule to give an intermediate complex, which slowly disproportionates to give the final product and the hydride species of ruthenium(III).

It was previously observed that transition metal complexes are good abstracting agents for the hydride ion.<sup>18-20</sup> They can adequately abstract a hydride ion, even from a hydrogen molecule. In the acidic medium, the abstraction of the hydride ion from the  $\alpha$ -carbon atom of 2-propanol has been observed.<sup>21</sup> Similar studies on alcohol or alkoxide oxidation have revealed that hydride ion transfer may take place from the  $\alpha$ -carbon atom of alcohol or an alkoxide ion to the metal atom.<sup>22,23</sup> This provided sufficient evidence that hydride ion transfer will take place during oxidation of TREN by the hexacyanoferrate(III) ion in aqueous alkaline medium using Ru(III) chloride as a homogeneous catalyst.

In the last step, the ruthenium(III) hydride species was reoxidized to its original ruthenium(III) reactive species  $[Ru(H_2O)_5OH]^{2+}$ . Equation (4) in the above proposed mechanism is the slowest and was therefore identified as the rate-determining step.

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = k'[\text{Intermediate complex}] \quad (6)$$

With the help of equations (2) and (3), equation (6) reduces to equation (7).

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = k'K_1K_2[Ru(III)][OH^-][\text{Substrate}] \quad (7)$$

Now, considering the equilibrium condition in equations (2) and (3), and knowing that

$$[Ru(III)]_T = [Ru(III)]_e + [Ru(H_2O)_5(OH)]^{2+} + [\text{Intermediate complex}],$$

the rate law (7) reduces to

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{k'K_1K_2[\text{Substrate}][OH^-][Ru^{III}]_T}{1 + K_1[OH^-] + K_1K_2[\text{Substrate}][OH^-]}$$

or

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{k'K_1K_2[\text{Substrate}][OH^-][Ru^{III}]_T}{1 + K_1[OH^-](1 + K_2[\text{Substrate}])}. \quad (8)$$

At lower concentrations of substrate, the inequality  $1 \gg K_2[S]$  may be assumed to hold good, and the rate law given in equation (8) is transformed to equation (9).

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{k'K_1K_2[\text{Substrate}][OH^-][Ru^{III}]_T}{1 + K_1[OH^-]} \quad (9)$$

Equation (8) shows first order kinetics at lower concentrations of substrate. Further, at lower concentrations of alkali,  $1 \gg K_1[OH^-]$ , then equation (9) reduces to

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = k'K_1K_2[\text{Substrate}][Ru^{III}]_T[OH^-]. \quad (10)$$

The rate law given in equation (10) is apparently consistent with the observed first order kinetics, with respect to the hydroxyl ion concentration at lower concentrations; however, at higher hydroxyl ion concentrations  $K_1[OH^-] \gg 1$  and under this condition equation (9) takes the following form:

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = k'K_2[\text{Substrate}][Ru^{III}]_T. \quad (11)$$

The rate law given in equation (11) evidently accounts for the zero order kinetics with respect to the hydroxyl ion at higher concentrations. Equation (8) at constant  $[Ru^{III}]_T$  becomes

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{k'K_1K_2[\text{Substrate}][OH^-]}{1 + K_1[OH^-] + K_1K_2[\text{Substrate}][OH^-]}. \quad (12)$$

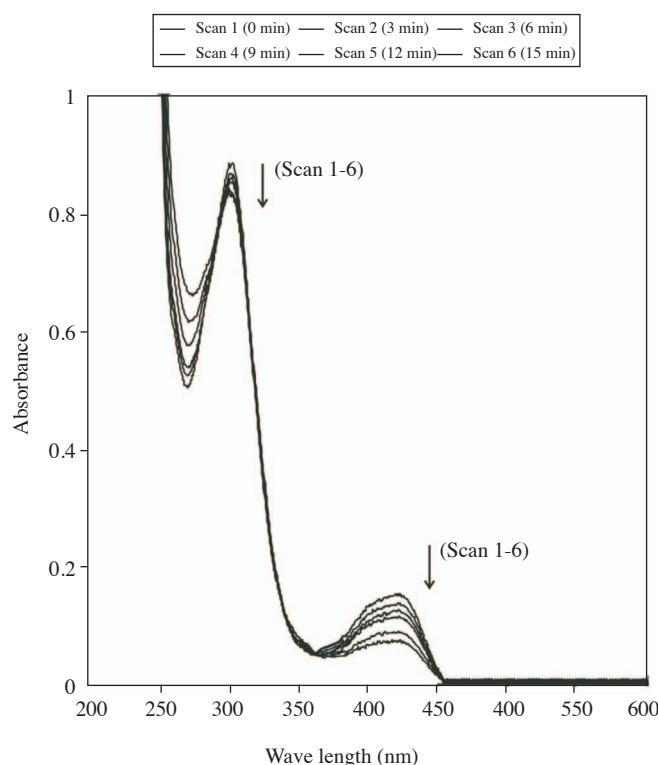
The reciprocal of equation (12) would give

$$\frac{1}{\text{Rate}} = \frac{1}{[\text{Substrate}]} \left[ \frac{1}{k'K_1K_2[OH^-]} + \frac{1}{k'K_2} \right] + \frac{1}{k'}. \quad (13)$$

The plot of  $(\text{Rate})^{-1}$  versus  $[\text{TREN}]^{-1}$  was found to be linear with the intercept on the rate axis. The intercept corresponds to  $1/k'$ , from which the value of  $k'$  comes out to be  $5.0 \times 10^{-5} \text{ min}^{-1}$  at  $45^\circ\text{C}$ . The value of  $k'$  was  $13.5 \times 10^{-5} \text{ min}^{-1}$  for Ru(III)-catalyzed oxidation of benzyl amine by hexacyanoferrate(III) in alkaline medium<sup>6</sup>, which is much less than the corresponding value for tris(2-amino ethyl)amine. It is therefore evident that the Ru(III)-catalyzed oxidation of tripodal tetraamine, i.e. tris(2-amino ethyl)amine, by alkaline hexacyanoferrate(III) is rather difficult in comparison to other amines like benzyl amine. Similarly, on the basis of equation (12), the plot of  $1/\text{Rate}$  versus  $1/[OH^-]$  at a constant substrate concentration yields a straight line with its slope and intercept equal to  $\frac{1}{k'K_1K_2[S]}$  and  $\frac{1}{k'K_2[S]} + \frac{1}{k'}$ , respectively. Now, with the help of the slope and intercept of the plot of  $1/\text{Rate}$  versus  $1/[OH^-]$  at a constant substrate concentration,

the calculated values of  $K_1$  and  $K_2$  were  $116.67 \pm 3.10$  and  $380.95 \pm 5.25$ , respectively. On the basis of the calculated values of  $K_1$  and  $K_2$ , and also the minimum and maximum concentration of alkali and substrate used in the present study, the 3 presumptions, namely  $1 \gg K_2[S]$  at lower substrate concentrations,  $1 \gg K_1[OH^-]$  at lower concentrations of alkali, and  $K_1[OH^-] \gg 1$  at higher concentrations of alkali can be verified. Thus, the above evidence supports the postulated mechanism. The evaluated values of activation parameters provide additional support for the proposed mechanistic scheme.

Lastly, a repetitive spectral scan was recorded for the Ru(III)-catalyzed oxidation of TREN by alkaline hexacyanoferrate(III) under the conditions, viz.  $[Fe(CN)_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[OH^-] = 1 \times 10^{-2}$  M,  $[TREN] = 1.5 \times 10^{-3}$  M,  $I = 0.1$  M ( $KNO_3$ ), and  $[RuCl_3] = 2.0 \times 10^{-6}$  M at  $45 \pm 0.1$  °C (Figure 4).



**Figure 4.** Spectral scan of the reaction mixture of  $[Fe(CN)_6]^{3-}$ , and TREN  $[Fe(CN)_6]^{3-} = 3.75 \times 10^{-4}$  M,  $[TREN] = 1.5 \times 10^{-3}$  M,  $[Ru^{3+}] = 2.0 \times 10^{-6}$  M, Ionic = 0.1 M ( $KNO_3$ ), and  $[OH^-] = 1.0 \times 10^{-2}$  M at  $45 \pm 0.1$  °C.

This shows that there is a continuous decrease in absorbance at 420 nm (broadband) and a corresponding decrease in the peak height at 303 nm (sharp band). The  $[Fe(CN)_6]^{3-}$  is consumed in the reaction by its reduction to  $[Fe(CN)_6]^{4-}$  by TREN; thus, the height of all the peaks due to  $[Fe(CN)_6]^{3-}$  show a continuous decrease with time due to its eventual conversion to  $[Fe(CN)_6]^{4-}$ . The  $[Fe(CN)_6]^{4-}$  also has a weak absorption band near 325 nm, but it could not be observed because it was buried in the shoulder of  $[Fe(CN)_6]^{3-}$  at 325 nm. An isosbestic point at 282 nm was also observed in the above spectrum, which points to the co-existence of 2 species, viz.  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$ , as assumed in the proposed mechanism of equation (5).



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