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Kinetics and mechanistic investigation of persulfate anion-mediated oxidation of hexacyanoruthenate(II) in aqueous medium

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The proposed study aimed to explore the kinetics of $[Ru(CN)_6]^{4-}$ oxidation in an aqueous media by persulfate anion ($S_2O_8^{2-}$). The increment in absorbance at 460 nm, which is indicative of the concentration of $[Ru(CN)_6]^{3-}$, was measured to determine the reaction rate. Applying the pseudo-first-order state, the reaction's progression was analyzed as an indicator of $[Ru(CN)_6^{4-}]$, temperature, $[S_2O_8^{2-}]$, ionic strength, and *p*H. The findings indicate that the *p*H of the medium is the crucial factor that significantly affects the rate of the reaction. The $[Ru(CN)_6]^{4-}$ undergoes a 2:1 stoichiometric interaction with $S_2O_8^{2-}$. The observed reaction exhibits first-order kinetics with regard to $[Ru(CN)_6^{4-}]$, and $[S_2O_8^{2-}]$, within the range of concentrations investigated. The observed invariance in reaction rate upon electrolyte's introduction is suggestive of a zero salt effect. The electron transfer from $[Ru(CN)_6]^{4-}$ to $S_2O_8^{2-}$ proceeds *via* the formation of ion-pair, which leads to the formation of $[Ru(CN)_6]^{3}$, sulfate ion, and sulfate radical ion. The formation of ion-pair is strengthened by the zero salt effect, while, the comparatively low activation energy and free radical test supports the formation of sulfate radical ion during the course of the reaction. The outer-sphere electron transfer pathway, *via* the formation of ion-pair as proposed by us, is further supported by the negative entropy of activation value.

Keywords: Persulfate, Oxidation, Hexacyanoruthenate(II), Kinetics and Mechanism, Ion-pair, Salt effect

The cyano complexes-based magnetic materials have garnered significant attention[1-4], as they represent a class of materials that include magnets with ordering temperatures equivalent to or surpassing room temperatures[5-7]. In the past few years, there has been a simultaneous surge in fascination towards the fabrication of uncomplicated paramagnetic cyano complexes, such as $[Ti(CN)_6]^{3-}$, $[Fe(CN)_6]^{2-}$, and $[Mn(CN)_6]^{2}$, which could be used as building blocks for magnetic materials[8-11]. Another potential paramagnetic building block is $[Ru(CN)_6]^{3-}$. The presence of $[Ru(CN)_6]^{3-}$ has been acknowledged for over a century, yet its chemical properties remain only partially elucidated. For several decades, this intricate compound was solely recognized as a yellow aqueous solution acquired through the oxidation of $[Ru(CN)_6]^{4-}$using H_2O_2, Ce(IV), or PbO_2[12, 13]. Nevertheless, efforts to successfully isolate simple salts from such solutions proved futile, and the unstable nature of the aqueous $[Ru(CN)_6]^{3-}$ has even been the focus of in-depth research[14]. Eler & Fischer showed how analytically pure $[Ru(CN)_6]^{3-}$ would be produced as its Bu_4N^+ salt employing DMF as the reaction solvent[15]. Nevertheless, through the careful selection of appropriate conditions, it is now feasible and advantageous to achieve the direct extraction of $[Ru(CN)_6]^{3-}$ from an aqueous solution with exceptional efficiency and convenience[14]. Previous literature reveals that the formation of aqueous $[Ru(CN)_6]^{3-}$ can be achieved through the reaction of $[Ru(CN)_6]^{4-}$ in the presence of potent oxidizing agents[16,17].

The persulfate ion exhibits remarkable oxidizing capabilities in aqueous solution, making it one of the most potent oxidizing agents[18-23]. The reaction: $2SO_4^{-}\,(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^{-}$ is thought to have a typical oxidation-reduction potential of –2.01 volts[23]. Reactions including this particular ion, nevertheless, typically exhibit sluggish kinetics at ambient temperatures. Numerous investigations have been conducted to study the kinetic aspects of various persulfate oxidations. Despite the favorable standard free energy change, persulfate oxidation of numerous reducing agents at 25°C requires a catalyst[23]. The Ag(I) catalyst has been examined the most, while Cu(II) reactions were also investigated [24-28]. Studies on persulfate oxidation have been discovered to be vital in synthetic[29,30], spectroscopy[31], and thermodynamic aspects[32, 33]. Haim elucidated the mechanistic pathways underlying the reactions involving mononuclear and binuclear ruthenium complexes with the potentially two-electron oxidizing agent, persulfate[34]. The application of persulfate as an oxidizing agent is ascribed to its notable stability throughout a broad spectrum of *p*H values[23]. The oxidation of $[Fe(CN)_5L]^{3-}$, $[Ru(NH_3)_5L]^{2+}$ (L = N-aromatic heterocyclicligands), and $[Fe(CN)_6]^{4-}$ by persulfate are reported to proceed through an outer-sphere electron transfer mechanism[35-37].

Numerous scientific studies have documented the oxidation of substituted cyano complexes of Ru(II) using distinct oxidizing agents[38, 39]. Nevertheless, a limited number of investigations have been conducted to directly oxidize $[Ru(CN)_6]^{4-}$ [16, 17]. Henceforth, in the present investigation, an endeavor is undertaken to explore the kinetics and mechanistic approach to oxidize $[Ru(CN)_6]^{4-}$ using persulfate ion.

Materials and Methods

Reagent Used

Double-deionized water and analytical-grade chemicals were employed consistently throughout the entirety of the kinetic investigation. In order to mitigate the risk of photo-induced degradation of $K_4[Ru(CN)_6].3H_2O$ (Fisher Scientific), an amber-colored vessel was employed to safeguard its stock solution. Himedia supplied potassium persulfate, which was utilized without subsequent purification. NaCl (Molechem) controlled ionic strength, while $HClO_4$ and NaOH (Merck) regulated the *p*H of the reaction mixture.

Instrumentation

The *p*H of the reactive solution was measured utilizing a DD LAB (model LAB.PHM.66800620) automated digital *p*H meter, duly calibrated with a predetermined buffer solution.The experimental setup involved the utilization of an Electronics India model 2375 double-beam UV-Visible spectrophotometer for conducting repeating spectral scans and quantifying absorbance at a wavelength of 460 nm.

Kinetic Measurements

With the exclusion of the $[Ru(CN)_6]^{3-}$, neither of the interacting solutions displayed substantial absorption at the relevant wavelength (460 nm), therefore the absorption readings were left unchanged. Following thermal equilibration at different temperatures for 30 minutes, all of the reactive solutions were quickly mixed in succession: $[Ru(CN)_6]^{4-}$, NaCl, and $S_2O_8^{2-}$. The reacting mixture was placed into the spectrophotometric cell right away after being vigorously shaken. The cell compartment was maintained at a consistent temperature by a self-designed water circulation system. The absorbance increase related to the $[Ru(CN)_6]^{3-}$ was recorded. Utilizing the slope of the line between $\log(A_\infty - A_t)$ and time, the reaction's rate constant (k_{obs}) was calculated. Where A_t and A_∞ are the absorbance at time t and at an infinite time respectively.

Results and Discussion

The kinetic study of $[Ru(CN)_6]^{4-}$ oxidation by $S_2O_8^{2-}$ in an aqueous medium was examined by assessing the increment in absorbance at 460 nm. The observed increase in absorbance can be attributed to the $[Ru(CN)_6]^{4-}$ oxidation to $[Ru(CN)_6]^{3-}$. Due to the significant instability of the $[Ru(CN)_6]^{3-}$ in an aqueous environment, the kinetic investigation was performed under acidic conditions[17]. The pseudo-first-order rate constants (by taking minimum 10-fold excess) of $[S_2O_8^{2-}]$ over $[Ru(CN)_6^{4-}]$) were computed as a function of $[S_2O_8^{2-}]$, $[Ru(CN)_6^{4-}]$, *p*H, and ionic strength at three distinct temperatures.

The measured quantities of $S_2O_8^{2-}$ were permitted to undergo a reaction with a surplus of ten times the amount of $[Ru(CN)_6]^{4-}$ under acidic conditions (*p*H = 4.0) at a temperature of 318 K within a sealed container until the reaction reached its conclusion. Through spectrophotometric analysis at a wavelength of 460 nm, the concentration of produced $[Ru(CN)_6]^{3-}$ was determined. The experimental findings indicate that $S_2O_8^{2-}$ and $[Ru(CN)_6]^{4-}$ undergo a chemical reaction with a stoichiometric ratio of 1:2, as represented by the following equation.

$$2[Ru(CN)_6]^{4-} + S_2O_8^{2-} \longrightarrow 2[Ru(CN)_6]^{3-} + 2SO_4^{2-} \qquad \dots (1)$$

To evaluate the participation of free radicals in the oxidation mechanism, a polymerization assay has been conducted. With defined amounts of acrylonitrile scavenger, reaction mixtures are kept inert for six hours. The formation of white precipitates upon dilution with methanol demonstrates the involvement of free radicals in this process. These studies failed in the detection of $S_2O_8^{2-}$ under comparable circumstances, suggesting the participation of $S_2O_8^{2-}$ in the generation of free radicals.

Impact of variation of $[S_2O_8^{2-}]$ on oxidation rate

The remaining parameters were held unchanged while the concentration of $S_2O_8^{2-}$ was varied from 2.0×10^{-2} M to 5.0×10^{-2} M to evaluate the implications of $[S_2O_8^{2-}]$ on the oxidation rate. The plot of $[S_2O_8^{2-}]$ against k_{obs} (Fig 1) illustrates the linear enhancement in the oxidation rate with zero intercepts. The experimental findings indicate that the $[S_2O_8^{2-}]$ exhibits first-order kinetics in its examined concentration range.

At fixed *p*H, the mechanism of $[Ru(CN)_6]^{4-}$ oxidation by $S_2O_8^{2-}$ *via* ion-pair formation can be represented by equation 2-4 (Scheme 1)[34], where Q_{IP} denotes the equilibrium constant for the formation of ion-pair.

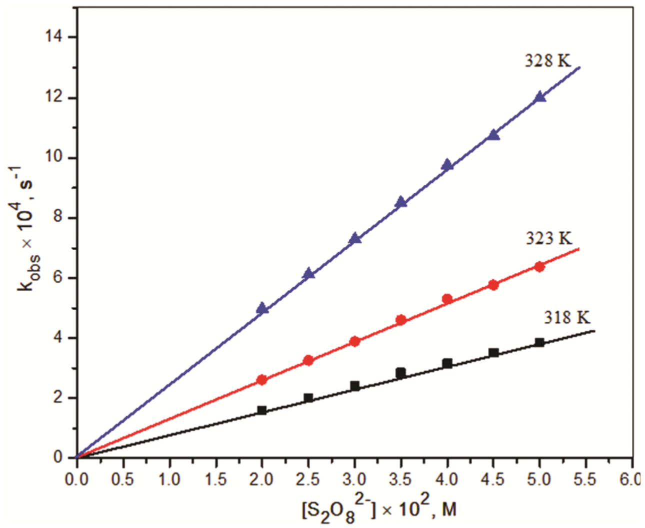
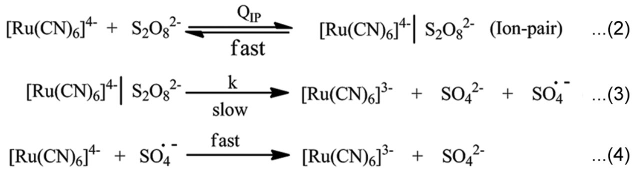


Fig 1 — Effect of variation of $[S_2O_8^{2-}]$ on rate constant (k_{obs})at I = 0.25 M (NaCl), *p*H = 4.0 ± 0.02, Temp = 318 K, 323 K, 328 K, and $[Ru(CN)_6^{4-}] = 2.5 \times 10^{-3}$ M



Scheme 1 — Mechanism of $[Ru(CN)_6]^{4-}$ oxidation by $S_2O_8^{2-}$ *via* ion-pair formation

$$\text{Rate of Reaction} = -\frac{d[Ru(CN)_6{}^{4-}]}{dt} = k\,[\text{Ion}-\text{pair}]$$
$$= k\,Q_{IP}[Ru(CN)_6{}^{4-}][S_2O_8^{2-}] \quad \ldots(5)$$

Eq. 6 symbolizes the cumulative [Ru(II)] throughout the course of the chemical reaction.

$$[Ru(CN)_6{}^{4-}]_T = [Ru(CN)_6{}^{4-}]_F + [\text{Ion}-\text{pair}] \quad \ldots(6)$$

Using equations 2, 3, and 6 we get:

$$[Ru(CN)_6{}^{4-}]_F = \frac{[Ru(CN)_6{}^{4-}]_T}{1 + Q_{IP}[S_2O_8^{2-}]} \quad \ldots(7)$$

Eq. 7 modifies the resultant rate law upon the substitution of $[Ru(CN)_6{}^{4-}]_F$ value,

$$\text{Rate} = \frac{k\,Q_{IP}[S_2O_8^{2-}]\,[Ru(CN)_6{}^{4-}]_T}{1 + Q_{IP}[S_2O_8^{2-}]} \quad \ldots(8)$$

$$\frac{\text{Rate}}{[Ru(CN)_6{}^{4-}]_T} = k_{obs} = \frac{k\,Q_{IP}[S_2O_8^{2-}]}{1 + Q_{IP}[S_2O_8^{2-}]} \quad \ldots(9)$$

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{1}{k\,Q_{IP}[S_2O_8^{2-}]} \quad \ldots(10)$$

Fig. 2 shows that the $1/k_{obs}$*vs* $1/[S_2O_8^{2-}]$ plots are linear, as expected by Eq. 10. The gradient and intercepts of the plot were used to compute the values of Q_{IP} and k, which are represented in Table 1. The results exhibit a rise in the Q_{IP} and k values as the temperature is elevated.

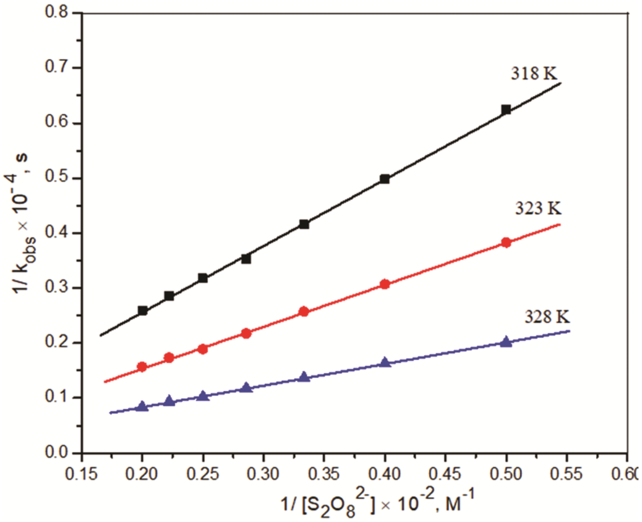


Fig 2 — $1/k_{obs}$ against $1/[S_2O_8^{2-}]$ plotat I = 0.25 M (NaCl), *p*H = 4.0 ± 0.02, Temp = 318 K, 323 K, 328 K, and $[Ru(CN)_6^{4-}] = 2.5 \times 10^{-3}$ M

Impact of variation of *p*H on oxidation rate

Previous investigations on the oxidation of organic moieties, both catalyzed and unanalyzed, involving $S_2O_8^{2-}$, have elucidated the significance of *p*H in governing the rate of oxidation[22-28]. The investigation focused on exploring the reaction rate within *p*H spanning from 1.0 to 6.0 M by calculating the oxidation rate constant under different *p*H.

Fig 3 illustrates a correlation between *p*H and k_{obs}. The reaction rate is slow at low *p*H, increases precisely up to *p*H = 4.0, and then remains constant as *p*H is increased to 6.0.The presence of a less responsive protonated state of $[Ru(CN)_6]^{4-}$ is hypothesized to be responsible for the decreased reaction observed in lower *p*H. $[Ru(CN)_6]^{4-}$ predominantly manifests in its deprotonated state at elevated *p*H[40]. The occurrence of deprotonated state of the reducing agent is responsible for the witnessed enhancement in reaction rate with an increase in *p*H. Above *p*H=4.0, the predominant existence of deprotonated state of $[Ru(CN)_6]^{4-}$ may be liable for the invariance in oxidation rate with *p*H.

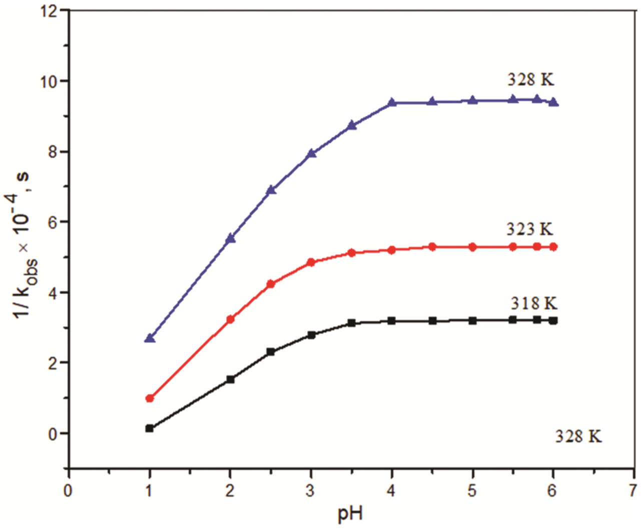


Fig 3 — Effect of variation of *p*H on rate constant (k_{obs}) at I = 0.25 M (NaCl), $[S_2O_8^{2-}]$ = 4.0 × 10^{-2} M, Temp = 318 K, 323 K, 328 K, and $[Ru(CN)_6^{4-}]$ = 2.5 × 10^{-3} M

Table 1 — Ion-Pair Formation Constants and rate Constants for the reaction of $[Ru(CN)_6]^{4-}$ with $S_2O_8^{2-}$

Temp (K)	Q_{IP}, M^{-1}	k × 10^2, s^{-1}
318	0.471	1.74
323	0.783	1.88
328	1.267	2.01

Table 2 — Effect of variation of $[Ru(CN)_6^{4-}]$ on rate constant (k_{obs}) Experimental Condition: I = 0.25 M(NaCl), *p*H =4.0 ± 0.02, Temp = 318 K, 323 K, 328 K, and $[S_2O_8^{2-}]$ = 4×10^{-2} M

$[Ru(CN)_6^{4-}]$ × 10^3, M	k_{obs} × 10^4, s^{-1}		
	318 K	323 K	328 K
0.5	3.16	5.12	9.38
1.0	3.10	5.19	9.39
2.0	3.15	5.22	9.40
2.5	3.18	5.20	9.43
3.0	3.21	5.19	9.47
4.0	3.12	5.16	9.42
5.0	3.15	5.18	9.46

Impact of variation of $[Ru(CN)_6^{4-}]$ on oxidation rate

Under the ideal circumstances of *p*H and $[S_2O_8^{2-}]$, while keeping the remaining reaction variables unchanged, the rate constant was determined as an indicator of $[Ru(CN)_6]^{4-}$ in the concentration ranging from 0.5 × 10^{-3} M to 5.0 × 10^{-3} M. Based on the determined k_{obs} value for every $[Ru(CN)_6]^{4-}$ (Table 2), it can be observed that the $[Ru(CN)_6^{4-}]$ range being studied demonstrates first-order kinetics.

Impact of variation of ionic strength on oxidation rate

In order to investigate the effect of ionic strength on the rate of reaction, the concentrations of a neutral electrolyte (NaCl) were varied within the range of 0.1 to 0.5 M. The remaining process parameters were maintained constant at Temp. = 318/323/328 ± 0.1 K, $[Ru(CN)_6^{4-}]$ = 2.5 × 10^{-3} M, *p*H = 4.0 ± 0.02, and $[S_2O_8^{2-}]$ = 4 × 10^{-2} M. The observed trend of k_{obs} with respect to ionic strength (I) displayed a zero salt effect, as depicted in Table 3. The invariance in oxidation rate with ionic strength also supports the participation of ion-pair rather than ionic species in the rate-determining step.

Effect of temperature

As anticipated, the oxidation rate is augmented under the optimum reaction conditions with the increases in temperature from 318 to 328 K. The values of activation parameters were computed using the Eyring equation (11).

Table 3 — Effect of variation of Ionic strength on rate constant (k_{obs}) Experimental Condition: $[Ru(CN)_6^{4-}]$ = 2.5×10^{-3} M, *p*H =4.0 ± 0.02, Temp = 318 K, 323 K, 328 K, and $[S_2O_8^{2-}]$ = 4×10^{-2} M

Ionic strength (I) M	k_{obs} × 10^4, s^{-1}		
	318, K	323, K	328, K
0.10	3.21	5.18	9.39
0.20	3.16	5.24	9.40
0.25	3.18	5.20	9.43
0.30	3.20	5.22	9.46
0.40	3.12	5.19	9.41
0.50	3.16	5.50	9.38

$$\frac{\mathrm{k_f}}{\mathrm{T}} = \frac{\mathrm{k_B}}{\mathrm{h}} \mathrm{e}^{\Delta S/R}.\,\mathrm{e}^{-\Delta H/RT} \qquad \ldots(11)$$

The plot of ln(k_f/T) *versus* (1/ T) yield a straight line (Fig 4). The values of entropy of activation ($\Delta S^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) were computed from the intercept and slope of the plot respectively. The calculated activation energy (E_a), enthalpy of activation ($\Delta H^{\neq}$), and entropy of activation ($\Delta S^{\neq}$) values are 82.49 kJ mol^{-1}, 79.81 kJ mol^{-1} and –28.89 $JK^{-1}mol^{-1}$ respectively.

The oxidation of $[Ru(CN)_6]^{4-}$ by $S_2O_8^{2-}$ was elucidated through a comprehensive analysis of the kinetic investigation and relevant literature[17,34,41]. The proposed mechanism, as depicted in Equations (12)-(15), represents the most probable pathway for this chemical transformation (Scheme 2).

Based on the observations, the oxidation of $[Ru(CN)_6]^{4-}$ by $S_2O_8^{2-}$ proceeds through a series of intricate steps, progressing through the creation of soluble ion-pair between $[Ru(CN)_6]^{4-}$ and $S_2O_8^{2-}$, as $[Ru(CN)_6]^{4-}$ is inert to substitution under uncatalyzed conditions and there is not another site accessible for $S_2O_8^{2-}$ coordination. The reaction rate demonstrates a first-order relationship with both $[Ru(CN)_6]^{4-}$ and $S_2O_8^{2-}$, indicating the probable emergence of the ion-pair during the equilibrium stage. The formation of an ion-pair between entities with comparable charges is additionally supported by the zero salt effect. In the subsequent step (rate determining step), the ion-pair by one electron transfer from $[Ru(CN)_6]^{4-}$ to $[S_2O_8]^{2-}$ yield $[Ru(CN)_6]^{3-}$, sulfate ion, and sulfate radical ion. The resultant radical ion promptly reacts with $[Ru(CN)_6]^{4-}$ yielding $[Ru(CN)_6]^{3-}$ and sulfate ion.

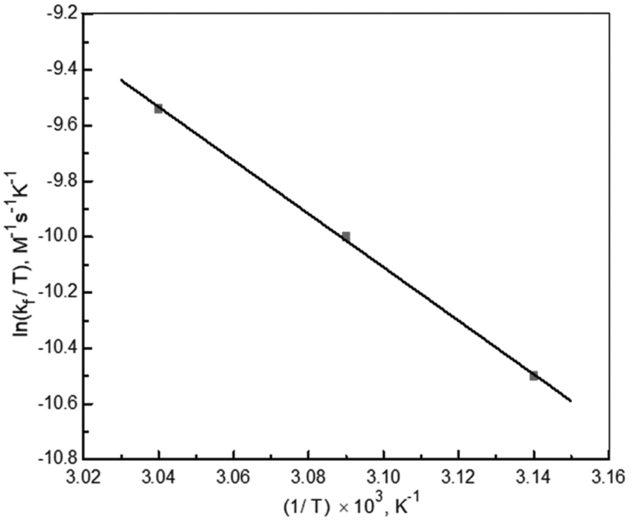


Fig 4 — Effect of variation of temperature on rate constant (k_{obs}) at I = 0.25 M (NaCl), $[S_2O_8^{2-}] = 4.0 \times 10^{-2}$ M, *p*H = 4.0 ± 0.02, and $[Ru(CN)_6^{4-}] = 2.5 \times 10^{-3}$ M

$$[H\,Ru(CN)_6]^{3-} \xrightleftharpoons{K_1} [Ru(CN)_6]^{4-} + H^+ \qquad \ldots(12)$$

$$[Ru(CN)_6]^{4-} + S_2O_8^{2-} \xrightleftharpoons[\text{fast}]{Q_{IP}} [Ru(CN)_6]^{4-} | S_2O_8^{2-} \text{ (Ion-pair)} \qquad \ldots(13)$$

$$[Ru(CN)_6]^{4-} | S_2O_8^{2-} \xrightarrow[\text{slow}]{k} [Ru(CN)_6]^{3-} + SO_4^{2-} + SO_4^{\cdot -} \qquad \ldots(14)$$

$$[Ru(CN)_6]^{4-} + SO_4^{\cdot -} \xrightarrow{\text{fast}} [Ru(CN)_6]^{3-} + SO_4^{2-} \qquad \ldots(15)$$

Scheme 2 — Probable pathway for $[Ru(CN)_6]^{4-}$ oxidation by $S_2O_8^{2-}$

$$\text{Rate of Reaction} = -\frac{d[Ru(CN)_6{}^{4-}]}{dt} = k\,[\text{Ion} - \text{pair}]$$

$$= \frac{k\,K_1 Q_{IP}[H\,Ru(CN)_6{}^{3-}][S_2O_8^{2-}]}{[H^+]} \qquad \ldots(16)$$

Eq. 17 symbolizes the cumulative [Ru(II)] throughout the course of the chemical reaction.

$$[Ru(CN)_6{}^{4-}]_T = [Ru(CN)_6{}^{4-}]_F + [H\,Ru(CN)_6{}^{3-}] + [\text{Ion} - \text{pair}] \qquad \ldots(17)$$

Using equations 12, 13, and 17 we get:

$$[H\,Ru(CN)_6{}^{3-}] = \frac{[Ru(CN)_6{}^{4-}]_T}{1 + \frac{K_1}{[H^+]} + \frac{K_1 Q_{IP}[S_2O_8^{2-}]}{[H^+]}} \qquad \ldots(18)$$

Eq. 18 modifies the resultant rate law upon the substitution of $[Ru(CN)_6{}^{4-}]_F$ value,

$$\text{Rate} = \frac{k\,K_1 Q_{IP}[Ru(CN)_6{}^{4-}]_T[S_2O_8^{2-}]}{[H^+]\,(1 + \frac{K_1}{[H^+]} + \frac{K_1 Q_{IP}[S_2O_8^{2-}]}{[H^+]})} \qquad \ldots(19)$$

$$\frac{\text{Rate}}{[Ru(CN)_6{}^{4-}]_T} = k_{obs}$$

$$= \frac{kK_1 Q_{IP}[S_2O_8^{2-}]}{[H^+]\,(1 + \frac{K_1}{[H^+]} + \frac{K_1 Q_{IP}[S_2O_8^{2-}]}{[H^+]})} \qquad \ldots(20)$$

The equilibrium constant (K_1) for the deprotonation of $[H\,Ru(CN)_6]^{3-}$ was computed utilizing the values of Q_{IP} and k, calculated by the $1/k_{obs}$ *vs* $1/[S_2O_8^{2-}]$ plots at fixed *p*H. The calculated K_1 value (6.25×10^{-3} at 318 K) agrees well with the previously reported value (2.97×10^{-3} M) at 298 K[17]. The proposed rate law also supports the first-order dependence on $[Ru(CN)_6]^{4-}$ and $S_2O_8^{2-}$ (as 1 >> Q_{IP} $[S_2O_8^{2-}]$) and a decreasing trend in reaction rate with increasing $[H^+]$.

Previously, it was hypothesized that persulfate ion oxidation typically proceeds *via* an outer-sphere

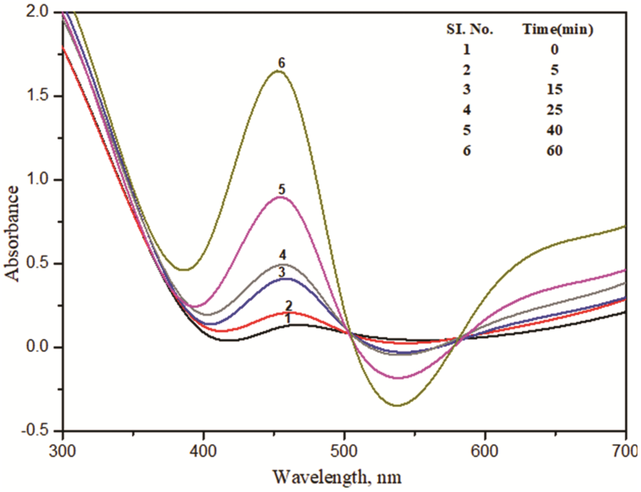


Fig 5 — Spectral scan of the reaction mixture at different time intervals at I = 0.25 M (NaCl), [$S_2O_8^{2-}$] = 4.0 × 10^{-2} M, pH = 4.0 ± 0.02, Temp = 318 K, and [$Ru(CN)_6^{4-}$] = 2.5 × 10^{-3} M

electron transfer mechanism [35-37]. Kinetic evidence establishes the existence of the ion pair at discernible concentrations, within the framework of the Rehm-Weller mechanism[42,43]. However, this outcome does not provide conclusive evidence regarding the reactivity of the ion pair. Nevertheless, for the sake of simplicity, it shall be postulated that the ion pair is indeed an intermediate species along the reaction pathway leading to the formation of products. Instead of being straightforward one-electron transfers, persulfate reactions with transition-metal complexes include the reductive breaking of the peroxide bond and the production of the sulfate radical ion[18,19]. The production of the sulfate ion as one of the final products was confirmed by precipitation as $BaSO_4$[44]. Henceforth, it is anticipated that the product of $S_2O_8^{2-}$ *via* one-electron reduction undergoes dissociation along the O—O coordinate, resulting in the formation of an ion pair consisting of sulfate ion and sulfate radical ion.

The energy of activation in the present case is much lower than the energy of activation 141 KJ Mol^{-1} for homolysis of peroxide bond[45]. The comparatively lower activation energy for the reaction has been taken as being indicative of the transfer of an electron from $[Ru(CN)_6]^{4-}$ to produce nascent sulfate radical ion[17]. The moderate value of $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ were favorable for electron transfer processes. The observed enthalpy of activation and relatively low negative value of entropy of the slow step indicate that the oxidation presumably occurs *via* an outer-sphere mechanism.

The $[Ru(CN)_6]^{4-}$ oxidation by the $S_2O_8^{2-}$ ion, in an acidic medium, as observed in the repetitive scan of the reaction mixture (Fig 5), demonstrates a consistent increase in peak intensity at 460 nm. A progressive increase in the intensity of peaks, associated with $[Ru(CN)_6]^{3-}$ over time, can be attributed to the oxidation of $[Ru(CN)_6]^{4-}$ by $S_2O_8^{2-}$ during the reaction, as $[Ru(CN)_6]^{4-}$ undergoes conversion to $[Ru(CN)_6]^{3-}$.

Conclusion

The current research adds to our understanding of the oxidation of cyano metal complexes by $S_2O_8^{2-}$ in an aqueous milieu. Within the investigated range of [$Ru(CN)_6^{4-}$], and [$S_2O_8^{2-}$] the observed reaction exhibits first-order kinetics. The reaction rate is slow at low pH, increases precisely up to pH = 4.0, and then remains constant with a further increase in pH. The production of $[Ru(CN)_6]^{3-}$ proceeds *via* the formation of ion-pair between $[Ru(CN)_6]^{4-}$ and $S_2O_8^{2-}$. The invariance in oxidation rate with ionic strength also supports the participation of ion-pair rather than ionic species in the rate-determining step. The comparatively low activation energy and free radical test supports the formation of sulfate radical ions during the course of the reaction. The outer-sphere electron transfer pathway, *via* the formation of ion-pair as proposed by us, is further supported by the negative entropy of activation value.

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