

The Kinetics and Mechanism of Oxidation of Hexacyanoferrate(II) by Periodate Ion in Highly Alkaline Aqueous Medium

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The oxidation of hexacyanoferrate(II) by periodate ion has been studied spectrophotometrically by registering an increase in absorbance at 420 nm (λ_{max} of yellow colored $[\text{Fe}(\text{CN})_6]^{3-}$ complex under pseudo first-order conditions by taking excess of $[\text{IO}_4^-]$ over $[\text{Fe}(\text{CN})_6]^{4-}$. The reaction conditions were: pH = 9.5 ± 0.02 , I = 0.1 M (NaCl) and Temp. = 25 ± 0.1 °C. The reaction exhibited first-order dependence on each $[\text{IO}_4^-]$ and $[\text{Fe}(\text{CN})_6]^{4-}$. The effects of variations of pH, ionic strength and temperature were also studied. The experimental observations revealed that the periodate ion exists in its protonated forms viz. $[\text{H}_2\text{IO}_6]^{3-}$ and $[\text{H}_3\text{IO}_6]^{2-}$ while $[\text{Fe}(\text{CN})_6]^{4-}$ is present in its deprotonated form throughout the pH region selected for the present study. It has also been observed that deprotonated form of $[\text{Fe}(\text{CN})_6]^{4-}$ and protonated forms of periodate ion are the most reactive species towards oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$. The repetitive spectral scan is provided as an evidence to prove the conversion of $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ in the present reaction. The activation parameters have also been computed using the Eyring's plot and found to be, $\Delta H^\ddagger = 51.53 \pm 0.06$ kJ mol⁻¹, $\Delta S^\ddagger = -97.12 \pm 1.57$ J K⁻¹ mol⁻¹ and provided in support of a most plausible mechanistic scheme for the reaction under study.

Keywords: Kinetics and mechanism, Hexacyanoferrate(II) oxidation, Periodate oxidation, Hexacyanoferrate(II), Periodate

INTRODUCTION

The periodate ion has been widely used as an oxidizing agent in aqueous medium [1-5]. The periodate oxidation of several inorganic and organic substrate takes place through either inner sphere or outer sphere mechanism. The periodate oxidation of $[\text{M}^{\text{IV}}(\text{CN})_8]^{4-}$ (M = W or Mo) [6-7] and some polyaminocarboxylato complexes of Co(II) [8-13], V(IV) [14], Fe(II) [15] and Cr(III) [16-18] proceeds through an inner sphere electron transfer pathway.

The oxidation of hexacyanoferrate(II) by peroxydisulfate [19] and peroxyxynitrite [20] has been recently investigated and found to follow an outer sphere electron transfer. The kinetic

and mechanistic study of oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by periodate ion was investigated earlier in weakly alkaline medium in the pH range of 6.8-8.5 by taking excess of $[\text{Fe}(\text{CN})_6]^{4-}$ over $[\text{IO}_4^-]$ [18]. The reacting species of periodate was reported as $[\text{IO}_4^-]$, $[\text{H}_4\text{IO}_6]^{2-}$ and $[\text{H}_3\text{IO}_6]^{2-}$ [23,24]. However, the effect of nature of the periodate ion when it is present in excess over $[\text{Fe}(\text{CN})_6]^{4-}$ in highly alkaline medium has not received much attention and needs detailed investigation.

Therefore, in the present paper, we have considered it worthwhile to investigate the kinetics of periodate oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by taking its large excess over $[\text{Fe}(\text{CN})_6]^{4-}$ in much wider alkaline medium, in order to understand the reactivities of different protonated and deprotonated forms of periodate ion.

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EXPERIMENTAL

Materials

Analytical grade potassium hexacyanoferrate(II), purchased from Glaxo was used to prepare the stock solution without further purification and stored in dark amber-colored bottle to avoid photodecomposition. The calculated amount of sodium metaperiodate (S.d Fine-Chemicals, India) was used to prepare its solution and always wrapped with aluminium foil in order to avoid photodecomposition. Ionic strength of reaction medium was maintained by sodium chloride (Merck). The pH of each solution was adjusted by dilute solutions of sodium hydroxide and hydrochloric acid.

Apparatus and Kinetic Measurements

All pH measurements were made on a digital pH meter model CL-46 (India) after its standardization using potassium hydrogen phthalate buffers of pH 4.0 and 7.0. The temperature of reactants were maintained at a desired value by putting the solutions for at least half an hour in a Remi Ultracryostat, model-702C (India). The extent of reaction, UV-Vis spectrum of reactants and products and the repetitive spectral scans of the reaction mixture were recorded on a UV-240 double beam spectrophotometer (Shimadzu, Japan) equipped with a thermostated cell compartment.

The reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and periodate ion was studied under pseudo-first-order conditions by taking excess of periodate over $[\text{Fe}(\text{CN})_6]^{4-}$. The reaction was initiated by injecting 5.0 ml of $[\text{IO}_4^-]$ through a syringe to a solution of 5.0 ml of $[\text{Fe}(\text{CN})_6]^{4-}$ taken in a 25.0 ml borosil beaker. The reaction mixture was properly shaken and transferred quickly to a 10 mm matched quartz cuvettes in the temperature controlled cell compartment of the spectrophotometer. The progress of reaction was subsequently followed by monitoring the increase in absorbance at $\lambda = 420 \text{ nm}$, due to the formation of yellow colored hexacyanoferrate(III) complex. The pseudo first order rate constants (k_{obs}) where $[\text{IO}_4^-]$ is in excess on $[\text{Fe}(\text{CN})_6]^{4-}$ were obtained from the slopes of $\log(A_\infty - A_t)$ vs. time plots.

RESULTS AND DISCUSSION

Effect of $[\text{IO}_4^-]$ on the Rate of Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ion

The oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ was investigated as a function of periodate ion concentration under pseudo-first-order conditions by taking its large excess at $\text{pH} = 9.5 \pm 0.02$, $I = 0.1 \text{ M}$ (NaCl), $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$ and $\text{temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$. The periodate concentration was varied in the range of 2.25×10^{-3} - $1.4 \times 10^{-2} \text{ M}$. The linear regression plot of pseudo-first-order rate constant (k_{obs}) vs. $[\text{IO}_4^-]$ yields a straight line (Fig. 1, $r = 0.9986$, $\text{sd} \geq 0.2247$) passing through origin.

Effect of pH on the Rate of Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ion

The rate of oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by $[\text{IO}_4^-]$ was investigated as a function of pH in a highly alkaline medium in the pH range of 8.25-10.5, while keeping all other variables constant. The pseudo first order rate constants (k_{obs}) were evaluated at each pH. The values of second order rate constants $k = k_{\text{obs}}/[\text{IO}_4^-]$ were also calculated.

The plot of second order rate constant (k) vs. $[\text{H}^+]$ is shown in Fig. 2 ($r = 0.9890$, $\text{sd} \geq 0.056$). It is evident from this plot that the rate constant increases linearly with increasing $[\text{H}^+]$, over the entire pH range studied.

Effect of Ionic Strength on the Rate of Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ion

The influence of ionic strength on the rate constant was also studied employing NaCl for maintaining ionic strength in the range of 0.025-0.40 M. The values of rate constants at different ionic strength under the reaction conditions $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$, $[\text{IO}_4^-] = 3.0 \times 10^{-3} \text{ M}$, $\text{pH} = 9.5 \pm 0.02$ and $\text{temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$ are compiled in Table 1. The plot of second order rate constant (k) vs. \sqrt{I} clearly indicates that the rate constant (k) increases linearly with increase in ionic strength. This also suggests that the two ionic species are involved in rate determining step.

Effect of $[\text{Fe}(\text{CN})_6]^{4-}$ on Rate of Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ion

The rate of oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by periodate ion was

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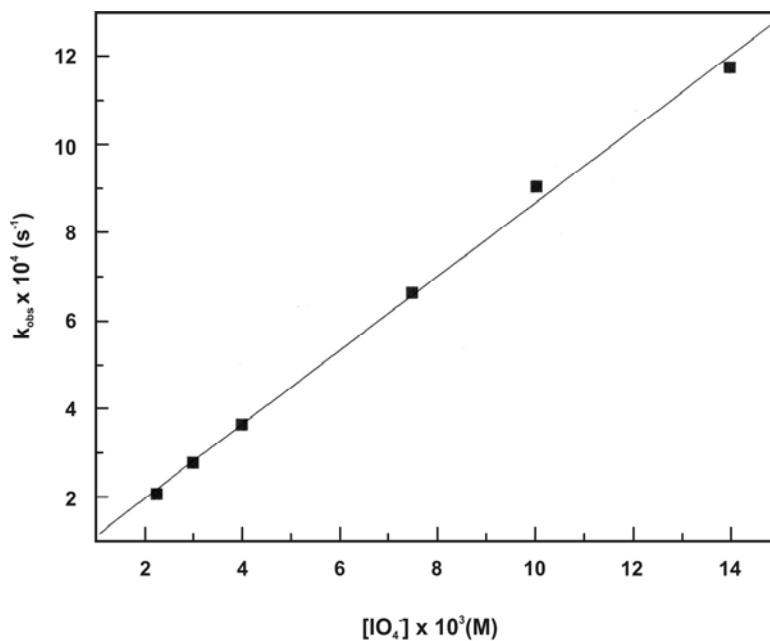


Fig. 1. The periodate dependence of observed rate constant for oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by periodate ion. Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$, $I = 0.1 \text{ M}$ (NaCl), $\text{pH} = 9.5 \pm 0.02$ and $\text{Temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$.

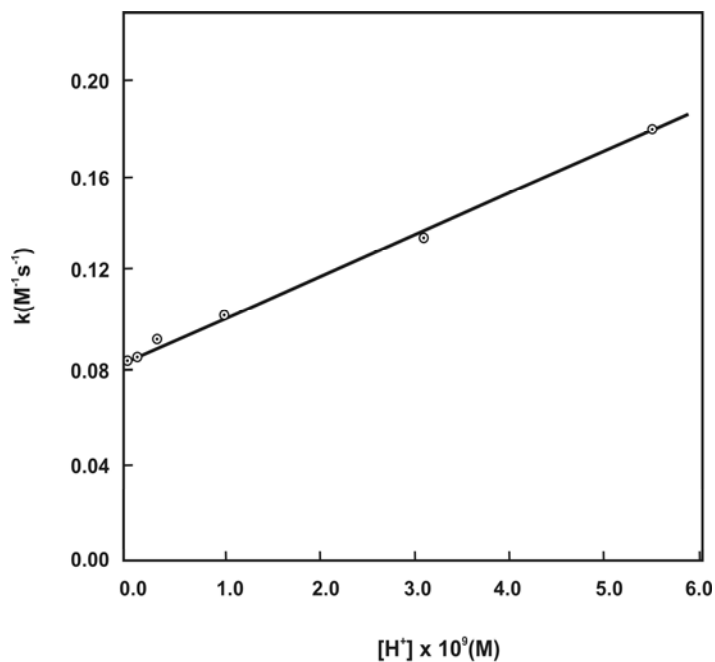


Fig. 2. Effect of $[\text{H}^+]$ on oxidation of Hexacyanoferrate(II) by periodate ion. Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$, $[\text{IO}_4^-] = 3.0 \times 10^{-3} \text{ M}$, $I = 0.1 \text{ M}$ (NaCl) and $\text{Temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$.

Table 1. Effect of Ionic Strength on $[\text{IO}_4^-]$ Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$

I (M)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$	$k \text{ (M}^{-1} \text{ s}^{-1}\text{)}$
0.025	2.63	0.088
0.05	2.69	0.090
0.10	2.75	0.092
0.20	2.89	0.096
0.30	2.96	0.099
0.40	3.02	0.101

$[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$, $[\text{IO}_4^-] = 3.0 \times 10^{-3} \text{ M}$, $\text{pH} = 9.5 \pm 0.02$ and $\text{Temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$.

Table 2. Effect of Variation of Hexacyanoferrate(II) on Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ions

$[\text{Fe}(\text{CN})_6]^{4-} \times 10^4 \text{ (M)}$	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
1.25	3.09
1.90	3.05
2.20	3.04
2.50	3.08
3.00	3.07

Average = 3.06 ± 0.02

$[\text{IO}_4^-] = 3.0 \times 10^{-3} \text{ M}$, $\text{pH} = 9.5 \pm 0.02$, $I = 0.1 \text{ M}$ (NaCl) and $\text{Temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$.

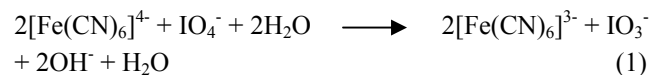
studied as a function of $[\text{Fe}(\text{CN})_6]^{4-}$ by varying its concentration from $1.5 \times 10^{-4} \text{ M}$ to $3.5 \times 10^{-4} \text{ M}$ keeping all other variables fixed at an optimum value. The dependence of rate constant on $[\text{Fe}(\text{CN})_6]^{4-}$ is compiled in Table 2, which clearly shows that the rate constant vary linearly with $[\text{Fe}(\text{CN})_6]^{4-}$ in the beginning and remains constant.

Effect of Temperature on Rate of Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by Periodate Ion

The rate of oxidation reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{IO}_4^-]$ was studied as a function of temperature in the range of 25-45 $^\circ\text{C}$, keeping all other reaction variables fixed at optimum values. The plot of $\ln(k/T)$ vs. $1/T$ yields a straight line, as shown in Fig. 3 ($r = 0.9979$, $\text{sd} \geq 0.0380$). The values of activation parameters *viz.* enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) evaluated from the slope and intercept of the above plot, were found to be $51.53 \pm 0.06 \text{ kJ mol}^{-1}$ and $-97 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

The hexacyanoferrate(II) is substitutionally inert and provides no additional site available for the coordination of $[\text{IO}_4^-]$ on it and, thus, the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ is expected to proceed like all other $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ systems investigated previously [25-27].

Our experimental observations on the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by periodate ion where $[\text{IO}_4^-] > [\text{Fe}(\text{CN})_6]^{4-}$ enabled us to consider various species of periodate and $[\text{Fe}(\text{CN})_6]^{4-}$ ions before proposing a plausible mechanistic scheme. The stoichiometry of the reaction is given by Eq. (1).



The stoichiometry given in Eq. (1) was verified spectrophotometrically at 420 nm (λ_{max} of $[\text{Fe}(\text{CN})_6]^{3-}$) by evaluating the concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ produced at infinite time.

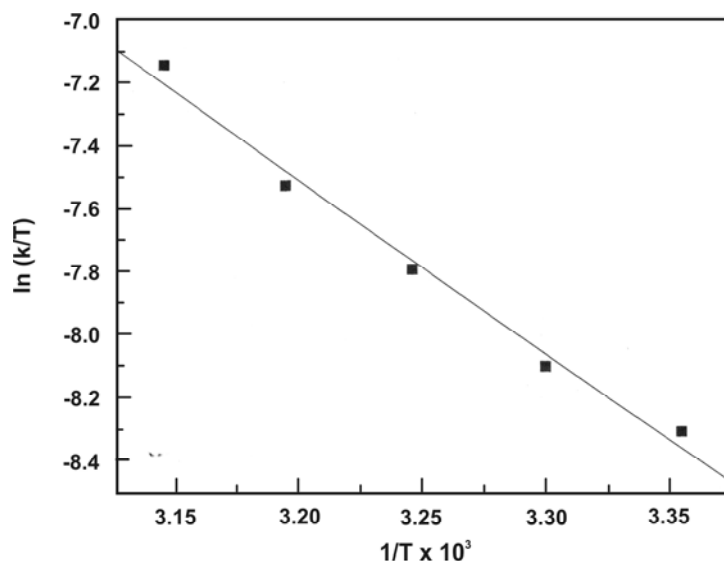
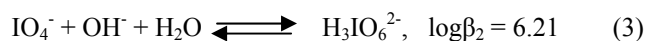
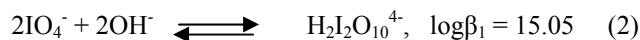


Fig. 3. Plot of $\ln(k/T)$ vs. $1/T$ of the $[\text{Fe}(\text{CN})_6]^{4-}$ - $[\text{IO}_4^-]$ oxidation reaction. Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4}$ M, $[\text{IO}_4^-] = 3.0 \times 10^{-3}$ M, $I = 0.1$ M (NaCl) and $\text{pH} = 9.5 \pm 0.02$.

The $[\text{Fe}(\text{CN})_6]^{4-}$ is known to exist in various protonated and deprotonated forms. The species distribution of $[\text{Fe}(\text{CN})_6]^{4-}$ as a function of pH, obtained using a computer programme developed by Perin and Sayee [28], is shown in Fig. 4. This clearly indicates that the deprotonated form of hexacyanoferrate(II), *i.e.* $[\text{Fe}(\text{CN})_6]^{4-}$, is the predominant reacting species in the whole pH region selected for the present study. On the other hand, the behavior of periodate ion in aqueous alkaline medium is best described by the following equilibria (Eqs. 2-4) [29]:



The distribution of all periodate ion species in aqueous alkaline solution can be calculated from equilibria (2-4). However, in the pH range used in the present work, the amount of dimer $[\text{H}_2\text{I}_2\text{O}_{10}^{4-}]$ and $[\text{IO}_4^-]$ species of periodate is negligible. The predominant reacting species of periodate are $[\text{H}_2\text{IO}_6^{3-}]$ and $[\text{H}_3\text{IO}_6^{2-}]$. Our results are also consistent with the

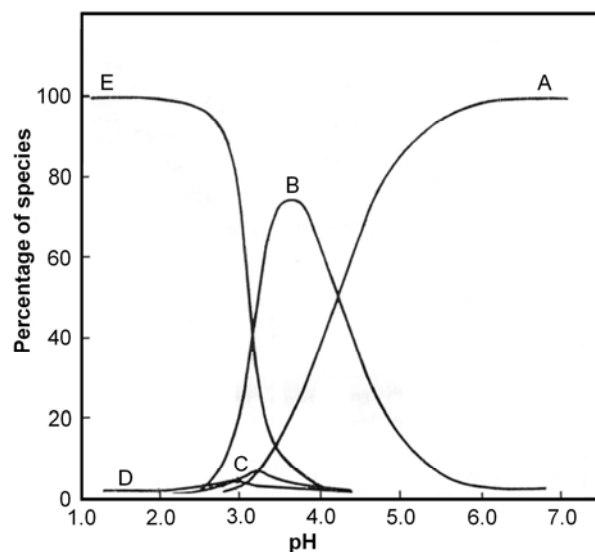
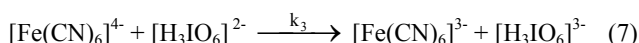
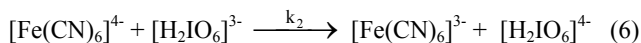


Fig. 4. Species distribution of $[\text{Fe}(\text{CN})_6]^{4-}$ as a function of pH. Conditions: Temp. = 25 ± 0.1 °C. $[\text{Fe}(\text{CN})_6]^{4-} = 5 \times 10^{-3}$ M, A = $[\text{Fe}(\text{CN})_6]^{4-}$, B = $\text{H}[\text{Fe}(\text{CN})_6]^{3-}$, C = $\text{H}_2[\text{Fe}(\text{CN})_6]^{2-}$, D = $\text{H}_3[\text{Fe}(\text{CN})_6]^{1-}$ and E = $\text{H}_4[\text{Fe}(\text{CN})_6]$.

recent results reported in the literature [30-32].

Therefore, the following possible rate determining reactions (Eqs. 5-7) can be proposed for the reaction at hand:



The total periodate concentration $[\text{IO}_4^-]_{\text{T}}$ may expressed by equation (8).

$$[\text{IO}_4^-]_{\text{T}} = [\text{IO}_4^-] + [\text{H}_2\text{IO}_6]^{3-} + [\text{H}_3\text{IO}_6]^{2-} \quad (8)$$

Equation (8) can be expressed in terms of $[\text{IO}_4^-]$ using the equilibria described in Eqs. (2-4).

$$[\text{IO}_4^-]_{\text{T}} = [\text{IO}_4^-] + \beta_2 [\text{OH}^-] [\text{IO}_4^-] + \beta_3 [\text{OH}^-]^2 [\text{IO}_4^-]$$

or

$$[\text{IO}_4^-]_{\text{T}} = [\text{IO}_4^-] + \beta_2 \frac{K\omega}{[\text{H}^+]} [\text{IO}_4^-] + \beta_3 \frac{K\omega^2}{[\text{H}^+]^2} [\text{IO}_4^-]$$

$$[\text{IO}_4^-]_{\text{T}} = \left\{ \left(\beta_2 + \frac{\beta_3 K\omega}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} + 1 \right\} [\text{IO}_4^-] \quad (9)$$

The rate of present reaction is described by Eq. (10).

$$\text{Rate} = k [\text{Fe}(\text{CN})_6]_{\text{T}}^{4-} [\text{IO}_4^-]_{\text{T}} \quad (10)$$

Since $[\text{Fe}(\text{CN})_6]^{4-}$ exists in its deprotonated form in the pH range used in the present study (Fig. 4) and $[\text{IO}_4^-]_{\text{T}}$ is described by Eq. (9), one can easily deduce the following rate law (Eq. 11) using Eq. (9).

$$\text{Rate} = k_1 [\text{Fe}(\text{CN})_6]^{4-} [\text{H}_2\text{IO}_6]^{3-} + k_2 [\text{Fe}(\text{CN})_6]^{4-} [\text{H}_3\text{IO}_6]^{2-} + k_3 [\text{Fe}(\text{CN})_6]^{4-} [\text{IO}_4^-]$$

or

$$\text{Rate} = \left\{ k_3 + \left(k_2 \beta_2 + \frac{k_1 \beta_3 K\omega}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} \right\} [\text{Fe}(\text{CN})_6]^{4-} [\text{IO}_4^-] \quad (11)$$

Now, from Eqs. (9), (10) and (11) one can deduce the following relationship.

$$k \left\{ \left(\beta_2 + \frac{\beta_3 K\omega k_3}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} + 1 \right\} [\text{Fe}(\text{CN})_6]^{4-} [\text{IO}_4^-] = \left\{ k_3 + \left(k_2 \beta_2 + \frac{\beta_2 K\omega k_1}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} \right\} [\text{Fe}(\text{CN})_6]^{4-} [\text{IO}_4^-]$$

or

$$k = \frac{\left\{ \left(k_2 \beta_2 + \frac{\beta_3 K\omega k_1}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} + k_3 \right\}}{\left\{ \left(\beta_2 + \frac{\beta_3 K\omega}{[\text{H}^+]} \right) \frac{K\omega}{[\text{H}^+]} + 1 \right\}} \quad (12)$$

Since, at pH \gg 8.5, the term $[\beta_2 + (\beta_3 K\omega/[\text{H}^+])] K\omega/[\text{H}^+] \ll 1$ and the rate constant (k_3) due to $[\text{IO}_4^-]$ is relatively small, Eq. (12) can be written as:

$$k = \frac{k_1 K\omega \beta_3 + k_2 \beta_2 [\text{H}^+]}{\beta_2 K\omega + \beta_2 [\text{H}^+]}$$

or

$$k (\beta_2 K\omega + \beta_2 [\text{H}^+]) = k_1 K\omega \beta_3 + k_2 \beta_2 [\text{H}^+] \quad (13)$$

The plot of left hand side of Eq. (13) vs. $[\text{H}^+]$ yields a straight line ($r = 0.9850$, $\text{sd} \geq 0.046$) and the value of rate constants k_1 and k_2 can be evaluated from the slope and intercept of this plot, respectively. The evaluated k_1 and k_2 values for the reaction of $[\text{H}_2\text{IO}_6]^{3-}$ and $[\text{H}_3\text{IO}_6]^{2-}$ with $[\text{Fe}(\text{CN})_6]^{4-}$ were found to be 0.16 ± 0.02 and $0.012 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The evaluated value of k_1 is in good agreement with experimentally found value of a second order rate constant (k). Thus, the rate equation derived from the

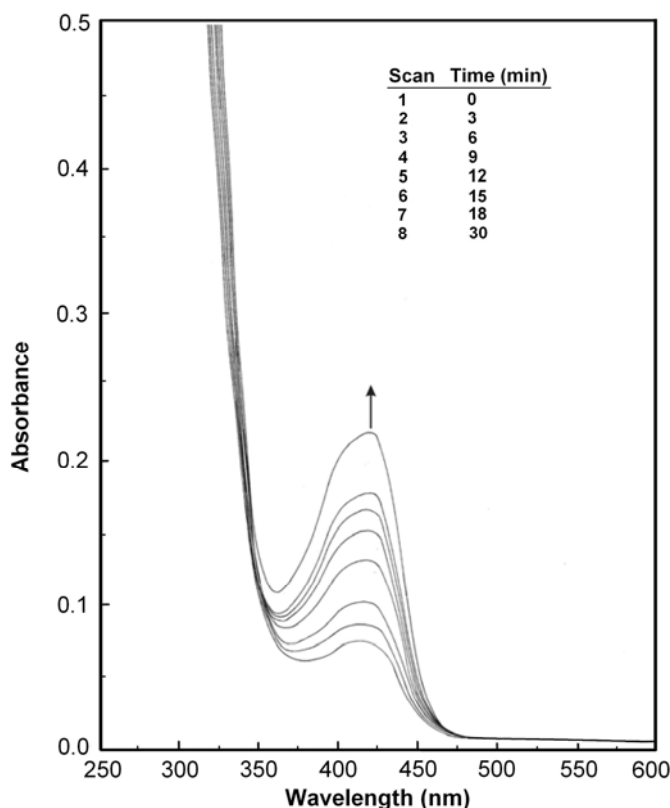


Fig. 5. Repetitive spectral scans of the reaction mixture of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{IO}_4^-]$. Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \times 10^{-4} \text{ M}$, $[\text{IO}_4^-] = 3.0 \times 10^{-3} \text{ M}$, $I = 0.1 \text{ M}$ (NaCl), $\text{pH} = 9.5 \pm 0.02$ and $\text{Temp.} = 25 \pm 0.1 \text{ }^\circ\text{C}$.

reaction mechanism is consistent with the experimental findings.

The lability of periodate ion [29] points to suggest an inner-sphere mechanism in which a cyanoligand bridges one of the periodate reactive species ($\text{H}_2\text{IO}_6^{3-}$ or $\text{H}_3\text{IO}_6^{2-}$) to a hexacyanoferrate(II) ion. There is a lack of direct evidence on involvement of periodate ion as an inner-sphere oxidant. However, on the basis of its behavior towards the oxidation of organic [33] and inorganic substrates [6-7], it is quite reasonable to expect that periodate ion should also behave in a similar way for the system under investigation.

The repetitive spectral scans recorded for the oxidation of hexacyanoferrate(II) by periodate ion are shown in Fig. 5, which clearly indicates that there is a continuous increase in the peak height at 420 nm. This is attributed to the formation of hexacyanoferrate(III) as a function of time. The hexacyanoferrate(III) is therefore the final reaction product.

The effect of temperature and ionic strength further support to the proposed mechanistic scheme.

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REFERENCES

- [1] E.L. Jackson, *Org. React.* 2 (1944) 341.
- [2] J.M. Bobbit, *Rec. Adv. Carbohydrate Chem.* II (1956) 1.
- [3] A.Y. Kasim, Y. Sulfab, *Inorg. Chem. Acta* 24 (1977) 247.
- [4] G.J. Buist, in: C.H. Boneford, C.F.H. Tripper (Eds.), *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam,

- 1972, pp. 435-456.
- [5] A. Indelli, F. Ferranti, F. Secco, *J. Phys. Chem.* 70 (1966) 631.
- [6] P. Guardado, A. Maestra, M. Baton, *J. Inorg. Nucl. Chem.* 43 (1981) 1392.
- [7] M.A. Hussein, Y. Sulfab, *Trans. Met. Chem.* 7 (1982) 181.
- [8] A.A. Abdel-Khalek, Y. Sulfab, *J. Inorg. Nucl. Chem.* 43 (1981) 3257.
- [9] M.A. Hussein, A.A. Abdel-Khalek, Y. Sulfab, *J. Chem. Soc., Dalton Trans.* (1983) 317.
- [10] M.H. Abu-Elenien, N.I. Al-Shatti, M.A. Hussein, Y. Sulfab, *Polyhedron* 9 (1990) 99.
- [11] R.M. Naik, J. Sarkar, A. Verma, *Indian J. Chem. Sec. A* (2003).
- [12] M.A. Mansour, *Trans. Met. Chem.* 28 (2003) 276.
- [13] G.R. Babu, K. Ramakrishna, G. Venkateswarlu, P.V. Subba Rao, *Indian J. Chem. Sec. A* 42A (2003) 1053.
- [14] Y. Sulfab, Y. Abu-Shadi, *Inorg. Chem. Acta* 21 (1977) 115.
- [15] F.R. El-Eziri, Y. Sulfab, *Inorg. Chem. Acta* 25 (1977) 15.
- [16] S.S. Anis, M.A. Mansour, *Trans. Met. Chem.* 26 (2001) 695.
- [17] H.A. Ewais, F.D. Al-Otaibi, A.A. Abdel-Khalek, *Inorg. Rect. Mech.* 6 (2006) 39.
- [18] A.A. Abdel-Khalek, H.A. Ewais, F.D. Al-Otaibif, *Inorg. Rect. Mech.* 6 (2006) 31.
- [19] X.-L. Meng, C.-X. Yuan, Q.-H. Zhou, M.-Y. Li, P. Yang, *Chinese J. Chem.* 22 (2004) 841.
- [20] E. Martinez, A.E. Mucientes, F.J. Pobleto, A. Rodriguez, *Polish. J. Chem.* 78 (2004) 261.
- [21] Y. Sulfab, *J. Inorg. Nucl. Chem.* 38 (1976) 2271.
- [22] M.B. Ibora, A.M. Alvarez, B. Almedia, *React. Kinet. Cat. Lett.* 22 (1983) 1.
- [23] *Stability Constants, Special Publication No. 17, The Chemical Society, London, 1964, p. 352.*
- [24] *Stability Constants, Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971, p. 226.*
- [25] A.J. Miralles, R.E. Armstrong, A.J. Haim, *J. Am. Chem. Soc.* 99 (1977) 1416.
- [26] N. Sutin, in: G.L. Eichhorn (Ed.), *Inorganic Chemistry, Vol. 2, Elsevier Science, Amsterdam, 1973, p. 611.*
- [27] U. Furholz, A. Haim, *Inorg. Chem.* 26 (1987) 3243.
- [28] D.D. Perrin, I.G. Sayce, *Talanta* 14 (1967) 833.
- [29] J. Aveston, *J. Chem. Soc. A* (1969) 273.
- [30] S.M. Tuwar, S.T. Nandibewoor, J.R. Raju, *J. Ind. Chem. Soc.* 69 (1992) 651.
- [31] J.H. Shan, S.M. Li, S.Y. Huo, S.G. Shen, H.W. Sun, *J. Iran. Chem. Soc.* 2 (2005) 226.
- [32] S.D. Kulkarni, S.T. Nandibewor, *Trans. Met. Chem.* 31 (2006) 1034.
- [33] I. Pechet, Z. Luz, *J. Am. Chem. Soc.* 87 (1965) 4068.