Kinetics of Oxidation of Diethylenetriaminepentaacetic Acid (DPTA) by Hexacyanoferrate(III)

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Received 25 March 1985; revised and accepted 16 July 1985

The kinetics of the title reaction has been investigated spectrophotometrically at 410 nm, pH = 10.5, I = 0.25 mol dm$^{-3}$ (NaClO$_4$) and temp. = 35 ± 0.1°C. The rate data indicate first order dependence each in [hexacyanoferrate(III)] and [DPTA] with a second order rate constant, $k = 7.93 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The rate constant increases in the pH range 8.5 to 12. The reaction species of DPTA in the above pH region are H$_2$L$^3-$, HL$^4-$ and L$^5-$.

This pH dependence makes it possible to resolve the rate constants due to reactions of [Fe(CN)$_6$]$^{3-}$ with L$^5-$ ($k_1 = 1.05 \times 10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$) and HL$^4-$ ($k_2 = 4.9 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$) respectively. The rate of reaction between [Fe(CN)$_6$]$^{3-}$ and H$_2$L$^3-$ is very slow. The effect of ionic strength is found to be positive. The activation parameters evaluated from Arrhenius plots are: $\Delta H^* = 28.2$ kJ mol$^{-1}$ and $\Delta S^* = -175.6$ JK$^{-1}$ mol$^{-1}$. An electron transfer from [Fe(CN)$_6$]$^{3-}$ to the substrate followed by decomposition of the latter is proposed.

Materials and Methods

Potassium hexacyanoferrate(II) (AR, Sarabhai M Chemicals), potassium hexacyanoferrate(III) (AR, SDS), sodium cyanide (May & Baker, England) and diethylenetriaminepentaacetic acid (Sigma) were used as such. Sodium hydroxide or perchloric acid was used to maintain pH at any desired value. Standard BDH buffers were used for standardization of pH meter. Sodium cyanide solution was standardized argentometrically$^2$. Sodium perchlorate (AR, BDH) or potassium nitrate (GR, Sarabhai M Chemicals) was used to maintain ionic strength.

A Toshniwal spectrophotometer model RL-02 fitted with a circulatory arrangement for thermostating the cell compartment was used for kinetic study. The temperature could be controlled to within ± 0.1°C. A Shimadzu double beam spectrophotometer model UV-190 and Cary 17D spectrophotometer were used for recording the spectral changes. All pH measurements were made on an Elico digital pH meter model LI-120.

Kinetic measurements

The reaction between DTPA and hexacyanoferrate(III) was followed at 410 nm (broad band of [Fe(CN)$_6$]$^{3-}$, $\varepsilon = 1020$ dm$^3$ mol$^{-1}$ cm$^{-1}$), pH = 10.5, I = 0.25 $M$ (NaClO$_4$) and temp. = 35 ± 0.1°C. The kinetics were studied under pseudo-first order conditions using large excess of DTPA. Solutions of hexacyanoferrate(III) and DTPA were pre-equilibrated at the desired temperature for 30 min before mixing. Ionic strength and pH were adjusted each time before equilibrating the reactants.

The pseudo-first order rate constants were calculated from plots of log $C_A$ versus time, where $C_A$ refers to [hexacyanoferrate(III)] remaining at any time $t$. The absorbance changes were observed for at least 70% of the reaction.

Results

The kinetic data of this reaction are given in Table 1 and the dependence of pseudo-first order rate constant on [DTPA] is shown in Fig. 1.

Dependence of rate on pH

The reaction was studied in the pH range 8.5-12. The species distribution of DTPA at various pH values was calculated with an IBM 7044 computer using a programme developed by Perrin and Sayce$^3$ and is shown in Fig. 2. The predominant species of DTPA in the pH range of interest are H$_2$L$^3-$, HL$^4-$ and L$^5-$ in varying proportions. It is observed that between pH...
Table I—Evaluation of Pseudo-first Order Rate Constants and Second Order Rate Constants

\[
\begin{align*}
[\text{Fe(CN)}_6^{3-}] &= 5 \times 10^{-4} \text{ mol dm}^{-3}; \text{pH} = 10.5; \text{temp.} = 35^\circ\text{C} \pm 0.1^\circ\text{C}; \\
I &= 0.25 \text{ mol dm}^{-3} (\text{NaClO}_3) \\
10^3 [\text{DTPA}]_T & k_{obs} \times 10^4 (\text{s}^{-1}) k_f = \frac{[\text{DTPA}]_T}{k_{obs}} \\
(\text{mol dm}^{-3}) & (\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) \\
5.0 & 4.17 \quad 8.34 \\
7.5 & 6.69 \quad 8.92 \\
10.0 & 7.90 \quad 7.90 \\
12.5 & 9.30 \quad 7.44 \\
15.0 & 10.56 \quad 7.04 \\
\text{Average} &= 7.93 \pm 0.4
\end{align*}
\]

8.5 and 10.0 the reaction rate increases linearly with increase in pH and levels off at higher pH (Fig. 3). Below pH 8.5 the rate is extremely slow. The data on pH-dependence of rate fit Eq. (2).

\[
\text{Rate} = k_f [\text{Fe(CN)}_6^{3-}] [\text{L}]_T 
\]

In Eq. (2) the concentration term, [L]_T includes all protonated and unprotonated forms of DTPA.

The rate of oxidation of DTPA by [Fe(CN)_6]^{3-} can also be given by the expression (3)

\[
\text{Rate} = [\text{Fe(CN)}_6^{3-}] \{ k_1 [\text{L}^5^-] + k_2 [\text{HL}^4^-] + k_3 [\text{H}_2\text{L}^3^-] \} \\
= [\text{Fe(CN)}_6^{3-}] \{ k_1 [\text{L}^5^-] + k_2 K_1 [\text{H}^+] [\text{L}^5^-] + k_3 K_1 K_2 [\text{H}^+]^2 \} \\
= [\text{Fe(CN)}_6^{3-}] \{ k_1 + k_2 K_1 [\text{H}^+] + k_3 K_1 K_2 [\text{H}^+]^2 \} 
\]

where \( k_1, k_2, k_3 \) are the rate constants for the species \( \text{L}^5^- \), \( \text{HL}^4^- \) and \( \text{H}_2\text{L}^3^- \) respectively and \( K_1 \) and \( K_2 \) are the respective protonation constants of DTPA.

Comparing Eqs (2) and (3) we get,

\[
k_f \frac{[\text{L}]_T}{[\text{L}^5^-]} = k_1 + k_2 K_1 [\text{H}^+] + k_3 K_1 K_2 [\text{H}^+]^2
\]

where

\[
\frac{[\text{L}]_T}{[\text{L}^5^-]} = 1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2
\]

At pH above 10, \([\text{H}^+]^2 \) can be ignored. So Eq. (4) is simplified to Eq. (5)

\[
k_f [1 + K_1 [\text{H}^+]] = k_1 + k_2 K_1 [\text{H}^+]
\]

In the higher pH region a plot of left hand side of Eq. (5) versus \([\text{H}^+]\) is linear (Fig. 4), the slope of which gives the value of \( k_2 \) (i.e. reaction rate between \([\text{Fe(CN)}_6]^{3-} \) and \([\text{HL}]^4^- \)) equal to \( 4.9 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). The intercept of the linear plot gives \( k_1 \) (i.e. the reaction rate between \([\text{Fe(CN)}_6]^{3-} \) and \([\text{H}_2\text{L}^3^-] \)).
Fig. 3—Effect of pH on the reaction of $[\text{Fe(CN)}_6]^{3-}$ with DTPA ($[\text{Fe(CN)}_6]^{3-} = 5 \times 10^{-4}$ mol dm$^{-3}$, [DTPA]$=10^{-2}$ mol dm$^{-3}$, temp. $= 35 \pm 0.1^\circ$C, $I = 0.25$ mol dm$^{-3}$ (NaClO$_4$)).

Fig. 4—Resolution of rate constants due to the reactions of $[\text{Fe(CN)}_6]^{3-}$ and $L^-$ and $[\text{Fe(CN)}_6]^{3-}$ and $HL^-$. The rate constant for reaction between $L^-$ and Fe(CN)$_6^{2-}$ is equal to $1.05 \times 10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Further, transforming expression (4) and taking logarithm, we get:

$$\log \frac{k_f}{[H^+]} = \log(k_3K_1K_2) + \log[H^+]$$

A plot of left hand side of Eq. (6) versus log $[H^+]$ is linear (Fig. 5) the slope of which is close to one and the intercept gives an estimated value of $k_3$ equal to $5.6 \times 10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$. This is consistent with the observation that the rate below pH 8.5 is extremely slow.

Effect of temperature on rate

Activation parameters for this reaction have been calculated from Arrhenius plot in the temperature range 25-40°C and the values are: $\Delta H^* = 28.2 \pm 0.04$ kJ mol$^{-1}$ and $\Delta S^* = -175.6 \pm 0.5$ JK$^{-1}$ mol$^{-1}$. Figure 6 shows a plot of enthalpies of activation versus the entropies of activation for the oxidation of a few aminocarboxylic acids, viz. DTPA, ethylenediaminetetraacetic acid (EDTA), ethylenediaminetetrapropionic acid (EDTPA), iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA) by $[\text{Fe(CN)}_6]^{3-}$.
relationship indicates that the oxidation of all these substrates proceeds by a common mechanism. The slope of this line gives the isokinetic temperature as \(26 \pm 3^\circ C\). At this temperature all these aminocarboxylic acids react with \([\text{Fe(CN)}_6]^{3-}\) at comparable rates. It may be pointed out that our conditions were not identical with the conditions used for other aminocarboxylate reactions.5

Discussion

The kinetic data given in Table I and plotted in Fig. 1 are consistent with the interaction of \(L^5-\) with hexacyanoferrate(III) in the rate-determining step. Added hexacyanoferrate(II) in the concentration range \(5 \times 10^{-4}\) to \(5 \times 10^{-3}\) mol dm\(^{-3}\) does not retard the reaction rate indicating that the reaction is essentially irreversible. The presence of cyanide in the concentration range \(2.5 \times 10^{-2}\) to \(7.5 \times 10^{-2}\) mol dm\(^{-3}\) also does not materially affects the forward rate ruling out the possibility of prior dissociation.

The effect of ionic strength on the rate constant presents an interesting feature in that the value of \(ZAZ_B\) obtained from the linear plot of \((\sqrt{I}) / (1 + \sqrt{I})\) versus log \(k_2\) is smaller than the expected value if the only reactants were \([\text{Fe(CN)}_6]^{3-}\) and \([\text{DTPA}]^5-\). This is not entirely unexpected because DTPA and other aminocarboxylates are known to form complexes with alkali metals of moderate stabilities \((K_{\text{NaDTPA}} = 10.0, K_{\text{KDTPA}} = 4.84)\). In the presence of three \(K^+\) ions released from dissociation of \(K_3[\text{Fe(CN)}_6]_6^0\) and large excess of \(Na^+\) present due to addition of \(NaClO_4\), significant concentration of DTPA is present as complexes of either \(Na^+\) or \(K^+\) and hence smaller effective value of \(ZAZ_B\).

Specific salt effects have also been observed in the present reaction system. The second order rate constants increase on changing \(Na^+\) to \(K^+\) at constant ionic strength. A similar behaviour has been observed in the hexacyanoferrate(III) oxidation of EDTA and also in the hexacyanoferrate(III)-hexacyanoferrate(II) exchange reaction. The values of rate constants in the presence of \(Na^+\) and \(K^+\) ions (0.25 mol dm\(^{-3}\) each) are 7.93 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} and 2.5 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} respectively. A third factor, which appears to affect the values of \(ZAZ_B\), is the possible formation of ion pairs between \([\text{Fe(CN)}_6]^{3-}\) and \([\text{DTPA}]^5-\) with the cations present in sufficiently high concentration in the reaction medium.

The spectral changes occurring during a typical kinetic run have been recorded and the results are shown in Fig. 7. There is a continuous decrease of absorbance at 410 nm and a corresponding decrease in the peak height of the peak at 303 nm as well. \([\text{Fe(CN)}_6]^{4-}\) has a weak absorption band at 325 nm but is not observed because it gets lost in a shoulder of \([\text{Fe(CN)}_6]^{3-}\) at 325 nm.

An isosbestic point at 281 nm indicates coexistence of two species, viz. \([\text{Fe(CN)}_6]^{3-}\) and \([\text{Fe(CN)}_6]^{4-}\). The absence of any new peak points to the fact that no reaction intermediate is possibly present in any appreciable concentration. The absorption peaks of other products are likely to be in the UV region where DTPA absorbs strongly and are, therefore, not identifiable. The oxidation products of EDTA have been identified as iminodiacetic acid and glycollic acid. Two specific tests for hexacyanoferrate (II), viz. ammonium molybdate and thorium nitrate tests confirm the formation of \([\text{Fe(CN)}_6]^{4-}\) as one of the reaction products.
GUPTA et al.: KINETICS OF OXIDATION OF DIETHYLENETRIAMINEPENTAACETIC ACID

The results presented above point to an outer sphere mechanism of electron transfer from hexacyanoferrate(III) to the DTPA in a bimolecular step. Under the conditions employed the reactants are [Fe(CN)₆]³⁻ on the one hand and DTPA⁵⁻ and HDTPA⁴⁻ on the other depending upon pH of the medium. The presence of Na⁺ and K⁺ in the reaction medium complicates the reaction due to the formation of complexes of DTPA with Na⁺ and K⁺ and possibly ion pairs. Specific salt effects are also observed. The highly negative value of entropy of activation shows that the activated complex obtained in the bimolecular process is highly charged.

References