

Study of the effect of structure on the kinetics and mechanism of the redox reactions of Fe(III)/Fe(II) complexes

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This study reveals the kinetics and mechanism of the redox reactions between a few selected Fe(III) and Fe(II) complexes. Through comparison, the outcomes of the study highlight the effect of structural variation upon the electron-transfer mechanism. Structural variation exhibits effects on the properties of transition metal complexes, more specifically, reduction potential and reaction mechanism. A change in the reduction potential may lead to altering the electron-transfer mechanism and biochemical applications of the compounds. We oxidized acetylferrocene, 1-ferrocenylethanol, and ferrocyanide by ferricyphen in the aqueous-organic co-solvent mixture. All of the reactions were completed in three phases, and followed a complex kinetics such as an overall second order, and, the zeroth order in the second and the first phases, respectively with a subsequent competition phase until the reaction was completed. The concentration of nitric acid was varied and its effect on the rate constant(s) was probed in each phase of the reaction(s) to recognize the probable protonation of the reducing agent(s), and its participation in the electron-transfer mechanism(s). The reactions, although, followed the same kinetic orders, but the rate-controlling species were specific to each phase in each reaction.

Keywords: Redox reaction, Fe(III)/Fe(II) complexes, ferrocyanide, acetylferrocene, 1-ferrocenylethanol, ferricyphen

INTRODUCTION

The chemical structure of the coordination compounds plays a leading role in their electrochemical behaviour. The electron-transfer chemistry mostly revolves around the structure of these compounds, which are oxidized and reduced during a reaction [1]. An outer-sphere or an inner-sphere mechanism can lead the redox chemistry, consequently. Each of these mechanisms is structure-dependent, which further divides the applications of the coordination compounds in our everyday life such as industry, pharmacy, technology, etc. Our interest was to study the effect of structure on the kinetics of the electron-transfer mechanism of a total of three selected reducing agents and an oxidizing agent, where Fe(II) or Fe(III) was the central metal part, respectively. For such purpose, we chose those compounds, which were structurally correlated. They were derivatives, for example, two derivatives of ferrocene were chosen for this study, which show solubility in the aqueous medium to a certain extent. We considered this property in order to avoid the use of expensive organic solvents during the study and to keep this project environmentally friendly. Alcohols cannot be used to compose the reaction media during such redox processes considering the oxidation of alcohols by the Fe(III) complexes [2]. 1,4-dioxane was used for its miscibility in water, as well as

neriness towards oxidation. Acetylferrocene and 1-ferrocenylethanol were the target compounds to oxidize in this study. The reduction potential ($E_{1/2}$) of acetylferrocene was reported to be 0.740 V and of 1-ferrocenylethanol - 0.204 V [3,4]. The redox ability of these compounds has previously been studied electrochemically without exploring the thorough mechanisms of the electron-transfer [5-9]. However, the reaction of these compounds with other transition metal complexes has rarely been focused yet. The importance of the derivatives of ferrocene appears from their antineoplastic characteristics, and their probable use in chemotherapy [10,11]. We also chose the well-known compound ferrocyanide for this study and oxidized it by ferricyphen. The reduction potential ($E_{1/2}$) of the mixed ligand complex (ferricyphen) increased to 0.80 V over ferrocyanide (0.40 V) upon addition of 1,10-phenanthroline chelate [3, 12]. A few of its studies appeared, where this compound has been used as an oxidizing agent for different compounds of biological importance [3,4, 12-16]. However, the literature review shows the oxidation of ferrocyanide by various other compounds [17-20]. Our study will significantly include the data, and surface the effect of structural variation upon the kinetics and mechanism of the reduction of ferricyphen ($[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$) by either acetylferrocene (FcCOMe), 1-ferrocenylethanol (FcCHOHMe), and/or,

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R. Khattak, I. Imam Naqvi: Study of the effect of structure on the kinetics and mechanism of the redox reactions of ... ferrocyanide ($[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) in aqueous-organic and aqueous media. We determined the effects of various experimental parameters such as the concentration of the reducing agents, the oxidizing agent, and the acid (nitric acid) on the rate constants of each reaction in each phase. In view of our results and literature, we found the reactive species that are involved in the rate-determining step(s), and that control the mechanism(s). We proposed a rate law for each of the electron-transfer processes with an outer-sphere mechanism. Through comparison, we surfaced the effect of the structure upon the kinetics and the electron-transfer mechanism of the compounds.

EXPERIMENTAL

We used Analar-grade materials. The oxidizing agent; $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ was synthesized and crystallized out by following all steps of the procedures mentioned earlier [3, 21]. The reagents such as potassium ferrocyanide, potassium nitrate, nitric acid and 1,4-dioxane were provided by Merck and used without any treatment. Acetylferrocene and 1-ferrocenylethanol were purchased from Sigma Aldrich and used without purification. The double-beam spectrophotometer (UV-Visible range/200 to 800 nm, Shimadzu UV-160A) helped to analyze the reactants and the products of the reaction(s).

The instrumental assembly was home-built in our laboratory to monitor the rapid reactions [3,4]. The increase in absorbance along time was recorded upon the reduction of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$, and the formation of ferrocyphe; $[\text{Fe}^{\text{II}}(\text{phen})_2(\text{CN})_2]$ was monitored at 510 nm and

530 nm in aqueous and dioxane-aqueous (20% v/v) media, respectively. The pseudo-first order condition was maintained to probe the reactions. The oxidation reactions of acetylferrocene and 1-ferrocenylethanol were studied in 20% (v/v) dioxane-aqueous co-solvent mixture at 0.18 mM ionic strength (I) and at room temperature. However, the oxidation of ferrocyanide was probed in the aqueous medium at 60 mM ionic strength and room temperature. The concentration of the reducing agent such as acetylferrocene, 1-ferrocenylethanol, and ferrocyanide was always in excess over the oxidizing agent such as ferricyphen. The results acquired through kinetic studies showed that the reduction of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ was completed in three phases (Fig. 1) regardless of the reducing agent, i.e., an overall zeroth order (first phase), an overall second order (second phase), and a competition between the rate of reaction and insolubility of ferrocyphe (third phase).

Three to six experimental trials helped to deduce an average value of the slope to determine the rate constant with standard deviation. The integration method was preferred over others to determine the pseudo-first order rate constant ($k'_{\text{obs}}/\text{s}^{-1}$) because of the completion of reactions in the phases. The increase in absorbance was monitored with respect to time as the ferricyphen reduced. The plot of log natural of the absorbance at a certain time point "t" ($\ln [\text{Absorbance}]_t$) versus time yielded a straight line with an intercept such as the log natural of the absorbance at zero time ($\ln [\text{Absorbance}]_0$), i.e., before starting the reaction. The slope of the plot yielded a pseudo-first order rate constant.

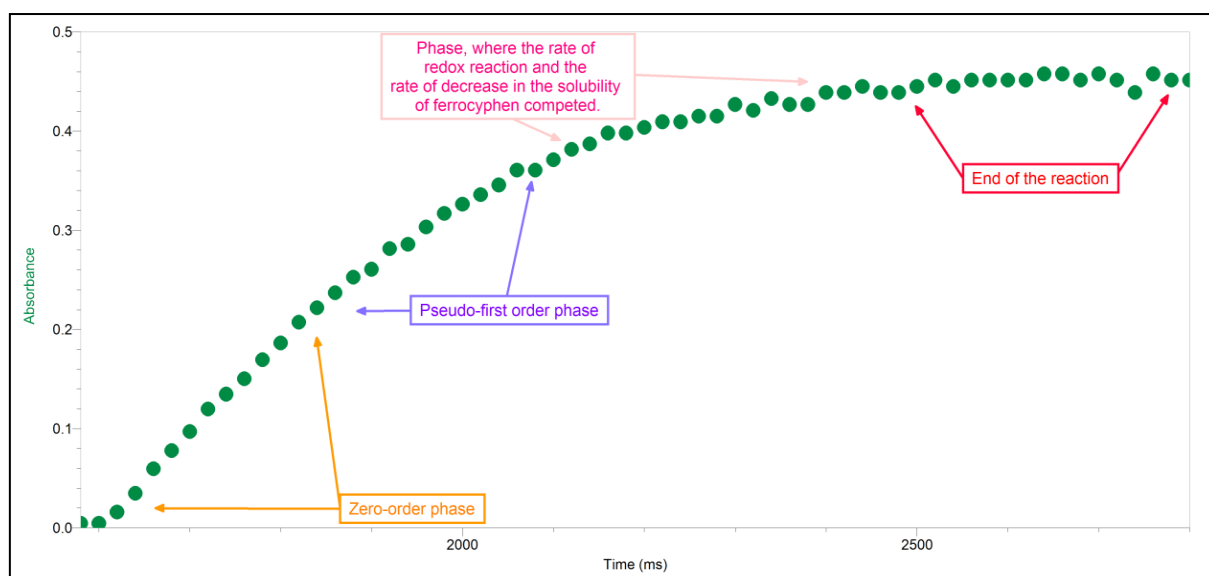


Fig. 1. A representative plot to show the kinetic pathway of the redox reaction between $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ (0.08 mM) and FcCHOHMe (1.3 mM) at 0.18 mM ionic strength and 291 ± 0.5 K in 20% (v/v) dioxane-aqueous medium.

The zeroth order kinetic data were also acquired by the integration method. The plots of absorbance at time point “t” $[Absorbance]_t$ versus time passed through the origin and the slopes of the plots yielded the observed zeroth order kinetic data. We did not observe any intercept because we did not have any concentration of the product; ferrocphen, initially. The slope of the plot ($\epsilon \cdot b \cdot k_{obs}$; s^{-1}) was not converted into the observed zero-order rate constant (k_{obs} ; $M s^{-1}$). The symbols “ $\epsilon \cdot b$ ” have their conventional meanings to represent the molar absorptivity ($M cm$)⁻¹ of ferrocphen and the path length of the cuvette (1 cm). The slope reduces to ‘ $\epsilon \cdot k_{obs}/s^{-1}$ ’ if we put ‘1’ for b, whereas “ ϵ ” carries a constant value and does not change our result of the rate constant (k_{obs}) except the addition of a constant number in all such data.

RESULTS AND DISCUSSION

Kinetic parameters

The effects of varying concentration of the reactants were studied to determine the order of reaction with respect to each reactant. All the other parameters were kept constant for these experiments. The ionic strength was maintained by potassium nitrate (KNO₃) considering the common ions; potassium and nitrate that come from the oxidizing agent and the reducing agent. However, dioxane was used to maintain a 20% (v/v) dioxane-aqueous co-solvent mixture. The experiments were performed at constant concentration (0.08 mM) of $[Fe^{III}(phen)_2(CN)_2]^+$ when the effect of varying concentration of the reducing agent(s) was studied. Meanwhile, 1.3 mM of FcCOMe/FcCHOHMe/ $[Fe^{II}(CN)_6]^{4-}$ was maintained constant and the concentration of the oxidizing agent was varied in the experimental setup to study the effect of the concentration of the oxidizing agent on the rate constants. The rest of the experimental conditions were constant such as 0.18 mM (I), 20% (v/v) dioxane-aqueous medium, 304 ± 0.5 K (FcCOMe), and 291 ± 0.5 K (FcCHOHMe) for the reactions of FcCOMe/FcCHOHMe. However, the oxidation of $[Fe^{II}(CN)_6]^{4-}$ was studied at 60 mM (I) and 298 ± 0.5 K in aqueous medium.

In the first phase of the reactions, we did not observe any effect of change in the concentration of $[Fe^{III}(phen)_2(CN)_2]^+$, FcCOMe, FcCHOHMe, and $[Fe^{II}(CN)_6]^{4-}$ over the value of the product of molar absorptivity of $[Fe^{II}(phen)_2(CN)_2]$ and observed zeroth order rate constant(s) ($\epsilon \cdot k_{obs}$). The results are shown in Fig. 2. The results confirmed an initial zeroth order with respect to $[Fe^{III}(phen)_2(CN)_2]^+$, FcCOMe, FcCHOHMe, and $[Fe^{II}(CN)_6]^{4-}$ in the first phase of the reaction. We also did not observe

any influence of the increasing concentration of $[Fe^{III}(phen)_2(CN)_2]^+$ upon the value of the observed pseudo-first order rate constant(s) (k'_{obs}) in the second phase of the reactions (Fig. 3). This supported the suitability of our maintained experimental conditions because under the pseudo-first order conditions the observed rate constant remains constant, however the rate of reaction changes with respect to the concentration of $[Fe^{III}(phen)_2(CN)_2]^+$ as follows.

$$Rate = k_{obs} + k'_{obs}[Fe^{III}(phen)_2(CN)_2]^+ \quad (1)$$

where, $FcCOMe/FcCHOHMe/[Fe^{II}(CN)_6]^{4-} \gg \gg [Fe^{III}(phen)_2(CN)_2]^+$

k_{obs} = observed zeroth order rate constant

$$k_{obs} = k_1[FcCOMe/FcCHOHMe/Fe^{II}(CN)_6]^{4-} = k_1 \quad (2)$$

$$k'_{obs} = \text{pseudo-first order rate constant} = k_2 [FcCOMe/FcCHOHMe/Fe^{II}(CN)_6]^{4-} \quad (3)$$

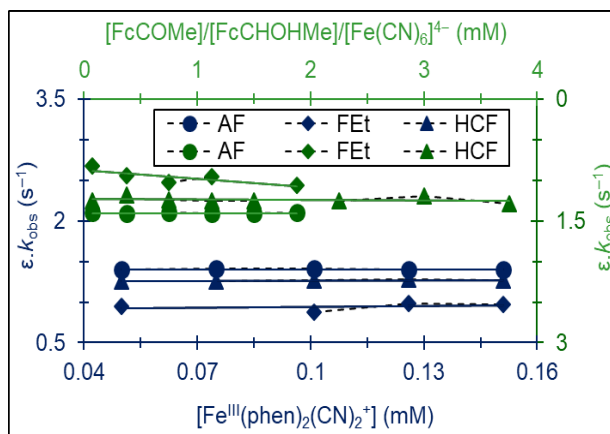


Fig. 2. Effect of variation in the concentration of oxidant and reductant on the observed zeroth order rate constant(s). The AF/FET/HCF corresponds to acetylferrocene/1-ferrocenylethanol/ferrocyanide.

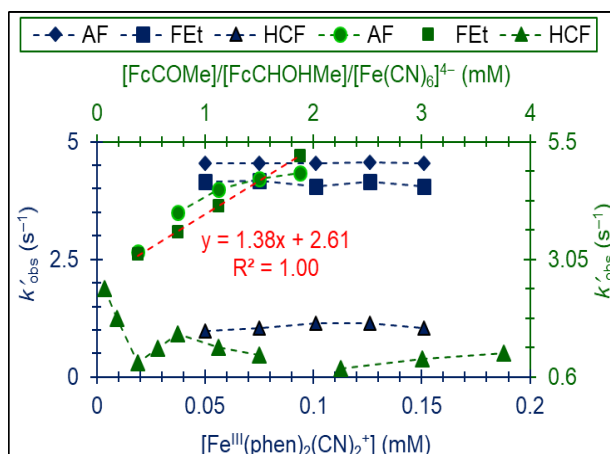


Fig. 3. Effect of variation in the concentration of oxidant and reductant on the observed pseudo-first order rate constant(s). The AF/FET/HCF corresponds to acetylferrocene/1-ferrocenylethanol/ferrocyanide.

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Different results on the effect of increasing concentration of the reducing agents in the reaction mixture upon the observed pseudo-first order rate constants (k'_{obs}) were observed (Fig. 3). The effect was an increasing curvature in case of FcCOME (acetylferrocene), a linear dependence with respect to FcCHOHMe (1-ferrocenylethanol), and a sine-wave pattern of k'_{obs} when the concentration of ferrocyanide ($[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) was increased. The value of the rate constant (k'_{obs}) increased initially, then decreased and then at the higher concentration of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, it again increased. The results are shown in Fig. 3. All of the reactions followed the first order with respect to the oxidizing agent ($[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$) in the second phase of the reactions according to the outcomes of the integration method. The increasing curvature with respect to the increasing concentration of acetylferrocene when plotted against k'_{obs} shows the formation of other species in the reaction mixture. A well-known characteristic of the carbonyl group is to get protonated. We assume the formation of the conjugate acid of acetylferrocene, and its oxidation subsequently during the reaction. The rate constant, k'_{obs} , showed a linear increase with increasing concentration of 1-ferrocenylethanol, and confirmed the first order reaction corresponding to 1-ferrocenylethanol. The sine-wave pattern of k'_{obs} upon increasing concentration of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ revealed that the oxidation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ involved its other species as well. The protonation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ may yield mono-, di-, tri-, and/or, tetra-protonated species. The protonation of ferrocyanide is condition-dependent such as the concentration of ferrocyanide in the reaction mixture, and/or, the composition of the medium for reaction to occur with the available concentration of the proton/ H^+ ions [3]. However, the protonation of ferricyphen does not take place under the experimental conditions employed for this study [3, 21]. In order to confirm our assumptions and to rectify the results, we studied the effect of acid (H^+) on the rate constants.

Effect of the concentration of acid (H^+) on the rate constants

The concentration of proton (H^+) was varied by increasing the concentration of nitric acid in the reaction mixture. We used nitric acid (HNO_3) regardless of its strong oxidizing properties because its concentrated solution was employed initially to oxidize the reduced form of the oxidizing agent during the synthesis of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ [3,4]. The oxidizing agent is stable in the nitric acid, consequently. The concentrations of the nitric acid used in this study were dilute, and unable to oxidize

the stable reducing agents such as FcCOME, FcCHOHMe, and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. The nitrate ion was, however, the common ion because the nitrate salt of the oxidizing agent was the reactant to prepare the solutions. We observed that $\varepsilon \cdot k_{\text{obs}}$ did not accept any effect of increasing concentration of H^+ ions in the reaction(s) mixture, as was expected due to obeying the zeroth order rate law in the first phase (Fig. 4). The molar concentrations of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ and FcCOME/FcCHOHMe/ $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ were maintained at a ratio of “1” (0.08 mM) and “10” (0.75 mM), respectively, to follow the reactions under the condition of pseudo-first order. The concentration of acid/proton (H^+) was always in excess over the concentration of FcCOME/FcCHOHMe/ $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. The other parameters were kept constant such as 5.1 mM (I) and 306 ± 0.5 K (FcCOME) or 291 ± 0.5 K (FcCHOHMe) in 20% dioxane-aqueous (v/v) medium. For the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ system, the experimental conditions were settled at 0.12 M (I) and 302 ± 0.5 K in the aqueous medium. The observed pseudo-first order rate constant; k'_{obs} , decreased upon increasing the concentration of proton (acid/ H^+) in each of the reactions between $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ and FcCHOHMe or $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and gradually became constant at the higher concentration of acid (proton/ H^+). In case of the reduction of FcCOME, the value of the rate constant, k'_{obs} , increased rather than showing a decrease, as was observed in the former two cases, and became constant at the higher concentration of acid (H^+) similar to that of the other two reactions. The results are shown in Fig. 5 (plot of k'_{obs} versus $[\text{H}^+]$). The effect of acid (H^+) rectifies our result with a clear conclusion of the formation of protonated FcCOME/FcCHOHMe/ $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. These protonated reducing agents influenced the rate of reactions, and the rate constants consequently. The oxidizing agent did not protonate, because, during its synthesis, we did not observe any protonated product/yield. The product was the hydrated salt of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ in the form of $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$. (FcC⁺OHMe/FcCO⁺HMe). The rate acceleration upon increasing the concentration of acid (H^+) in the reaction mixture leads to the conclusion that the protonated acetylferrocene (FcC⁺OHMe/FcCO⁺HMe) is basically the reactant involved in the rate-determining step of the redox reaction between $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{CN})_2]^+$ and FcCOME. The reducing agent, 1-ferrocenylethanol (FcCHOHMe) has an oxygen atom in its structure also, with two lone pairs of electrons that attract the proton (H^+) from the medium and gets protonated to form FcCHO⁺H₂Me.

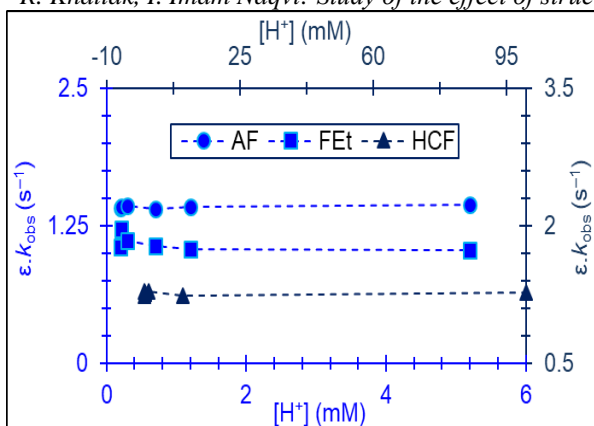


Fig. 4. Effect of variation in the concentration of acid (H^+) on the observed zeroth order rate constant(s). The AF/FEt/HCF corresponds to acetylferrocene/1-ferrocenylethanol/ferrocyanide.

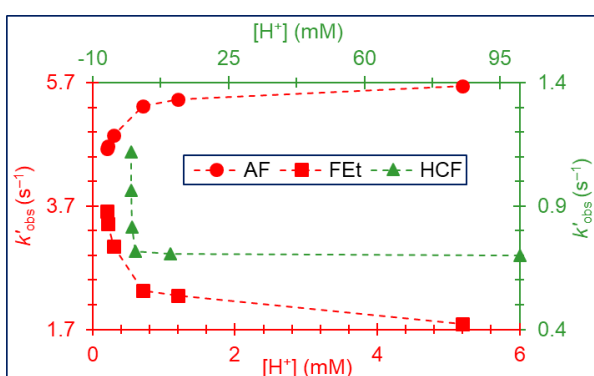
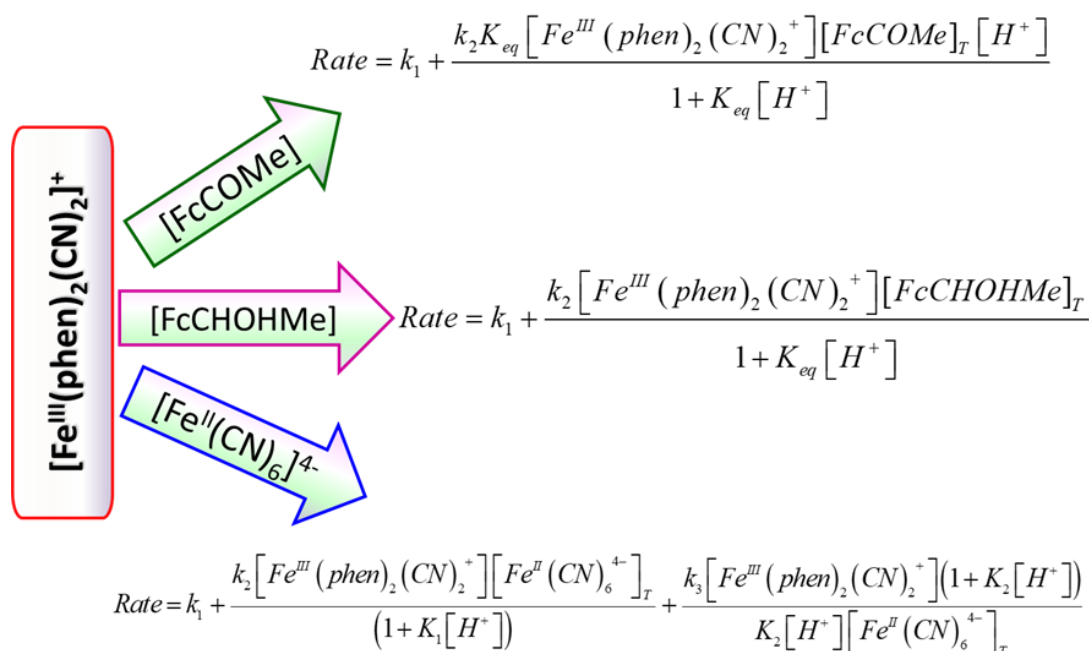


Fig. 5. Effect of variation in the concentration of acid (H^+) on the observed pseudo-first order rate constant. The AF/FEt/HCF corresponds to acetylferrocene/1-ferrocenylethanol/ferrocyanide.

The deceleration of the rate upon protonation of FcCHOHMe helped to conclude that the free compound (FcCHOHMe) donates an electron in the rate-determining step of the reaction. However, under the conditions we maintained for our reaction between $[Fe^{III}(phen)_2(CN)_2]^+$ and $[Fe^{II}(CN)_6]^{4-}$, the existence of $H_4[Fe^{II}(CN)_6]$ and $H_3[Fe^{II}(CN)_6]^-$ was not possible, but that of $H_2[Fe^{II}(CN)_6]^{2-}$ and $H[Fe^{II}(CN)_6]^{3-}$ was possible at the high concentrations of ferrocyanide and proton (H^+). The decrease in the rate constant (k'_{obs}) with increasing proton (H^+) concentration reflected the formation of protonated ferrocyanide either in the form of monobasic or dibasic acid such as $H[Fe^{II}(CN)_6]^{3-}$ and $H_2[Fe^{II}(CN)_6]^{2-}$ in the reaction mixture, which retarded the rate of reaction by decreasing the concentration of free ferrocyanide ion in the vicinity. This leads to the conclusion that free $[Fe^{II}(CN)_6]^{4-}$ gets oxidized in the rate-determining step. The rate constant (k'_{obs}) became constant at the higher concentration of proton/ H^+ because of the constant concentration of the limiting reactant, i.e., FcCOMe/FcCHOHMe/ $[Fe^{II}(CN)_6]^{4-}$.

The structural difference between the reducing agents containing Fe(II) as a central metal ion exhibited the explicit effect on the oxidation of these compounds by the same oxidizing agent containing Fe(III). Each of the redox reactions followed an outer-sphere mechanism and a complex kinetics with the different rate law as follows (Scheme 1).



Scheme 1. Proposed rate law(s) of the oxidation of Fe(II) complex(es) by $[Fe^{III}(phen)_2(CN)_2]^+$.

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