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Mechanism of the electron-exchange reactions between mixed ligand Fe(III) complexes and cyano complex of Fe(II)

Rozina Khattak[1,2*], Muhammad Sufaid Khan[3], Iftikhar Imam Naqvi[2]

[1]*Department of Chemistry, Shaheed Benazir Bhutto Women University, Peshawar, Pakistan*
[2]*Department of Chemistry, University of Karachi, Karachi-75270, Pakistan*
[3]*Departamento de Fısico-Quımica, Instituto de Quımica, Universidade Estadual Paulista (UNESP) - Araraquara 14800-900, SP, Brazil*

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Our interest was to study the reactions of those mixed ligand complexes of Fe(III), where cyanide plays its role as a ligand. We synthesized the mixed ligand complexes of Fe(III) with diimine and cyanide as ligands to form octahedral geometry with high stability. We adopted previously cited procedures with improvements. The synthesized complexes, $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ were reduced by the hexacyano complex of Fe(II) that is well-known for its high stability and octahedral geometry. The reduction was performed in aqueous medium at constant ionic strength of 0.06. The progress of the reactions was monitored spectrophotometrically by measuring the formation of $[Fe^{II}(phen/bpy)_2(CN)_2]$, i.e., the increase in absorbance with time. We found that the reduction of the mixed ligand Fe(III) complexes takes place in two phases. The first phase, when the Fe(III) complex is reduced to the neutral Fe(II) complex followsing zeroth order kinetics. The second phase was observed to be the rate-determining or slow step in the reduction of each complex, and the electron-exchange took place by an overall second order kinetics. In order to refine our results and to differentiate between the species which were taking part in the rate-determining step (slow step) and those which were taking part in the fast step, we studied the effect of protons and ionic strength on the rate constants in aqueous medium. We proposed an outer-sphere mechanism for the electron-exchange between Fe(III) and Fe(II) complexes.

Keywords: Dicyanobis(phen)iron(III), Dicyanobis(bpy)iron(III), Hexacyanoferrate(II)

INTRODUCTION

The redox chemistry of the coordination complexes is specifically important considering the wide ranging applications of those compounds [1-5]. We chose the redox reactions of Fe(III)/Fe(II) complexes, and studied the electron-exchange mechanism of the reactions of the mixed ligand complexes of Fe(III) with a well-known stable cyano complex of Fe(II). Dicyanobis(diimine)iron(III) was selected as an oxidizing agent due to its stability and solubility in aqueous medium, high molar absorptivity of its reduced form and the moderate value of the reduction potential (0.80 - 0.76 V) [6]. We selected 1,10-phenanthroline and 2,2'-bipyridine ligands as the representatives of the diimine group. Dicyanobis(phen/bpy)iron(III)/(II); $[Fe^{III/II}(phen/bpy)_2(CN)_2]^{+/0}$ were the outer-sphere mixed ligand complexes. They were synthesized in the 1960s [7] and their structure and properties, such as electrochemical behavior, were subsequently studied [8-17]. The derivatives of these compounds were also synthesized and characterized [18-20]. Later on, their applications were found through extensive research work on photosensitizing ability, acid hydrolysis, solvatochromism, indicators (nonaqueous acid-base and redox), and kinetic studies [2, 21-52]. The kinetic studies involve the redox reactions of these compounds, but such reactions have rarely been studied since the compounds have been synthesized in the 1960s. $[Fe^{II}(bpy)_2(CN)_2]$ was oxidized by $S_2O_8^{2-}$, and the effect of various parameters were determined [36, 39, 40]. The effects of solvents and the solvation in the transition state, as well as the reorganization energy were discussed [41]. Bromate ion, BrO_3^-, has been used to oxidize $[Fe^{II}(bipy)(CN)_4]^{2-}$, $[Fe^{II}(bipy)_2(CN)_2]$ and $[Fe^{II}(bipy)_3]^{2+}$ in acidic medium, and the kinetic parameters were reported [5, 43]. Meanwhile, the literature survey surfaced oxidation of a number of biologically active compounds by dicyanobis(bpy)iron(III); $[Fe^{III}(bpy)_2(CN)_2]^+$ and dicyanobis(phen)iron(III); $[Fe^{III}(phen)_2(CN)_2]^+$. Dicyanobis(phen/bpy)iron(III) is a sufficiently stable compound in aqueous, mixed aqueous and non aqueous media. This electrochemical stability draws the interest of the chemists to use this coordination complex in various redox reactions. Hydroquinone, ascorbic acid, sulfatoiron, rusticyanin, derivatives of ferrocene, Piloty's acid, iodide, cysteine and catechol were oxidized by

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* To whom all correspondence should be sent:
E-mail: rznkhattak@sbbwu.edu.pk,
rznkhattak@yahoo.com

$[Fe^{III}(phen/bpy)_2(CN)_2]^+$ in different media under various conditions [2-4, 44-47, 49-52]. The kinetic parameters of these studies show that the reactions follow an outer-sphere mechanism which was discussed in the view of Marcus theory. We chose to oxidize hexacyanoferrate(II); $[Fe^{II}(CN)_6]^{4-}$ by each of dicyanobis(phen)iron(III) and dicyanobis(bpy)iron(III) in order to compile the results of a thorough kinetic study. Hexacyanoferrate(II) has been oxidized by cumene hydroperoxide, chloroperoxidase compounds I and II, horseradish peroxidase compounds I and II, lactoperoxidase compound II, hydrogen peroxide, bromate, iodate, *N*-bromosuccinimide, and permanganate [53-62]. The kinetic parameters such as rate constants of some of these reactions were monitored and reported, and the mechanisms were discussed. Our study contributes the results of the kinetic study of the redox reactions between $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ and $[Fe^{II}(CN)_6]^{4-}$ in aqueous medium. We determined the effects of various parameters such as proton and ionic strength on the rate constants. In the view of the results and their comparison, we aimed to know the reactive species that were involved in the slow step(s) to control the mechanism(s).

EXPERIMENTAL

Analar grade materials were used. The nitrate salt of $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ was synthesized and purified by implementing the reported procedures [2, 6, 7]. We purchased potassium salt of hexacyanoferrate(II), potassium nitrate, nitric acid and dioxane from Merck and used them without further purification. We used a rapid reaction monitoring system (home built) by following changes in absorbance with respect to time in the visible region [2, 6]. A total of 3 mL of the reaction mixture was put into the quartz cuvette (1 cm path length). We recorded the formation of dicyanobis(phen/bpy)iron(II) at 510 nm and 522 nm, respectively.

The reactions were studied under the condition of pseudo-first order in aqueous medium at 0.06 ionic strength and room temperature. The concentration of $[Fe^{II}(CN)_6]^{4-}$ was always in excess over $[Fe^{III}(phen/bpy)_2(CN)_2]^+$. The results helped to conclude that the electron-exchange reaction of dicyanobis(phen/bpy)iron(III) with hexacyanoferrate(II) was completed in three phases (Fig. 1). We observed the first phase soon after starting the reaction(s). In this phase, the rate of reaction(s) remained independent of the concentrations of the reactants, and the order of reaction(s) with respect to the oxidant and reductant was zero. A ~69 (bpy system) and ~72 (phen system) percent fraction of the reactions obeyed an overall zeroth order. The second phase started soon after the first phase. In this phase, the order of reaction with respect to the oxidant and the reductant was first, and we observed an overall second order. The third phase was the competition phase. The competition occurred between the rate of redox reaction(s) and the rate of precipitation of the neutral product, dicyanobis(phen/bpy)iron(II); $[Fe^{II}(phen/bpy)_2(CN)_2]$. We followed the progress of reaction(s) by monitoring the formation of product species, $[Fe^{II}(phen/bpy)_2(CN)_2]$, i.e., the increase in absorbance with respect to time. The monopositive oxidizing agent, $[Fe^{III}(phen/bpy)_2(CN)_2]^+$, was gaining an electron to yield neutral $[Fe^{II}(phen/bpy)_2(CN)_2]$. The increasing concentration of the neutral product near completion of the reaction(s) tended to decrease its solubility in aqueous medium. Due to this decrease in the solubility, we observed precipitates in the cuvette, and changes in the absorbance occurred. The decrease in absorbance changed the data near the end of each reaction. We implemented an integration method to determine the rate constant in each phase of the reaction(s). The values; observed zeroth order ($\varepsilon.b.k_{obs}$; s^{-1}) and observed pseudo-first order (k'_{obs}; s^{-1}), are the average values of 3-6 experimental trials.

We collected data to characterize the synthesized complexes by using UV-Visible spectrophotometer (UV-160A Shimadzu) and elemental analyzer (Carlo Erba 1106). We used pH meter (HANNA HI 8314), and circulating water bath (Haake KT 33) to monitor pH and maintain temperature at a desired value, respectively.

RESULTS AND DISCUSSION

Kinetic parameters

We studied the effect of variation in the concentration of $[Fe^{III}(phen/bpy)_2(CN)_2]^+$, and or, $[Fe^{II}(CN)_6]^{4-}$ upon the product of molar absorptivity of $[Fe^{II}(phen/bpy)_2(CN)_2]$ and observed zeroth order rate constant ($\varepsilon.k_{obs}$) i.e., the first phase of the reaction(s), and, observed pseudo-first order rate constant (k'_{obs}) i.e., the second phase of the reaction(s). There was no effect of $[Fe^{III}(phen/bpy)_2(CN)_2{}^+]$ on '$\varepsilon.k_{obs}$' and 'k'_{obs}' (Fig. 2). This confirms the zeroth order with respect to $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ and the suitability of the pseudo-first order condition to probe the reaction(s) according to the following Eqns. 1-3.

$$Rate = k_{obs}[Fe^{III}(phen/bpy)_2(CN)_2^+]^0 + k'_{obs}[Fe^{III}(phen/bpy)_2(CN)_2^+] \qquad (1)$$

where, $[Fe^{II}(CN)_6^{4-}] >>> [Fe^{III}(phen/bpy)_2(CN)_2^{+}]$

k_{obs} = observed zeroth order rate constant = $k_1[Fe^{II}(CN)_6^{4-}]^0$ (2)

k'_{obs} = observed pseudo-first order rate constant = k_2 $[Fe^{II}(CN)_6^{4-}]$ (3)

The value of ‘k'_{obs}’ varied in a sine-wave pattern and ‘$\varepsilon.k_{obs}$’ remained unchaged with respect to $[Fe^{II}(CN)_6^{4-}]$ (Fig. 3).

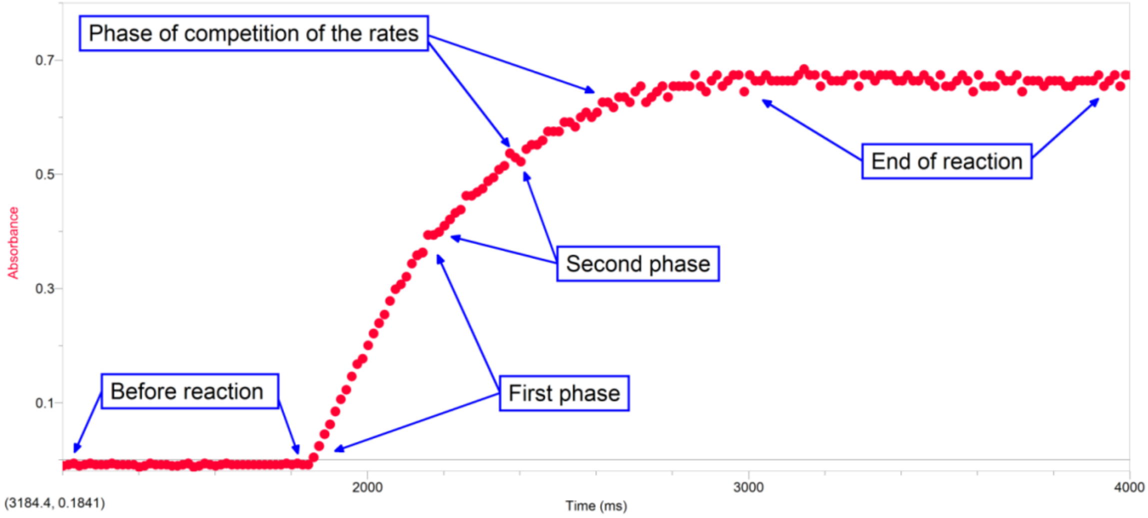

Fig. 1. A representative plot to show the phases of the reaction of $[Fe^{III}(phen)_2(CN)_2]^+$ with $[Fe^{II}(CN)_6]^{4-}$ at $[Fe^{III}(phen)_2(CN)_2^{+}]$ = 0.1 mM, $[Fe^{II}(CN)_6^{4-}]$ = 1.3 mM, I = 0.06, T = 298 ± 0.5 K and λ_{max} = 510 nm.

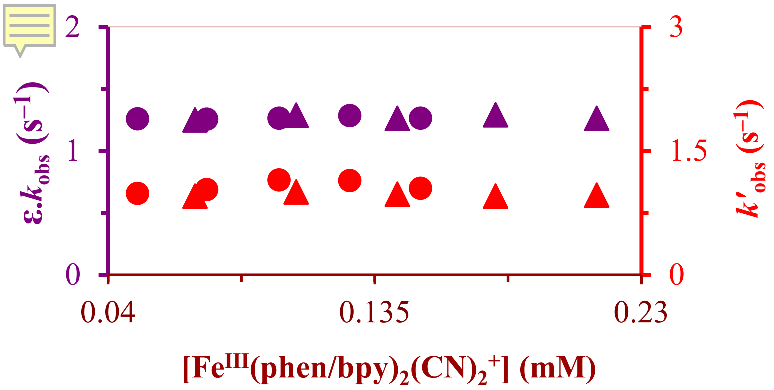

Fig. 2. Effect of the concentration of $[Fe^{III}(phen/bpy)_2(CN)_2]^+$ on the rate constants “$\varepsilon.k_{obs}$” and “k'_{obs}” at 298 ± 0.5 K, $[Fe^{II}(CN)_6^{4-}]$ = 1.8/1.3 mM, and I = 0.06 (● phenanthroline and ▲ bipyridine systems).

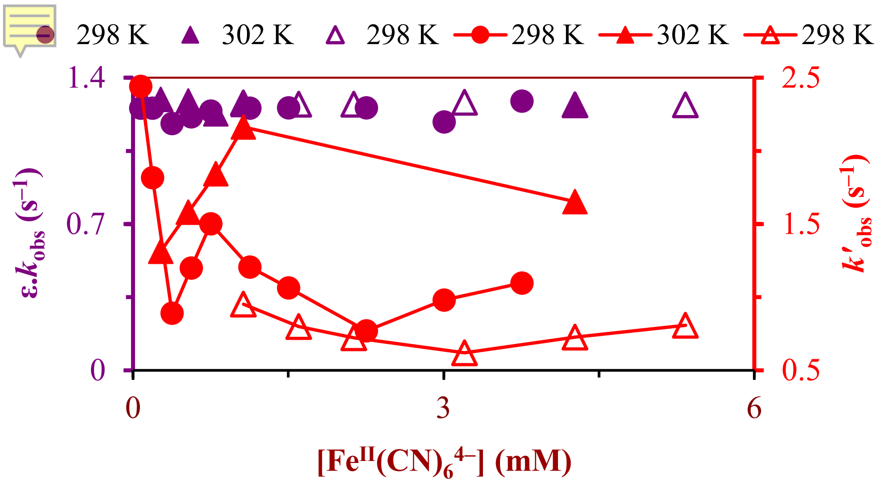

Fig. 3. Effect of the concentration of $[Fe^{II}(CN)_6]^{4-}$on the rate constants “$\varepsilon.k_{obs}$” and “k'_{obs}” at 298/302 ± 0.5 K, $[Fe^{III}(phen/bpy)_2(CN)_2^{+}]$ = 0.08/0.11 mM, and I = 0.06 (● phenanthroline and Δ/▲ bipyridine systems).

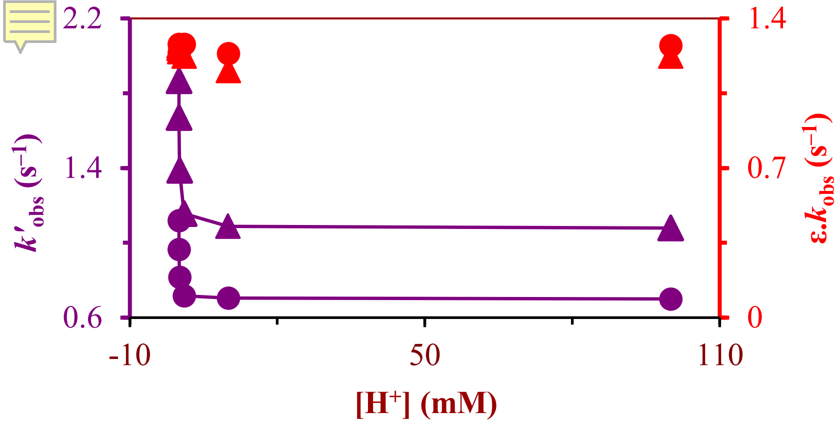

Fig. 4. Effect of the concentration of H^+ on the rate constants "$\varepsilon.k_{obs}$" and "k'_{obs}" at 298/302 ± 0.5 K, $[Fe^{III}(phen/bpy)_2(CN)_2{}^+]$ = 0.08/0.11 mM, $[Fe^{II}(CN)_6{}^{4-}]_T$ = 0.8/1.1 mM, and I = 0.12 (● phenanthroline and ▲ bipyridine systems).

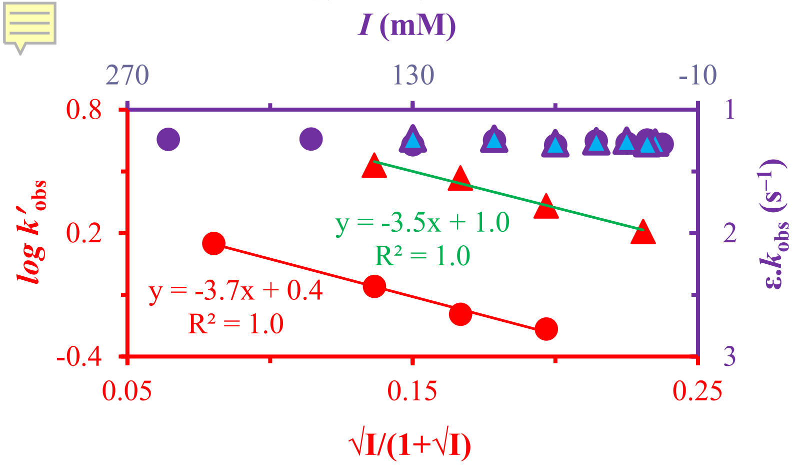

Fig. 5. Effect of the ionic strength on the rate constants "$\varepsilon.k_{obs}$" and "k'_{obs}" in aqueous medium at 300/302 ± 0.5 K, $[Fe^{III}(phen/bpy)_2(CN)_2{}^+]$ = 0.08/0.11 mM, and $[Fe^{II}(CN)_6{}^{4-}]_T$ = 0.8/1.1 mM (● phenanthroline and ▲ bipyridine systems).

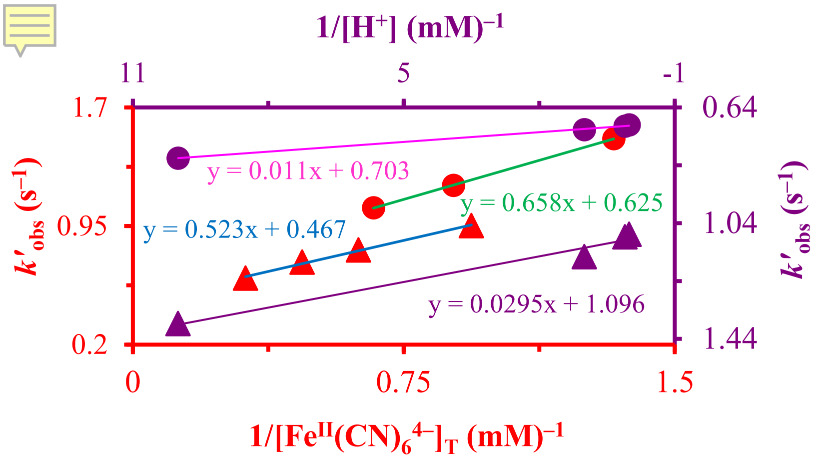

Fig. 6. The plot of k'_{obs} against $1/[Fe^{II}(CN)_6{}^{4-}]_T$ or $1/[H^+]$ at 298 ± 0.5 K, $[Fe^{III}(phen/bpy)_2(CN)_2{}^+]$ = 0.08/0.11 mM, $[Fe^{II}(CN)_6{}^{4-}]_T$ = 0.8/1.1 mM, and I = 0.06/0.12 (● phenanthroline and ▲ bipyridine systems).

We observed a similar effect for each reaction. The results confirmed an initial zeroth and then first order with respect to $[Fe^{II}(CN)_6]^{4-}$ in the first and second phase of the reaction, respectively. The sine-wave pattern corresponding to the increasing concentration of $[Fe^{II}(CN)_6]^{4-}$ shows that the oxidation of $[Fe^{II}(CN)_6]^{4-}$ may involve its protonated species as well.

Effect of protons on the rate constants

Hexacyanoferrate(II) may protonate and form $H[Fe^{II}(CN)_6]^{3-}$, $H_2[Fe^{II}(CN)_6]^{2-}$, $H_3[Fe^{II}(CN)_6]^{-}$, and $H_4[Fe^{II}(CN)_6]$, which depends upon the acidity of the reaction mixture, concentration of $[Fe^{II}(CN)_6]^{4-}$, and the conditions employed [6]. However, there is no evidence of protonation of $[Fe^{III}(phen/bpy)_2(CN)_2]^{+}$ under the experimental conditions [7]. In order to rectify the outcomes (Fig. 3), we varied the concentration of protons (H^+) in the reaction mixture by adding HNO_3 and determined its effect on the rate constants. The pseudo-first order condition was maintained by keeping $[Fe^{II}(CN)_6{}^{4-}]$ in a 10-fold excess over $[Fe^{III}(phen/bpy)_2(CN)_2{}^{+}]$, and $[H^+]$ in excess over $[Fe^{II}(CN)_6{}^{4-}]$. We did not observe any change in '$\varepsilon.k_{obs}$'. This was obvious due to the zeroth order rate law in the first phase of the reaction(s). The value of k'_{obs} decreased gradually with increase in $[H^+]$ and became constant at the higher concentration of proton. Each reaction underwent similar effect (Fig. 4). The results confirm the formation and participation of $H[Fe^{II}(CN)_6]^{3-}$ and $H_2[Fe^{II}(CN)_6]^{2-}$in the reaction(s) because under the experimental conditions, the existence of $H_3[Fe^{II}(CN)_6]^{-}$ and $H_4[Fe^{II}(CN)_6]$ is not possible. The value of k'_{obs} became constant at the higher concentration of proton because of the constant concentration of the limiting reactant i.e., $[Fe^{II}(CN)_6]^{4-}$. The decrease in the value of k'_{obs} indicates that the rate-determining step involves free $[Fe^{II}(CN)_6]^{4-}$. The findings were confirmed by studying the effect of ionic strength on the rate constants.

Effect of ionic strength on the rate constants

The effect of ionic strength was studied by adding KNO_3 in the reaction mixture and maintaing the pseudo-first order condition at constant temperature in aqueous medium. The ionic strength was varied from 7.6 mM to 250 mM for each reaction and the rate constant was determined in each phase. The zeroth order rate constant ($\varepsilon.k_{obs}$) remained neutral and confirmed the zeroth order rate law in the first phase of each reaction (Fig. 5). The value of k'_{obs} decreased upon increasing the ionic strength. The plot of log k'_{obs} *vs* $\sqrt{I}/(1+\sqrt{I})$ yielded a negative slope and an intercept equivalent to the value of log k'_{obs} at zero ionic strength (Fig. 5). From the slope ($1.02\ z_A z_B$) of the plot (Fig. 5), we deduced the product of the charges on the reactive species ($z_A z_B$) that take part in the rate-determining step to form the activated complex. The slopes were –3.7 and –3.5 for the reaction between $[Fe^{III}(phen)_2(CN)_2]^{+}$ and $[Fe^{II}(CN)_6]^{4-}$, and, $[Fe^{III}(bpy)_2(CN)_2]^{+}$ and $[Fe^{II}(CN)_6]^{4-}$, respectively. The negative sign represents the electron-exchange between opposite charge carriers such as $[Fe^{III}(phen)_2(CN)_2]^{+}$ or $[Fe^{III}(bpy)_2(CN)_2]^{+}$ and $[Fe^{II}(CN)_6]^{4-}$. The value of the slope is around 4, which confirms the electron-exchange between $[Fe^{III}(phen)_2(CN)_2]^{+}$ or $[Fe^{III}(bpy)_2(CN)_2]^{+}$ and $[Fe^{II}(CN)_6]^{4-}$ in the rate-determining step of the reaction i.e., the second phase of the reactions. However, the decrease in the value of k'_{obs} upon increasing the concentration of proton in the reaction mixture confirms the oxidation of $H[Fe^{II}(CN)_6]^{3-}$ in the fast step of the reactions i.e., the first phase of the reactions.

CONCLUSION

The results of our studies enabled us to propose a common outer-sphere electron-exchange mechanism for the two reactions. Following rate-law was proposed for the reactions:

$$-\frac{d\left[Fe(II)\right]}{dt} = k_1 + k_2\left[Fe(III)\right]\left[Fe(II)\right]_T + \frac{k_3\left[Fe(III)\right]}{K_2\left[H^+\right]\left[Fe(II)\right]_T} \cdots\cdots\cdots\cdots (4)$$

According to Eqn. (4) the rate should be independent of the reactants in the first phase, and should be of first order with respect to each reactant in the second phase. Our results are in conformity with the rate law (Figs. 2-3). The conversion of free hexacyanoferrate(II) into mono and diprotonated species reduces the concentration of the reactive entity $[Fe^{II}(CN)_6{}^{4-}]$ that controls the rate-determining step and leads to the decrease in the value of the rate constant upon increasing $[H^+]$ and $[Fe^{II}(CN)_6{}^{4-}]$, (Figs. 3-4). If we plot k'_{obs} *versus* the reciprocal of $[H^+]$, and or, $[Fe^{II}(CN)_6{}^{4-}]$, the straight line should yield a +ve slope, which may be used to deduce k_3. Our results are consistent with the rate law (Fig. 6). From our resuts we calculated the values of the rate constants for each reaction as follows.

- k_1, k_2, and k_3 for $[Fe^{III}(phen)_2(CN)_2]^{+}$ + $[Fe^{II}(CN)_6]^{4-}$ reaction = 2.1×10^{-5} M s^{-1}, 1.63×10^{3} M^{-1} s^{-1}, and 2.94×10^{-8} M s^{-1} respectively at 298 ± 0.5 K
- k_1, k_2, and k_3 for $[Fe^{III}(bpy)_2(CN)_2]^{+}$ + $[Fe^{II}(CN)_6]^{4-}$ reaction = 1.1×10^{-4} M s^{-1} at 302 ± 0.5 K, 1.1×10^{3} M^{-1} s^{-1} at 302 ± 0.5 K, 2.34×10^{-8} M s^{-1} at 298 ± 0.5 K

We concluded from the results that the phen complex (0.80 V, [6]) has a high affinity of electron-exchange with hexacyanoferrate(II) (0.4 V, [6]) than that of bpy complex (0.74 V, [6]).

REFERENCES

1. R. Khattak, I. I. Naqvi, M. A. Farrukh, *J. Iran. Chem. Soc.,* **5,** 631 (2008).
2. R. Khattak, I. I. Naqvi, S. Summer, M. Sayed, *Arabian Journal of Chemistry,* (2016), DOI: https://doi.org/10.1016/j.arabjc.2016.05.007
3. R. Khattak, M. Nazir, S. Summer, M. Sayed, A. Minhaz, I. I. Naqvi, *Chemical Papers,* **72,** 883 (2018).
4. R. Khattak, M. Nazir, S. Summer, M. Sayed, A. Minhaz, I. I. Naqvi, *Chemical Papers,* **72,** 895 (2018).
5. S. Summer, I. I. Naqvi, R. Khattak, S. Gulzar, F. Reyaz, *J. Chem. Soc. Pak*., **38,** 384 (2016).
6. R. Khattak, Department of Chemistry, University of Karachi, Karachi, Pakistan, 2011.
7. A. A. Schilt, *J. Am. Chem. Soc.* **82,** 3000 (1960).
8. Sh. Zhan. Q. Meng. X. You. G. Wang, P.-J. Zheng, *Polyhedron,* **15,** 2655 (1996).
9. T.-H. Lu, H.-Y. Kao, D. I. Wu, K. C. Kong, C. H. Cheng, *Acta Cryst.* **C44,** 1184 (1988).
10. W. M. Reiff, R. E. Desimone, *Inorg. Chem.,* **12,** 1793 (1973).
11. J. R. Winkler, N. Sutin, *Inorg. Chem.,* **26,** 220 (1987).
12. T. Sagij, S. Aoyagui, *Bull. Chem. Soc. Jpn*., **49,** 1399 (1976).
13. M. F. A. Dove, J. G. Hallett, *J. Chem. Soc*. A, 1204 (1969).
14. H. Kobayashi. B. V. Agarwala, Y. Kaizu, *Bull. Chem. Soc. Jpn*., **48,** 465 (1975).
15. O. S. Esan. C. O. Aboluwoye. N. A. Oladoja, O. Bankole, *Int. J. Phys. Sci.*, **4,** 764 (2009).
16. O. S. Esan, C. O. Aboluwoye, N. A. Oladoja, J. Ige, O. Owoyomi, G. O. Ogunlusi, *Afr. J. Pure Appl. Chem*., **2,** 92 (2008).
17. A. Yamagishi, *Inorg. Chem.,* **21,** 1778 (1982).
18. S. Gou, F. Renz, Y. Fukuda, W. Linert, *Inorg. Chim. Acta*, **287,** 95 (1999).
19. D. F. Shriver, J. Posner, *J. Am. Chem. Soc*., **88,** 1672 (1966).
20. B. J. C. Lima, F. David, P. G. David, *J. Chem. Soc., Dalton Trans.,* 680 (1974).
21. S. Ferrere, *Inorg. Chim. Acta*, **329,** 79 (2002).
22. S. Ferrere, *Chem. Mater*., **12,** 1083 (2000).
23. V. Balzani, V. Carassiti, L. Moggi, *Inorg. Chem.,* **3,** 1252 (1964).
24. Y. Zimmermann, S. Spange, *New J. Chem*., **26,** 1179 (2002).
25. A. Taha, A. A. T. Ramadan, M. A. El-Behairy, A. I. Ismail, M. M. Mahmoud, *New J. Chem.,* **25,** 1306 (2001).
26. R. Lungwitz, M. Friedrich, W. Linert, S. Spange, *New J. Chem.,* **32,** 1493 (2008).
27. K. Harada, J. Yuzurihara, Y. Ishii, N. Sato, H. Kambayashi, Y. Fukuda, *Chem. Lett.,* 887 (1995).
28. A. Alousy, N. J. Blundell, J. Burgess, C. D. Hubbard, R. V. Eldik, *Transition Met. Chem*., **27,** 244 (2002).
29. M. J. Blandamer, J. Burgess, B. Shraydeh, *J. Chem. Soc., Faraday Trans.,* **89,** 531 (1993).
30. A. A. Schilt, *Anal. Chim. Acta,* **26,** 134 (1962).
31. A. A. Schilt, J. Bacon, *Anal. Chem*., **41,** 1669 (1969).
32. A. A. Schilt, J. W. Sutherland, *Anal. Chem*., **36,** 1805 (1964).
33. O. O. Soriyan, O. Owoyomi, J. Ige, *Transition Met. Chem.,* **33,** 121 (2008).
34. P. Cokie, J. E. Erman, *Biochim. Biophys. Acta*, **913,** 257 (1987).
35. O. O. Soriyan, J. Ige, A. O. Fadiran, O. Owoyomi, *J. Applied Sci.,* **5,** 773 (2005).
36. F. Sánchez, M. L. Moyá, A. Rodríguez, R. Jiménez, C. Gómez-Herrera, C. Yánes, P. López-Cornejo, *Langmuir,* **13,** 3084 (1997).
37. J. Benko, O. Vollárová, J. Burgess, P. López, *Transition Met. Chem.,* **25,** 674 (2000).
38. J. Benko, J. Burgess, P. L. Cornejo, O. Vollárová, *Croatica Chemica Acta* (CCACAA), **74,** 607 (2001).
39. M. J. Blandamer, J. Burgess, N. V. Reed, P. Wellings, *J. Inorg. Nucl. Chem.,* **43,** 3245 (1981).
40. J. Blandamer, J. Burgess, *J.C.S. Chem. Comm.,* **963,** (1978).
41. M. S. Matamoros-Fontenla, P. López-Cornejo, P. Pérez, R. Prado-Gotor, R. D. L. Vega, M. L. Moya, F. Sanchez, *New J. Chem.,* **39** (1998).
42. O. Horváth, K. L. Stevenson, *J. Photochem. Photobiol. A: Chem*., **120,** 185 (1999).
43. J. P. Birk, S. G. Kozub, *Inorg. Chem.,* **17,** 1186 (1978).
44. E. Pelizzetti, E. Mentasti, E. Pramauro, *Inorg. Chem*., **17,** 1181 (1978).
45. H. D. Takagi, N. Kagayama, M. Matsumoto, T. Tarumi, S. Funahashi, *J. Mol. Liq*., **65-66,** 277 (1995).
46. M. Matsumoto, T. Tarumi, K.-I. Sugimoto, N. Kagayama, S. Funahashi, H. D. Takagi, *Inorg. Chim. Acta,* **255,** 81 (1997).
47. R. Blake, K. J. White, E. A. Shute, *J. Biol. Chem.,* **266,** 19203 (1991).
48. T. Saji. T. Yamada, S. Aoyagui, *Bull. Chem. Soc. Jpn.,* **48,** 1641 (1975).
49. P. C. Wilkins, H. K. Jacobs, M. D. Johnson, A. S. Gopalan, *Inorg. Chem*., **43,** 7877 (2004).
50. X. Wang, D. M. Stanbury, *J. Phys. Chem. A*, **108,** 7637 (2004).
51. X. Wang, D. M. Stanbury, *Inorg. Chem.,* **45,** 3415 (2006).
52. X. Wang, D. M. Stanbury, *Inorg. Chem.,* **47,** 1224 (2008).
53. D. M. Kardel, H. B. Dunford, S. Alexandre, *Eur. J. Biochem.,* **194,** 259 (1990).
54. A.-M. Lambeir, H. B. Dunford, M. A. Pickard, *Eur. J. Biochem.,* **163,** 123 (1987).
55. H. Boardman, *J. Am. Chem. Soc.,* **75,** 4268 (1953).

56. B. B. Hasinoff, H. B. Dunford, *Biochemistry,* **9,** 4930 (1970).
57. M. L. Cotton, H. B. Dunford, *Can. J. Chem.*, **51,** 582 (1973).
58. G. Rabai, I. R. Epstein, *Inorg. Chem.,* **28** 732 (1989).
59. A. A. Abdel-Khalek, *Transition Met. Chem.*, **11,** 67 (1986).
60. G. Rabai, K. Kustin, I. R. Epstein, *J. Am. Chem. Soc.*, **111,** 8271 (1989).
61. M. A. Rawoof, J. R. Sutter, *J. Phys. Chem.*, **71,** 2767 (1967).
62. A. E. M. Abdel-Hady, *Transition Met. Chem.*, **33,** 887 (2008).

МЕХАНИЗЪМ НА РЕАКЦИИТЕ НА ОБМЕН НА ЕЛЕКТРОНИ МЕЖДУ СМЕСЕНИ ЛИГАНДНИ КОМПЛЕКСИ НА Fe(III) И ЦИАНО КОМПЛЕКС НА Fe(II)

Розина Хатак[1,2]*, Мухамад Суфаид Хан[3], Ифтихар Имам Накви[2]

[1] Департамент по химия, Женски университет Шахеед Беназир Бхуто, Пешавар, Пакистан
[2]Департамент по химия, Университет на Карачи, Карачи-75270, Пакистан
[3]Департамент по физикохимия, Институт по химия, Държавен университет Паулиста(UNESP)–Араракуара 14800-900, СП, Бразилия

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(Резюме)

В статията са изследвани реакциите на смесени лигандни комплекси на Fe(III) с цианиденлиганд. Синтезирани са смесени лигандни комплекси на Fe(III) с лиганди диимин и цианид, характеризиращи се с октаедрична геометрия и висока стабилност. За целта са модифицирани известни процедури. Синтезираните комплекси, Fe^{III}(фенантролин/бипиридил)$_2(CN)_2]^+$ са редуцирани от хексациано комплекса на Fe(II), който е известен с високата си стабилност и октаедрична геометрия. Редукцията се извършва във водна среда при постоянна йонна сила = 0.06. Напредването на реакциите се проследява спектрофотометрично чрез измерване на нарастването на абсорбцията с времето, т.е. образуването на [Fe^{II}(фенантролин/бипиридил)$_2(CN)_2$]. Установено е, че редукцията на смесените лигандни комплекси на Fe(III) става на два етапа. Първият етап на редукция на Fe(III) комплекса до неутрален Fe(II) комплекс е с кинетика от нулев порядък. Вторият етап е скоростоопределящ или бавен етап при редукцията на комплексите и електронният обмен е с обща кинетика от втори порядък. За прецизиране на резултатите и разграничаване на формите, участващи в скоростоопределящия етап (бавен етап) и тези, участващи в бързия етап е изучено влиянието на протоните и йонната сила върху скоростните константи във водна среда. Предложен е външно-сферен механизъм на електронния обмен между комплексите на Fe(III) and Fe(II).