

A Free Energy Relationship for the Reactions Involving Bis (dipicolinate) Cobaltate (III) and Various Pentacyanoferrate (II) - N - Heterocycle Complexes

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As velocidades de transferência de elétrons envolvendo a redução de bis (dipicolinato) cobaltato (III), $[\text{Co}(\text{dipic}_2)]^-$, através de uma série de complexos pentacianoferratos (II)-N-heterocíclicos, $[(\text{NC})_5\text{Fe L}]^{n-}$ (L = ácido pirazina-2,6-dicarboxílico nas formas mono e diprotionada, pirazina piridina e ácido isonicotínico) e a redução de $[\text{Co}(\text{dipic}_2)]^-$ e $[\text{Co}(\text{EDTA})]^-$ (EDTA = ácido etilenodiamino tetraacético) através do redutor $[(\text{CN})_5\text{Fe}^{\text{II}}\text{th}]^{3-}$ (th = tiouréia) foram investigadas em meio ácido perclórico aquoso. Os resultados cinéticos sugerem que todas as reações estudadas estão de acordo com a lei de velocidade de segunda ordem, $-\text{d}[\text{Fe}^{\text{II}}]/\text{dt} = k_2 [\text{Fe}^{\text{II}}][\text{Co}^{\text{III}}]$. A aplicação da teoria de Marcus aos parâmetros experimentais resulta numa energia de ativação de $117.15 \text{ kJ}\cdot\text{mol}^{-1}$ ($k_{11} = 3.0 \times 10^{-6} \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) para a reação de auto-troca eletrônica no sistema $[\text{Co}(\text{dipic})]^{-/ -2}$. Este valor é comparado com valores existentes na literatura para outros sistemas e discutido em termos de configuração de spin, barreira de Franck-Condon e capacidade acceptora π dos grupos aromáticos. A boa concordância entre as constantes de velocidade determinadas experimentalmente e aquelas calculadas através da teoria de Marcus, sugerem que as reações são adiabáticas, o que pode ser atribuído ao eficiente acoplamento eletrônico π dos anéis aromáticos nos pares iônicos formados durante o processo de transferência de elétrons.

Intermolecular electron - transfer rate involving the reduction of bis (dipicolinate) cobaltate (III), $[\text{Co}(\text{dipic}_2)]^-$, by a series of pentacyanoferrate (II)-N-heterocycle Complexes, $[(\text{NC})_5\text{Fe L}]^{n-}$ (L = pyrazine-2,6-dicarboxylic acid in their mono and diprotionated forms, pyrazine, pyridine and isonicotinic acid) and the reduction of $[\text{Co}(\text{dipic}_2)]^-$ (dipic = dipicolinate (pyridine-2,6-dicarboxylate) and $[\text{Co}(\text{EDTA})_2]^-$ (EDTA = ethylenediamine tetraacetic acid) by the reductant $[(\text{CN})_5\text{Fe}^{\text{II}}\text{th}]^{3-}$ (th = thiourea) have been investigated in aqueous perchloric acid media. The kinetic results suggest that the electron transfer for all species fit the second - order rate law, $-\text{d}[\text{Fe}^{\text{II}}]/\text{dt} = k_2 [\text{Fe}^{\text{II}}][\text{Co}^{\text{III}}]$. The application of the Marcus theory to the experimental parameters leads to an activation energy of $117.15 \text{ kJ}\cdot\text{mol}^{-1}$ ($k_{11} = 3.0 \times 10^{-6} \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) for the $[\text{Co}(\text{dipic})]^{-/ -2}$ self - exchange reaction. This electron-exchange rate value is compared with values for other systems reported in the literature and discussed in terms of the spin configurations, thermal Franck Condon factor, and the π acceptor capability of the aromatic groups. A good agreement between the experimentally determined electron transfer rate constants and the theoretical values calculated from the Marcus theory suggests that the outer-sphere reactions are in the adiabatic regime, which may be achieved by an efficient electronic coupling caused by a stacked π - π overlap of the aromatic moieties of the ion-pairs or the encounter complexes.

Key words: pentacyanoferrate (II), free energy.

Introduction

Kinetic studies involving oxidation of metallo-proteins by the oxidant bis (dipicolinate) cobaltate (III), $[\text{Co}(\text{dipic}_2)]^-$, have been extensively reported in the literature¹⁻⁵. Particularly, this oxidant was employed for the understanding of the electron-transfer reactivities in cytochrome C² and blue copper protein¹. Similarly, Sykes and co-workers⁵, reported a two phase electron reduction mechanism, observed in the kinetic of the interconversion of hemerythrin in their dioxy. and met. forms. In an attempt to obtain further information on the redox chemistry of this Co^{III} complex and to elucidate the total disagreement

among kinetic data reported in the literature^{1,2,6}, a study of the kinetics and mechanism of the reduction of $[\text{Co}(\text{dipic}_2)]^-$, by the series of pentacyanoferrate (II)-N-heterocycle complexes, $[(\text{NC})_5\text{Fe}^{\text{II}}\text{L}]^{n-}$ (L equals pyrazine-2,6-dicarboxylic acid in their mono and diprotionated forms, pyrazine, pyridine and isonicotinic acid) (Table 1) and the reductions of both, $[\text{Co}(\text{dipic}_2)]^-$ and $[\text{Co}(\text{EDTA})]^-$ (EDTA = ethylene diamine tetraacetic acid) by the reductant $[(\text{CN})_5(\text{th})]^{3-}$ (th = thiourea) was undertaken. Kinetic measurements were made in aqueous perchloric media and $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ electron exchange parameters were derived using Marcus theory⁷.

Table 1. Electronic spectra and formal redox potentials of the iron (II)/iron (III) complexes

Complexes	Medium ^a	λ max, nm (ϵ , L mol ⁻¹ cm ⁻¹)		E ^o , V ^b
		Fe(II)	Fe(III)	
I. [(NC) ₅ Fe(pyraz-2,6H) ₂] ^{2-/3-}	A	448 (4.5 x 10 ³) ^c		0.69 ^c
II. [(NC) ₅ Fe(pyraz-2,6-H)] ^{3-/4-}	B	512 (4.5 x 10 ³) ^c		0.60 ^c
III. [(NC) ₅ Fe(pyraz-2,6)] ^{4-/5-}	C	478 (4.5 x 10 ³) ^c	345 (shoulder) ^d 396 (shoulder)	0.56 ^c
IV. [(NC) ₅ Fe(pz)] ^{2-/3-}	C	455 (5.0 x 10 ³) ^e		0.55 ^h
V. [(NC) ₅ Fe(isonic)] ^{3-/4-}	C	420 (3.1 x 10 ³) ⁱ	360 (shoulder) ^d 416 (1.1 x 10 ³)	0.45 ^h
VI. [(NC) ₅ Fe(py)] ^{2-/3-}	C	365 (3.7 x 10 ³) ^e	368 (8.0 x 10 ⁴) ^f 414 (1.1 x 10 ³)	0.47 ^h
VII. [(NC) ₅ Fe(Th)] ^{2-/3-}	C	406 (3.2 x 10 ²) ^g	600 (2.3 x 10 ³) ^g	0.30 ^h

a. Legend: A = 0.1M HClO₄, B = Citrate buffer (pH = 3.0), C = 0.1M NaClO₄.

b. V vs NHE; c. ref. 11; d. This work; e. ref. 19; f. ref. 23; g. ref. 22; h. ref. 20; i. ref. 21.

Experimental

Abbreviation of Ligands – Pyraz-2,6 = pyrazine-2,6-dicarboxylate (C₆H₂N₂O₄), pyraz-2,6-H (pyraz-2,6-H₂) = mono and diprotonated forms of pyrazine-2,6-dicarboxylic acid; pz = pyrazine; py = pyridine; isonic = isonicotinate; dipic = dipicolinate (pyridine-2,6-dicarboxylate); EDTA = ethylene diamine tetraacetic acid; th = thiourea; dien = N-(2-aminoethyl)-1,2-ethanediamine; dpt = N-(3-amino-propyl)-1,3-propanediamine.

Reagents – Pyridine-2,6-dicarboxylic acid, pyrazine, pyridine-4-carboxylic acid and ascorbic acid were Merck reagent grade chemicals; sodium nitroprusside and cobalt nitrate were purchased from Riedel. All the above chemicals were used without further purification. Pyrazine-2,6-dicarboxylic acid was prepared as described in the literature from the decarboxylation of pyrazine-2,3,5-tricarboxylic acid⁹.

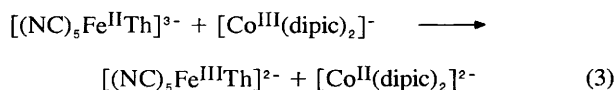
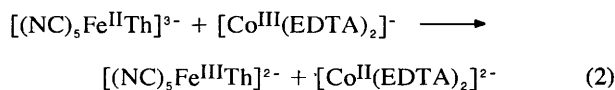
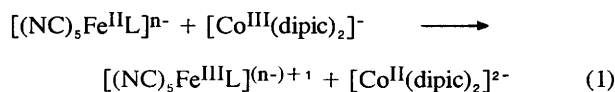
Synthesis – The complexes NH₄[Co(dipic)₂]²⁺, K[Co(EDTA).4H₂O]³⁻, Na₃[Fe^{II}(CN)₅NH₃].3H₂O¹⁰ were prepared according to previously published procedures. The complexes, I – VII¹¹⁻¹⁸ were prepared *in situ* from a freshly prepared solution of [Fe(CN)₅OH₂]³⁻. The resulting solution was spectrophotometrically and electrochemically characterized and the obtained data are in agreement with those reported in the literature (Table 1). Solutions of [Fe(CN)₅OH₂]³⁻ were obtained by aquation of [Fe(CN)₅NH₃]³⁻ according to previously published procedure^{14,16}.

Electrochemistry – Cyclic Voltammograms were recorded with a Bioanalytical System Inc. CV – 27 apparatus, equipped with an X – Y recorder (Houston Instruments, model Omnigraphic 100). The electrochemical cell employed was the standard three – electrode configuration: the gold working electrode and glassy carbon electrode, a Pt-wire auxiliary electrode, and the reference electrode (Ag/AgCl in saturated KCl). The potential in the Argon – scrubbed aqueous solutions of complexes I – VII (10⁻³M) containing 0.1M supporting electrolyte (HClO₄ or LiClO₄) were measured at scan rates ranging from 20 to 200 mV s⁻¹ at 25°C. Potentials were corrected to the normal hydrogen electrode (NHE) by adding 0.204 V to the measured potential. The half – wave potentials were taken as the average of the anodic and cathodic peak potentials of reversible (or quasi-reversible) cyclic voltammograms.

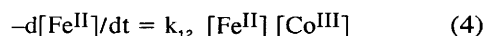
Kinetic Studies – Kinetic measurements and spectra were obtained using a UV/Visible Shimadzu UV-190 spectrophotometer equipped with thermostated (\pm 0.05°C) cell compartments and interfaced to an IBM XT computer. All runs were carried out under pseudo-first-order conditions employing at least a 10-fold molar excess of oxidant. The wavelengths of observation for the kinetics runs were at the maxima for the most absorbing species (Table I). All kinetics measurements were prepared using syringe-septa methods under atmosphere of vanadium-scrubbed argon. The kinetic runs for reactions involving complexes I and II were carried out at pH 3.00 (citrate buffer) and ionic strength 0.1M. The ionic strength was maintained at 0.1 M with LiClO₄ for reactions involving complexes III – VII. Plots of ln(A_t – A_∞) against time, derived from the absorbance data, were linear for at least 3 half-lives.

Results

The stoichiometries of overall oxidation reactions of complexes I – VII used in this study were determined by spectrophotometric titration monitored at the maxima for the most absorbing species (Table I). The numbers of moles reduced per mole of [(NC)₅Fe^{II}L]ⁿ⁻ was found as 1 : 1 ratio, eq.(1 – 3).



All the kinetic data obtained fit the second-order rate law shown by equation (4) for each of the species under study.



The values of the rate constants, together with the corresponding activation parameters, are summa-

Table 2. Summary of kinetic Parameters on the Reduction of $[Co(dipic)_2]^-$ by various Iron (II) Complexes.

Reductant	K_{12}^a	k_{12}^b $dm^3 \cdot mol^{-1} \cdot s^{-1}$	f_{12}^c	ΔH^\ddagger $kJ \cdot mol^{-1}$	ΔS^\ddagger $J \cdot K^{-1} \cdot mol^{-1}$	ΔG_{12}^\ddagger $kJ \cdot mol^{-1}$	$\Delta G_{12}^{o\ddagger}$ $kJ \cdot mol^{-1}$
I	8.5	0.7 ± 0.05^d	0.98	59.0 ± 3.51	-49.8 ± 3.43	74.5	-5.4
II	2.8×10^2	3.6 ± 0.2^e	0.86	58.6 ± 3.76	-36.4 ± 2.51	69.4	-13.8
III	1.1×10^3	9.2 ± 0.6	0.78	63.2 ± 3.55	-14.6 ± 2.72	67.4	-17.6
IV	2.0×10^3	11.4 ± 0.9	0.76	54.4 ± 3.64	-41.8 ± 2.42	66.5	-18.8
V	1.0×10^5	78.0 ± 3.8	0.54	60.7 ± 3.68	-2.9 ± 3.55	61.5	-28.4
VI	4.6×10^4	218.5 ± 12.5	0.56	32.2 ± 3.80	-90.8 ± 3.55	58.8	-26.4
VII	3.5×10^7	1120.0 ± 86.0	0.25	36.8 ± 3.22	-59.8 ± 1.42	54.8	-43.1

a. Calculated from electrochemical data (Table 1); b. Conditions unless otherwise stated: I = 0.1M NaClO₄; by using two-three fold excess of ligand in the kinetics experiments; c. Calculated from equations 6 and 7; d. Conditions: I = 0.1M; $[H^+] = 0.1 M HClO_4$; e. Conditions: I = 0.1M NaClO₄; pH = 3 (Citrate buffer).

Table 3. The Dependence of Second-order Rate Constants, k_{12} on pH, for the Reduction of $[Co(dipic)_2]^-$ by $[(NC)_5Fe(pyraz-2,6)]^{5-}$ at 25°C and I = 0.1M.

Complex	pH	$k_{12}(dm^3 \cdot mol^{-1} \cdot s^{-1})$
$[(NC)_5Fe(pyraz-2,6-H_2)]^{3-}$	1.0 ^a	0.68
$[(NC)_5Fe(pyraz-2,6-H)]^{4-}$	3.0 ^b	3.60
$[(NC)_5Fe(pyraz-2,6)]^{5-}$	6.5 ^c	9.20

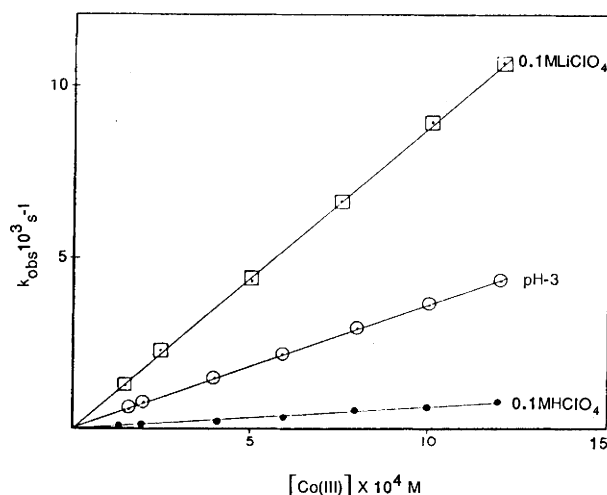
a. 0.1 M HCl₄; b. Citrate buffer; c. 0.1M LiClO₄.

ized in Table II. Detailed experimental kinetic data and results from calculation on the effects of electrostatic interaction on the rate constants are also available as supplementary material. The parameters obtained under these conditions were used in the formulation of a Marcus theory correlation. In addition, the dependence of the kinetic rates on the hydrogen ion concentration was studied at 25°C (Table III).

The kinetic dependence of the oxidation of $[(NC)_5Fe^{II}(pyraz-2,6)]^{5-}$ by $[Co(dipic)_2]^-$ on $[H^+]$ - According to Wieghardt and co-workers¹¹, the iron complexes can be found in the diprotonated $[(NC)_5Fe(pyraz-2,6-H_2)]^{3-}$, monoprotated $[(NC)_5Fe(pyraz-2,6-H)]^{4-}$ and deprotonated $[(NC)_5Fe(pyraz-2,6)]^{5-}$ forms, each species showing characteristic redox potential behavior and $d\pi(M) \rightarrow \pi^*(L)$ charge-transfer band (Table 1). Both the reducing ability and kinetic inertness of such species in aqueous solution make these species appropriate reactants for outer-sphere electron transfers reactions. A compilation of second order rate constants of the reactions of $[Co(dipic)_2]^-$ as a common oxidant and of iron complexes, is shown in Table 3. Figure 1 clearly shows the linear dependence of k_{obs} on $[Co^{III}]$ for diprotonated, monoprotated and deprotonated $[(NC)_5Fe^{II}]^n$ species in solution. Such reactivity differences are interpreted in terms of different driving forces of the Fe(II) complexes¹¹.

Analysis of Reaction Products - The reactional final products were separated by ion-exchange chromatography and revealed the presence of pentacyano-N-heterocycle iron (III) complexes identified by its characteristic absorption spectra in the 340-420 nm range (Table 4) in complete agreement with those reported in the literature^{22,23}. The pentacyano-N-heterocycles iron (III) complexes can be recovered quantitatively as the correspond-

ing iron (II) complex by using of ascorbic acid. The visible spectra from this species remain invariant over periods of at least 2 h.

**Figure 1:** Plot of $k_{obs}(s^{-1})$ versus $[Co(III)]$, M for the reaction of $[Co(dipic)_2]^-$ with complexes: $[(NC)_5Fe(pyraz-2,6-H_2)]^{3-}$ (●) $[(NC)_5Fe(pyraz-2,6-H)]^{4-}$ (○); and $[(NC)_5Fe(pyraz-2,6)]^{5-}$ (□) at 25°C.

Discussion

The inertness of the reductants and oxidant involved in this study suggests that the electron transfer reactions occur by an outer-sphere mechanism. It is clear from the spectroscopic identification of the final products that the first coordination sphere of the reactive species is unaffected during and after the electron transfer reaction has been taken. Effects of electrostatic interaction on the rate constants for the electron exchange reaction of $Co(dipic)_2^{1-}$ couple was estimated by the extensive use of mathematical models for charge correction described by Wherland and Gray²⁴. The corrected results are found to be negligible as compared with the estimates from the classical treatment of Marcus and Hush⁷ and uncorrected values for charge effects are being considered in discussing the rate constants in this work. The theories of Mar-

Table 4. Reactivity Ratio $(k_{12})_1/(k_{12})_2$ on the Reduction of $[\text{Co}(\text{dipic})_2]^-$ by $[(\text{NC})_5\text{Fe}(\text{L})]^{3-}$ Complexes at 25°C.

Complexes	$(k_{12})_1/(k_{12})_2^a$	$(k_{12})_1/(k_{12})_2^b$	$(k_{12})_1/(k_{12})_2$ (measured)
$[(\text{NC})_5\text{Fe}(\text{Th})]^{3-}/[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-H}_2)]^{3-}$	4.0×10^6	1.1×10^3	1.6×10^3
$[(\text{NC})_5\text{Fe}(\text{py})]^{3-}/[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-H}_2)]^{3-}$	5.3×10^3	55.6	311
$[(\text{NC})_5\text{Fe}(\text{pz})]^{3-}/[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-H}_2)]^{3-}$	2.4×10^2	13.5×10^3	16.7

a. Using the equation $\log(k_{12})_1 - \log(k_{12})_2 = 16.9(E_{(2)}^0 - E_{(1)}^0)$

b. Using the equation $(k_{12})_1/(k_{12})_2 = [(K)_1(f_{12})_1/(K)_2(f_{12})_2)]^{1/2}$

$(K)_n$ and $(k_{12})_n$ ($n = 1, 2$) are the equilibrium and rate constants for the reactions 1 and 2 respectively.

cus and Hush⁷ for explaining the rate constants of homogeneous outer-sphere electron-transfer reactions, establish a relationship (eq. 5) between the free energy of reaction (ΔG_{12}^\ddagger) and the free energies of activation for the cross reaction (ΔG_{12}^\ddagger), and the free energies of the self-exchange reactions (ΔG_{11}^\ddagger and ΔG_{22}^\ddagger) of the oxidant $[\text{Co}(\text{dipic})_2^-$ and the reductant (I – VII).

$$\Delta G_{12}^\ddagger = 0.5 \Delta G_{11}^\ddagger + 0.5 \Delta G_{22}^\ddagger + 0.5 \Delta G_{12}^\ddagger - 1.15 RT \log f_{12} \quad (5)$$

where eq. 5 was derived from:

$$k_{12} = (k_{11} k_{22} k_{12} f_{12})^{1/2} \quad (6)$$

$$\text{and} \quad \log f_{12} = (\ln k_{12})^{2/4} \log (k_{11} k_{22} / Z^2) \quad (7)$$

where k_{12} is the rate constant for the cross-reaction, k_{11} and k_{22} are the self-exchange rate constant of the reactants, k_{12} is the equilibrium constant for the cross-reaction, and Z the collision frequency for the uncharged species taken to be $10^{11} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Thus eq 5 can be used to calculate the free energy of activation for the self-ex-

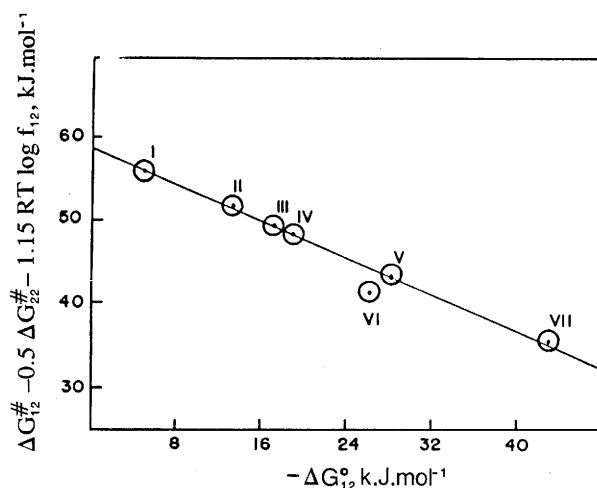


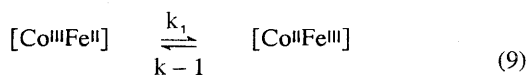
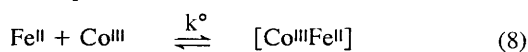
Figure 2. Relation between $(\Delta G_{12}^\ddagger - 0.5 \Delta G_{22}^\ddagger + RT \log f_{12})$ and the standard free energy of the reduction of $[\text{Co}(\text{dipic})_2]^-$ by various $(\text{NC})_5\text{Fe}^{\text{II}} \text{L}^n$ complexes. (I) $[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-H}_2)]^{3-}$; (II) $[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-H})]^{4-}$; (III) $[(\text{NC})_5\text{Fe}(\text{pyraz-2,6-})]^{5-}$; (IV) $[(\text{NC})_5\text{Fe}(\text{pz})]^{3-}$; (V) $[(\text{NC})_5\text{Fe}(\text{isonic})]^{4-}$; (VI) $[(\text{NC})_5\text{Fe}(\text{py})]^{3-}$; (VII) $(\text{NC})_5\text{Fe}(\text{Th})]^{3-}$.

change reaction for the oxidant. ΔG_{11}^\ddagger , from the rate and equilibrium data of Table 2, and the free energy of activation for the self-exchange reaction for the reductant, ΔG_{22}^\ddagger , which corresponds to $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple (I – VII). This latter value has been taken to be very similar to that of self-exchange free energy for the complex of $[(\text{NH}_3)_5\text{Ru}(\text{pyraz-2,6-H}_2)]^{3+/2+}$,¹¹ and has been reported as $35.81 \text{ kJ} \cdot \text{mol}^{-1}$, which corresponds to a self-exchange rate constant of $3.2 \times 10^6 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 25°C and $I = 0.1 \text{ M}$ upon comparisons of the self-exchange rate constant of $[(\text{CH}_3)_5\text{Ru}(\text{Py})]^{3+/2+}$ and $[(\text{NC})_5\text{Fe}(\text{Py})]^{2+/3-}$ which are found to be very similar¹⁵. A plot of $(\Delta G_{12}^\ddagger - 0.5 \Delta G_{22}^\ddagger + 1.15 RT \log f_{12})$ against ΔG_{12}° for reactions involving complexes I – VII and oxidant $[\text{Co}(\text{dipic})_2]^{1-}$ shows a slope of 0.54 ± 0.05 in excellent agreement with the expected value of 0.5 from eq. 5 (Figure 2). From the intercept in figure 2, the value of free energy of activation, ΔG_{11}^\ddagger , was found to be $117.15 \text{ kJ} \cdot \text{mol}^{-1}$ which corresponds to a self-exchange rate constant k_{11} of $3.0 \times 10^{-8} \text{ dm}^3 \cdot \text{mol}^{-1}$ for the couple $[\text{Co}(\text{dipic})_2]^{1-/2-}$.

This value is in complete disagreement with Gray and coworkers^{1,2} reported value of $4 \times 10^{-1} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ which has been derived from kinetic data for the reaction of $[\text{Co}(\text{dipic})_2]^-$ with $[\text{Fe}(\text{EDTA})]^{2-}$. However, such dramatic discrepancy has originated from the conventional electrochemical estimate of redox potential, 0.40 V ,² for $[\text{Co}(\text{dipic})_2]^{1-/2-}$. Williams and Yandell's⁶ value of 0.747 V was found by using potentiometric titration method, and $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ as electron mediator which corroborates very well with Wiegand's²⁵ estimate of 0.745 V from cyclic voltammetry with gold working electrode. By this way, by using the correct value for the redox potential of 0.747 V ,²⁵ for $[\text{Co}(\text{dipic})_2]^{1-/2-}$ couple, and adopting values for the self-exchange rate constant k_{22} of $3.10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ²⁴ for $[\text{Fe}(\text{EDTA})]^{1-/2-}$, k_{12} of $2.3 \times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,^{1,2} for the cross reaction of $[\text{Fe}(\text{EDTA})]^{1-/2-}$ and $[\text{Co}(\text{dipic})_2]^-$ and by using $E^\circ = 0.12 \text{ V}$ ²⁴ for $[\text{Fe}(\text{EDTA})]^{1-/2-}$, the self-exchange rate constant evaluated by the treatment reported previously^{1,2} was reestimated as being $7.0 \times 10^{-6} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ which agrees fairly well with our value.

Additional, indirect support for results obtained from this work, are found from self-exchange rate constant k_{11} of $7.0 \times 10^{-10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for $[\text{Co}(\text{dien})(\text{dipic})]^{+/0}$ and k_{11} of $1.5 \times 10^{-8} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for $[\text{Co}(\text{dpt})(\text{dipic})]^{+/0}$ couples by using $[(\text{NH}_3)_5\text{Ru}(\text{pyraz-2,6-H}_2)]^{2+}$ as reductor at 25°C and ionic strength, I of 0.1 M (where dien = N-(2-aminoethyl)-1,2-ethanediamine and dpt = N-(3-aminopropyl) 1,3 propanediamine)¹¹. This system may also be compared with structurally, similar, $[\text{Co}(\text{dien})(\text{pyraz-2,6})]^{+/0}$ and $[\text{Co}(\text{dpt})(\text{pyraz-2,6})]^{+/0}$. The cobalt

self-exchange rate constants of $3.4 \times 10^{-3} \text{ dm}^3 \cdot \text{mol}^{-1}$ for the former and $0.7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for the later, are much higher¹¹ and it may be accounted for in part by consideration of the energy for the inner sphere reorganization being slightly lower in good π acceptor ligand like pyraz-2,6. The differences in π acceptor capabilities may reflect by the changes in metal-ligand reorganization of the ground-state reactants in forming the Franck-Condon activated complex and consequently be correlated with the electron-exchange parameters¹¹. Considerations have been given to those reactions in which a set of the iron (II) complex possesses the same negative charge (complexes I, IV, VI and VII). For these systems, it seems reasonable to assume that there is no contribution of a work term to bring together the reactants and to separate the products. So the coulombic work term in the electron-transfer and self-exchange processes in similarly charged reactants partially cancel each other, or are negligibly small in cross reaction and self-exchange reactions given the following proposed mechanism (eq. 8 – 10).

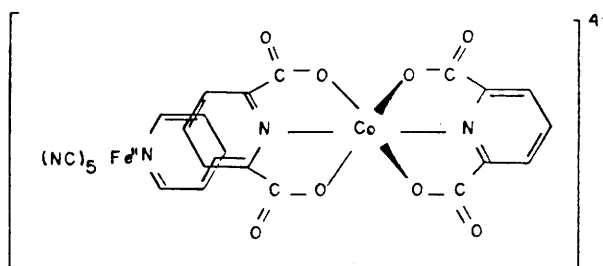


We must now decide which step is the rate-determining. To provide an appropriate answer to the question, two plausible possibilities are to be considered in this analysis. The first one is based on the assumption that dissociation and spin change at the cobalt (II) center on eq. 10 is the rate-determining step. To be more consistent with such assumption, the observed rate constant should be expressed as, $k_{12} = k \cdot k_2$, where $K = k_1 / k_{-1}$. Under this condition, the difference of reactivities between the pentacyanoferrate (II) complexes and $[\text{Co}(\text{dipic})_2]^-$ should vary linearly as K values increase, assuming a constant value of k_2 in the related series of complexes. The resulting calculated and found values of rate constant ratio are given in Table 5 and the complete lack of agreement found among the calculated and found values, rules out this possibility. Finally, it is also possible to assume that the rate determining step is the electron transfer described in eq. 9. If this is true, a $K^{1/2}$ dependence on the reaction rate (k_{12}) can be analysed by using the Marcus cross relation for outer-sphere electron-transfer reactions (eq. 6), assuming the electron self-exchange rate constant to be reasonably constant for a series of Fe(II)/Fe(III) complexes. The good agreement between the theoretical and the experimental value, corroborates the assignment of the outer-sphere electron-transfer in eq. 9 as the rate-determining step. It is instructive to compare the resulting analyses with that proposed for a thermodynamically unfavorable reaction involving $[\text{Co}(\text{EDTA})]^-$ and $[\text{Fe}(\text{CN})_6]^{4-}$ which has been assigned to be an outer-sphere electron-transfer reaction²⁶. It is also possible to calculate the cross-reaction rate constant for $[\text{Co}(\text{EDTA})]^-$ (eq. 2) and $[\text{Co}(\text{dipic})_2]^-$ (eq. 3) with the common reductor $[(\text{CN})_5\text{Fe}(\text{Th})]^{3-}$ by using the self-exchange rate constants $k_{11} = 3.0 \times 10^{-8} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for $[\text{Co}(\text{dipic})]^{1-/2-26}$ (this work) and²⁶ $k_{11} = 3.2 \times 10^{-7} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for $[\text{Co}(\text{EDTA})]^{1-/2-}$. The calculated result, $k_{12} = 940 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for eq. 2 and $k_{12} = 4.7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for eq. 3 are in good agreement with the experimental values $k_{12} = 1.120 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $k_{12} = 1.7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. This analysis gives a consistent picture supporting the outer-sphere

Table 5. Pseudo first-order rate constants for the reduction of $[\text{Co}(\text{dipic})_2]^-$ by various $[(\text{NC})_5\text{Fe}(\text{L})]^{n-}$ complexes ($I = 0.1\text{M NaClO}_4$). Reductant: $[(\text{NC})_5\text{Fe}(\text{pyraz-2,6})]^{5-}$; $[\text{Fe}(\text{II})] = 2.5 \times 10^{-5} \text{ M}$, with three-fold excess of L .

t, °C	$10^4 [\text{Co}(\text{III})], \text{M}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$
25	1.5	1.3
25	2.5	2.3
25	5.0	4.3
25	7.5	6.6
25	10.0	8.9
25	12.0	10.6
20	6.9	3.8
25	6.9	6.0
30	6.9	9.3
35	6.9	14.2
40	6.9	21.4

electron-transfer step (eq. 9) to be rate-determining. Since the adiabaticity factor in eq. 6 is set to be unity, the above agreement strongly supports an adiabatic regime for the reaction involving Co(III) and Fe(II)²⁷. Gray and coworkers^{1,2} have attempted to rationalize the efficient electron transfer processes found in metalloprotein – $[\text{Co}(\text{dipic})_2]^-$ system on the basis of extensively π – electrons coupling through the pyridine ring and aromatic moieties on the protein surface. By using different redox systems, Chaudhuri and Sigel²⁸, Wieghard and coworkers^{11,29}, have shown that a stacked structure formed by aromatic ligands of the ion pair formed during the electron transfer reaction, allows a sufficient degree of coupling between oxidant and reductant. A stacked structure was attributed to the ion pair $\{[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyraz-2,6-H}_2)]/[\text{Co}(\text{dien})(\text{pyraz-2,6})]^{+}\}$. As has been the case for the reported systems, a comparison seems to be reasonable for the present systems.



Finally, to our surprise, the rate for the pyridine derivative is particularly high relative to the other reductants. In addition to this fact one notes that the enthalpy of activation for this reductant is ca. $2\text{g kJ} \cdot \text{mol}^{-1}$ less than the other aromatic N-heterocyclic complex (see table 2). On the other hand, the entropy of activation has a relatively negative value. This fact is at least quantitatively consistent with the formation of a somewhat associative precursor complex in the $[(\text{NC})_5\text{Fe}(\text{Py})]^{3-}$ complex.

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Supplementary Material Available

Listing of detailed kinetic data on the outer-sphere reduction of $[\text{Co}(\text{dipic})_2]^-$ by complexes I-VII and reduction of $[\text{Co}(\text{EDTA})]^-$. A table listing the effects of electrostatic interaction on the rate constants for the electron exchange reactions of $[\text{Co}(\text{dipic})_2]^{1-/2-}$ couple is also available. All upon request.