Table I. Statistical Factors for Successive Stability Constants

ligand type and coord symm	K_1/K_2	K_2/K_3
unidentate		
octahedral	2.40	1.88
tetrahedral/square planar	2.67	2.25
bidentate		
octahedral	4.80	9.38
tetrahedral	12	
square planar	8	
terdentate		
octahedral		
facial	16	
meridional	24	
facial or meridional	40	

ligand leaves only five edges available for a second bidentate ligand. Hence, $K_1/K_2 = (12/1)/(5/2) = 4.8$. An additional statistical problem emerges when K_2/K_3 is calculated in that a third ligand cannot add at all if the second ligand is trans to the first. Of the five positions available for addition of the second ligand, four are cis and one is trans. In computing K_2/K_3, the number of available edges for an incoming ligand must be taken as the average number of edges available in the two possible bis complexes.[10] Hence, $K_2/K_3 = (5/2)/(0.8/3) = 9.38$. The extension of this method to terdentate ligands in octahedral symmetry is straightforward. Results of calculations for a number of common examples are presented in Table I.

The method presented here is extremely simple and leads to results identical with those obtained by the application of symmetry and isomer effects. The importance of taking into account statistical effects in the evaluation of thermodynamic data is clear when one considers that, in relatively simple systems, such factors may be as large as 40.

---

(10) An earlier analysis (Sen, B. *Anal. Chim. Acta* **1962**, *27*, 515) of bidentate ligands in square-planar symmetry has been criticized by Chung. However, it should be pointed out that that paper also contains a discussion of bidentate ligands in octahedral symmetry, which leads to conclusions identical with those presented here.

Contribution from the Cátedra de Química Inorgánica,
Facultad de Química, Montevideo, Uruguay,
and the Department of Chemistry, State University
of New York, Stony Brook, New York 11794

Electron-Transfer Reactions of Ion Pairs: Reduction of Various (Carboxylato)pentaamminecobalt(III) Complexes by Hexacyanoferrate(II)

Eduardo Kremer, Gisela Cha, Marta Morkevicius,
Madeleine Seaman, and Albert Haim*

Received December 8, 1983

The importance of measuring rates of electron-transfer reactions in the intramolecular mode has been emphasized repeatedly.[1] In previous publications we reported both inner-sphere[2,3] and outer-sphere[4,5] internal electron-transfer reactions involving positively charged (pyridine)pentaamminecobalt(III) and negatively charged hexacyanoferrate(II) complexes. For the inner-sphere reactions, the relative orientation of the cobalt(III) and iron(II) centers is firmly established[3] and the effects of electronic[2] and geometric[3] factors can be ascertained. However, for outer-sphere reactions, because of the lability of the ion pairs, the relative orientation of cation and anion, when at least one of these does not possess octahedral symmetry, is unknown. Under these circumstances, indirect criteria[3] must be invoked to obtain information about the detailed pathway for the electron transfer and it becomes important to accumulate kinetic data for first-order, outer-sphere reactions. In the present paper we report such data for the reduction of a variety of (carboxylato)pentaamminecobalt(III) complexes by hexacyanoferrate(II). By utilizing relatively high concentrations of the iron reagent, we have been able to measure the ion-pair formation constants (eq 1) and the rate constants for internal electron transfer within the ion pairs (eq 2).

$$\mathrm{Co(NH_3)_5O_2CR^{2+} + Fe(CN)_6^{4-} \underset{}{\overset{Q_{IP}}{\rightleftharpoons}} Co(NH_3)_5O_2CR^{2+}|Fe(CN)_6^{4-}} \quad (1)$$

$$\mathrm{Co(NH_3)_5O_2CR^{2+}|Fe(CN)_6^{4-} \xrightarrow{k_{et}} Co(NH_3)_5O_2CR^{+}|Fe(CN)_6^{3-}} \quad (2)$$

Experimental Section

Materials. The perchlorate salts of the cobalt(III) complexes were synthesized by standard procedures.[6,7] Each complex was recrystallized several times from water. The purification of the water and of the lithium perchlorate was described previously.[4] All other chemicals were of reagent grade and were used as received.

Kinetic Measurements. Solutions containing the desired concentrations of the cobalt(III) complex, ascorbic acid, sodium ethylenediaminetetraacetate (Na_2EDTA), Tris buffer, and lithium perchlorate were prepared and brought to the desired temperature. The desired volume of a freshly prepared solution of hexacyanoferrate(II) was added, and the resulting solution was treated by one of two alternative procedures. For the experiments with $Co(NH_3)_5O_2CCH_3^{2+}$ performed at Stony Brook, the resulting solution was poured into a spectrophotometric cell that was then placed in the modified[8] water-filled cell compartment of a Cary 17 spectrophotometer. A recording of the absorbance at 500 nm vs. time was obtained. For the experiments with the benzoate and nitrobenzoate complexes performed in Montevideo, the resulting solutions were kept in a constant-temperature bath. At the desired time intervals, aliquots were withdrawn and their absorbances at 500 nm were measured in a Beckman DB spectrophotometer. First-order rate constants, k_{obsd}, were obtained by linear least-squares fitting of $\ln (A_t - A_\infty)$ to t. A_t and A_∞ are the absorbances of the solution at time t and after 10 half-lives, respectively.

Results and Discussion

The kinetic measurements of the $Co(NH_3)_5O_2CR^{2+}$–$Fe(CN)_6^{4-}$ reactions were carried out in the presence of $EDTA^{2-}$ and ascorbic acid. The addition of $EDTA^{2-}$ serves to sequester the free cobalt(II) released upon reduction of the cobalt(II) complexes and thus prevents the precipitation of cobalt(II) hexacyanoferrate(II).[8] Ascorbic acid reduces hexacyanoferrate(III) very rapidly[9] and therefore serves to keep the iron complex in the +2 oxidation state and at constant concentration. Under these circumstances, the disappearance of cobalt(III) obeys first-order kinetics even when the $Fe(CN)_6^{4-}$ is not in excess with respect to the initial concentration of the cobalt(III) complex.[9] Moreover, the rapid reduction of $Fe(CN)_6^{3-}$ by the added ascorbic acid prevents the occurrence

---

* To whom correspondence should be addressed at the State University of New York.

(1) Haim, A. *Pure Appl. Chem.* **1983**, *55*, 89.
(2) Jwo, J. J.; Gaus, P. L.; Haim, A. *J. Am. Chem. Soc.* **1979**, *101*, 6189.
(3) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679.
(4) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.
(5) Miralles, A. J.; Szecsy, A. P.; Haim, A. *Inorg. Chem.* **1982**, *21*, 697.
(6) Sebera, D. K.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1785.
(7) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.
(8) Gaswick, D. G.; Haim, A. *J. Am. Chem. Soc.* **1974**, *96*, 7845.
(9) Rosenhein, L.; Speiser, D.; Haim, A. *Inorg. Chem.* **1974**, *13*, 1571.

Table I. Ion-Pair Formation Constants and Internal Electron-Transfer Rate Constants for Reactions of $Fe(CN)_6^{4-}$ with $Co(NH_3)_5L^{2+}$ [a]

L	10^4k_{et}, s^{-1}			$10^{-2}Q_{IP}$, M^{-1}		
	25 °C	30 °C	35 °C	25 °C	30 °C	35 °C
acetate	3.7 ± 0.2		22 ± 1	3.0 ± 0.4		2.2 ± 2
benzoate	6.2 ± 0.3	9.6 ± 0.2	20 ± 1	2.4 ± 0.3	3.0 ± 0.3	2.3 ± 2
o-nitrobenzoate	27.6 ± 0.8	87 ± 5	120 ± 5	2.8 ± 0.2	1.7 ± 0.2	3.1 ± 2
m-nitrobenzoate	9.1 ± 0.3	13.8 ± 0.6	31 ± 1	1.5 ± 0.1	2.0 ± 0.2	2.5 ± 0.2
p-nitrobenzoate	7.6 ± 0.2	20 ± 1	29 ± 1	2.9 ± 0.2	2.2 ± 0.3	4.3 ± 0.3

[a] $[Co(NH_3)_5L^{2+}] = (1-2) \times 10^{-3}$ M, [ascorbic acid] $= 5.0 \times 10^{-3}$ M, $[EDTA^{4-}] = 3.1 \times 10^{-3}$ M, and pH 8.0.

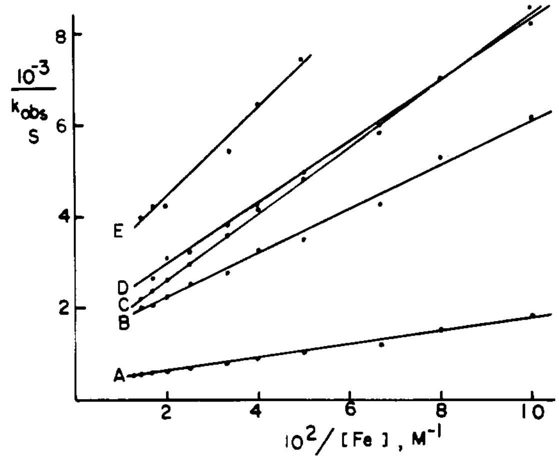

Figure 1. Double reciprocal plot ($1/k_{obsd}$ vs. $1/[Fe(II)]$) for reduction of various (carboxylato)pentaamminecobalt(III) complexes by hexacyanoferrate(II) at 25 °C, pH 8.0, $[EDTA^{2-}] = 3.1 \times 10^{-3}$ M, [ascorbic acid] $= 5.0 \times 10^{-3}$ M, $\mu = 0.10$ M, $[Co(III)] = (1-2) \times 10^{-3}$ M. Complexes: A, *o*-nitrobenzoate; B, *p*-nitrobenzoate; C, *m*-nitrobenzoate; D, benzoate; E, acetate.

of the reaction between $CoEDTA^{2-}$ and $Fe(CN)_6^{3-}$,[9] a reaction that interferes with $Co(III)-Fe(CN)_6^{4-}$ reactions[5,9] when the latter ones are rather slow as is the case in the present system.

The kinetic results obtained in the present work parallel those obtained earlier[5] with the analogous (pyridine)pentaamminecobalt(III) complexes. Values of $1/k_{obsd}$ vs. $1/[Fe(CN)_6^{4-}]$ are plotted in Figure 1. It will be seen that the results for every complex conform to eq 3, the characteristic

$$k_{obsd} = \frac{k_{et}Q_{IP}[Fe(CN)_6^{4-}]}{1 + Q_{IP}[Fe(CN)_6^{4-}]} \tag{3}$$

functional dependence that obtains when there is strong association between the reactants. Values of k_{obsd} vs. $[Fe(CN)_6^{4-}]$ were treated by nonlinear least squares to obtain values of k_{et} and Q_{IP} for each complex. The resulting values, given in Table I, reproduce the experimental results quite well (compare solid curves and experimental points in Figure 1).

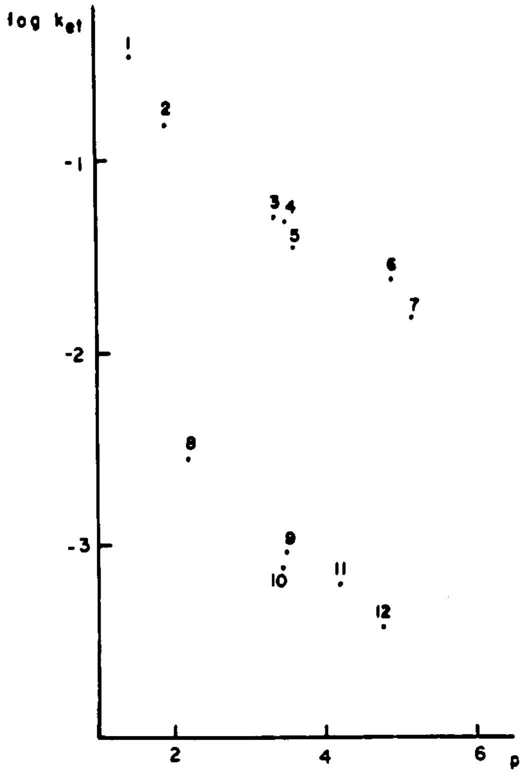

Figure 2. Rate constants (k_{et}) for internal electron transfer within $Co(NH_3)_5L^{n+}|Fe(CN)_6^{4-}$ ion pairs vs. pK_a of HL: 1,3-cyanopyridine; 2, 4-cyanopyridine; 3, nicotinamide; 4, *N*-methyl-4,4′-bipyridinium; 5, isonicotinamide; 6, 4,4′-bipyridine; 7, pyridine; 8, *o*-nitrobenzoate; 9, *m*-nitrobenzoate; 10, *p*-nitrobenzoate; 11, benzoate; 12, acetate.

Values of Q_{IP} at 25 °C and 0.10 M ionic strength fall into the range $(1.5-3.0) \times 10^2$ M^{-1}. The value calculated from eq 4 and 5[5] with the radii of $Fe(CN)_6^{4-}$ and $Co(NH_3)_5O_2CR^{2+}$

$$K_0 = \frac{4Na^3}{3000}\exp(-U(a)/RT) \tag{4}$$

$$U(a) = Z_1Z_2e^2/Da(1 + \kappa a) \tag{5}$$

taken as 4.5×10^{-8} and $\sim 5 \times 10^{-8}$ cm^{10} is 44 M^{-1} at 25 °C and ionic strength 0.10 M. Measured values of Q_{IP} are consistently higher[3-5,8] (factors of 3–5) than those calculated from eq 4 and 5 for ion pairs formed between pentaamminecobalt(III) complexes and $Fe(CN)_6^{4-}$. Perhaps, hydrogen bonding between the ammonia N on Co(III) and the cyanide N on Fe(II) adds to the already favorable Coulombic interaction between the cobalt and iron complexes.[3]

The rate constants for internal electron transfer within the ion pairs fall into a relatively narrow range, $(3.7-27.6) \times 10^{-4}$ s^{-1} at 25 °C, and vary inversely with the pK_a of the carboxylic acid bound to the cobalt(III) center (see Figure 2). The analogous electron-transfer reactions of the ion pairs $Fe(CN)_6^{4-}|Co(NH_3)_5L^{3+}$, where L is a pyridine derivative, also follow a similar trend; namely, as the pK_a of the protonated pyridine increases, k_{et} decreases. Previously, the reductions of various pyridine complexes of $Co(en)_2Cl^{2+}$ by iron(II)[11] and of various (pyridine)- and (carboxylato)pentaamminecobalt(III) complexes by $Ru(NH_3)_6^{2+}$ [12] were found to conform to similar patterns. The trends can be rationalized by considering the thermodynamic and intrinsic barriers for electron transfer. For a series of related ligands bound to the petaamminecobalt(III) moiety, it is expected[13] that the reduction potential of the cobalt(III) center will increase with decreasing σ-donor strength of the sixth ligand. It is reasonable[11,13] to estimate the σ-donor strength from the pK_a of the conjugated protonated

---

(10) The radius for $Co(NH_3)_5O_2CR^{2+}$ is calculated from $0.5(d_1d_2d_3)^{1/3}$, where d_1, d_2, and d_3 are the diameters along the three principal axes, and represents the radius equivalent to the sphere of equal volume.

(11) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.

(12) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(13) Phillips, C. S. G.; Williams, R. J. P. "Inorganic Chemistry"; Oxford University Press: New York, 1966; Vol. II, p 312.

Table II. Comparison of Rate Constants (25 °C) for Reductions by Fe(CN)$_6^{4-}$ and Ru(NH$_3$)$_6^{2+}$

oxidant	k_{Fe}, s^{-1}	k_{Ru},[a] s^{-1}	k_{Ru}/k_{Fe} obsd[b]	k_{Ru}/k_{Fe} calcd[c]
Co(NH$_3$)$_5$O$_2$CCH$_3^{2+}$	3.7×10^{-4}	0.10	2.8×10^2	2.2×10^2
Co(NH$_3$)$_5$py^{3+}	1.5×10^{-2} [d]	6.56[e]	4.4×10^2	1.7×10^2
Ru(NH$_3$)$_5$py^{3+}	9.7×10^3 [d]	4.5×10^6 [d]	4.6×10^2	1.7×10^2

[a] Calculated from k_{obsd}/Q_{IP}, where k_{obsd} is the measured second-order rate constant and Q_{IP} is the association constant between ruthenium and cobalt complexes calculated from eq 4 and 5. [b] Ratio of first-order rate constants given in columns 2 and 3. [c] Calculated from the Marcus relationship; see text. [d] Reference 4. [e] Reference 12.

ligand. Therefore, the observed increase in k_{et} with decreasing pK_a can be ascribed, at least in part, to the increased reduction potential of the cobalt(III) center.[14] Turning to a consideration of the intrinsic barrier, it must be recognized that, in the inner-sphere reduction of cobalt(III)[15] and chromium(III)[16] complexes, outward motion of the ligands along the z axis obtains in order to bring down the energy of the d_{z^2} orbital that accepts the electron. Such motion, part of the inner-shell reorganization energy, depends on the σ-donor ability of the ligands.[11] As the σ-donor strength increases, more energy is necessary for outward motion and the rate constant decreases. It was noted[11] that the above treatment does not depend on whether the reaction is inner sphere or outer sphere and that the σ-bonding theory of nonbridging ligand effects[17] is also applicable to outer-sphere reactions. Therefore, the observed increase in k_{et} with decreasing pK_a of the carboxylate ligand (which measures the σ-bonding strength of the ligand) can be ascribed, at least in part, to the intrinsic barrier. Whether the thermodynamic or the intrinsic barrier is more important in governing the observed trends cannot be ascertained because the reduction of the cobalt(III) complexes is irreversible and thus their reduction potentials are not known.

It is instructive to compare the rate constant for the reduction of Co(NH$_3$)$_5$O$_2$CCH$_3^{2+}$ by Fe(CN)$_6^{4-}$ with the corresponding value for the reduction by Ru(NH$_3$)$_6^{2+}$. The pertinent data are listed in Table II together with the values for the reductions of Co(NH$_3$)$_5$py^{3+} and Ru(NH$_3$)$_5$py^{3+} by Fe(CN)$_6^{4-}$[4] and Ru(NH$_3$)$_6^{2+}$.[12] The measured rate constants for reductions by Fe(CN)$_6^{4-}$ correspond to the elementary first-order processes for internal electron transfer within the ion pairs. In contrast, the measured rate constants for reductions by Ru(NH$_3$)$_6^{2+}$ are composite constants ($k_{et}Q_{IP}$) that include the desired rate constants for internal electron transfer and the ion-pair formation constant. Therefore, values of k_{et} for the reductions by Ru(NH$_3$)$_6^{2+}$ were calculated from the measured[4,12] second-order rate constants and the values of Q_{IP} (0.21, 0.10, 0.16 M^{-1}) estimated by utilization of eq 4 and 5. It will be seen (column 4 of Table II) that the ratio of the rate constants for internal electron transfer in Ru(NH$_3$)$_6^{2+}$ and in Fe(CN)$_6^{4-}$ reactions are independent of the nature of the oxidant. This is the expected result if the three reactions under consideration obey the Marcus relationship since the properties that depend upon the identity of the oxidant cancel out when ratios are taken. In fact, the ratio can be calculated from the known reduction potentials[18,19] and rate constants for self-exchange[18,20,21] of the Fe(CN)$_6^{3-/4-}$ and Ru(NH$_3$)$_6^{3+/2+}$ couples. The results of the calculations are listed in column 5 of Table II, and it will be seen that they are in excellent agreement with observed values (column 4). It is noteworthy that the calculation is equally successful for oxidants that are σ-electron acceptors (Co(NH$_3$)$_5$O$_2$CCH$_3^{2+}$ and Co(NH$_3$)$_5$py^{3+}) and for Ru(NH$_3$)$_5$py^{3+}, a π-electron acceptor (in all cases the reductants are π-electron donors). The agreement between observed and calculated ratios indicates that the electronic factors[22] in the exchange and cross-reactions are similar and, banning some fortuitous cancellation, that all of these electron-transfer reactions proceed at or near the adiabatic regime.

Acknowledgment. The research carried out at Stony Brook was supported by the National Science Foundation under Grant CHE 8203887. The research carried out in Montevideo was initiated in 1979 while A.H. was a Fulbright lecturer at the University of Uruguay.

Registry No. Fe(CN)$_6^{4-}$, 13408-63-4; Co(NH$_3$)$_5$O$_2$CCH$_3^{2+}$, 16632-78-3; Co(NH$_3$)$_5$O$_2$CC$_6$H$_5^{2+}$, 30931-77-2; Co(NH$_3$)$_5$O$_2$C-*o*-C$_6$H$_4$NO$_2^{2+}$, 62714-55-0; Co(NH$_3$)$_5$O$_2$C-*m*-C$_6$H$_4$NO$_2^{2+}$, 62714-56-1; Co(NH$_3$)$_5$O$_2$C-*p*-C$_6$H$_4$NO$_2^{2+}$, 36445-08-6; Co(NH$_3$)$_5$O$_2$CCH$_3^{2+}$|Fe(CN)$_6^{4-}$, 91443-82-2; Co(NH$_3$)$_5$O$_2$CC$_6$H$_5^{2+}$|Fe(CN)$_6^{4-}$, 91443-83-3; Co(NH$_3$)$_5$O$_2$C-*o*-C$_6$H$_4$NO$_2^{2+}$|Fe(CN)$_6^{4-}$, 91443-84-4; Co(NH$_3$)$_5$O$_2$C-*m*-C$_6$H$_4$NO$_2^{2+}$|Fe(CN)$_6^{4-}$, 91443-85-5; Co(NH$_3$)$_5$O$_2$C-*p*-C$_6$H$_4$NO$_2^{2+}$|Fe(CN)$_6^{4-}$, 91443-86-6.

---

(14) Assuming that the Marcus relaation is applicable, the maximum change in rate constants for the carboxylate systems corresponds to an $E°$ of 0.10 V.

(15) Benson, P.; Haim, A. *J. Am. Chem. Soc.* **1965**, *87*, 3826.

(16) Ogard, A. E.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1084.

(17) Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *9*, 303.

(18) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

(19) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

(20) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.

(21) The measured second-order rate constants divided by the ion-pair formation constants calculated from eq 6 and 7 yield first-order rate constants for internal electron transfer in Ru(NH$_3$)$_6^{3+}$/Ru(NH$_3$)$_6^{2+}$ and in Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ of 4.4×10^5 s^{-1} and 1.4×10^6 s^{-1}, respectively.

(22) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273.

Contribution from the Istituto Chimica Generale
and Istituto Chimica Fisica, University of Pisa,
56100 Pisa, Italy

Comparison between Carbonyl Derivatives of Palladium and Those of Nickel and Platinum

Daniela Belli Dell'Amico, Fausto Calderazzo,*
Carlo Alberto Veracini, and Nicola Zandonà

Received January 5, 1984

Palladium is an important element in several catalytic carbonylations.[1] Some features of the chemistry of palladium carbonyl complexes appear to be unusual with respect both to its congener elements in the nickel subgroup and to other transition elements. In particular, some structural, spectroscopic, and chemical properties of palladium carbonyl complexes cannot easily be explained by the usual mechanism of synergic σ–π contributions to the Pd–CO bond.

Recent work in these laboratories led to the convenient preparations of palladium and platinum carbonyl complexes[2] with the same valence electron count and presumably the same molecular structure, thus allowing a comparison of properties to be made within elements belonging to the same vertical sequence (a group trend).

Experimental Section

All of the reactions reported in this paper were carried out under an atmosphere of prepurified carbon monoxide or dinitrogen, as specified. Solvents were dried prior to use by the conventional pro-

---

* To whom correspondence should be addressed at the Istituto Chimica Generale.