On the Reactivity of Precursor Complexes in the System Pentacyanoferrate(II) and Pentaammine(dimethylsulfoxide)cobalt(III)

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Received September 15, 1976

In the search for evidence of precursor complexes in electron transfer reactions, a binuclear intermediate was detected in the system pentaammine(dimethylsulfoxide)cobalt(III) and aquopentacyanoferrate(II). Cyclic voltammetry measurements and careful analysis of the products indicated that the formation of a sulfur–iron bond stabilizes the intermediate with respect to electron transfer reaction. Interpretation of the kinetics data is consistent to the formation of an outer sphere complex (K = 350 M^{-1}) which undergoes internal substitution (k = 20 s^{-1}) to yield the dimethyl sulfoxide bridged intermediate. The binuclear intermediate aquates by breaking the cobalt(III)–sulfoxide bond, with a specific rate of 0.106 s^{-1}, $\Delta H^{\ddagger}$ = 20 Kcal mol^{-1} and $\Delta S^{\ddagger}$ = 4 cal mol^{-1} deg^{-1}, at 25 °C and μ = 0.10 M (lithium perchlorate).

Using the less labile amminopentacyanoferrate(II) ion instead of the aquopentacyanoferrate(II) complex, an outer sphere electron transfer reaction with saturation behavior has been observed. For this system, an ion pair association constant of 470 M^{-1} (ΔH = +2 Kcal mol^{-1} and ΔS = 20 cal mol^{-1} deg^{-1}) and an intramolecular transfer rate of 1.22 s^- ($\Delta H^{\ddagger}$ = 22 Kcal mol^{-1}, $\Delta S^{\ddagger}$ = 17 cal mol^{-1} deg^{-1}) have been obtained at 25 °C, μ = 0.10 M (lithium perchlorate).

Introduction

Most electron transfer reactions between transition metal complexes display mixed second-order kinetics, unless there is strong association between the reactants. Depending on the association constant of the precursor complexes, a typical saturation behavior can be observed, with the kinetics gradually approaching to a simple first order rate law. The special interest on this limiting situation is mainly associated to the possibility of measuring directly the intramolecular transfer rates [1–5] without complications usually involved in assembling the reaction partners.

Resembling [6] in many aspects the ruthenium–ammine complexes [7], the pentacyanoferrates have been shown [8, 9] to be potentially useful for studies on reactivity of precursor complexes. The labile nature of the aquopentacyanoferrate(II) ion allows to generate the intermediates much more rapidly in comparison to the rates of outer-sphere redox reactions, for example, with the cobalt(III)–ammine complexes [8–10]. For the ruthenium–ammine complexes, more elaborate methods, as those ingeniously designed by Taube *et al.* [4] are necessary to generate similar intermediates.

Using the high affinity of the pentacyanoferrate(II) ion for the dimethyl sulfoxide ligand [11], we succeeded in detecting a precursor intermediate in the reaction

$$(NH_3)_5Co-O{=\!\!=}S(CH_3)_2^{3+} + Fe(CN)_5H_2O^{3-} \rightarrow$$
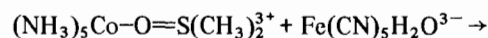
Products

The binuclear intermediate is formed and decomposed very rapidly, however both steps can be conveniently investigated by the stopped-flow technique. To our knowledge, binuclear intermediates with dimethyl sulfoxide (dmso) acting as bridging ligand have never been reported before.

To evaluate the importance of ion pairing and outer sphere mechanisms, the aquopentacyanoferrate(II) ion was substituted by the less labile amminopentacyanoferrate(II) complex. Genuine intramolecular electron transfer rates were obtained for this system.

Experimental

Materials

The complex [Co(NH_3)_5(dmso)](ClO_4)_3·2H_2O was prepared and recrystallized according to the procedure of Beyer and McColl [12]. Na_3[Fe(CN)_5NH_3]·3H_2O was prepared from analytical grade sodium nitroprusside, according to the conventional procedure [13].

Solutions of the complexes were prepared by dissolving the pure solid in argon saturated, distilled, deionized water, at the appropriate ionic strength. The pH was controlled with acetate buffer. Lithium perchlorate was used to adjust the ionic strength. Whenever possible, the solutions were used within the first half hour to minimize aquation of the dmso complex [14] and ageing processes associated to the aquopentacyanoferrate(II) ion.

Analysis and Ionic Exchange Separations

Analyses of the several products were carried out spectrophotometrically, after their separation in a Dowex 50W–X4 cationic, or a Biorad Ag1–X2 anionic resin, under argon atmosphere. The spectra were recorded with a Cary 14 or Cary 17 Spectrophotometer.

Kinetic Measurements

The kinetic experiments were carried out using a Durrum D–110 stopped-flow apparatus, with a 2.00 cm pathlength cell. The progress of the reaction was monitored at several wavelengths (360–540 nm), and was displayed on a Hewlett–Packard storage type oscilloscope. Under the conditions employed in this work, no evidence for precipitation has been observed.

Cyclic Voltammetry Measurements

A Princeton Applied Research Corporation system, consisting of a Model 173 Potentiostat and a Model 175 Universal Programmer was employed in the cyclic voltammetry measurements. Platinum wires were used as auxiliary and working electrodes, with saturated calomel as the reference electrode.

Results and Discussion

Reaction of $Fe(CN)_5H_2O^{3-}$ with $Co(NH_3)_5dmso^{3+}$

As shown in Fig. 1, an intermediate is formed and decomposed within a few seconds when 10^{-3} M solutions of pentaammine(dimethylsulfoxide)cobalt(III) and aquopentacyanoferrate(II) (10^{-5} M) are mixed.

Although the decomposition of the intermediate occurs with a much slower rate in comparison to the formation, it is apparently the major responsible for a deviation in the linearity of plots of log (A_∞ – A) *versus* time, for the kinetics of the first reaction. The problem arises from the changes in A_∞, the absorbance associated to the infinite time. To minimize this effect, we have employed a treatment similar to that of Francis and Jordan [15].

Basically, the procedure consists in extrapolating the kinetic plots of the second reaction to the initial time to obtain a limiting transmittance at the infinite time for the first reaction. Then, to correct for the induction period of the second reaction, the best
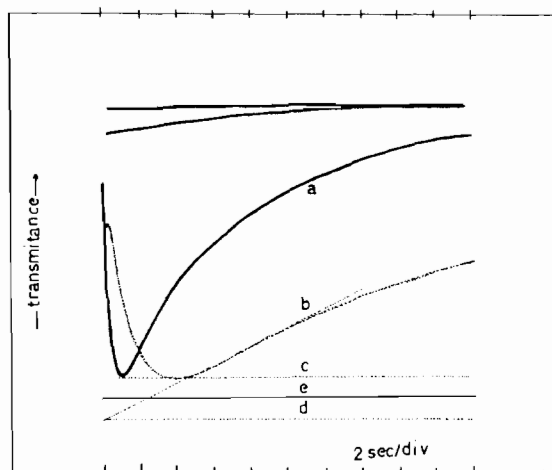

Figure 1. Oscilloscope traces for the $Fe(CN)_5H_2O^{3-}$ + Co-$(NH_3)_5dmso^{3+}$ reaction (expt. 4, Table I), showing (a) the formation and the decay of the intermediate. Curve (b) is the same as (a), but with the horizontal scale expanded 4 times. (c) is the value measured for the intermediate at infinite time. (d) is the highest limiting value, neglecting the induction period for the decomposition reaction. (e) is the best estimated value for infinite time.

value in the range of the observed and limiting values is chosen, which linearizes the logarithmic plots. The procedure is illustrated in Fig. 1.

To characterize the intermediate, we have obtained its visible spectrum, starting from equimolar solutions of the reactants (10^{-4} M), with the stopped-flow apparatus. The spectrum reveals the existence of a broad band with a maximum at nearly 420 nm ($\epsilon = 8 \times 10^2$ M^{-1} cm^{-1}) and a shoulder at 540 nm. However, in general, it does not differ appreciably from the spectra of the reactants (λ_{max} = 440 nm, $\epsilon = 6 \times 10^2$ M^{-1} cm^{-1} for $Fe(CN)_5H_2O^{3-}$ and λ_{max} = 515 nm, $\epsilon = 60$ M^{-1} cm^{-1} for $Co(NH_3)_5dmso^{3+}$). Experimentally we have chosen 540 nm to monitor the kinetics, because at this wavelength the absorbance changes for both reactions are of comparable magnitudes.

Analogously to the system $Fe(CN)_6^{4-}$ and $Co-(NH_3)_5H_2O^{3+}$ investigated by Gaswick and Haim [1], outer sphere electron transfer reactions between $Co(NH_3)_5dmso^{3+}$ and $Fe(CN)_5H_2O^{3-}$ should occur rapidly. However, in the last case, the lability and the facility of the aquopentacyanoferrate(II) ion to form stable S-bonded complexes with sulfoxides [11] should favor the formation of binuclear intermediates. Therefore, as the outer sphere mechanism, the inner sphere seems also very likely to occur in this system. To elucidate this point, we have investigated the kinetics of formation and decomposition of the intermediate. The dependence of the rates on the concentration of reactants, pH, ionic strength and temperature can be seen in Table I.

An important observation that can be drawn from Table I is that only the rates of formation of the

TABLE I. Rate Constants for the Reaction $Fe(CN)_5H_2O^{3-} + Co(NH_3)_5dmso^{3+}$.

Expt. no.	T (±0.2 °C)	μ^a (M)	$[Co(NH_3)_5dmso^{3+}]$ × 10^{+3} M	k_f (s⁻¹)	k_2 (s⁻¹)
1	8.2	0.10	4.0	1.67	–
2	19.7	"	"	6.9	0.052
3	25.0	"	0.50	3.7	0.103ᵇ
4	"	"	0.50	3.0	0.111ᵇ
5	"	"	0.50	4.6	0.108ᵇ
6	"	"	1.00	5.1	0.112
7	"	"	2.00	9.0	0.109
8	"	"	3.00	9.8	0.104
9	"	"	4.00	11.7	0.102
10	"	"	5.5	13.8	0.103
11	"	"	6.0	12.5	0.108
12	"	"	1.00	4.7	0.105ᶜ
13	"	"	"	5.0	0.107ᶜ
14	"	"	"	5.5	0.120ᶜ
15	"	0.050	4.00	–	0.105
16	"	0.20	"	5.2	0.106
17	"	0.50	"	3.2	0.097
18	30.0	0.10	"	18.1	0.163
19	34.5	"	"	–	0.275

ᵃLithium perchlorate was used to adjust the ionic strength.   ᵇExpts. 3, 4, 5 refer to pH 3.7, 4.7 and 5.7 respectively. For all other expts, the pH was maintained at 4.7 with acetate buffer, 10^{-2} M. For expt. 5, the acetate ion concentration was 0.050 M, contributing to 50% of the total ionic strength.   ᶜExpts. 12, 13 and 14 refer to $[Fe(CN)_5H_2O^{3-}]$ = 6 × 10^{-5} M, 1.2 × 10^{-4} M and 3.2 × 10^{-4} M, respectively. At higher concentrations, appreciable amounts of the reactant remain in the form of the amminopentacyanoferrate(II) complex. For all other expts., $[Fe(CN)_5H_2O^{3-}]$ = 1 × 10^{-4} M.

intermediate depend on the concentration of the reactants (expts 3–11), The rates of decomposition (k_2) are essentially invariant, suggesting that it takes place under a saturation condition with practically all the reactants converted to the intermediate.

As can be seen in Fig. 2, the rates of formation increase non-linearly with the concentration of the pentaammine(dimethyl sulfoxide)cobalt(III) ion. This fact suggests that the substitution reaction is preceded by strong ion pair formation.

The simplest mechanism that accommodate these observations is the following:

$$(NH_3)_5Co(dmso)^{3+} + Fe(CN)_5H_2O^{3-} \xrightarrow{K}$$

$$[(NH_3)_5Co(dmso)^{3+}][Fe(CN)_5H_2O^{3-}]$$

$$[(NH_3)_5Co-O=S(CH_3)_2^{3+}][Fe(CN)_5H_2O^{3-}]\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$[(NH_3)_5Co-O=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{S}}-Fe(CN)_5] + H_2O$$

$$[(NH_3)_5Co-O=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{S}}-Fe(CN)_5] \xrightarrow{k_2} Products$$
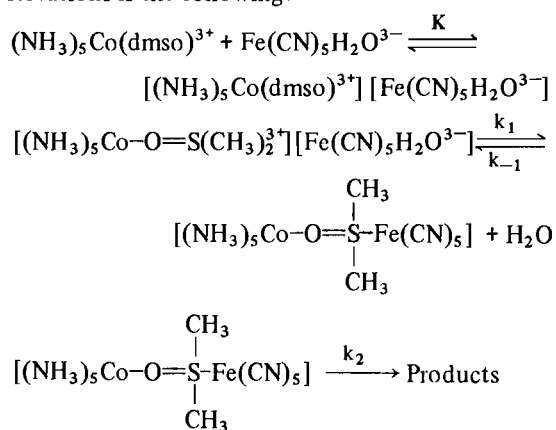
Since the rates of formation and decomposition of the binuclear intermediate differ by a factor of at least 30, the two processes can be considered separately. For the formation reaction, the expression derived for the observed rate constant has the form

$$k_{obsd} = \frac{k_1K[Co(NH_3)_5(dmso)^{3+}]}{1 + K[Co(NH_3)_5(dmso)^{3+}]} + k_{-1} \quad (eq\ 1)$$

According to the extrapolated plot of Fig. 2, k_{-1} seems to be negligible in comparison to the cobalt-(III) dependent term. Therefore, eq. 1 can be converted to

$$1/k_{obsd} = 1/k_1 + 1/k_1K[Co(NH_3)_5dmso^{3+}] \quad (eq\ 2)$$

The plot of k_{obsd}^{-1} *versus* $[Co(NH_3)_5(dmso)^{3+}]^{-1}$ is strictly linear (see internal plot in Fig. 1), with k_1 = 20 ± 5 s⁻¹ and K = 3.5 ± 0.8 × 10^2 M^{-1}.

The rate constant of substitution in the ion pair is of one order of magnitude smaller than the rates of substitution in the aquopentacyanoferrate(II) ion by neutral ligands [16]. The theoretical value of the association constant for the ion pair can be estimated from the equation [17]

$$K = \frac{4\pi Na^3}{3000} e^{-U(a)/kT}$$

where U(a) is the Debye–Hückel interaction potential. Agreement between the calculated and the experimental value can be obtained only if a is 6.2 × 10^{-8} cm. This value is probably smaller than the
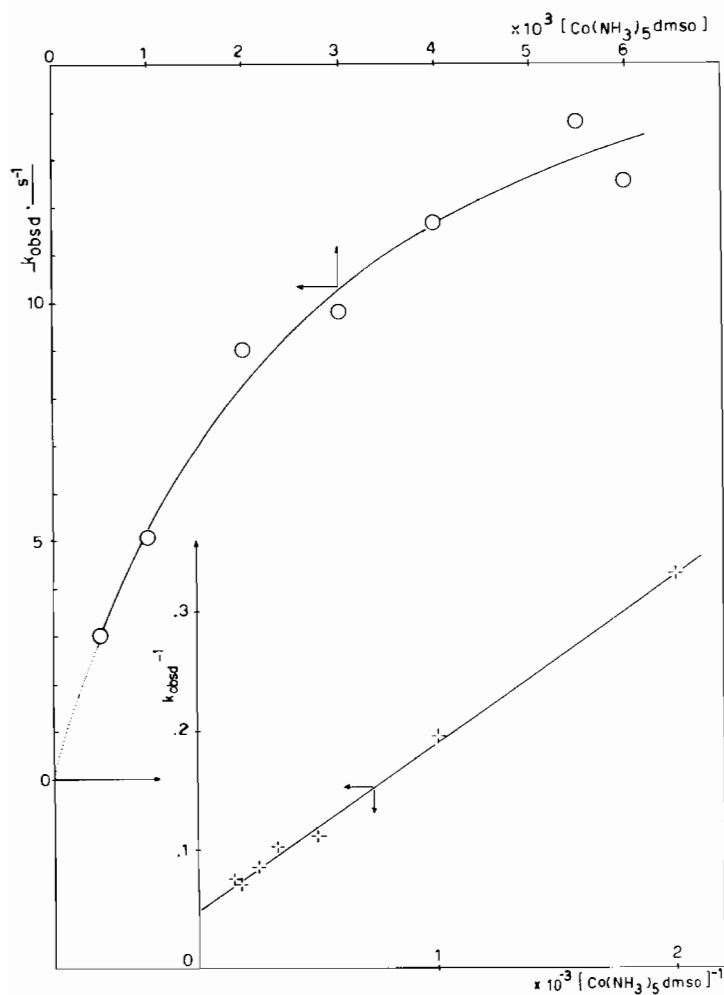
Figure 2. Saturation behavior for the $Fe(CN)_5H_2O^{3-} + Co(NH_3)_5dmso^{3+}$ reaction (expts. 4–11, Table I), showing internally the linear inverse plot used to calculate the ion pair and substitution constants.

actual distance between the centers of the reactants. As in the cases reported by Haim and Sutin [18], it seems that specific ion effects may be of comparable importance to the general electrostatic effects, in determining the magnitude of ion pair interactions.

For the decomposition of the intermediate, the expression derived for the observed rate constant has the form

$$k_{obsd} = \frac{k_2 K_T [Co(NH_3)_5dmso^{3-}]}{1 + K_T[Co(NH_3)_5dmso^{3+}]}$$

where K_T is the overall equilibrium constant for the first reaction. The saturation behavior observed in this case indicates that $K_T[Co(NH_3)_5dmso^{3+}] \gg 1$. In this case, k_{obsd} is reduced simply to k_2. Since saturation is observed even for the lowest cobalt(III) concentration we have employed, it is possible to predict that K_T must be greater than $2 \times 10^3 \ M^{-1}$.

Therefore, substituting the values of K and k_1 in $K_T = Kk_1/k_{-1}$, k_{-1} can be estimated to be smaller than 3 s^{-1}.

Identification of the products of decomposition of the intermediate presented many difficulties associated mainly to the necessity of using small amounts of the aquopentacyanoferrate(II) ion to prevent precipitation and formation of dimeric species [19].

To work under the same conditions of the kinetic experiments, it was necessary to cancel the undesirable influence of the remaining pentaammine(dimethylsulfoxide)cobalt(III) complex on the spectra of the products. We solved the problem by separating the products using anionic or cationic resin in the conventional way, under argon atmosphere, to prevent any influence from the air [20].

Surprisingly, the major products have been spectrophotometrically identified as the pentacyano-(dimethylsulfoxide)ferrate(II) complex (>80%) and

TABLE II. Rate Constants for the Reaction $Fe(CN)_5NH_3^{3-}$ + $Co(NH_3)_5dmso^{3+}$
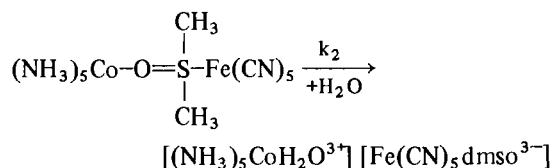
Exp no.	T (±0.2 °C)	μ^a (M)	$[Co(NH_3)_5dmso^{3+}]$ ($\times 10^{-3}$ M)	k_{obsd}^a (s^{-1})
1	13.9	0.10	1.00	0.096
2	"	"	2.00	0.130
3	"	"	3.00	0.163
4	"	"	4.00	0.180
5	"	"	5.00	0.198
6	"	"	6.00	0.223
7	25.0	"	1.00	0.38
8	"	"	2.00	0.62
9	"	"	4.00	0.83
10	"	"	4.00	0.91[b]
11	"	0.20	"	0.53
12	"	0.60	"	0.160
13	"	0.10	5.0	0.86
14	"	"	6.0	0.91
15	32.0	0.10	1.00	1.02
16	"	"	2.00	1.54
17	"	"	4.00	2.03
18	"	"	5.0	2.18
19	"	"	6.0	2.19

[a]Lithium perchlorate, pH 4.8 (acetate buffer, 10^{-2} M), $[Fe(CN)_5NH_3^{3-}]$ = 1.0×10^{-4} M, λ = 390 nm. [b]*ibidem*, $[Fe(CN)_5NH_3^{3-}]$ = 2.0×10^{-4} M.

the aquopentacyanoferrate(III) complex (<20%). We have also observed that in the presence of excess dimethyl sulfoxide and ascorbic acid, the aquopentacyanoferrate(III) ion can be completely converted to the pentacyano(dimethylsulfoxide)ferrate(II) complex.

Since the products are known [11, 21] to be quite inert to substitution [22], the only reasonable explanation for this unexpected result is to consider that the intermediate decomposes, by breaking the cobalt—sulfoxide bond [23] to form $Fe(CN)_5dmso^{3-}$ and $Co(NH_3)_5H_2O^{3+}$.

The ionic strength data shown in Table I reveal that only the rates of formation of the binuclear intermediate depend on the electrolyte concentration. The lack of this dependence for the second reaction seems to indicate that the immediate products of the dissociation remain attached in an ion pair, so that no net change of charges is produced during the reaction. This is also consistent to the small value of the activation entropy of 4 cal mol^{-1} deg^{-1}. The activation enthalpy of 20 kcal mol^{-1} is reasonable for substitution in cobalt(III)—ammine complexes [24]. Therefore, k_2 can be associated to the process

$$(NH_3)_5Co-O=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{S}}-Fe(CN)_5 \xrightarrow[+H_2O]{k_2}$$

$$[(NH_3)_5CoH_2O^{3+}] \ [Fe(CN)_5dmso^{3-}]$$

To explain for the non-occurrence of electron transfer reactions in the binuclear intermediate or in the immediate products, we carried out the determination of the oxidation potential for the (S-bonded [11]) pentacyano(dimethylsulfoxide)ferrate(II) complex.
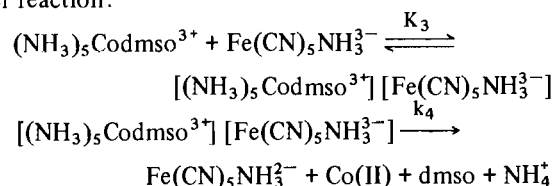
Potentiometric titrations of the colorless $Fe(CN)_5$$dmso^{3-}$ complex with Ce(IV) yielded a yellow product with absorption bands at nearly 410 and 340 nm. The product, presumably $Fe(CN)_5dmso^{2-}$, decomposes rapidly to the $Fe(CN)_5H_2O^{2-}$ complex and this precludes the direct potentiometric determination of the formal potentials for the couple. Using cyclic voltammetry, however, well behaved and reversible waves have been obtaind, with a peak separation of 0.062 V and $E_{1/2}$ equal to 0.89 V, at pH 4.7, 27 °C and 1.0 M sodium chloride.

Based on this highly negative value for the oxidation potential of the dimethylsulfoxide complex, we suggest that the high barrier for electron transfer arises from the strong stabilization of the donor ion when the iron—sulfur bond is formed. Also associated to the high stability of the product [11] is the complete retention of the iron—sulfoxide bond, during the cleavage of the binuclear complex.

Reaction of $Fe(CN)_5NH_3^{3-}$ with $Co(NH_3)_5dmso^{3+}$

The kinetics of the outer sphere electron transfer reaction between $Fe(CN)_5NH_3^{3-}$ and $Co(NH_3)_5$$dmso^{3+}$ have been investigated, starting from 10^{-4} M solutions of the amminopentacyanoferrate(II) complex [25] in the presence of ammonia (10^{-3} M) to prevent the aquation of coordinated NH_3. For this system, electron transfer occurs rapidly, yielding exclusively $Fe(CN)_5NH_3^{2-}$, according to the electronic spectra of the products [26].

In contrast to the aquopentacyanoferrate(II) complex, the rates of oxidation of $Fe(CN)_5NH_3^{3-}$ depend on the concentration of the pentaammine(dimethylsulfoxide)cobalt(III) ion, as can be seen in Table II. However, instead of a linear behavior, the plots of the observed rate constants *versus* the cobalt complex concentration reveal the occurrence of saturation, as shown in Figure 3. This fact was assigned to ion pair formation, preceding the outer sphere electron transfer reaction:

$$(NH_3)_5Codmso^{3+} + Fe(CN)_5NH_3^{3-} \underset{}{\overset{K_3}{\rightleftharpoons}}$$

$$[(NH_3)_5Codmso^{3+}] \ [Fe(CN)_5NH_3^{3-}]$$

$$[(NH_3)_5Codmso^{3+}] \ [Fe(CN)_5NH_3^{3-}] \xrightarrow{k_4}$$

$$Fe(CN)_5NH_3^{2-} + Co(II) + dmso + NH_4^+$$

For the mechanism above, the observed rate constant can be expressed by

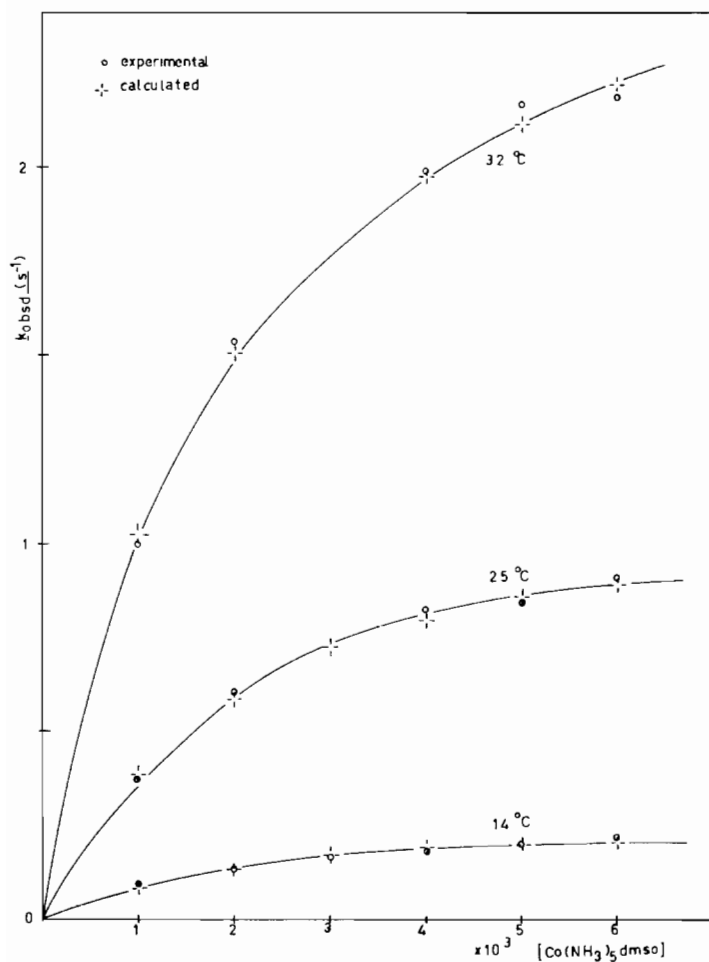$$k_{obsd} = \frac{k_4K_3[Co(NH_3)_5dmso^{3+}]}{1 + K_3[Co(NH_3)_5dmso^{3+}]}$$

Figure 3. Saturation behavior for the $Fe(CN)_5NH_3^{3-} + Co(NH_3)_5dmso^{3+}$ reaction, at several temperatures.

From the inverse linear plots, the ion pair association constant was calculated to be nearly 430, 470 and 550 M^{-1}, with k_4 equal to 0.30, 1.22 and 2.9 s^{-1} at 13.8 °C, 25.0 °C and 32.0 °C respectively. The rate constants, k_4, in this case are associated to direct intramolecular electron transfer, as in the system reported by Haim and Gaswick [1].

The calculated thermodynamic parameters were: $\Delta H = 2 \pm 1$ kcal mol^{-1}, $\Delta S = 20 \pm 4$ cal mol^{-1} deg^{-1}, $\Delta H^{\ddagger} = 22 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 17 \pm 8$ cal mol^{-1} deg^{-1} for ion pairing and electron transfer, respectively.

From the known values [22] of the oxidation potentials of $Fe(CN)_5NH_3^{3-}$ and $Fe(CN)_5H_2O^{3-}$, (0.399 and 0.409 V, respectively) one can estimate the rate of the outer sphere electron transfer reaction between $Fe(CN)_5H_2O^{3-}$ and $Co(NH_3)_5dmso^{3+}$. Using the Marcus [27] relationship, $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$, the rates of two similar crossed reactions, k_{12} and k'_{12}, can be related to their equilibrium constants K_{12} and K'_{12}, according to $k_{12} = k'_{12}(K_{12}/K'_{12})^{1/2}$

(assuming the differences in self exchange constants and work terms negligible).

Using this simplified approach, the calculated rate constant for the intramolecular electron transfer reaction between $Fe(CN)_5(H_2O)^{3-}$ and $Co(NH_3)_5$-dmso^{3+} was equal to 1.0 s^{-1} in comparison to 20 s^{-1} for substitution in the ion pair. These values offer a good explanation for the small yield in $Fe(CN)_5H_2$-O^{2-} observed in the reaction above, as reported in the initial part of this article. To test for the validity of Marcus' theory in these systems, a number of similar reactions involving substituted pentacyano-ferrates are being investigated at this laboratory.

Acknowledgements

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