

# Reaction and Reorganization Free Energies of Electron-Transfer Reactions under Restricted Geometry Conditions

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Electron-transfer reactions between iron and cobalt complexes were studied in  $\beta$ -cyclodextrin ( $\beta$ CD), 2-hydroxypropyl- $\beta$ -cyclodextrin (H $\beta$ CD), and 18-crown-6 ether (18C6) solutions. The results were rationalized taking as the basis the Marcus–Hush formalism. We employed two different approaches, depending on the kind of receptor and solvent, to obtain the reorganization and reaction free energies that determine the reaction rate constant. The opposite trends in reactivity observed in  $\beta$ CD and H $\beta$ CD solutions and the behavior in solutions of 18C6 are explained.

## Introduction

At present, there is great interest in the study of changes in reactivity caused by restricted geometry conditions (r.g.c.), that is, under conditions in which one or both reactants are bound to some receptors such as micelles, cyclodextrins (CDs), polymers, and so forth.<sup>1</sup> This interest is due to (i) model studies on r.g.c. that offer valuable insights into many biological processes,<sup>2</sup> (ii) reactions under r.g.c. which experience changes in the rate constant of several orders of magnitude that depend on the concentration of receptors, this allowing control in the reaction rate,<sup>3</sup> and (iii) in some cases, r.g.c. changing the course of the reaction through a change of its mechanism.<sup>4,5</sup> Thus, different orientations of a given guest in different CDs, as a consequence of different CD sizes, can lead to conformational control of reactivity because of the exposition of different moieties of the guest to a second reactant.<sup>5</sup>

In our studies in this field, we preferred electron-transfer reactions<sup>1,3,6,7</sup> due to the existence of a well-founded theoretical framework for this kind of reaction, the Marcus–Hush formalism,<sup>8,9</sup> which allows deeper insight into rationalization of the effects of r.g.c. on electron-transfer reactions. In fact, a careful analysis of experimental data for electron-transfer reactions permits the separation of the electron-transfer rate constant,  $k_{\text{et}}$ , from the experimentally measured rate constant,  $k_{\text{obs}}$ , and then obtaining of the parameters that determine  $k_{\text{et}}$

$$k_{\text{et}} = Ae^{-\Delta G^\ddagger/RT} \quad (1a)$$

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \quad (1b)$$

In previous equations,  $A$  is the pre-exponential factor,  $\Delta G^\ddagger$  and  $\lambda$  are the activation and the reorganization free energies, respectively, and  $\Delta G^\circ$  is the free energy for the process

precursor complex  $\rightarrow$  successor complex. For electron-transfer reactions under r.g.c., to obtain  $\lambda$  and  $\Delta G^\circ$  requires developing some of the strategies that we have employed in micellar systems.<sup>7a,b,h</sup> These strategies are extensions of those contained in papers in which the relation between optical and thermal processes has been studied.<sup>10</sup>

In this paper, we extend these studies to electron-transfer reactions in two different kinds of receptors, 18-crown-6 (18C6) and cyclodextrins  $\beta$ -cyclodextrin ( $\beta$ CD) and 2-hydroxypropyl- $\beta$ -cyclodextrin (H $\beta$ CD). Two different procedures were employed depending on the kind of receptor (and solvent) in order to have the reaction free energy. The analysis permitted obtaining  $\lambda$  and  $\Delta G^\circ$  in the different cases, as well as explaining the opposite trend in reactivity observed for  $\beta$ CD and H $\beta$ CD.

## Experimental Section

**Materials.**  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  was prepared according to a published procedure<sup>11,12</sup> as a perchlorate salt.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  was obtained as by Schlessinger.<sup>13</sup>  $[\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-}$  was prepared in situ from a solution of the commercially available  $[\text{Fe}(\text{CN})_5(\text{NH}_3)]\text{Na}_3$  (from Aldrich), after adding the stoichiometric amount of the 4-phenylpyridine ligand (from Fluka). The rapid hydrolysis of the ammonia complex produced the corresponding aquocomplex<sup>14</sup>  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ . Complete formation of the  $[\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-}$  complex was checked spectrophotometrically.  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  was from Sigma-Aldrich, and  $\text{K}_4[\text{Ru}(\text{CN})_6]$  was from the Johnson Matthey Company. Cyclodextrins were commercial products from Fluka and were used as received. The average degree of substitution per glucose unit was 0.6–0.8 units of 2-hydroxypropyl ( $\text{C}_3\text{H}_7\text{O}$ ) in H $\beta$ CD. 18-crown-6 (18C6) was from Fluka and was stored in a vacuum desiccator for several days before being used. Acetonitrile from Merck was used in the experiments. Purified water used in the preparation of solutions was obtained from a Millipore Milli-Q water system. Its conductivity was less than  $10^{-6} \text{ S m}^{-1}$  and was deoxygenated before use.

**Spectra.** The spectra corresponding to the metal-to-metal charge-transfer (MMCT) band within the ion pair  $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  were obtained with a Cary 500 (Varian) spectrophotometer. The final solutions containing this ion pair were prepared by mixing equal volumes of the ruthenium and

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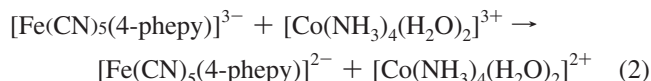
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cobalt solutions. The concentrations of the final solutions were always  $6 \times 10^{-3}$  and  $6 \times 10^{-4}$  mol dm $^{-3}$ , respectively.

**Electrochemical Measurements.** The standard formal redox potentials of the  $[\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-}$  in water and in solutions containing CDs were obtained by differential pulse voltammetry, after checking the reversibility of the system, using the apparatus, electrodes, and procedures previously described.<sup>15</sup> The concentration of the iron complex in these experiments was  $3 \times 10^{-3}$  mol dm $^{-3}$ , and the ionic strength of the solutions was maintained at 0.118 mol dm $^{-3}$  by addition of NaCl. The estimated uncertainty in the values of the potentials was  $\pm 2.5$  mV.

**Kinetic Measurements.** The kinetics of the reaction between  $[\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ :



were followed by measuring the absorbance changes at 405 nm. This wavelength corresponds to the absorbance maximum of the iron complex in water (it was also checked that changing the observation wavelength does not change the value of the rate constants).

Kinetic runs were performed in a stopped-flow apparatus from Applied Photophysics. Concentrations of the iron and cobalt complexes were  $10^{-4}$  and  $6 \times 10^{-3}$  mol dm $^{-3}$ , respectively. That is, the work was done under pseudo-first-order conditions. The estimated uncertainty in the values of the rate constants was  $\pm 0.6$  s $^{-1}$ .

The temperature in all of the experiments in this work was maintained at  $298.2 \pm 0.1$  K.

## Results and Discussion

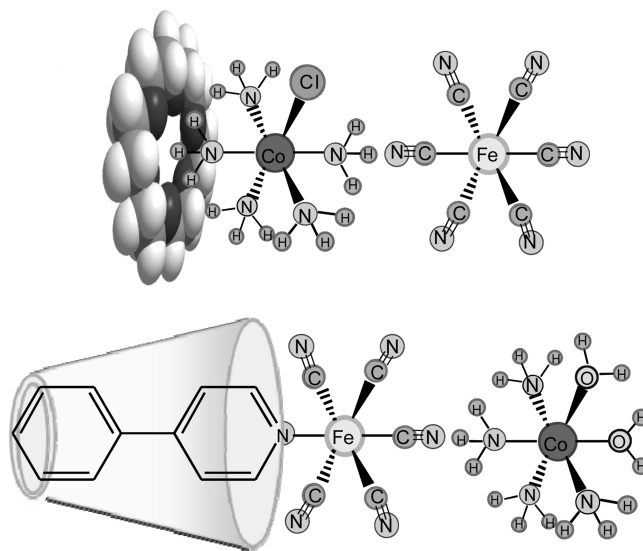
**General.** As mentioned in the Introduction, the first step in the determination of the reorganization free energies was to separate  $k_{\text{et}}$  (eq 1) from the experimentally measured rate constant ( $k_{\text{obs}}$ ). There are different approaches to accomplish this. Here, irreversible electron-transfer reactions were studied. In this case, this irreversible character comes from the decomposition of Co(II) complexes. Under this circumstance, and working in the excess of one of the reactants, as here, it can be shown that the experimental rate constant is given by

$$k_{\text{obs}} = \frac{k_{\text{et}}K_{\text{IP}}[\text{A}]}{1 + K_{\text{IP}}[\text{A}]} \quad (3)$$

where  $K_{\text{IP}}$  is the equilibrium constant for the formation of the precursor (encounter) complex from the separate reactants (see Scheme 1) and A is the acceptor complex (the cobalt one), which is in high excess over the donor. Reactants highly charged and bearing opposite charge signs were selected. Therefore, in our experiments,  $K_{\text{IP}}[\text{A}] \gg 1$ . Thus,  $k_{\text{obs}} = k_{\text{et}}$ .

All of the kinetic data in this paper are  $k_{\text{et}}$  rate constants. This was checked experimentally by changing the concentration of the reactant in excess. For different concentrations of this reactant in the range of  $4 \times 10^{-3}$ – $8 \times 10^{-3}$  mol dm $^{-3}$ , no changes in  $k_{\text{et}}$  were observed. Therefore, we are measuring, in fact, rate constants for the electron transfer within the precursor complex. Schematic representations of encounter complexes, corresponding to the case in which one of the reactants is bound to the receptor, are given in Scheme 1. These representations are inspired by the structures given in refs 16 and 17.

## SCHEME 1: Schematic Representations of the Encounter Complexes Formed by Bound Reactants<sup>a</sup>



<sup>a</sup> The charges are omitted.

**TABLE 1: Values of  $k_{\text{et}}$ ,  $\Delta G^\ddagger$ ,  $\Delta G^{\circ'}$ , and  $\lambda$  for the Reaction  $[\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-} + [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  in Aqueous Solutions of  $\beta\text{CD}$**

$[\beta\text{CD}] \times 10^3 /$ mol dm $^{-3}$	$k_{\text{et}}^a / \text{s}^{-1}$	$\Delta G^\ddagger /$ kJ mol $^{-1}$	$\Delta G^{\circ' b} /$ kJ mol $^{-1}$	$\lambda^c /$ kJ mol $^{-1}$
0	16.2	63.9	−36.6	325
1	14.7	64.1	−36.5	325
2	14.9	64.2	−36.4	325
4	13.6	64.4	−36.0	325
6	13.1	64.5	−35.8	325
8	12.0	64.5	−35.6	325
10	13.3	64.6	−35.4	325
12	12.1	64.6	−35.2	325
14	12.5	64.6	−35.1	325

<sup>a</sup> The values of the parameters obtained from the fit to eq 4 are  $K = 291$  mol $^{-1}$  dm $^3$  and  $(k_{\text{et}})_{\text{CD}} = 11$  s $^{-1}$ . <sup>b</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 0.1$  kJ mol $^{-1}$ . <sup>c</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 2$  kJ mol $^{-1}$ .

**CD Solutions.** Tables 1 and 2 contain the values of  $k_{\text{et}}$  for the reaction of  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+} / [\text{Fe}(\text{CN})_5(4\text{-phepy})]^{3-}$  in solutions which contained  $\beta\text{CD}$  and  $\text{H}\beta\text{CD}$ , respectively. The influence of the CD concentrations can be described by a two-state model<sup>18</sup> (see Figure 1)

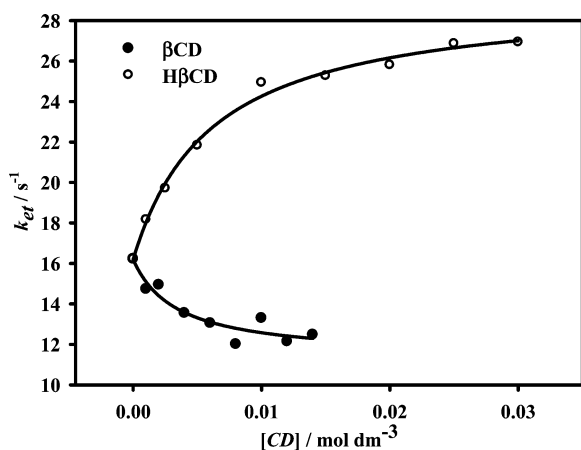
$$k_{\text{et}} = \frac{(k_{\text{et}})_w + (k_{\text{et}})_{\text{CD}}K[\text{CD}]}{1 + K[\text{CD}]} \quad (4)$$

In this equation  $(k_{\text{et}})_w$  is the rate constant for the precursor complex formed from the free reactants,  $(k_{\text{et}})_{\text{CD}}$  is the rate constant corresponding to the precursor complex formed from the reactants bound to the CD (see Scheme 1), and  $K$  is the equilibrium constant of the binding process. It is worth pointing out that, for reactions in which two reactants participate, the fact that kinetic data fit eq 4 implies that only one of them is present in the two states. In the present case, this reactant is the iron complex, as established in a previous paper.<sup>19</sup> Despite the fact that the same model holds in the presence of the two CDs studied here, there is a striking difference between the binding effect; in  $\beta\text{CD}$  solutions, the rate constant decreases when the

**TABLE 2: Values of  $k_{\text{et}}$ ,  $\Delta G^\ddagger$ ,  $\Delta G^{\circ'}$ , and  $\lambda$  for the Reaction  $[\text{Fe}(\text{CN})_54\text{phepy}]^{3-} + [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$  in Aqueous Solutions of  $\text{H}\beta\text{CD}$** 

$[\text{H}\beta\text{CD}] \times 10^3 /$ $\text{mol dm}^{-3}$	$k_{\text{et}} / \text{s}^{-1}$	$\Delta G^\ddagger /$ $\text{kJ mol}^{-1}$	$\Delta G^{\circ'} /$ $\text{kJ mol}^{-1}$	$\lambda /$ $\text{kJ mol}^{-1}$
0	16.2	63.9	-36.6	325
1	18.2	63.7	-37.5	325
2.5	19.7	63.4	-38.3	326
5	21.8	63.2	-38.9	326
10	24.9	62.9	-39.4	326
15	25.3	62.8	-39.7	326
20	25.8	62.7	-39.8	326
25	26.9	62.7	-39.9	326
30	26.9	62.7	-39.9	326

<sup>a</sup> Data obtained from ref 19. The values of the parameters obtained from the fit to eq 4 are  $K = 162 \text{ mol}^{-1} \text{ dm}^3$  and  $(k_{\text{et}})_{\text{CD}} = 29 \text{ s}^{-1}$ . <sup>b</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 0.1 \text{ kJ mol}^{-1}$ . <sup>c</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 2 \text{ kJ mol}^{-1}$ .

**Figure 1.** Plot of the electron-transfer rate constant,  $k_{\text{et}}/\text{s}^{-1}$ , for the reaction  $[\text{Fe}(\text{CN})_54\text{phepy}]^{3-} + [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$  in aqueous solutions at different concentrations of  $\beta\text{CD}$  (●) and  $\text{H}\beta\text{CD}$  (○).

concentration of  $\beta\text{CD}$  increases; the opposite effect is found in the presence of  $\text{H}\beta\text{CD}$ .

In order to shed light on the cause of this different behavior, it is necessary to determine  $\lambda$  and  $\Delta G^{\circ'}$ . The first step is to calculate  $\Delta G^\ddagger$  from  $k_{\text{et}}$ . This can be done using eq 1a. In this equation, the pre-exponential term,  $A$ , is given by<sup>20,21</sup>

$$A = \kappa_{\text{el}} \frac{k_{\text{B}} T}{h} \quad (5)$$

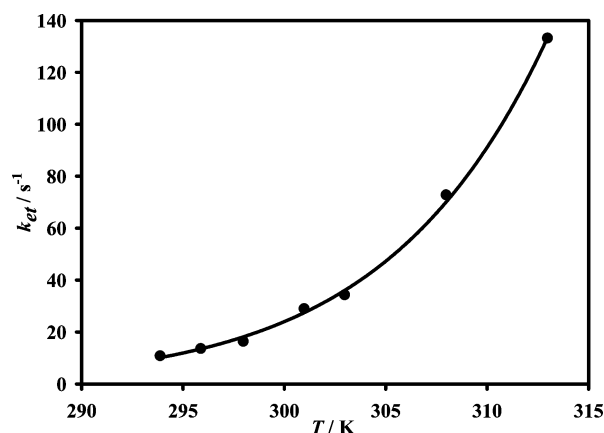
where  $\kappa_{\text{el}}$  is the electronic transmission coefficient ( $\sim 1$  for an adiabatic process),  $k_{\text{B}}$  is the Boltzmann constant,  $h$  is the Planck constant, and  $T$  is the work temperature.

As the purpose was to calculate  $\Delta G^\ddagger$ , it is necessary to know  $\kappa_{\text{el}}$ . There are several procedures to estimate this factor. We have used a procedure that consists of taking as a starting point

$$k_{\text{et}} = a T e^{-\Delta G^\ddagger / RT} \quad (6a)$$

$$k_{\text{et}} = a T e^{-(\Delta H^\ddagger - T \Delta S^\ddagger) / RT} \quad (6b)$$

Obviously,  $a = \kappa_{\text{el}} k_{\text{B}} / h$  if one accepts the frequency factor given by the Transition-State Theory, as in refs 20 and 21. Equation

**Figure 2.** Plot of the electron-transfer rate constant,  $k_{\text{et}}/\text{s}^{-1}$ , for the reaction  $[\text{Fe}(\text{CN})_54\text{phepy}]^{3-} + [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$  in aqueous solutions at different temperatures,  $T/\text{K}$ .

6b can be fitted directly using a nonlinear fitting procedure. Using this method, the following results were found (see Figure 2):  $a = 8.6 \times 10^9 \pm 1 \times 10^9 \text{ s}^{-1} \text{ K}^{-1}$ ,  $\Delta H^\ddagger = 101 \pm 5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 124 \pm 17 \text{ J mol}^{-1} \text{ K}^{-1}$ . This would imply that  $A = aT = 2.6 \times 10^{12} \pm 0.3 \times 10^{12} \text{ s}^{-1}$  at  $298 \text{ K}$ .

In order to check the values of the activation parameters obtained following this fitting procedure, we have also obtained the value of  $\Delta H^\ddagger$  following the conventional procedure, that is, from the slope of the Eyring plot  $\ln(k_{\text{et}}/k_{\text{B}}T)$  versus  $1/T$ . The value obtained was  $104 \pm 5 \text{ kJ mol}^{-1}$ , which is close to the value obtained from the nonlinear fitting. This gives support to the values of the activation parameters obtained by us.

Notice that this value of  $A$  is obtained directly from experimental data. Therefore, its value is independent of using  $\kappa_{\text{el}} k_{\text{B}} T / h$  as a frequency factor. However, if one accept this value for the pre-exponential term, one obtains  $\kappa_{\text{el}} = A h / k_{\text{B}} T = 0.42 \pm 0.05$ . Therefore, the reaction would be close to the adiabaticity limit ( $\kappa_{\text{el}} = 1$ ). Notice that our procedure for obtaining the preexponential term permits the separation of  $\kappa_{\text{el}}$  and  $\Delta S^\ddagger$ , whereas that based on the Eyring plot does not permit this separation.

With the value of the pre-exponential term obtained as previously indicated,  $\Delta G^\ddagger$  can be calculated from  $k_{\text{et}}$

$$\Delta G^\ddagger = -RT \ln \frac{k_{\text{et}}}{2.6 \times 10^{12}} \quad (7)$$

The values of  $\Delta G^\ddagger$  are given in Tables 1 and 2 for  $\beta\text{CD}$  and  $\text{H}\beta\text{CD}$ , respectively.

Once  $\Delta G^\ddagger$  is known, one can have  $\lambda$ , provided that the reaction free energy,  $\Delta G^{\circ'}$ , is known. This free energy can be calculated from the redox potentials of the iron and cobalt redox couples. The redox potentials of the iron couple were measured in the presence of CDs and appear in Table 3. In order to combine these values with those of the activation free energy, the potential values were corrected from the ionic strength, and the potential data for the same CD concentrations used in the kinetic measurements were interpolated. However, the redox potential for the cobalt couple cannot be obtained by conventional electrochemical techniques due to the electrochemical irreversibility of this couple. (Notice that this irreversible character guarantees that eq 3 holds.)

For this reason, a different procedure was employed. This procedure is based on the relation between the optical and thermal electron-transfer processes.<sup>22</sup> According to Hush, the

**TABLE 3: Values of the Redox Potentials for the Complex  $[\text{Fe}(\text{CN})_5\text{4phepy}]^{3-}$  ( $E_{\text{Fe}}^\circ$ ) in Solutions of  $\beta\text{CD}$  and  $\text{H}\beta\text{CD}$** 

$[\beta\text{CD}] \times 10^3 / \text{mol dm}^{-3}$	$E_{\text{Fe}}^\circ / \text{V}$	$[\text{H}\beta\text{CD}] \times 10^3 / \text{mol dm}^{-3}$	$E_{\text{Fe}}^\circ / \text{V}$
0	0.442	0	0.442
1	0.439	1	0.431
2.5	0.444	3	0.422
3.5	0.445	6	0.416
5	0.452	10	0.413
8	0.452	16	0.408
12	0.458		
16	0.458		

energy of the maximum of the MMCT band,  $E_{\text{op}}$ , is related to the parameters of the corresponding thermal electron transfer by

$$E_{\text{op}} = \lambda + \Delta G^{\circ'} \quad (8)$$

Starting from eq 8, some of us developed a procedure for the determination of redox potentials of chemically and electrochemically irreversible inorganic redox couples, such as the cobalt couple here.<sup>23,24</sup> Following this procedure, the redox potentials of a series of cobalt complexes were determined. The reliability of this method is illustrated in Figure 3. In this figure, the redox potentials of the cobalt couples determined by the procedures in refs 23 and 24 (see Appendix) are plotted versus the redox potentials of the corresponding ruthenium couples (obtained from conventional electrochemical measurements). The linear relationship of the two sets of potentials is in line with the ideas of Lever.<sup>25</sup> This gives support to our determinations of the potentials of the redox couples of the cobalt complexes. On the other hand, Figure 4 gives the plot of  $\ln k_{\text{et}}$  for the oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  by the cobalt complexes versus the redox potentials of these complexes. There is a linear relationship between  $\ln k_{\text{et}}$  and  $E^\circ$ , as expected according to the Marcus theory. This gives further support to the procedures in refs 23 and 24. In fact, we have used the relation illustrated in Figure 4 to determine the redox potential of  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ . Thus,  $k_{\text{et}} = 32 \text{ s}^{-1}$  for the oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  with the cobalt complex. From this value of  $k_{\text{et}}$ , a value of  $E^\circ = 0.82 \text{ V}$  is obtained (the estimated uncertainty is  $\pm 30 \text{ mV}$ , which is obtained from standard errors on the slope and the intercept, appearing in Figure 4, and the usual propagation errors).

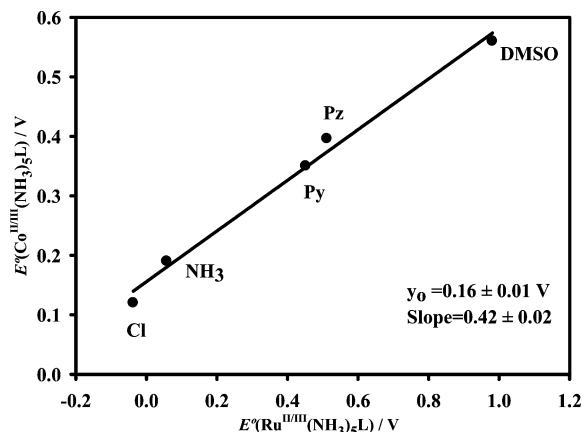
The linearity of the plot in Figure 4 deserves some comments because, according to eq 1

$$\ln k_{\text{et}} = \ln A - \left( \frac{\lambda}{4RT} + \frac{\Delta G^{\circ'}}{2RT} + \frac{(\Delta G^{\circ'})^2}{4\lambda RT} \right) \quad (9)$$

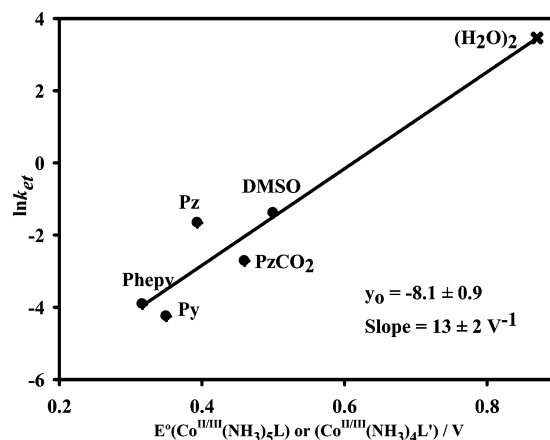
Therefore, a quadratic dependence of  $\ln k_{\text{et}}$  on  $\Delta G^{\circ'}$  should be expected. However, as Marcus and Sutin established,<sup>26</sup> this quadratic term is small for reactions with low values of  $\Delta G^{\circ'}$  and/or high values of  $\lambda$ . In fact, for data in Figure 4, the change in the quadratic term is about  $2 \text{ kJ mol}^{-1}$ , whereas the linear term changes by about  $25 \text{ kJ mol}^{-1}$ .

Once the value of the potential for the  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  couple has been estimated and the values of  $E^\circ$  for the iron complex have been measured,  $\Delta G^\circ$  for the reaction can be calculated

$$\Delta G^\circ = -F(E_{\text{Co}}^\circ - E_{\text{Fe}}^\circ) \quad (10)$$

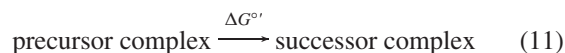


**Figure 3.** Plot of the redox potentials of the cobalt couples,  $E^\circ(\text{Co}^{\text{III/II}}(\text{NH}_3)_5\text{L})/\text{V}$ , determined by the procedures in refs 23 and 24 versus the redox potentials of the corresponding ruthenium couples,  $E^\circ(\text{Ru}^{\text{III/II}}(\text{NH}_3)_5\text{L})/\text{V}$ , obtained from conventional electrochemical measurements. L = Cl (chloride), Pz (pyrazine), Py (pyridine), and DMSO (dimethyl sulfoxide).



**Figure 4.** Plot of  $\ln k_{\text{et}}$  for the oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  by  $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}]$  or  $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{L}']$  complexes versus the redox potentials (V) of the corresponding  $\text{Co}^{\text{III/II}}$  couples. L = Phepy (4-phenylpyridine), Py (pyridine), Pz (pyrazine), and DMSO (dimethyl sulfoxide); L' =  $\text{PzCO}_2$  (pyrazine-2-carboxylate) and  $(\text{H}_2\text{O})_2$  (diaquo).

However, the free energy in eq 10 is not the value of  $\Delta G^{\circ'}$  to be used in the calculation. The latter corresponds to the process



and the free energy in eq 10 corresponds to the process



However,  $\Delta G^\circ$  and  $\Delta G^{\circ'}$  are related by

$$\Delta G^{\circ'} = \Delta G + (w_p - w_r) \quad (13)$$

The difference of these work terms can be expressed as

$$w_p - w_r = -RT \left( \ln \frac{K_p}{K_r} \right) \quad (14)$$



where  $K_p$  and  $K_r$  represent the equilibrium constants corresponding to formation of the successor complex from the separate products and the precursor complex from separate reactants, respectively, which were calculated by

$$K_i = \frac{4}{3} 10^3 \pi N_A r^3 \exp(-\beta V_{AD}^{EF}(r, I)) \quad (15)$$

$V_{AD}^{EF}(r, I)$  being the mean force potential between the reactants or products (electronic acceptor and donor) at the contact distance ( $r$ ),  $\beta = 1/k_B T$ , and  $N_A$  being Avogadro's constant. The interaction potential was calculated by the Eigen–Fuoss approach<sup>27</sup>

$$V_{AD}^{EF}(r, I) = \frac{Z_A Z_D e^2}{4\pi\epsilon_0 \epsilon_s r(1 + \kappa r)} \quad (16)$$

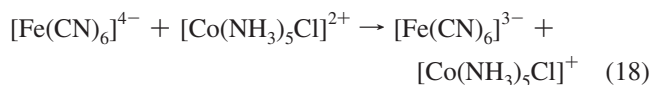
$Z_A$  and  $Z_D$  are the charge type of the electronic acceptor and donor, respectively,  $e$  is the proton charge,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_s$  is the relative dielectric constant,  $r$  is the encounter distance between the ions (taken as the sum of ionic radii)<sup>28</sup> (see also ref 29), and  $\kappa$  is the Debye screening parameter that is a function of the ionic strength,  $I$ . Taking into account an ionic strength of 0.037 mol dm<sup>-3</sup>, the value for  $w_p - w_r$  was 7.9 kJ mol<sup>-1</sup>, in agreement with the estimation performed in refs 23 and 24 for similar reactants. In this way, the values of  $\Delta G^{o'}$  appearing in Tables 1 and 2 were obtained. Finally, from  $\Delta G^\ddagger$  and  $\Delta G^{o'}$ , the values of  $\lambda$  were calculated.

As can be seen in the tables, the reorganization free energy does not change appreciably in the presence of CDs. Therefore, the different behavior is due to the differences in reaction free energies,  $\Delta G^{o'}$ , which, in turn, are due to the differences in the behavior of the redox potentials of the iron complex in the two CDs; in the case of  $\beta$ CD,  $\Delta G^{o'}$  becomes less favorable when the iron complex is bound, whereas in the case of  $H\beta$ CD, the opposite effect is observed. Notice that the influence of the receptor on the redox potential of an included guest depends on the binding of the oxidized and reduced forms of this couple to the host<sup>30</sup>

$$E^o = E_o^o + RT \ln \frac{\gamma_{ox}}{\gamma_{red}} = E_o^o + RT \ln \frac{1 + K_{red}[CD]}{1 + K_{ox}[CD]} \quad (17)$$

Thus, one must conclude that the presence of the 2-hydroxypropyl moiety in  $H\beta$ CD implies that the binding of the oxidized form is stronger than the binding of the reduced form of the iron complex couple. The opposite is true for the  $\beta$ CD.

**Crown Ether Solutions.** In the case of solutions containing 18-crown-6, our task was the same as that in the case of CD solutions, to find out if the influence of the binding in the kinetics of the reaction



comes from the effects of this binding on  $\lambda$  or  $\Delta G^{o'}$  (or both). However, in this case, the redox potential of the cobalt complex couple cannot be determined through the same procedure as that employed in the case of CDs. This difficulty arises from

**TABLE 4: Values of  $k_{et}$ ,  $\Delta G^\ddagger$ ,  $(E_{op})_{exp}$ ,  $(E_{op})_{corr}$ ,  $\Delta G^{o'}$ , and  $\lambda$  for the Reaction  $[\text{Fe}(\text{CN})_6]^{4-} + [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  in a Mixture of Acetonitrile and Water ( $x_{ACN} = 0.4$ ) at Different Concentrations of 18C6**

[18C6]/ mol dm <sup>-3</sup>	$k_{et}^a/s^{-1}$	$\Delta G^\ddagger^b/kJ mol^{-1}$	$(E_{op})_{exp}^c/kJ mol^{-1}$	$(E_{op})_{corr}^c/kJ mol^{-1}$	$\Delta G^{o'd}/kJ mol^{-1}$	$\lambda^e/kJ mol^{-1}$
0	1.06	70.7	324	275	7	268
0.02	1.22	70.3	321	272	9	263
0.035	1.34	70.1	320	271	9	261
0.05	1.46	69.9	319	270	10	260
0.1	1.61	69.7	317	268	10	258
0.2	1.72	69.4	316	267	10	257
0.3	1.77	69.4	316	267	10	257
0.4	1.87	69.3	316	267	10	257
0.5	1.9	69.3	316	267	10	256

<sup>a</sup> Data obtained from ref 31. The values of the parameter obtained from the fit to eq 4 are  $K = 13 \text{ mol}^{-1} \text{ dm}^3$  and  $(k_{et})_{18C6} = 2 \text{ s}^{-1}$ . <sup>b</sup> The uncertainties from the experimental errors are  $\pm 0.1 \text{ kJ mol}^{-1}$ . <sup>c</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 1 \text{ kJ mol}^{-1}$ . <sup>d</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 3 \text{ kJ mol}^{-1}$ . <sup>e</sup> The uncertainties calculated using the usual procedure on the propagation errors are  $\pm 2 \text{ kJ mol}^{-1}$ .

the fact that kinetic results, which appear in Table 4, were taken from a previous paper<sup>31</sup> in which a mixture of acetonitrile and water ( $x_{ACN} = 0.4$ ) was used as the solvent. For this solvent, redox potentials of  $\text{Co}^{3+/2+}$  couples were not available. Consequently, a different approach was used. This approach follows from the consideration of eqs 1b and 8, which permits one to write

$$\Delta G^\ddagger = \frac{E_{op}^2}{4\lambda} \quad (19)$$

This equation implies that by combining kinetic ( $\Delta G^\ddagger$ ) and optical ( $E_{op}$ ) data, one can obtain  $\lambda$ , and then, once  $\lambda$  is known, it is possible to use eq 8 to obtain  $\Delta G^{o'}$ .

However, having  $E_{op}$  for a reactive system presents difficulties. For this reason, instead of measuring  $E_{op}$  for the MMCT band in the  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  system, we have measured the values of  $E_{op}$  for the  $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  system. Of course, this implies correction of the measured values of  $E_{op}$ . Briefly, the corrections are the following:<sup>23,24</sup> (i) correction for the difference in the spin–orbit coupling of the iron and ruthenium complexes, (ii) corrections for the difference for the redox potentials in these complexes, and (iii) corrections for the differences of spin of  $\text{Co}(\text{II})$  complexes resulting in optical (low-spin) and thermal (high-spin) electron transfer. After applying these corrections (see Appendix), the values of  $E_{op}$  to be used in eq 19,  $(E_{op})_{corr}$  appearing in Table 4, were obtained. Notice that  $(E_{op})_{corr}$  corresponds to the same optical transition as that in the thermal process. That is,  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$  (low spin)  $\rightarrow$   $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Co}^{\text{II}}(\text{NH}_3)_5\text{Cl}]^{1+}$  (high spin).

From the values of  $(E_{op})_{corr}$  in Table 4 and those of  $\Delta G^\ddagger$ ,  $\lambda$  was determined using eq 19 for the different concentrations of 18C6. Finally, from the values of  $\lambda$  and employing eq 1b (or 8), the values of  $\Delta G^{o'}$  were obtained (see Table 4).

It is important to realize that by using eq 19, one can obtain  $\lambda$  without employing the bandwidth<sup>22</sup> because the latter procedure overestimates  $\lambda$  values due to the problem of inhomogeneous broadening.<sup>32</sup>

The data in Table 4 show that the behavior of the primary kinetic data,  $k_{et}$ , is similar to the behavior of this parameter in CD solutions in the sense that it can be described employing a

two state model (eq 4). However, in the case of 18C6, the increase in  $k_{\text{et}}$  is mainly controlled by  $\lambda$ , whereas  $\Delta G^{\circ'}$  exerts only a minor influence (in the opposite sense to  $\lambda$  but in agreement with eq 17<sup>17</sup>). In the case of CDs, on the contrary, changes in  $\Delta G^{\circ'}$  cause the changes in  $k_{\text{et}}$ ,  $\lambda$  being practically constant.

In conclusion, two electron-transfer processes, in which one of the reactants participates as a bound species, were studied. Working under conditions in which the measured rate constant is directly  $k_{\text{et}}$  and following two different approaches,  $\lambda$  and  $\Delta G^{\circ'}$  were calculated for these electron-transfer processes. These data show that similar behavior in  $k_{\text{et}}$  (in 18C6 and H $\beta$ CD) can arise from different causes. It also made it possible to explain the different behavior in the two CD-type receptors. We think that this kind of analysis may be useful in gaining a deeper knowledge of the electron-transfer reactions under restricted geometry conditions.

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## Appendix

It is clear that one cannot obtain the energy of the maximum optical transfer band directly within the ion pairs  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}/[\text{Fe}(\text{CN})_6]^{4-}$ ,  $(E_{\text{op}})_{\text{corr}}$ , because the reactions are too fast at room temperature. Instead, the energy of the maximum optical transfer band within the ion pairs  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}/[\text{Ru}(\text{CN})_6]^{4-}$ ,  $(E_{\text{op}})_{\text{exp}}$ , was measured. Thus,  $(E_{\text{op}})_{\text{exp}}$  must be corrected for

(a) the spin–orbit coupling contribution of the hexacyanoruthenate (III) complex by using

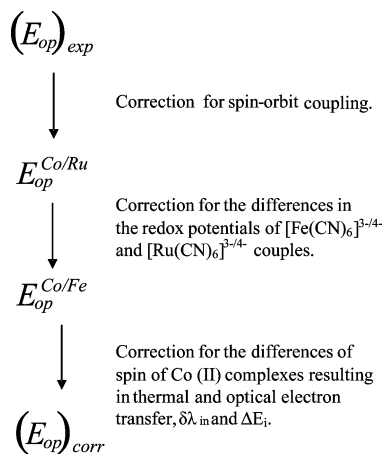
$$E_{\text{op}}^{\text{Co/Ru}} = (E_{\text{op}})_{\text{exp}} - \lambda_{\text{so}} \quad (\text{A-1})$$

where  $\lambda_{\text{so}}$  is the spin–orbit coupling parameter. A value of 14.9 kJ mol<sup>−1</sup> was used for this parameter.<sup>28b</sup>

(b) the difference in the redox potential of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  ( $E_{\text{Fe}}^{\circ}$ ) and  $[\text{Ru}(\text{CN})_6]^{3-/4-}$  ( $E_{\text{Ru}}^{\circ}$ ) couples in order to obtain the maximum of the MMCT band corresponding to the ion pair  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}/[\text{Fe}(\text{CN})_6]^{4-}$

$$E_{\text{op}}^{\text{Co/Fe}} = E_{\text{op}}^{\text{Co/Ru}} + F(E_{\text{Fe}}^{\circ} - E_{\text{Ru}}^{\circ}) \quad (\text{A-2})$$

## SCHEME 2: Correction of $(E_{\text{op}})_{\text{exp}}$ to Obtain $(E_{\text{op}})_{\text{corr}}$ for Optical Electron-Transfer Processes



(c) the differences between free energies of thermally equilibrated high-spin and low-spin Co(II) complexes,  $\Delta E_i$ , and the inner-shell reorganization free-energy difference between the thermal and optical processes, owing to the differences in the spin of Co(II),  $\delta\lambda_{\text{in}}$

$$(E_{\text{op}})_{\text{corr}} = E_{\text{op}}^{\text{Co/Fe}} + \Delta E_i + \delta\lambda_{\text{in}} \quad (\text{A-3})$$

A value of  $-79.5$  kJ mol<sup>−1</sup> was taken for  $\Delta E_i$  according to the data of Brunschwig,<sup>28b</sup> and a value of  $127.8$  kJ mol<sup>−1</sup> was calculated for  $\delta\lambda_{\text{in}}$  using eq A-4 and the corresponding force constants and bond lengths (see ref 23)

$$\lambda_{\text{in}} = \sum_k \frac{1}{2} f_k^r (\Delta q_k)^2 \quad (\text{A-4a})$$

$$f_k = \frac{2f_k^r f_k^p}{f_k^r + f_k^p} \quad (\text{A-4b})$$

Scheme 2 summarizes the steps of the correction procedure.

Once one has  $(E_{\text{op}})_{\text{corr}}$ , from experimental  $k_{\text{et}}$  and the corresponding values of  $\Delta G^{\ddagger}$  by using eqs 19 and 8, the values of  $\Delta G^{\circ'}$  and  $\lambda$  for a given reaction can be calculated. In this way, the values of these parameters appearing in Table 4 were obtained.

On the other hand, once one has  $\Delta G^{\circ'}$ , to have the values of  $E^{\circ}$  for the cobalt couples is a straightforward matter using eq 13 and the redox potential of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  couple.

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