

# The Effects of Cyclodextrin Inclusion of the Ferrocenemonocarboxylate Anion on the Kinetics of Its Oxidation by Bis(pyridine-2,6-dicarboxylato)cobaltate(III) in Aqueous Solution

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**Abstract.** The effects of  $\alpha$ -,  $\beta$ -,  $\text{dm}\beta$ -(heptakis(2,6-di-*O*-methyl)- $\beta$ -) and  $\gamma$ -cyclodextrins (CD) on the kinetics of the electron-transfer reaction of the ferrocenemonocarboxylate anion ( $\text{FCA}^-$ ) with bis(pyridine-2,6-dicarboxylato)cobaltate(III) have been investigated in aqueous solution (0.20 M  $\text{Na}_2\text{HPO}_4$ , pH 9.2) at 25.0°C. Substantial decreases in the rate constants for the electron-transfer reactions were observed upon cyclodextrin inclusion of the reductant, due to an increase in the  $\text{FCA}^{0/-}$  reduction potential and to the insulation of the reductant from oxidant. The inclusion stability constants for  $\{\text{FCA}\cdot\text{CD}\}^-$  were evaluated from the  $^1\text{H}$  NMR and kinetic data, and the order of the stability constants was found to be  $\beta\text{-CD} \approx \text{dm}\beta\text{-CD} \gg \gamma\text{-CD} > \alpha\text{-CD}$ .

**Key words.** Cyclodextrins, ferrocenemonocarboxylate, bis(pyridine-2,6-dicarboxylato)cobaltate(III), electron transfer kinetics, inclusion stability constants.

## 1. Introduction

Cyclodextrins (CD) are cyclic oligosaccharide molecules, most commonly comprised of six ( $\alpha$ -CD), seven ( $\beta$ -CD), or eight ( $\gamma$ -CD)  $\alpha$ -(1  $\rightarrow$  4)-linked D-(+)-glucopyranose units, which are capable of including a wide variety of organic and inorganic guests within their hydrophobic cavities [1]. Despite a wealth of information on the cyclodextrin inclusion complexes of organic compounds [2], comparatively less information is known about cyclodextrin inclusion of transition metal complexes [3]. Among the earliest transition metal complexes to be investigated were ferrocene and its substituted derivatives [4]. It has been reported that ferrocene forms a 2:1 (host: guest) inclusion complex with  $\alpha$ -CD and 1:1 inclusion complexes with both  $\beta$ -CD and  $\gamma$ -CD [5]. From recent studies of substituted ferrocene derivatives using induced circular dichroism, it has been suggested that the inclusion of ferrocenes in  $\beta$ -CD is axial while that of  $\gamma$ -CD is equatorial [6, 7]. The effects of cyclodextrins on the electrochemical properties of ferrocene and its derivatives have been reported [4, 8–11], and cyclic voltammetry has been employed in the determination of the stability constants of the complexation of ferrocene and its derivatives with  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrin [8–11].

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Recent research interests in our laboratory have been concerned with the effects of cyclodextrin inclusion on the kinetics and mechanisms of ligand substitution and electron transfer reactions of transition metal complexes in aqueous solution [12, 13]. We have found that CD inclusion of one or both of the reactants substantially decreases the rate constants for these processes. In particular, the inclusion of 4-*t*-butylcatechol by  $\alpha$ - and  $\beta$ -cyclodextrins significantly inhibits the rate of its oxidation by several transition metal complex oxidants [13]. The inclusion of the 4,4'-bipyridine ligand on  $[\text{Ru}(\text{NH}_3)_5(4,4'\text{-bpy})]^{2+}$  in heptakis(2,6-di-*O*-methyl) $\beta$ -cyclodextrin (dm $\beta$ -CD) has been reported to reduce the rate constant for its outer-sphere oxidation by  $[\text{Co}(\text{EDTA})]^-$  by partially shielding the reactants from each other [14]. In this paper, we report the results of an investigation into the effects of the inclusion of ferrocenecarboxylate ( $\text{FCA}^-$ ) in  $\alpha$ -,  $\beta$ -, dm $\beta$ - and  $\gamma$ -cyclodextrin on the kinetics of its outer-sphere electron-transfer reaction with substitutionally inert bis(pyridine-2,6-dicarboxylato)cobaltate(III) ( $[\text{Co}(\text{dipic})_2]^-$ ). The stability constants of the  $\alpha$ -,  $\beta$ -, dm $\beta$ - and  $\gamma$ -CD inclusion complexes with  $\text{FCA}^-$  have been determined by the application of simplex optimization and non-linear least squares programs to the kinetic data. The effects of cyclodextrin inclusion on the reductant electron-transfer rate constants are discussed and the stability constants compared with those obtained from cyclic voltammetry studies [8–10].

## 2. Experimental

### 2.1. MATERIALS

The  $\alpha$ -,  $\beta$ -, dm $\beta$ - and  $\gamma$ -cyclodextrins (Aldrich and Cyclolab) were dried at 80°C under vacuum for at least 12 hours prior to use. The ferrocenemonocarboxylic acid (Aldrich and Strem) was used as received. The ammonium bis(pyridine-2,6-dicarboxylato)cobaltate(III),  $\text{NH}_4[\text{Co}(\text{dipic})_2]$ , was prepared as reported in the literature [15]. Solutions were prepared immediately prior to use in a 0.20 M  $\text{Na}_2\text{HPO}_4$  solution (pH = 9.2) and the concentrations of the oxidant and reductant were determined spectrophotometrically at 510 nm ( $\epsilon = 630 \text{ M}^{-1} \text{ cm}^{-1}$ ) [15] and 440 nm ( $\epsilon = 205 \text{ M}^{-1}$ ), respectively.

### 2.2. PHYSICAL MEASUREMENTS

The kinetic measurements were performed by using a TDI Model IIA stopped-flow apparatus and data acquisition system (Cantech Scientific). Pseudo-first-order conditions of excess reductant concentrations ( $[\text{FCA}^-] = 0.50\text{--}4.45 \times 10^{-3} \text{ M}$ ) over oxidant concentration ( $5.0 \times 10^{-5} \text{ M}$ ) were employed, and plots of  $\ln(A_t - A_\infty)$  against time, monitoring the formation of iron(III) product  $\text{FCA}$  at 620 nm, were linear for at least three half-lives. The observed pseudo-first-order rate constants were determined from the average of four replicate experiments and the reaction temperature was maintained at  $25.0 \pm 0.1^\circ\text{C}$  by means of an external circulating water bath.

Cyclic voltammetric measurements on the  $\text{FCA}^{-/0}$  couple in the presence of dm $\beta$ -CD were performed by using a CV1B cyclic voltammograph (Bioanalytical

Systems) attached to a Houston Instruments 100 X-Y recorder. The working (platinum button) and auxiliary (Pt wire) electrodes in the sample solution ( $1.0 \times 10^{-3}$  M FCA<sup>-</sup>,  $0.2 \times 10^{-2}$  M dm $\beta$ -CD) were separated from the reference electrode (Ag/AgCl) by a glass frit. The <sup>1</sup>H NMR titrations of FCA<sup>-</sup> by dm $\beta$ - and  $\gamma$ -CD were performed on a Bruker AM-400 spectrometer at 25°C in D<sub>2</sub>O containing 0.20 M Na<sub>2</sub>HPO<sub>4</sub>.

### 2.3. STABILITY CONSTANT CALCULATIONS

The inclusion stability constants and the estimated errors were calculated from electron-transfer kinetic data and <sup>1</sup>H NMR chemical shift titration data by the application of Simplex optimization and non-linear least-squares programs [16, 17] to Equations (1) and (6). The concentrations of the 1:1 host-guest complex {FCA·CD}<sup>-</sup> (where FCA<sup>-</sup> = the ferrocenemonocarboxylate anion, and CD =  $\alpha$ -,  $\beta$ -, dm $\beta$ - or  $\gamma$ -CD) were determined from Equation (1).

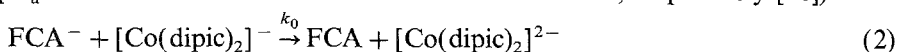
$$[\{\text{FCA}\cdot\text{CD}\}^-] = \frac{B - (B^2 - 4[\text{FCA}^-]_{\text{T}}[\text{CD}]_{\text{T}})^{1/2}}{2} \quad (1)$$

where  $B = ([\text{FCA}^-]_{\text{T}} + [\text{CD}]_{\text{T}} + K_{\text{CD}}^{-1})$ .

## 3. Results

### 3.1. KINETICS

The measurements of the kinetics of the oxidation of the ferrocenemonocarboxylate anion, FCA<sup>-</sup>, by bis(pyridine-2,6-dicarboxylato)cobaltate(III), [Co(dipic)<sub>2</sub>]<sup>-</sup>, were carried out in 0.20 M Na<sub>2</sub>HPO<sub>4</sub> solutions (pH 9.2) at 25.0°C. The reduced and oxidized forms of the iron reactant are present in the deprotonated forms at this pH (the pK<sub>a</sub> values of FCAH and FCAH<sup>+</sup> are 4.20 and 1.35, respectively [18]).

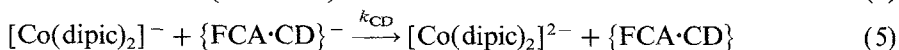


In the absence of added cyclodextrins, the pseudo-first-order rate constants for the formation of the iron(III) product, FCA, exhibited a first-order dependence on the concentration of FCA<sup>-</sup> present in a large excess ( $0.50\text{--}4.45 \times 10^{-3}$  M) over [Co(dipic)<sub>2</sub>]<sup>-</sup> ( $5.0 \times 10^{-5}$  M), according to the rate expression in Equation (3).

$$\frac{d[\text{FCA}]}{dt} = k[\text{Co}(\text{dipic})_2^-][\text{FCA}^-] \quad (3)$$

The second-order rate constant in the absence of cyclodextrin,  $k_0$ , is  $(2.03 \pm 0.02) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25.0°C.

The electron-transfer rate constants were observed to decrease as the concentrations of added  $\alpha$ -,  $\beta$ -, dm $\beta$ - and  $\gamma$ -cyclodextrins were increased (Figures 1 and 2). The reaction pathway for oxidation of the included FCA<sup>-</sup> reductant by [Co(dipic)<sub>2</sub>]<sup>-</sup> may be represented as follows.



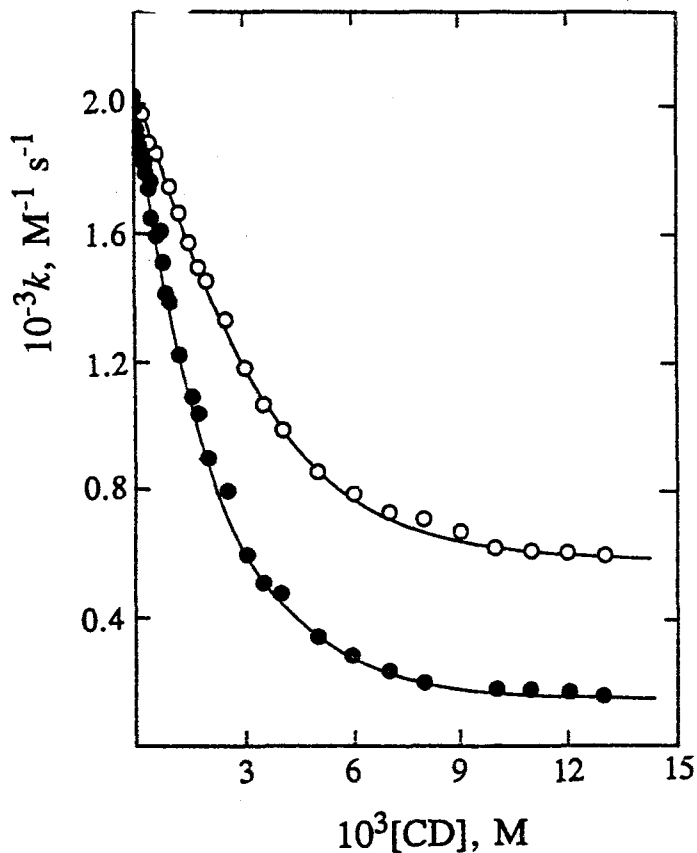


Fig. 1. Dependences of the second-order rate constants on  $[\beta\text{-CD}]$  (●) and  $[dm\beta\text{-CD}]$  (○) for the oxidation of  $\text{FCA}^-$  by  $[\text{Co}(\text{dipic})_2]^-$  at  $25.0^\circ\text{C}$  in  $0.20\text{ M Na}_2\text{HPO}_4$ . The solid curves represent a fit of the kinetic data to Equation (6) using the parameters in Table I.

The inclusion of the ferricinium monocarboxylate (FCA) in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD has been reported to be much weaker than the inclusion of  $\text{FCA}^-$  [8, 10]. The second order rate constant for the electron transfer reaction may be expressed in terms of the specific rate constant  $k_0$  and  $k_{\text{CD}}$ , as shown in Equation (6).

$$k = \frac{k_0[\text{FCA}^-] + k_{\text{CD}}[\{\text{FCA}\cdot\text{CD}\}]^-}{[\text{FCA}^-]_{\text{T}}} \quad (6)$$

Non-linear least-square fits of the kinetic data to Equations (1) and (6) for a 1:1 guest:host model yielded values for  $k_{\text{CD}}$  and  $K_{\text{CD}}$ , which are presented in Table I.

### 3.2. NMR TITRATIONS

The stability constants for the inclusion of  $\text{FCA}^-$  in the cavities of  $dm\beta$ - and  $\gamma$ -cyclodextrins were also determined by means of  $^1\text{H}$  NMR chemical shift titrations

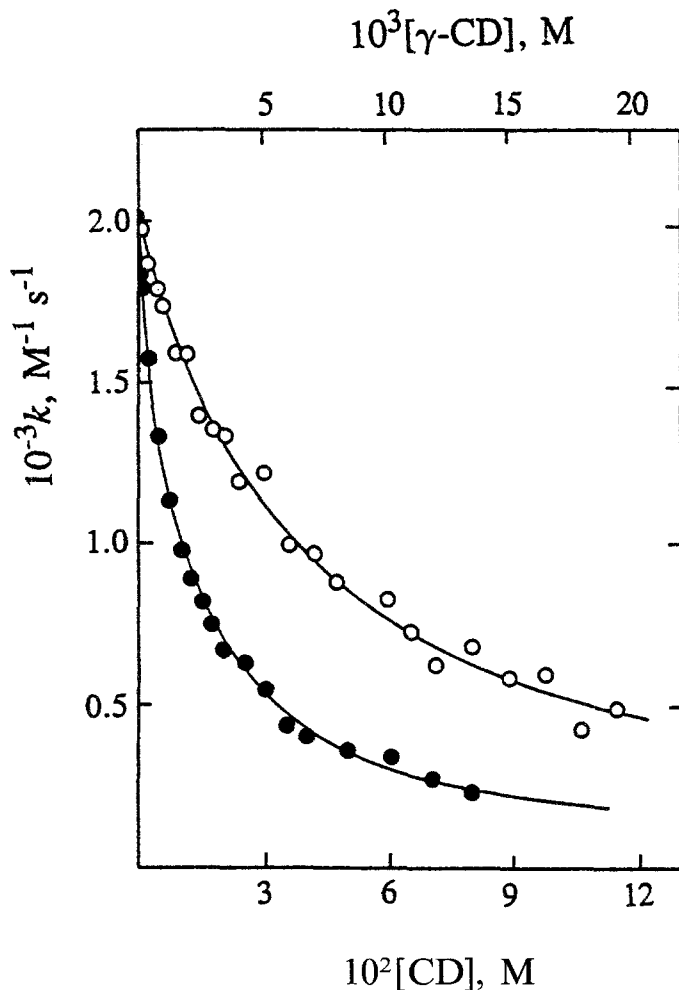


Fig. 2. Dependences of the second-order rate constants on  $[\alpha\text{-CD}]$  ( $\bullet$ ) and  $[\gamma\text{-CD}]$  ( $\circ$ ) for the oxidation of FCA<sup>-</sup> by  $[\text{Co}(\text{dipic})_2]^-$  at 25.0°C in 0.20 M  $\text{Na}_2\text{HPO}_4$ . The solid curves represent a fit of the kinetic data to Equation (6) using the parameters in Table I.

in  $\text{D}_2\text{O}$  containing 0.20 M  $\text{Na}_2\text{HPO}_4$  at 25°C. The H-3/H-4 resonance of the coordinated 1-cyclopentadienylcarboxylate ligand of FCA<sup>-</sup> shifted upfield in the presence of the added cyclodextrins and the chemical shift changes ( $\Delta\delta_{\text{obs}} = \Delta\delta_{\text{CD}}[\{\text{FCA}\cdot\text{CD}\}^-]/[\text{FCA}^-]_{\text{T}}$ ) were used (with Equation (1)) to determine the inclusion stability constants (Table I). Limiting chemical shift changes,  $\Delta\delta_{\text{CD}}$ , of  $-24 \pm 1$  and  $-50 \pm 3$  Hz were calculated for the  $\text{dm}\beta$ - and  $\gamma$ -CD inclusions, respectively.

The pyridine proton resonances on the oxidant  $[\text{Co}(\text{dipic})_2]^-$  exhibited negligible chemical shift changes in the presence of a large excess of added  $\text{dm}\beta$ - and  $\gamma$ -cyclodextrins, indicating very small ( $< 5 \text{ M}^{-1}$ ) stability constants for inclusion in the cyclodextrin cavities.

Table I. The rate constants for the oxidation of  $\text{FCA}^-$  by  $[\text{Co}(\text{dipic})_2]^-$  and the inclusion stability constants for  $\{\text{FCA}\cdot\text{CD}\}^-$  in 0.20 M  $\text{Na}_2\text{HPO}_4$  at 25.0°C

CD	$k_0, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{CD}}, \text{M}^{-1} \text{s}^{-1}$	$K_{\text{CD}}, \text{M}^{-1}$
$\alpha$ -CD	$2030 \pm 20$	$80 \pm 30$	$130 \pm 10^a$ $100^b$ $5.1 \pm 1.8^c$
$\beta$ -CD	$2030 \pm 20$	$80 \pm 30$	$2380 \pm 260^a$ $2200 \pm 100^b$ $2100 \pm 300^c$ $2200^d$
dm $\beta$ -CD	$2030 \pm 20$	$530 \pm 20$	$2390 \pm 320^a$ $2200 \pm 450^c$
$\gamma$ -CD	$2030 \pm 20$	$100 \pm 80$	$220 \pm 30^a$ $200^b$ $180 \pm 40^e$

<sup>a</sup> This work, from kinetic measurements at 25°C.

<sup>b</sup> Ref. [11], from cyclic voltammetry measurements at 18°C.

<sup>c</sup> Ref. [9], from cyclic voltammetry measurements.

<sup>d</sup> Ref. [8], from cyclic voltammetry measurements at 20°C.

<sup>e</sup> This work, from  $^1\text{H}$  NMR chemical shift titrations.

### 3.3. CYCLIC VOLTAMMETRY

While the effects of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin inclusions on the cyclic voltammograms of the  $\text{FCA}^{0/-}$  couple have been reported previously [8, 9, 11], studies on the effects of the presence of dm $\beta$ -CD had not been undertaken. As observed previously with  $\beta$ -CD, the half-wave potential ( $E_{1/2}^0 = 0.302$  versus Ag/AgCl) increases upon inclusion of  $\text{FCA}^-$  upon additions of dm $\beta$ -CD. The dependence of  $\Delta E_{1/2}$  for the  $\text{FCA}^{0/-}$  couple, measured in 0.20 M  $\text{Na}_2\text{HPO}_4$  solution (pH 9.2), on the concentration of dm $\beta$ -CD is presented in Figure 3. The half-wave potential for a 1:1 guest–host couple may be related to the concentration of the host by Equation (7),

$$\Delta E_{1/2} = (RT/F) \{ \ln(D_c/D_f)^{1/2} + \ln(1 + K_{\text{CD}}[\text{dm}\beta\text{-CD}]) \} \quad (7)$$

where  $D_c$  and  $D_f$  are the diffusion coefficients of  $\{\text{FCA}\cdot\text{dm}\beta\text{-CD}\}^-$  and  $\text{FCA}^-$ , respectively, and  $K_{\text{CD}}$  is the inclusion stability constant of  $\{\text{FCA}\cdot\text{dm}\beta\text{-CD}\}^-$  [8]. At higher concentrations of dm $\beta$ -CD ( $> 5 \times 10^{-3}$  M), such that the majority of the  $\text{FCA}^-$  anions ( $[\text{FCA}^-] = 1.0 \times 10^{-3}$  M) are included and  $K_{\text{CD}} \gg 1$ , a linear dependence of  $\Delta E_{1/2}$  on  $\ln[\text{dm}\beta\text{-CD}]$  is observed (Figure 3), with a slope of 22 mV, close to the expected value of 25 mV ( $RT/F$ ) for a 1:1 complex at 20°C. Using  $D_c/D_f = 0.41$ , determined for  $\beta$ -CD [8], and  $K_1 = 2300 \text{ M}^{-1}$  from the NMR titration and the electron-transfer kinetics, a reasonable fit of the linear portion of Figure 3 to Equation (7) requires a small value for the stability constant for  $\{\text{FCA}\cdot\text{dm}\beta\text{-CD}\}$ . The weak binding of the oxidized FCA to dm $\beta$ -CD is consistent with the relatively small values determined for  $\alpha$ - ( $4.4 \text{ M}^{-1}$  [11]),  $\beta$ - ( $< 20 \text{ M}^{-1}$  [8],  $36.9 \text{ M}^{-1}$  [11]), and  $\gamma$ -cyclodextrins ( $8.8 \text{ M}^{-1}$  [11]).

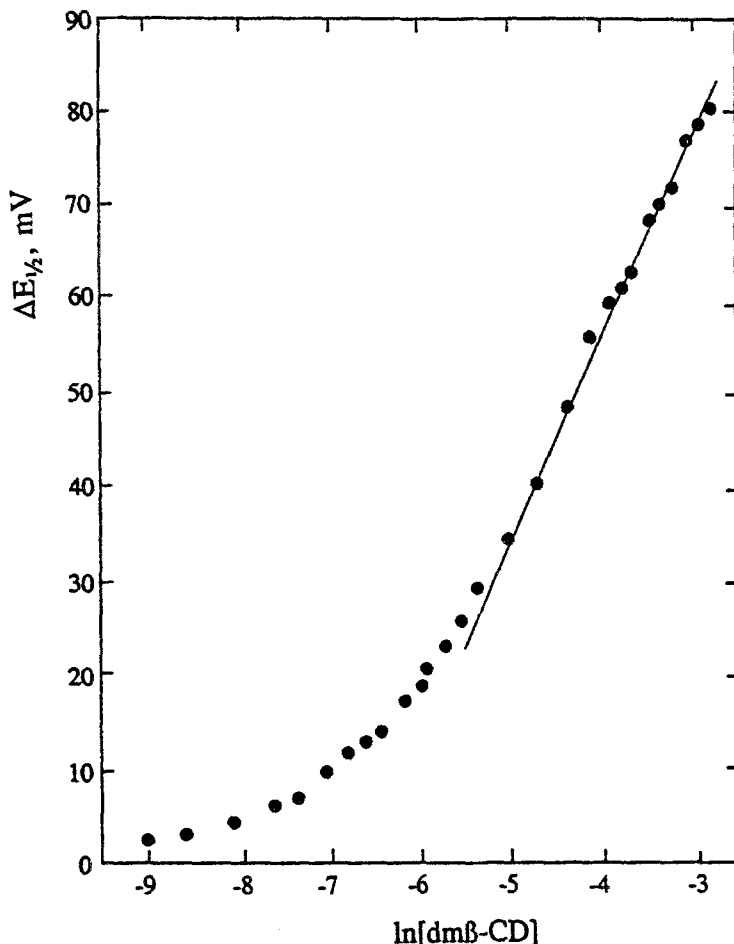


Fig. 3. A plot  $\Delta E_{1/2}$  against  $\ln[\text{dm}\beta\text{-CD}]$  from cyclic voltammetric measurements on the  $\text{FCA}^{0/-}$  couple ( $[\text{FCA}^-] = 1.0 \times 10^{-3} \text{ M}$ ) in  $0.20 \text{ M Na}_2\text{HPO}_4$  at a scan rate of  $100 \text{ mV s}^{-1}$ . The solid line represents a slope of  $22 \text{ mV}$  (see text).

#### 4. Discussion

The inclusion of the reductant  $\text{FCA}^-$  in cavities of the  $\alpha$ -,  $\beta$ -,  $\text{dm}\beta$ - and  $\gamma$ -cyclodextrins leads to a decrease in the rate constants for its outer-sphere oxidation by  $[\text{Co}(\text{dipic})_2]^-$ . From Table I, the order of the magnitude of the  $\{\text{FCA}\cdot\text{CD}\}^-$  stability constants was observed to be  $\beta\text{-CD} \approx \text{dm}\beta\text{-CD} \gg \gamma\text{-CD} > \alpha\text{-CD}$ , in good agreement with the values measured previously by means of cyclic voltammetry [8], and in this study by  $^1\text{H}$  NMR chemical shift titrations. The limiting rate constants for the oxidation of the included ferrocenemonocarboxylate anion are very similar for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD hosts at  $80\text{--}100 \text{ M}^{-1} \text{ s}^{-1}$ .

One explanation for the observed decrease in the rate constants for the electron-transfer reaction is that the inclusion of  $\text{FCA}^-$  and  $\text{FCA}$  in the cyclodextrin cavities lead to an increase in the reduction potential of the  $\text{FCA}^{0/-}$  couple. Cyclic

voltammetric investigations into the effects of added  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD at pH 9.2 (0.20 M  $\text{Na}_2\text{HPO}_4$ ) have revealed 70–100 mV increases [8, 10]. An increase in the redox potential of  $\text{FCA}^-$  upon inclusion will lead to a decrease in the driving force of the electron transfer reaction and hence a decrease in the rate constant. The dependence of the electron-transfer rate constant ( $k_{12}$ ) on the thermodynamic driving force of the reaction ( $K_{12}$ ) is given by the Marcus theory relationship [19, 20] in Equation (8),

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (8)$$

in which  $k_{11}$  and  $k_{22}$  are the self-exchange rate constants of the reductant and oxidant couples,  $W_{12}$  is an electrostatic work term (Equation (9)),

$$W_{12} = [(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (9)$$

and  $f_{12}$  is a non-linear correction term, given by Equation (10).

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22}) + (w_{11} + w_{22})/RT]} \quad (10)$$

The  $[\text{Co}(\text{dipic})_2]^{-2-}$  couple has a reduction potential of 0.747 V [21] and a self-exchange rate constant calculated to be  $1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  [15, 21]. While the self-exchange rate constant for the  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{COO})]^{-0}$  couple has not been reported, the values for the related  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{OH})]^{0/+}$  and  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_3)]^{+/2+}$  couples have been determined to be  $1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively in  $\text{D}_2\text{O}$  [22]. Using the former rate constant (couple with the same charge product) for  $k_{11}$  of the  $\text{FCA}^{-0}$  couple, the rate constant for the electron-transfer reaction between  $\text{FCA}^-$  and  $[\text{Co}(\text{dipic})_2]^-$  in the absence of the cyclodextrins is calculated (Equations (8)–(10), with  $A_{11}A_{22} = 1 \times 10^{24} \text{ M}^{-2} \text{ s}^{-2}$  [20]) to be  $1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with the measured value. The increase of 70–100 mV in the reduction potential of the  $\text{FCA}^{0/-}$  couple observed upon inclusion in the cyclodextrin cavities would decrease  $K_{12}$  by a factor of four to six, and partially account for the observed reduction in the electron-transfer rate constant for the  $\text{FCA}^-/[\text{Co}(\text{dipic})_2]^-$  reaction. The increase in the reduction potential of  $\beta$ -CD-included  $\text{FCA}$  is responsible for the accelerated rate of its oxidation of NADH at 7.0 [23].

A second effect of the cyclodextrin inclusion of  $\text{FCA}^-$  upon the rate constants for the electron transfer to  $[\text{Co}(\text{dipic})_2]^-$  is the shielding of the two reactants from each other imposed by the host CD. We have observed that the rate constants for the oxidations of 4-*t*-butylcatechol by several transition metal complexes are substantially reduced upon the inclusion of the reductant in  $\alpha$ - or  $\beta$ -cyclodextrins [13]. Johnson *et al.* [14] have reported a similar observation for the reduction of  $[\text{Co}(\text{EDTA})]^-$  by  $[\text{Ru}(\text{NH}_3)_5(4,4'\text{-bpy})]^{2+}$ , in which the coordinated 4,4'-bipyridine was included in the cavity of  $\text{dm}\beta$ -CD. The shielding of one of the reactants from the other upon cyclodextrin inclusion would hinder a close approach of the species and an effective overlap of the donor and acceptor orbitals. The rate constant  $k_{\text{CD}}$  determined for the reaction in the presence of  $\text{dm}\beta$ -CD was found to be larger than those for  $\alpha$ -,  $\beta$ -, or  $\gamma$ -CD. This may be a result of a shallower inclusion of the  $\text{FCA}^-$  in the  $\text{dm}\beta$ -CD cavity, and therefore greater access to the oxidant, due to the presence of the methyl groups which may occupy the narrow end of the hydrophobic host cavity [24].



The decreases calculated above for the electron-transfer rate constants, resulting from changes in the thermodynamic driving forces, are made assuming that the self-exchange rate constant for the FCA<sup>-/0</sup> couple is not changed upon CD inclusion. The self-exchange rate constants of the [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>OH)]<sup>0/+</sup> couple vary somewhat ( $0.5\text{--}1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) when measured in water and a variety of organic solvents [22]. The presence of the cyclodextrin as the second coordination sphere for the complex may play a role in the solvent reorganization required prior to electron transfer [20] and kinetic studies into the effects of inclusion on the electron self-exchange rate constants of several transition metal complexes are presently underway in our laboratory.

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## References

- (a) M. L. Bender and M. Komiyama: *Cyclodextrin Chemistry*, Springer-Verlag, Berlin, 1978.  
(b) J. Szejtli: *Cyclodextrins and their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.
- R. J. Clarke, J. H. Coates, and S. F. Lincoln: *Adv. Carbohydr. Chem. Biochem.* **46**, 205 (1988).
- J. F. Stoddart and R. Zarzycki: *Recl. Trav. Chim. Pays-Bas* **107**, 515 (1988).
- B. Siegel and R. Breslow: *J. Am. Chem. Soc.* **97**, 6869 (1975).
- A. Harada, Y. Hu, S. Yamamoto, and S. Takahashi: *J. Chem. Soc. Dalton Trans.* 729 (1988).
- N. Kobayashi and T. Osa: *Chem. Lett.* 421 (1986).
- N. Kobayashi and M. Opallo: *J. Chem. Soc., Chem. Commun.* 477 (1990).
- T. Matsue, D. H. Evans, T. Osa and N. Kobayashi: *J. Am. Chem. Soc.* **107**, 3411 (1985).
- A. D. Ryabov, E. M. Tyapochkin, S. D. Varfolomeev and A. A. Karyakin: *J. Electroanal. Chem., Bioelectrochem. Bioenerg.* **24**, 257 (1990).
- V. V. Strelets, I. A. Mamedjarova, M. N. Nefedova, N. I. Pysnograeva, V. I. Sokolov, L. Pospisil, and J. Hanzlik: *J. Electroanal. Chem.* **310**, 179 (1991).
- S. McCormack, N. R. Russell, and J. F. Cassidy: *Electrochimica Acta* **37**, 1939 (1992).
- (a) M. E. Shortreed, R. S. Wylie, and D. H. Macartney: *Inorg. Chem.* **32**, 1824 (1993). (b) R. S. Wylie and D. H. Macartney: *Inorg. Chem.* **32**, 1830 (1993).
- (a) J. A. Imonigie and D. H. Macartney: *J. Chem. Soc., Dalton Trans.* 891 (1993). (b) J. A. Imonigie and D. H. Macartney: *Inorg. Chem.* **32**, 1007 (1993).
- M. D. Johnson, V. C. Reinsborough, and S. Ward: *Inorg. Chem.* **31**, 1085 (1992).
- A. D. Mauk, C. L. Coyle, E. Bordignon and H. B. Gray: *J. Am. Chem. Soc.* **101**, 5054 (1979).
- (a) J. W. Cooper: *Introduction to Pascal for Scientists*, Wiley-Interscience, New York 1981. (b) G. E. Forsythe, M. A. Malcolm and C. B. Moler: *Computer Methods for Mathematical Computations*, Prentice-Hall, Englewood Cliffs, 1977.
- K. A. Connors: *Binding Constants. The Measure of Molecular Complex Stability*, Wiley-Interscience, New York, 1987.
- A. A. Pendin, P. K. Leont'evskaya, E. I. L'vova, and B. P. Nikol'skii: *Dokl. Akad. Nauk. SSSR* **189**, 115 (1969).
- R. A. Marcus: *Annu. Rev. Phys. Chem.* **15**, 155 (1964).
- N. Sutin: *Prog. Inorg. Chem.* **30**, 441 (1983).
- N. H. Williams and J. K. Yandell: *Aust. J. Chem.* **36**, 2377 (1983).
- (a) G. E. McManis, R. M. Nielson, A. Gochev, and M. J. Weaver: *J. Am. Chem. Soc.* **111**, 5533 (1989). (b) R. M. Nielson, G. E. McManis, and M. J. Weaver: *J. Phys. Chem.* **93**, 4703 (1989).
- T. Matsue, T. Kato, U. Akiba, and T. Osa: *Chem. Lett.* 843 (1986).
- R. Breslow, M. F. Czarniecki, J. Emert, and H. Hamaguchi: *J. Am. Chem. Soc.* **102**, 762 (1980).