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The kinetics of electron-transfer reactions of the $[FeCp(CpCH_2N(CH_3)_3]^{+/2+}$ couple in the presence of cyclodextrins in aqueous media

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Abstract

The stability constants for the inclusions of the $[FeCp(CpCH_2N(CH_3)_3]^+$ cation in α- (150 ± 10 M^{-1}), β- (4810 ± 600 M^{-1}), dmβ- (5010 ± 800 M^{-1}) and γ-cyclodextrins (500 ± 50 M^{-1}) have been determined at 25 °C by means of ^1H NMR chemical shift titrations. The effects of cyclodextrin inclusion of the substituted ferrocene couple on the kinetics of its electron-transfer reactions have been investigated in aqueous solution at 25.0 °C. The inclusions of $[FeCp(CpCH_2N(CH_3)_3]^+$ by cyclodextrins decrease the rate constant for its oxidation by bis(pyridine-2,6-dicarboxylato)cobaltate(III) (from 930 to 20 M^{-1} s^{-1} upon β-CD inclusion). The rate constants for the oxidations of ascorbic acid by $[FeCp(CpCH_2N(CH_3)_3]^{2+}$ increase (from 640 to 2600 M^{-1} s^{-1} for β-CD) upon inclusion of the oxidant by α- ($K_{CD} = 10 \pm 5$ M^{-1}), β- (150 ± 15 M^{-1}) and dmβ-cyclodextrin (140 ± 30 M^{-1}) inclusions of the oxidant. The γ-cyclodextrin has a negligible effect on the electron-transfer rate constant. The effects of cyclodextrin inclusion on the kinetics of these electron-transfer reactions are discussed in terms of changes in the thermodynamic driving force of the reaction and shielding of the reactants.

Keywords: Kinetics; Electron transfer; Cyclodextrin complexes; Ferrocene substituted complexes; Inclusion complexes

1. Introduction

The cyclodextrins (CD) are a family of cyclic oligosaccharide molecules, most commonly comprised of six (α-CD), seven (β-CD), or eight (γ-CD) α-(1→4)-linked D-(+)-glucopyranose units (Fig. 1), which are capable of including a wide variety of inorganic and organic guests within their hydrophobic cavities [1,2].

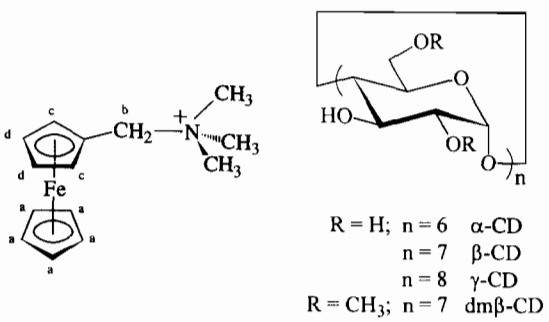

Fig. 1. Structures of $[FeCp(CpCH_2N(CH_3)_3)]^+$ and the cyclodextrins.

While there is a wealth of information concerning the cyclodextrin inclusion complexes of organic compounds [3], comparatively less is known about cyclodextrin inclusions of transition metal complexes [4] in solution. Among the first of the transition metal complexes to be investigated in this respect were ferrocene and its substituted derivatives [5]. It has been reported that ferrocene forms a 1:2 (guest:host) inclusion complex with α-CD and 1:1 inclusion complexes with both β-CD and γ-CD [6]. Recent studies of substituted ferrocene derivatives, using induced circular dichroism, have suggested that the inclusion of ferrocenes in β-CD is axial while that of γ-CD is equatorial [7,8]. The effects of cyclodextrins on the reduction potentials of several ferricinium/ferrocene couples have been reported [5,9–13], and cyclic voltammetry has been employed in the determination of the stability constants of the complexation of ferrocene and its derivatives with α-, β- and γ-cyclodextrin [9–12].

Several investigations in our laboratory have recently been concerned with the effects of cyclodextrin inclusions on the kinetics and mechanisms of ligand substitution [14,15] and electron-transfer reactions of tran-

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sition metal complexes in aqueous solution [16–18]. We have observed that the cyclodextrin inclusion of one or both of the reactants substantially decreases the rate constants for each of these processes. In particular, the inclusions of 4-tert-butylcatechol by α- and β-cyclodextrins significantly inhibits the rate of its oxidation by several transition metal complex oxidants [16,17]. The inclusion of the 4,4′-bipyridine ligand on $[Ru(NH_3)_5(4,4'\text{-bpy})]^{2+}$ in heptakis(2,6-di-*o*-methyl)β-cyclodextrin (dmβ-CD) has been reported to reduce the rate constant for its outer-sphere oxidation by $Co(EDTA)^-$ by partially shielding the reactants from each other [19]. We have recently investigated the effects of the inclusion of ferrocenemonocarboxylate in α-, β-, dmβ- and γ-cyclodextrin on the kinetics of its outer-sphere electron-transfer reaction with substitutionally inert bis(pyridine-2,6-dicarboxylato)-cobaltate(III) ($[Co(dipic)_2]^-$) [18], and observed similar behaviour.

In this paper we present the results of a kinetic study of the effect of α-, β-, dmβ- and γ-cyclodextrin inclusions on the electron-transfer reactions of the $[FeCp(CpCH_2N(CH_3)_3)]^{+/2+}$ couple (Fig. 1) in aqueous solution. These reactions (Eq. (1)) involve the use

$$\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+ + \text{oxidant} \rightleftharpoons \{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^{2+} + \text{reductant} \quad (1)$$

of $[Co(dipic)_2]^-$ as an oxidant and ascorbic acid as a reductant. The inclusion stability constants for the binding of reduced and oxidized forms of the substituted ferrocene were determined from the kinetics studies, as well as from ^1H NMR chemical shift titrations in the case of the reduced species. The effects of the cyclodextrin inclusions on the electron-transfer rate constants are discussed in terms of the thermodynamic driving forces of the reactions and abilities of the cyclodextrins to inhibit the reactions by shielding the guest molecule from the cross-reactant.

2. Experimental

2.1. Materials

The α-, β-, dmβ- and γ-cyclodextrins (Aldrich and Cyclolab) were dried at 80 °C under vacuum for at least 12 h prior to use. L-Ascorbic acid was used as received (Aldrich) and solutions were prepared in 0.10 M $HClO_4$ immediately prior to use. The $[FeCp(CpCH_2N(CH_3)_3)]I$ complex was prepared from $FeCp(CpCH_2N(CH_3)_2)$ (Strem) and methyl iodide (Aldrich) by the method of Lindsay and Hauser [20]. The tetrafluoroborate salt was prepared by anion exchange chromatography (Amberlite IRA-401, BDH) in methanol [21]. The $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ cation was prepared in situ by the oxidation of the $[FeCp(CpCH_2N(CH_3)_3)]^+$ ion using solid PbO_2 in 0.10 M $HClO_4$, and the concentrations determined spectrophotometrically at 628 nm ($\epsilon = 198\ M^{-1}\ cm^{-1}$). The ammonium bis(pyridine-2,6-dicarboxylato)cobaltate-(III) complex, $NH_4[Co(dipic)_2]$, was prepared as previously reported [22].

2.2. Physical measurements

The kinetic measurements on the electron-transfer cross-reactions 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 were employed and plots of $\ln(A_\infty - A_t)$ or $\ln(A_t - A_\infty)$ against time, monitoring the formation or disappearance of the iron(III) product, $[FeCp(CpCH_2N(CH_3)_3]^{2+}$ at 628 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 ± 0.1 °C by means of an external circulating water bath. The ionic strength of the reaction solutions was maintained at 0.10 M using $HClO_4$ (oxidation of ascorbic acid) or phosphate buffer (0.025 M NaH_2PO_4/0.025 M Na_2HPO_4, reduction of $[Co(dipic)_2]^-$).

Cyclic voltammetric measurements on the $[FeCp(CpCH_2N(CH_3)_3]^{+/2+}$ couple in the presence of the cyclodextrins were performed using a CV1B cyclic voltammograph (Bioanalytical Systems) attached to a Houston Instruments 100 X-Y recorder. The working (Pt button) and auxiliary (Pt wire) electrodes in the sample solution were separated from the reference electrode (Ag/AgCl) by a glass frit. The ^1H NMR spectra and chemical shift titrations were recorded on a Bruker AM-400 spectrometer at 25 °C in D_2O containing 0.025 M phosphate buffer at pH 6.8. The chemical shifts were referenced to TSP in D_2O in a sealed capillary.

2.3. Stability constant computations

The inclusion stability constants and estimated errors were calculated from the ^1H NMR chemical shift titrations and from the electron-transfer kinetic data by the application of non-linear least-squares and Simplex optimization programs [23–25]. The concentrations of the 1:1 host–guest complex $\{FeCp(CpR)\cdot CD\}^{n+}$ were determined from Eq. (2),

$$[\{FeCp(CpR)\cdot CD\}^{n+}] = \frac{B-(B^2-4[FeCp(CpR)^{n+}]_T[CD]_T)^{1/2}}{2} \quad (2)$$

where $B=([FeCp(CpR)^{n+}]_T+[CD]_T+K_{CD}^{-1})$.

3. Results and discussion

3.1. Inclusion stability constants

The stability constants for the inclusion complexes $\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+$, with α-, β-, dmβ- and γ-cyclodextrins (Eq. (3)) were determined at 25 °C in D_2O containing 0.025 M phosphate buffer (pH 7.0) by

$$[FeCp(CpCH_2N(CH_3)_3)]^+ + CD \overset{K_{CD}}{\rightleftharpoons} \{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+ \quad (3)$$

means of ^1H NMR chemical shift titrations. For a 1:1 binding model, the observed change in the chemical shift of a proton resonance, $\Delta\delta_{obs}$, is the product of the limiting chemical shift difference, $\Delta\delta_{CD}$, and the complexed fraction of the species whose resonance is being monitored (Eq. (4)).

$$\Delta\delta_{obs} = \frac{\Delta\delta_{CD}[\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+]}{[FeCp(CpCH_2N(CH_3)_3)^+]_T} \quad (4)$$

The inclusion stability constants K_{CD} and the limiting chemical shifts for the guest ferrocene protons were determined from the non-linear regressions of the chemical shift data to Eqs. (2) and (4). The parameters determined from the titrations of the complex with α-, β-, dmβ- and γ-cyclodextrins are presented in Table 1. The resonances for the symmetry-related protons on the substituted cyclopentadienyl ring are observed to split into separate resonances upon inclusion of the complex into the cavities of the β- and dmβ-cyclodextrins. In the case of β-CD, only splitting of the H^c protons (Fig. 2) is observed ($\Delta_{c,c'}=16$ Hz), whereas with the dmβ-CD host, both the H^c (22 Hz) and H^d (10 Hz) resonances split. The splitting pattern for this β-CD inclusion complex was observed previously by Isnin et al. [13] in the presence of a ten-fold excess of β-CD. They assigned the peaks at δ 4.36 and 4.33 to a splitting of resonance for the unsubstituted cyclopentadienyl ring. From the titration of the ferrocene with β-CD in this study it is clear that these peaks correspond rather to an upfield shift in the methylene protons and a downfield shift in the unsubstituted ring protons, respectively. With α-and γ-CD, no separation of the proton resonances upon inclusion is observed.

The limiting chemical shift displacements for the $[FeCp(CpCH_2N(CH_3)_3)]^+$ proton resonances upon cyclodextrin inclusion show marked dependences on the nature of the cyclodextrin. The $\Delta\delta_{CD}$ values for the ring protons decrease significantly on going from small α-CD cavity to the large γ-CD cavity, while the methyl protons show an opposite effect. The trend in the ring protons is understandable in terms of the proximity of the rings to the cavity wall of the cyclodextrin host. In the case of the methyl protons, the increase in the chemical shift changes upon increasing the cyclodextrin cavity diameter may indicate a deeper inclusion of the trimethylammonium group into the cavity. The splitting of the ^1H resonances for the symmetry-related nuclei of the substituted cyclopentadienyl ring upon inclusions of the $[FeCp(CpCH_2N(CH_3)_3)]^+$ complex in the β- and

Table 1
The inclusion stability constants, K_{CD}, and the ^1H NMR chemical shift displacements, $\Delta\delta_{CD}$, for the $\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+$ complexes in aqueous solution at 25 °C[a]

Proton[b]	$\Delta\delta_{CD}$[c] (Hz)			
	α-CD	β-CD	dmβ-CD	γ-CD
CH_3	+11.2±0.5	+21.9±1.0	+20.3±1.0	+30.1±0.7
H^b	+17.2±0.5	−5.6±1.7	−9.6±0.5	+16.0±0.6
H^a	+45.8±1.0	+28.0±0.7	+10.8±0.2	+3.4±0.2
H^d	+62.3±0.6	+41.9±1.7	+12.8±0.9	+2.6±0.2
$H^{d'}$	+62.3±0.6	+41.9±1.7	+22.9±0.6	+2.6±0.2
H^c	+55.9±0.7	+31.9±0.6	+8.1±1.7	−49.4±5.1
$H^{c'}$	+55.9±0.7	+47.4±0.9	+30.1±0.9	−49.4±5.1
K_{CD} (M^{-1})	150±10	4810±600	5010±800	500±50

[a]In D_2O containing 0.025 M phosphate buffer.
[b]Protons labelled as in Fig. 1.
[c]$\Delta\delta_{CD}$ is the chemical shift of the inclusion complex minus the chemical shift of the free metal complex.

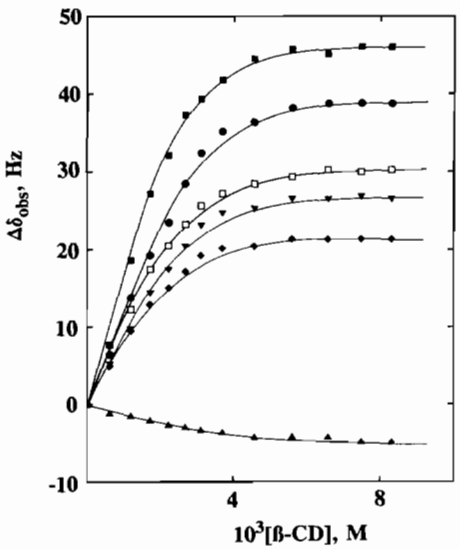

Fig. 2. Plots of the chemical shift changes, $\Delta\delta_{obs}$, for the protons of $[FeCp(CpCH_2N(CH_3)_3)]^+$ (2.96×10^{-3} M) against concentration of added β-CD in D_2O (0.025 M Na_2HPO_4/NaH_2PO_4) at 25 °C. The curves correspond to (▼) H^a, (▲) H^b, (□) H^c, (■) $H^{c'}$, (●) H^d and (♦) CH_3, according to the proton labelling in Fig. 1.

dmβ-CD cavities suggests that rotation of the bond between the ring and the substituent methylene group is hindered by the cyclodextrin ring.

3.2. Electron-transfer kinetics

The effects of cyclodextrin inclusion on the kinetics of the electron-transfer cross-reactions of the $[FeCp(CpCH_2N(CH_3)_3)]^{+/2+}$ couple were investigated using the inert complex bis(pyridine-2,6-dicarboxylato)-cobaltate(III) ion, $[Co(dipic)_2]^-$, as an oxidant and ascorbic acid as a reductant. Neither of these complexes exhibit any significant binding to the cyclodextrins. In the absence of added cyclodextrins the oxidation of $[FeCp(CpCH_2N(CH_3)_3)]^+$ by $[Co(dipic)_2]^-$ (Eq. (5)) proceed with a second-order rate constant of $(9.30 \pm 0.05) \times 10^2$ M^{-1} s^{-1} at 25.0 °C.

$$[FeCp(CpCH_2N(CH_3)_3)]^+ + [Co(dipic)_2]^- \xrightarrow{k_0} [FeCp(CpCH_2N(CH_3)_3)]^{2+} + [Co(dipic)_2]^{2-} \quad (5)$$

The additions of increasing concentrations of cyclodextrins resulted in significant decreases in the observed second-order rate constants (Figs. 3 and 4), as a result of inclusions of the reductant (Eq. (6)).

$$\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+ + [Co(dipic)_2]^- \xrightarrow{k_{CD}} \{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^{2+} + [Co(dipic)_2]^{2-} \quad (6)$$

The second-order rate constant for the electron transfer reaction may be expressed in terms of the specific rate constants k_0 and k_{CD}, as in Eq. (7).

$$k = \frac{k_0[FeCp(CpR)^+] + k_{CD}[\{FeCp(CpR)\cdot CD\}^+]}{[FeCp(CpR)^+]_T} \quad (7)$$

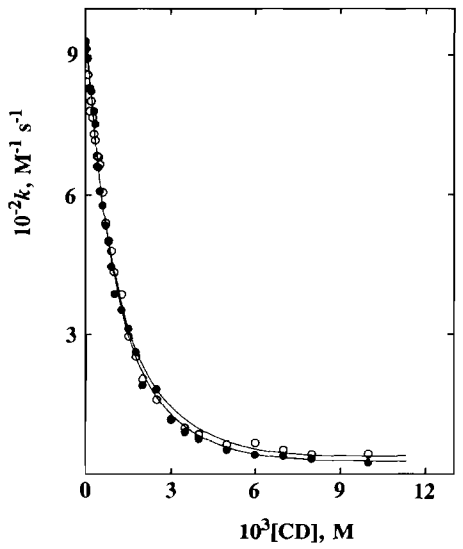

Fig. 3. Plots of the second-order rate constants against cyclodextrin concentration for the oxidation of $[FeCp(CpCH_2N(CH_3)_3)]^+$ by $[Co(dipic)_2]^-$ in the presence of (○) β-CD and (●) dmβ-CD at 25.0 °C and $I = 0.10$ M (Na_2HPO_4/NaH_2PO_4).

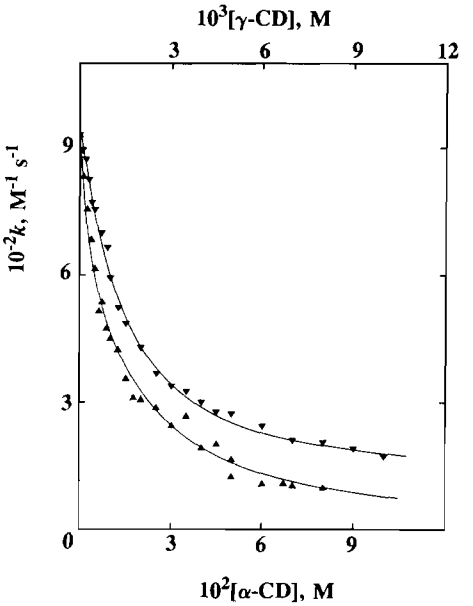

Fig. 4. Plots of the second-order rate constants against cyclodextrin concentration for the oxidation of $[FeCp(CpCH_2N(CH_3)_3)]^+$ by $[Co(dipic)_2]^-$ in the presence of (▲) α-CD and (▼) γ-CD at 25.0 °C and $I = 0.10$ M (Na_2HPO_4/NaH_2PO_4).

Table 2
Inclusion stability constants for $\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^+$ complexes and rate constants for the oxidation of $[FeCp(CpCH_2N(CH_3)_3]^+$ by $[Co(dipic)_2]^-$ at 25.0 °C and $I = 0.10$ M (Na_2HPO_4/NaH_2PO_4)

CD	k_0 (M^{-1} s^{-1})	k_{CD} (M^{-1} s^{-1})	K_{CD} (M^{-1})
α-CD	930 ± 5	70 ± 25	130 ± 30
β-CD	930 ± 5	20 ± 8	4820 ± 390
dmβ-CD	930 ± 5	10 ± 10	4960 ± 500
γ-CD	930 ± 5	140 ± 8	1620 ± 100

Plots of k against cyclodextrin concentrations are shown in Fig. 3 for β- and dmβ-cyclodextrins and in Fig. 4 for the α- and γ-cyclodextrins. The second-order rate constants k_{CD} and the inclusion stability constants k_{CD}, determined for each of the cyclodextrins by non-linear least-squares fits of the kinetic data to Eqs. (2) and (7), are presented in Table 2.

The inclusion stability constants determined from the ^1H NMR chemical shift titrations are generally in good agreement with the values determined from the kinetics of the reduction of $[Co(dipic)_2]^-$ by $[FeCp(CpCH_2N(CH_3)_3)]^+$ in the presence of the cyclodextrins. Similar values for α- (240 ± 15 M^{-1}) and γ-CD (400 ± 25 M^{-1}) stability constants have been reported by Isnin et al. [13] from diffusion coefficient measurements in 50 mM NaCl, although their value for β-CD (1900 ± 180 M^{-1}) was lower than those determined in this study. The trend in the magnitude of the stability constants, β- ≈ dmβ- > γ- > α-CD, is similar to that determined by

the kinetic and ^{1}H NMR methods for inclusions of the ferrocenemonocarboxylate anion [18].

The kinetics of the oxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A) by the $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ cation were investigated at 25.0 °C in 0.10 M $HClO_4$ (Eq. (8)).

$$2[FeCp(CpCH_2N(CH_3)_3)]^{2+} + H_2A \longrightarrow 2[FeCp(CpCH_2N(CH_3)_3)]^{+} + 2H^{+} + A \quad (8)$$

In the absence of added cyclodextrins the second-order rate constant for the rate-determining one-electron oxidation of H_2A to the $H_2A^{\cdot+}$ intermediate (Eq. (9) is $(6.40 \pm 0.35) \times 10^2$ M^{-1} s^{-1}.

$$[FeCp(CpCH_2N(CH_3)_3)]^{2+} + H_2A \xrightarrow{k_0} [FeCp(CpCH_2N(CH_3)_3)]^{+} + H_2A^{\cdot+} \quad (9)$$

Additions of α-, β- and dmβ-cyclodextrin resulted in increases in the observed rate constants (Eq. (10)) while γ-CD had no effect on the rate constant, as illustrated in Fig. 5.

$$[FeCp(CpCH_2N(CH_3)_3)\cdot CD]^{2+} + H_2A \xrightarrow{k_{CD}} [FeCp(CpCH_2N(CH_3)_3)\cdot CD]^{+} + H_2A^{\cdot+} \quad (10)$$

The kinetic data were fitted to Eqs. (2) and (7) with $[FeCp(CpCH_2N(CH_3)_3)^{2+}]$ and the resulting second-order rate constants k_{CD} and inclusion stability constants K_{CD} determined for each of the cyclodextrins are presented in Table 3.

The two factors resulting from the inclusions of the $[FeCp(CpCH_2N(CH_3)_3)]^{+/2+}$ couple which are expected to affect the rate constants for their electron-transfer

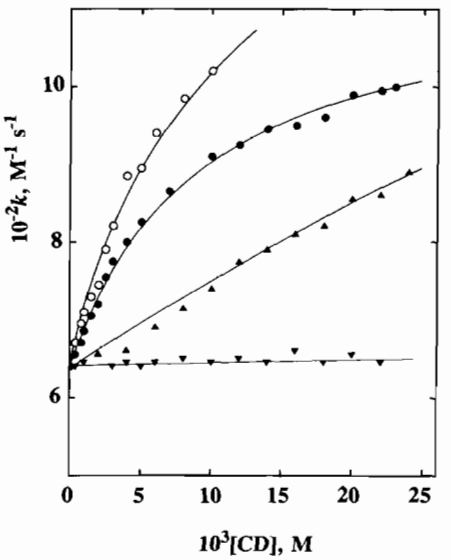

Fig. 5. Plots of the second-order rate constants against cyclodextrin concentration for the oxidation of ascorbic acid by $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ in the presence of (▲) α-CD, (○) β-CD, (●) dmβ-CD and (▼) γ-CD at 25.0 °C and $I = 0.10$ M ($HClO_4$).

Table 3
Inclusion stability constants for $\{FeCp(CpCH_2N(CH_3)_3)\cdot CD\}^{2+}$ complexes and rate constants for the oxidation of ascorbic acid by $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ at 25.0 °C and $I = 0.10$ M ($HClO_4$)

CD	k_0 (M^{-1} s^{-1})	k_{CD} (M^{-1} s^{-1})	K_{CD} (M^{-1})
α-CD	640 ± 35	2300 ± 800	10 ± 5
β-CD	640 ± 35	2600 ± 100	150 ± 15
dmβ-CD	640 ± 35	2200 ± 150	140 ± 30
γ-CD	640 ± 35	650 ± 50	< 1

reactions are the changes in the ferricinium/ferrocene reduction potential and the shielding of the cross-reactants from each other. The effects of cyclodextrin inclusions on the electrochemical half-wave potential of the $[FeCp(CpCH_2N(CH_3)_3)]^{2+/+}$ couple have been studied by Isnin et al. [13]. They reported increases of about 5, 10 and 80 mV in the presence of 10 mM concentrations of α-, γ- and β-cyclodextrins, respectively. We have observed similar changes in the reduction potential (measured by cyclic voltammetry) in the presence of dmβ-cyclodextrin as found for β-CD. Inclusions of the $[FeCp(CpCH_2N(CH_3)_3)]^{+}$ complex would therefore make it a poorer reductant and should lead to a diminution in its rate of oxidation. Significant decreases in electron-transfer rate constants have also been observed in systems in which cyclodextrin inclusion of the reductant does not change its electrochemical oxidation potential. In these reactions, involving metal complex oxidations of the cyclodextrin-included reductants $[Ru(NH_3)_5(4,4'\text{-bipyridine})]^{2+}$ [19] and 4-tert-butylcatechol [17], the extent to which the reaction is inhibited depends on the accessibility of the reductant to the cross-reactant in solution. Whereas only the coordinated 4,4'-bipyridine ligand is included in the dmβ-CD in the case of the Ru(II) complex, lowering the rate constant by about 50%, inclusion of the majority of the 4-tert-butylcatechol in the β-cyclodextrin cavity resulted in more significant decreases, in the range 75–85%. The encapsulation of the catechol by two α-CD host molecules led to a decrease of 95% in the observed rate constants.

In the present system the shielding of the reactants and the increase in the ferricinium/ferrocene reduction potential would both be expected to contribute to the decreases observed in the electron-transfer rate constants. The trend in the values of k_{CD}, $\beta \approx$ dmβ- $< \alpha$- $< \gamma$-CD, reflects both of these factors. In the case of γ-CD, the reductant would be expect to be most exposed to encounters with the $[Co(dipic)_2]^-$ anion. These rate constants may be compared with rate constants determined for the oxidation of $[FeCp(CpCOO)]^-$ by $[Co(dipic)_2]^-$ ($k_0 = 2030 \pm 20$ M^{-1} s^{-1}) in the presence of α- ($k_{CD} = 80 \pm 30$ M^{-1} s^{-1}), β- (80 ± 30 M^{-1} s^{-1}), dmβ- (530 ± 20 M^{-1} s^{-1}) and γ-CD (100 ± 20 M^{-1} s^{-1}) [18]. In this particular system the larger value for the

dmβ-CD was attributed to a more shallow inclusion of the $[FeCp(CpCOO)]^-$ species due to the presence of the methyl groups on both rims of the host molecule. The ferrocene in the present study has a more hydrophobic substituent and deeper inclusion may be anticipated.

The rate constants for the oxidation of ascorbic acid by the $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ cation exhibit a modest increase in the presence of the α-, β- and dmβ-cyclodextrins, with no change observed in the case of the γ-cyclodextrin. The weaker binding of this complex compared with the reduced form is likely due to an increase in the charge on the metal. Similar binding constants have been determined electrochemically by McCormack et al. [12] for the iron(III) species FeCp(CpCOO) with α- (4.4 M^{-1}), β- (36.9 M^{-1}) and γ-cyclodextrins (8.8 M^{-1}). The three- to four-fold increases in the rate constants for the oxidation of ascorbic acid upon inclusion of the $[FeCp(CpCH_2N(CH_3)_3)]^{2+}$ cation in α-, β- and dmβ-cyclodcxtrins appear to be the first examples of the acceleration of homogeneous thermal electron-transfer reactions as a result of the inclusion of an oxidant. The partial shieldings of the cross-reactants likely prevents the increases in rate constants from being more significant. A similar degree of acceleration has been reported for the electrocatalytic oxidation of NADH (β-nicotinamide adenine dinucleotide) by FeCp(CpCOO) in the presence of β-cyclodextrin [26].

The deceleration and acceleration of the electron-transfer reactions upon cyclodextrin inclusion of the reduced and oxidized ferrocenes, respectively, are primarily the result of an increase in the reduction potential of the $[FeCp(CpCH_2N(CH_3)_3)]^{+/2+}$ couple. It has recently been reported that inclusion of this couple in the *p*-sulphonated calix[6]arene host molecule results in a decrease in reduction potential, due to the greater stability for binding of the ferricinium species relative to that of the ferrocene [27]. This should lead to an acceleration in the rate of oxidation of the $[FeCp(CpCH_2N(CH_3)_3)]^{+}$ cation. Kinetic investigations of the electron-transfer reactions of this and other metal complex couples in the presence of cyclodextrins and calixarenes are ongoing in our laboratory.

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