Primitive Molecular Recognition Effects in Electron Transfer Processes: Modulation of ((Trimethylammonio)methyl)ferrocenium/ferrocene Self-Exchange Kinetics via Hydrophobic Encapsulation

Roger M. Nielson,*,† L. Andrew Lyon, and Joseph T. Hupp*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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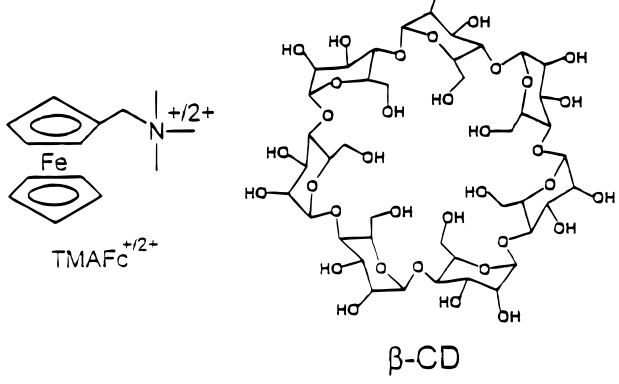
^{1}H NMR line broadening measurements show that the electron self-exchange rate constant for ((trimethylamino)-methyl)ferrocenium/ferrocene ($TMAFc^{2+/+}$) in D_2O as solvent is decreased by ca. 20−50 fold in the presence of excess β-cyclodextrin. The rate effect is associated with the selective hydrophobic encapsulation of the ferrocene form of the redox couple (i.e., the ferrocenium form is not significantly encapsulated). Selective encapsulation leads to a coupling of electron transfer to host (cyclodextrin) transfer. Optical intervalence absorption measurements for a closely related mixed-valence system strongly suggest that the coupling decreases the self-exchange rate by increasing the thermal activation barrier—an inference that is corroborated by activation parameter measurements. The barrier increase ultimately can be understood in terms of a redox asymmetry effect upon the isolated electron transfer event, where the overall exchange mechanism likely entails sequential electron and host transfer.

Introduction

We and others have been exploring the consequences of molecular recognition and macrocyclic inclusion upon both optical and thermal electron transfer reactivity.[1−3] Recently we discovered that hydrogen-bonding-based encapsulation of ammine ruthenium guests by crown ether hosts could induce large changes in electron self-exchange reactivity ($Ru^{III/II}$)—where the mechanism of rate modulation involved a coupling of electron transfer (ET) to subsequent host transfer.[3d] We reasoned that analogous redox reactivity effects might exist based on hydrophobic encapsulation: Here we report aqueous (D_2O) self-exchange kinetics studies for ((trimethylammonio)methyl)-ferrocenium/ferrocene ($TMAFc^{2+/+}$) as a function of β-cyclodextrin (β-CD) encapsulation. While the exact encapsulation geometry is unknown, a prior investigation has yielded evidence for β-CD inclusion of both the unsubstituted cyclopentadiene and the methylene substituent of $TMAFc^+$.[1c]



It should be noted that $TMAFc^{2+/+}$ and β-cyclodextrin have been examined previously in ET cross reactions, and that a variety of potential kinetic effects has been identified.[1] We felt that the conceptual simplification offered by self-exchange processes would enable us to identify the most important of these effects. In any case, we find that (1) $TMAFc^+$ is readily recognized and encapsulated by β-CD, (2) $TMAFc^{2+}$, on the other hand, is not, (3) the resulting differential encapsulation substantially increases the barrier to electron transfer, and (4) the barrier increase and related factors attenuate the $TMAFc^{2+/+}$ self-exchange rate by ca. 20- to 50-fold.

Experimental Section

Materials. β-Cyclodextrin septahydrate (Aldrich) was dried overnight at 100 °C. [TMAFc](I) was prepared from ((dimethylamino)-methyl)ferrocene (Aldrich) via a literature method.[4] Conversion to the BF_4^- salt was accomplished by adding aqueous [TMAFc](I) to saturated aqueous $NaBF_4$. The resulting precipitate was washed with cold water, dried, and recrystallized from CH_3CN/ether. $TMAFc^{2+}$ was obtained from $TMAFc^+$ by using benzoquinone in CH_2Cl_2 as a stoichiometric oxidant. Addition of HBF_4 yielded solid $[TMAFc](BF_4)_2$ which was washed with ether. (Anal. Calcd (found) for $C_{14}H_{20}NB_2F_8Fe$: C: 38.95 (38.67); H: 4.67 (4.68); N: 3.24 (3.32).) Since solutions of $TMAFc^{2+}$ are air sensitive, these were prepared in an argon atmosphere. Bis-(ferrocenyl)acetylene (BFA) and $[BFA](BF_4)$ were synthesized via literature methods.[5]

Measurements. The electron self-exchange rate constant, *k*, was obtained via ^{1}H NMR line broadening (Varian Gemini 300). In the

† Permanent address: Department of Chemistry, Southern Oregon State College, Ashland, OR 97520.

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(1) Representative kinetic studies: (a) Imonigie, J. A.; Macartney, D. H. *Inorg. Chem.* **1993**, *32*, 1007. (b) Imonigie, J. A.; Macartney, D. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1830. (c) Imonigie, J. A.; Macartney, D. H. *Inorg. Chim. Acta* **1994**, *225*, 51. (d) Johnson, M. D.; Reinsborough, V. C.; Ward, S. *Inorg. Chem.* **1992**, *31*, 1085.

(2) Representative thermodynamic studies: (a) Zhang, L.; Macias, A.; Lu, T.; Gordon, J. I.; Gokel, G. W.; Kaifer, A. E. *J. Chem. Soc., Chem. Commun.* **1993**, 1017. (b) Isnin, R.; Salam, C.; Kaifer, A. E. *J. Org. Chem.* **1991**, *37*, 1939. (c) Strelets, V. V.; Mamedjarov, I. A.; Nefedova, M. N.; Pysnograeva, V. I.; Sokolov, V. I.; Pospisil, L.; Hanzlik, J. *J. Electroanal. Chem.* **1991**, *310*, 179. (d) Ando, I.; Ishimura, D.; Ujimoto, K.; Kurihara, H. *Inorg. Chem.* **1994**, *33*, 5010.

(3) (a) Todd, M. D.; Yoon, D. I.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 4685. (b) Curtis, J. C.; Roberts, J. A.; Blackbourn, R. L.; Dong, Y.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 3856. (c) Todd, M. D.; Dong, Y.; Horney, J.; Yoon, D. I.; Hupp, J. T. *Inorg. Chem.* **1993**, *32*, 2001. (d) Nielson, R. M.; Yoon, D. I.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 9085.

(4) Lindsay, J. K.; Hauser, C. R. *J. Org. Chem.* **1957**, *22*, 355.

(5) (a) Rosenblum, M.; Brown, N.; Papenmeier, J.; Applebaum, M. J. *J. Organomet. Chem.* **1966**, *6*, 173. (b) Dong, T. Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *25*, 4233. (c) Blackbourn, R. L.; Hupp, J. T. *Chem. Phys. Lett.* **1988**, *150*, 399.

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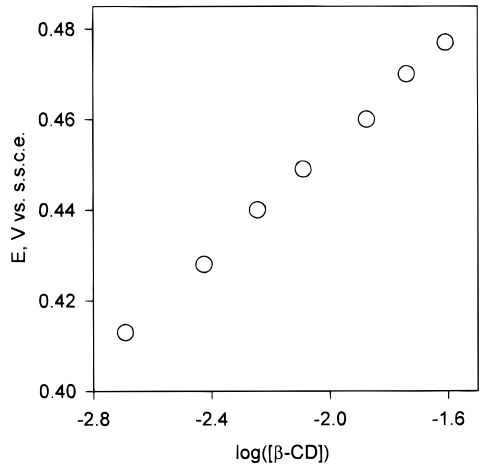

Figure 1. Apparent formal potentials for $TMAFc^{2+/+}$ vs log $[\beta\text{-CD}]_{total}$.

slow exchange limit[6] (generally applicable here)

$$k = \pi(W_{DP} - W_D)/[TMAFc^{2+}] \quad (1)$$

where W_{DP} is the full width at half-height for mixtures of $TMAFc^{+}$ and $TMAFc^{2+}$ and W_D is the peak width for $TMAFc^{+}$ only. The exchange kinetics for $TMAFc^{2+/+}$ in 0.1 *M* $NaClO_4$ or $NaBF_4$ without β-CD, however, proved too rapid for eq 1 to be applied; *k* was instead determined via the fast exchange analysis shown in eq 2.[7] In the

$$k = 4\pi\chi_P\chi_D(\Delta\nu)^2/(W_{DP} - \chi_D W_D - \chi_P W_P)C_{sum} \quad (2)$$

equation, $\Delta\nu$ is the contact shift in Hz, χ_D and χ_P are mole fractions of $TMAFc^{+}$ and $TMAFc^{2+}$, respectively, W_P is the peak width for $TMAFc^{2+}$ only, and C_{sum} is the combined total molar concentration of $TMAFc^{+}$ and $TMAFc^{2+}$. Except as specified, the line broadening measurements were made at 20 ± 2 °C.

Apparent formal potentials were determined by cyclic voltammetry by using a two-compartment cell containing a gold working electrode, a platinum counter electrode and a saturated (NaCl) calomel reference electrode (ssce). The electrolyte was 0.1 M $NaBF_4$. Variable temperature measurements (seven temperatures between 2 and 30 °C) were performed by using a nonisothermal cell. Voltammograms were generated with a PAR 273 potentiostat. Fast voltammograms (5−11000 V/s) were obtained by coupling a signal generator (PAR 175 programmer) to the potentiostat. Signals in the higher sweep rate range were collected and averaged with a digital oscilloscope (LeCroy 9400; 125 MHz bandwidth). To minimize *iR* distortions in the fast experiments, positive feedback was employed, 10 μm diameter carbon disks were used as working electrodes (single compartment cell) and the electrolyte concentration was increased to 0.5 M.

Near-infrared absorption measurements were made in D_2O with an OLIS-modified Cary 14 spectrophotometer.

Results and Discussion

Electrochemical Binding Studies. In the absence of β-CD, the observed formal potential (E_f) for $TMAFc^{2+/+}$ is 376 mV. Figure 1 shows that cyclodextrin addition induces a Nernstian shift in the apparent formal potential (E_f).[8] The sign of the shift indicates that cyclodextrin binding has occurred for the ferrocene form of the guest, but not for the ferrocenium form. The limiting slope at high cyclodextrin concentrations (60 mV) indicates that only a single host molecule is lost upon guest oxidation, in agreement with earlier reports.[2] The redox process occurring in the presence of β-CD, therefore, is

$$TMAFc^{+}\cdot\beta\text{-CD} \rightleftarrows TMAFc^{2+} + \beta\text{-CD} + e^{-} \quad (3)$$

As shown in eq 4, the magnitude of the potential shift at a given cyclodextrin concentration can be used to calculate the $TMAFc^{+}\cdot\beta$-CD association constant (*K*):[9]

$$E_{1/2} - E_f = (RT/F)\ln[\beta\text{-CD}] + (RT/2F)\ln(D_{ox}/D_{red}) + (RT/F)\ln K \quad (4)$$

In the equation, *F* is the Faraday constant and D_{ox} and D_{red} are diffusion coefficients for the oxidized and reduced species, respectively. The diffusion term typically is negligible, but contributes about −12 mV here because host−guest association diminishes *D* by ca. 65%. From eq 3, *K* is 4900 ± 600 M^{-1} (at 22 °C). (For comparison, Imonigie and Macartney report $K = 4800 \pm 600\ M^{-1}$.)[1c] Extension of the electrochemical studies to both lower and higher temperatures yields, for eq 5, an enthalpy of binding of −5.9 kcal mol^{-1} and an entropy of binding of −3 eu.

$$TMAFc^{+} + \beta\text{-CD} \rightleftarrows TMAFc^{+}\cdot\beta\text{-CD} \quad (5)$$

In principle, the corresponding binding constant for the ferrocenium species (*K′*) is available from the limiting potential shift at high cyclodextrin concentrations. In Figure 1, however, no evidence for high-concentration limiting behavior (i.e. loss of sensitivity of $E_{1/2}$ to cyclodextrin concentration) is observed. This indicates that within the accessible host concentration range, no appreciable amount of $TMAFc^{2+}$ is bound.[10] Consequently, *K′* must be less than ∼20 M^{-1}.[11]

Evans and co-workers have pointed out that in favorable circumstances cyclic voltammetry can also be used to determine the rate of host−guest dissociation (i.e. reverse of eq 5).[12,13] The requirements are that (1) the host−guest assembly is electrochemically inactive in the potential range where the guest is oxidized, (2) electrochemical oxidation proceeds by initial dissociation of the guest:host assembly (i.e. a "CE" mechanism is followed), and (3) the dissociation rate constant is small in comparison to a composite quantity that includes the voltammetry sweep rate and the pseudo-first-order rate of host−guest association. When these requirements are met, the normally symmetrical voltammetry response will be characterized by an attenuated and flattened oxidation peak and an approximately normal reduction peak. We were unable to observe such effects here, even with sweep rates as high as 11 000 V/s and cyclodextrin concentrations as great as 10 mM. The negative results imply either that the dissociation rate constant is large ($> 2 \times 10^7\ s^{-1}$, assuming that a 50% attenuation in the oxidative voltammetry peak would have been observable) or that requirement 1 (above) is not met for this system. Consistent with either

(6) Nielson, R. M.; McManis, G. E.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 4703.
(7) See, for example: Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542.
(8) Reported formal potentials (Figure 1) will differ slightly from true formal potentials because of differences in diffusion coefficients for $TMAFc^{2+}$ vs $TMAFc^{+}\cdot\beta$-CD (see eq. 4).
(9) It is important to note that the relevant concentration in eq 4 is the free host concentration, not the total concentration. The concentrations of free host were determined iteratively.
(10) Additional (negative) evidence is provided by NMR measurements on β-CD. Significant shifts in two of the six proton resonances are induced by $TMAFc^{+}$, but none are induced by $TMAFc^{2+}$.
(11) The solubility limit for β-CD was ∼23 mM (achieved by gently heating the host solution followed by spontaneous cooling to room temperature). Assuming that a 15 mV deviation from Nernstian behavior would be detectable at the highest host concentration, eq 1 and the data in Figure 1 yield the indicated upper limit estimate for *K′*.
(12) Matsue, T.; Evans, D. H.; Osa, T.; Kobayashi, N. *J. Am. Chem. Soc.* **1985**, *107*, 3411.
(13) See also: Bard, A. J.; Faulkner, L. *Electrochemical Methods: Fundamentals and Applications*; John Wiley and Sons: New York, 1980 p 445.

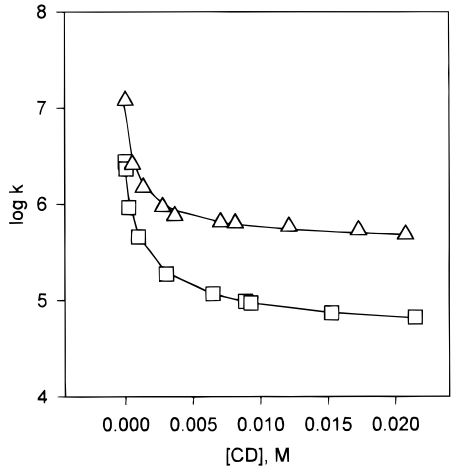

Figure 2. Logarithm of the $TMAFc^{2+/+}$ self-exchange rate constant vs free β-cyclodextrin concentration in D_2O as solvent. $[TMAFc^{2+}] = (0.1-2.3) \times 10^{-4}\ M^{-1}$. $[TMAFc^{+}] = (1.59-2.11) \times 10^{-3}\ M^{-1}$. Lines drawn are best fit lines to a logarithmic analog of eq 8: (□) without added electrolyte; (△) with 0.1 *M* $NaClO_4$.

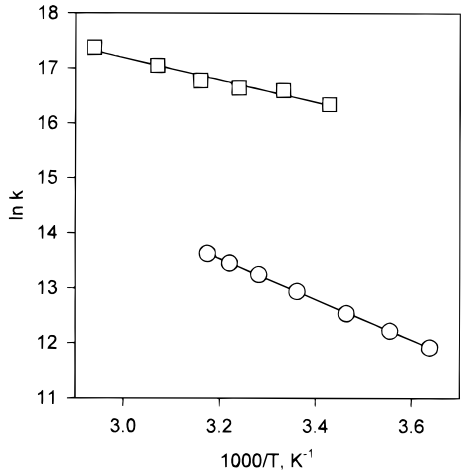

Figure 3. Ln *k* vs 1/*T*: (□) [β-CD] = 0; (○) [β-CD] = 0.017 *M*.

interpretation, Johnson has independently observed (via stopped-flow spectroscopy) that the dissociation rate constant exceeds 350 s^{-1}.[14]

NMR Kinetics Studies. Figure 2 shows plots of the log of the $TMAFc^{2+/+}$ self-exchange rate constant vs β-CD concentration—both with added electrolyte and without. Rates in the presence of electrolyte are significantly faster, as expected from work term considerations. More importantly, rates under both conditions are attenuated by as much as 20- to 50-fold following β-CD addition. In contrast to the behavior of ruthenium ammines and crowns,[4d] however, the reactivity does not recover with further additions of the host species. The electrochemical (thermodynamic) experiments point to the existence of two forms of $TMAFc^{+}$, suggesting the possibility of a parallel reaction scheme involving free $TMAFc^{+}$ (k°; eq 6) and encapsulated $TMAFc^{+}$ (k^{β}; eq 7a) pathways.[15] Fits of

$$TMAFc^{+} + TMAFc^{2+} \overset{k^{\circ}}{\rightleftharpoons} TMAFc^{2+} + TMAFc^{+} \quad (6)$$

$$TMAFc^{+}\cdot\beta\text{-CD} + TMAFc^{2+} \overset{k^{\circ}}{\rightleftharpoons} TMAFc^{2+}\cdot\beta\text{-CD} + TMAFc^{+} \quad (7a)$$

$$TMAFc^{2+}\cdot\beta\text{-CD} + TMAFc^{+} \rightarrow TMAFc^{2+} + TMAFc^{+}\cdot\beta\text{-CD} \quad (7b)$$

the observed rate constant to a parallel scheme (eq 8) are shown

$$k = \{k^{\circ}[TMAFc^{+}] + k^{\beta}[TMAFc^{+}\cdot\beta\text{-CD}]\}/\{[TMAFc^{+}] + [TMAFc^{+}\cdot\beta\text{-CD}]\} \quad (8)$$

in Figure 2,[16] where the required concentrations of $TMAFc^{+}$ and $TMAFc^{+}\bullet\beta$-CD have been obtained from the independently measured host−guest association constant. On this basis, the values of k° and k^{β}, without electrolyte, are 2.5×10^{6} and $4.3 \times 10^{4}\ M^{-1}\ s^{-1}$, respectively. With electrolyte, they are 7×10^{6} and $3.0 \times 10^{5}\ M^{-1}\ s^{-1}$.[17] The diminishing reactivity with increasing cyclodextrin concentration can be interpreted, therefore, as an effect arising from both the decreasing concentration of free TMAFc+ and the inherently attenuated reactivity of the encapsulated compound in comparison to the free species. It should be noted, however, that a finite reactivity for $TMAFc^{+}\cdot\beta$-CD is required in order to achieve reasonable fits to the data in Figure 2.[18]

Figure 3 shows an extension of the kinetics experiments where the temperature was varied for [β-CD] = 0 and 17 mM. From the slopes, $\Delta H^{*}(0) = 4.0$ kcal mol^{-1} and $\Delta H^{*}(17) = 7.3$ kcal mol^{-1}.[19-21] While the parameters seem to suggest that enthalpic effects account for the decreased reactivity of the encapsulated species vs the free species, the comparison neglects complications from variations in *K* and, therefore, variations in the partitioning between reaction pathways 6 and 7. If the temperature dependence of *K* is considered, variable temperature estimates for k^{β} can be obtained and $\Delta H^{*}(\beta)$ can be estimated as 1.5 ± 0.7 kcal mol^{-1}.[21]

Intervalence Measurements. While activation parameters can offer insight into kinetic barrier effects, their interpretation

(14) We thank Prof. M. D. Johnson of New Mexico State University for communicating these results to us prior to publication.

(15) While eq 7b is written as a net host transfer reaction, presumably it involves sequential unimolecular dissociation and bimolecular association reaction components.

(16) To avoid excessively weighting the fit toward k° (large) at the expense of accuracy in k^{β} (small), rate data were fit to a logrithmic form of eq 8.

(17) The directly measured k° values (i.e. rate constants in the absence of cyclodextrin) are $1.2 \times 10^{7}\ M^{-1}\ s^{-1}$ (without electrolyte) and $2.8 \times 10^{7}\ M^{-1}\ s^{-1}$ (with electrolyte). The disparity between measured and fit values for the former might be due to noncancelling systematic errors associated with the intercomparison of kinetic data collected in both the slow (eq 1) and fast (eq 2) line broadening regimes.

(18) The analysis assumes rapid equilibration between bound and unbound reactant forms. An alternative scheme can be envisioned where guest: host dissociation is slow and direct reaction of $TMAFc^{+}\cdot\beta$-CD with $TMAFc^{2+}$ is neglected. At limiting high guest concentrations, *k* would correspond to the dissociation rate and the linewidth difference parameter, $W_{DP} - W_{D}$ (eq 5), would become insensitive to the $TMAFc^{2+}$ concentration. In contrast, the expected sensitivity is observed experimentally at all accessible host concentrations.

(19) Because of solubility problems with $NaClO_4$ solutions at low temperatures, activation parameters were obtained in $NaBF_4$ solutions. Room temperature rate constants in the two electrolyte solutions were identical in the absence of cyclodextrin, but differed by ~35% in the presence of cyclodextrin (17 mM).

(20) ΔH^{*} values were obtained from slopes of plots of ln *k* vs 1/*T*, where preexponentional factors were assumed (following conventional semiclassical electron transfer theory) to be temperature independent. Because of difficulties in observing sufficiently fast kinetics to render eq 2 applicable at low temperatures, values for k° were obtained only at 292 °C and higher. Subsequent estimation of k^{β} values at lower temperatures, therefore, required extrapolation of ln k° vs 1/*T* plots.

(21) In the absence of electrolyte, $\Delta H^{*}(0) = 4.7$ kcal mol^{-1}, $\Delta H^{*}(17) = 7.9$ kcal mol^{-1}, and $\Delta H^{*}(\beta) = 3.8$ kcal mol^{-1}. The apparent entropies of activation, assuming a frequency factor of 1.9×10^{12} (the longitudinal relaxation time of D_2O), are $\Delta S^{*}(0) = -10$ eu, $\Delta S^{*}(17) = -7$ eu, and $\Delta S^{*}(\beta) = -22$ eu. With electrolyte the parameters are $\Delta S^{*}(0) = -10$ eu, $\Delta S^{*}(17) = -6$ eu, and $\Delta S^{*}(\beta) = -28$ eu.

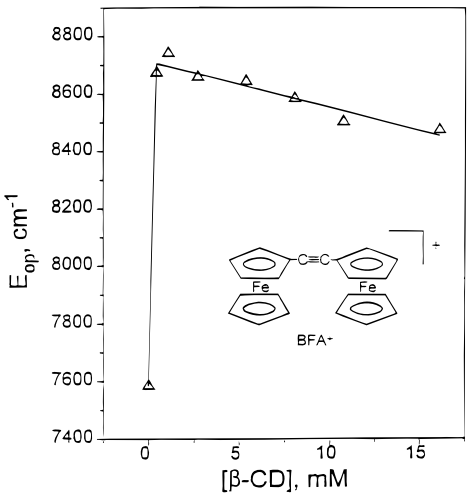

Figure 4. Intervalence absorption energy maximum for BFA^+ as a function of β-cyclodextrin concentration in D_2O as solvent. First point ([β-CD] = 0) estimated as described in ref 22.

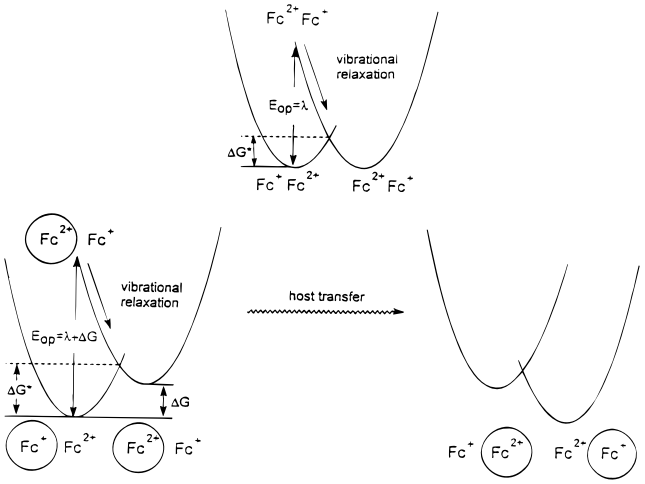

Figure 5. Schematic representations of energy surfaces for optical and thermal electron transfer: top, without β-CD; bottom, with β-CD.

is often complicated by work term effects, ion pairing effects, residual entropy effects and other secondary phenomena. In principle, a more direct approach to barrier evaluation is to obtain optical intervalence absorption spectra. Measurements of this kind for reaction 9 (Figure 4) show that the *optical*

$$Fc{-}C{\equiv}C{-}Fc^+ \rightarrow Fc^+{-}C{\equiv}C{-}Fc \qquad (9a)$$

$$\beta\text{-CD}\cdot Fc{-}C{\equiv}C{-}Fc^+ \rightarrow \beta\text{-CD}\cdot Fc^+C{-}C{\equiv}C{-}Fc \qquad (9b)$$

barrier to ferrocenium/ferrocene electron exchange (E_{op}) increases by 1100 ± 200 cm^{-1} following β-CD association.[22] The figure also reveals, however, a slight decrease in apparent barrier height in response to excess β-CD. The decrease is probably indicative of the onset of encapsulation at the ferrocenium site (i.e., binding of a second cyclodextrin). If, as in previous studies with crowns,[3a,d] the limiting intervalence energy with double encapsulation is approximately equal to that without encapsulation, then an association constant of ~10 M^{-1} for the ferrocenium site with β-CD can be inferred from the energy shifts. An alternate estimate based on the magnitude of the initial positive shift in E_{op} with β-CD addition yields $K \approx 25\ M^{-1}$.[23]

In contrast to the activation parameter measurements, the optical measurements clearly imply that cyclodextrin-induced electron exchange inhibition is associated with a thermal barrier increase. In the context of reactions 6 and 7 and a stepwise electron transfer/crown transfer reaction sequence (see above), the observed optical effects translate into a thermal barrier effect of ca. 1.6 kcal mol^{-1} (~550 cm^{-1} $\approx \Delta E_{op}/2$; see Figure 5). At ambient temperature, a barrier increase of this magnitude corresponds to a 14-fold decrease in rate. The remaining factor of 2−4 is presumably associated with "blocking effects" (nonadiabaticity effects) which have been implicated in other studies.[1]

To summarize, the available kinetic, thermodynamic and optical data indicate that ET reactivity diminution occurs when electron transfer becomes coupled—in a net sense—to host transfer:

$$TMAFc^+\cdot\beta\text{-CD} + TMAFc^{2+} \rightleftarrows TMAFc^{2+} + TMAFc^+\cdot\beta\text{-CD} \qquad (10)$$

While the overall reaction is energetically symmetrical ($\Delta G = 0$), the isolated ET step (eq 7a) in a sequential electron transfer/host transfer scheme is energetically unsymmetrical (Figure 5). The redox asymmetry induces a thermal barrier increase that can account for the majority of the observed 20- to 50-fold rate decrease caused by β-CD encapsulation. In principle, fast exchange kinetics should be recoverable (or partially recoverable) by additionally encapsulating the $TMAFc^{2+}$ reactant (eq 11) and thereby removing the redox asymmetry. The failure

$$TMAFc^+\cdot\beta\text{-CD} + TMAFc^{2+}\cdot\beta\text{-CD} \rightleftarrows TMAFc^{2+}\cdot\beta\text{-CD} + TMAFc^+\cdot\beta\text{-CD} \qquad (11)$$

to observe rate recovery here is consistent with the thermodynamic inability to achieve $TMAFc^{2+}$ encapsulation within the accessible β-CD concentration range.

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(22) Because of the extreme insolubility of free BFA^+ in water, the optical barrier (or intervalence absorption energy) in the absence of β-cyclodextrin has necessarily been estimated from optical and static dielectric constants for water, together with known correlations of $E_{op}(BFA^+)$ with dielectric properties in other solvents. The reported uncertainty represents two standard deviations in E_{op} in a previously published correlation of six solvents (Blackbourn, R. L.; Hupp, *J. T. J. Phys. Chem.* **1990**, *94*, 1788).

(23) If ΔE_{op} arises exclusively from redox asymmetry effects[3a,5c] (i.e., if reorganizational effects can be neglected) then this quantity can be equated with $-RT\ \ln\{K(\text{ferrocene}\cdot\beta\text{-CD})/K(\text{ferrocenium}\cdot\beta\text{-CD})\}$. If K(ferrocenium·β-CD) equals 4800 M^{-1},[1c] then K(ferrocene·β-CD) will equal 25 M^{-1}.