Electron Self-Exchange Kinetics for a Water-Soluble Ferrocenium/Ferrocene Couple: Rate Modulation via Charge Dependent Calix[6]arene-*p*-sulfonate Encapsulation

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Introduction

In several recent studies we have observed that stepwise encapsulation of simple redox partners by weakly interacting molecular hosts can exert substantial kinetic and/or energetic effects upon thermal (self exchange) and/or optical (intervalence) electron transfer (ET) reactions.[1−3] The previous studies featured encapsulation via either hydrogen bonding (ammine ruthenium guests with crown ether hosts[1,2]) or hydrophobic interactions (trimethylaminomethyl(ferrocenium/ferrocene) (TMAFc$^{2+/+}$) guests with a β-cyclodextrin host[3,4]). With either mode of encapsulation, substantial self-exchange rate decreases (i.e., 20- to 300-fold) are induced when only one redox partner serves as a guest. Under these conditions electron transfer effectively becomes coupled to host transfer and an energetically unfavorable redox asymmetry effect arises in the isolated ET step.[2,3] We reasoned that related effects could exist based on combined electrostatic/hydrophobic association of host and guests. Described below are TMAFc$^{2+/+}$ self-exchange studies in water with calix[6]arene-*p*-sulfonate,[5] a negatively charged molecular host. This system was chosen because strong host/guest association had previously been established electrochemically and because the association strength was reported to depend upon guest oxidation state.[6]

TMAFc$^{+/2+}$ calix[6]arene-*p*-hexasulfonate
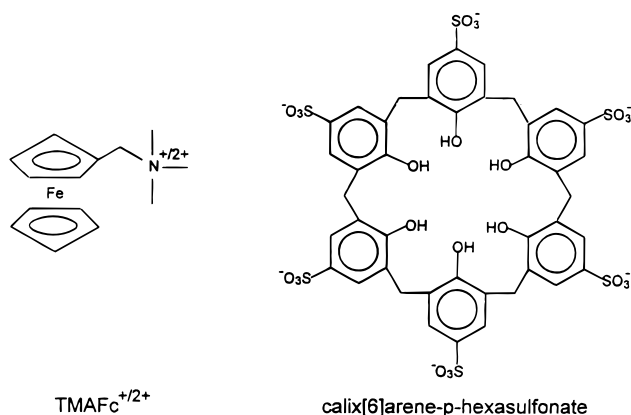
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(4) See also: (a) Imonigie, J. A.; Macartney, D. H. *Inorg. Chem.* **1993,** *32,* 1007. (b) Imonigie, J. A.; Macartney, D. H. *J. Chem. Soc., Dalton Trans.* **1993,** 1830. (c) Johnson, M. D.; Reinsborough, V. C.; Ward, S. *Inorg. Chem.* **1992,** *31,* 1085.

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Experimental Section

Materials. [TMAFc](BF$_4$), [TMAFc](BF$_4$)$_2$, and Na$_8$\{calix[6]arene-*p*-hexasulfonate (1-H)\} were prepared and purified by literature methods.[3,5,7]

Rate Measurements. The electron self-exchange rate constant, *k*, was obtained via ^{1}H NMR line broadening (Varian Gemini 300). In the fast exchange limit (applicable here):[8]

$$k = 4\pi\chi_D\chi_P(\Delta\nu)^2/(w_{DP} - \chi_D w_D - \chi_P w_P)C_{sum} \quad (1)$$

where $\Delta\nu$ is the contact shift in Hz, χ_D and χ_P are total mole fractions of TMAFc$^+$ and TMAFc^{2+}, respectively, w_D, w_P, and w_{DP} are line widths (half-height) for solutions containing TMAFc$^+$, TMAFc^{2+}, and mixtures of TMAFc$^+$ and TMAFc^{2+}, respectively, and C_{sum} is the combined total molar concentration of TMAFc$^+$ and TMAFc^{2+}. Total concentrations of TMAFc$^+$ and TMAFc^{2+} were ca. 5 and 0.2 mM, respectively. The total concentration of calix[6]arene-*p*-sulfonate was varied between 0 and 48 mM.

Our initial attempts to measure *k* were frustrated by the decomposition of TMAFc^{2+} in the presence of the host. While the nature of the decomposition reaction was not investigated, we found that it could be circumvented by recrystallizing the calixarene from 1 M HCl; presumably this protonates phenolate sites[5b] and subsequently yields in unbuffered solution a mix of the hexaanionic and heptaanionic forms (or possibly heptaanionic and octaanionic forms). Except as noted, all subsequent experiments were performed with the recrystallized calixarene and with 0.1 M NaBF$_4$ (measured solution pH(D) ≈ 5).

Results and Discussion

An NMR titration of TMAFc$^+$ (methyl resonances, δ = 2.84 to 2.37 ppm)[6] with the host yielded a value of 8600 ± 500 M^{-1} for the equilibrium encapsulation constant (K_1) for eq 2.

$$\text{TMAFc}^+ + \mathbf{1}^{n-} \rightleftharpoons \text{TMAFc}^+ \cdot \mathbf{1}^{n-} \quad (2)$$

For comparison, Zhang et al. report a value of 11 000 M^{-1} under slightly different conditions.[6] The equilibrium constant (K_2) for the corresponding reaction with TMAFc^{2+} can be obtained from eq 3, where ΔE_f is the limiting shift in the TMAFc$^{2+/+}$ formal
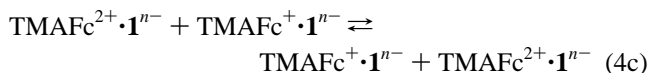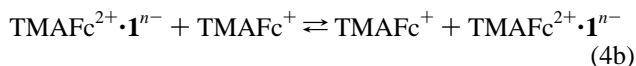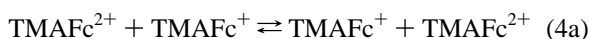
$$\Delta E_f = (RT/F) \ln[K_1/K_2] \quad (3)$$

potential following host addition and *F* is the Faraday constant. We observed a −47 mV shift, corresponding to $K_2 = 54000 \pm 5000$ M^{-1}.[9] Thus, the experiments offer an interesting contrast to TMAFc$^{2+/+}$ association with β-cyclodextrin, where only the ferrocene form is detectably encapsulated.[10]

Figure 1 summarizes the effects of $\mathbf{1}^{n-}$ upon TMAFc$^{2+/+}$ self-exchange kinetics. The unusual peaked response of *k* to added $\mathbf{1}^{n-}$ is strongly suggestive of stepwise encapsulation of the redox couple. Depending on the calixarene concentration, any of three reactions could contribute to the observed rate constant:[11]

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

(8) See, for example: Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1978,** *82,* 2542.

(9) Again under slightly different conditions (unbuffered 0.05 *M* KCl), Kaifer and co-workers[6] report a −120 mV potential shift−implying a 110-fold increase in *K* upon oxidation to the ferrocenium form. Under their conditions, we find $\Delta E_f = -60$ mV−corresponding to a 10-fold increase in *K*. The origin of the discrepancy is unclear. An additional experiment in 0.1 M NaCl with the pH adjusted to 10 with NaOH, however, yielded $\Delta E_f = 80$ mV (23-fold increase in *K*).

(10) A reviewer has pointed out that a TMAFc^{2+}·β-CD binding constant of 150 *M*$^{-1}$ has been reported recently by Imonigie and Macartney on the basis of electron transfer kinetics measurements (*Inorg. Chim. Acta* **1994,** *225,* 51). Direct electrochemical thermodynamics measurements, on the other hand, indicate a binding constant of 20 M^{-1} or less.[3]

(11) A fourth pathway involving TMAFc^{2+} and TMAFc$^+ \cdot \mathbf{1}^{n-}$ also must exist, but should be of negligible significance under our conditions.
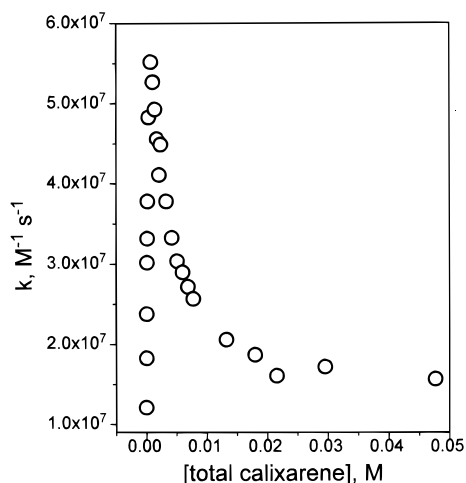
Figure 1. TMAFc$^{2+/+}$ self-exchange rate constant vs calixarene concentration (total concentration).

$$TMAFc^{2+} + TMAFc^+ \rightleftarrows TMAFc^+ + TMAFc^{2+} \quad (4a)$$

$$TMAFc^{2+} \cdot 1^{n-} + TMAFc^+ \rightleftarrows TMAFc^+ + TMAFc^{2+} \cdot 1^{n-} \quad (4b)$$

$$TMAFc^{2+} \cdot 1^{n-} + TMAFc^+ \cdot 1^{n-} \rightleftarrows$$
$$TMAFc^+ \cdot 1^{n-} + TMAFc^{2+} \cdot 1^{n-} \quad (4c)$$

On the basis of the encapsulation constants, reaction 4b should dominate in the peak region. More generally, the observed rate constant can be written as

$$k = (k_a[TMAFc^{2+}][TMAFc^+] +$$
$$k_b[TMAFc^{2+} \cdot 1^{n-}][TMAFc^+] +$$
$$k_c[TMAFc^{2+} \cdot 1^{n-}][TMAFc^+ \cdot 1^{n-}])/$$
$$[TMAFc^{2+}]_{tot}[TMAFc^+]_{tot} \quad (5a)$$

or equivalently (after algebraic manipulation)

$$k = \frac{k_a + k_b K_2[1^{n-}] + k_c K_1 K_2[1^{n-}]^2}{1 + K_1[1^{n-}] + K_2[1^{n-}] + K_1 K_2[1^{n-}]^2} \quad (5b)$$

For each rate measurement (each calixarene concentration), the specific reactant concentrations were calculated from the available equilibrium constants and the appropriate *total* TMAFc$^+$, TMAFc^{2+}, and 1^{n-} concentrations as follows:

$$[TMAFc^+]_{tot} = [TMAFc^+] + [TMAFc^+ \cdot 1^{n-}] =$$
$$[TMAFc^+] + K_1[TMAFc^+][1^{n-}] \quad (6)$$

$$[TMAFc^{2+}]_{tot} = [TMAFc^{2+}] + [TMAFc^{2+} \cdot 1^{n-}] =$$
$$[TMAFc^{2+}] + K_2[TMAFc^{2+} \cdot 1^{n-}] \quad (7)$$

$$[1^{n-}]_{tot} = [1^{n-}] + \frac{K_1[1^{n-}][TMAFc^+]_{tot}}{1 + K_1[1^{n-}]} +$$
$$\frac{K_2[1^{n-}][TMAFc^{2+}]_{tot}}{1 + K_1[1^{n-}]} \quad (8)$$

Figure 2 (k versus the concentration of *free* calixarene ([1^{n-}])) shows that the available kinetic data are well described by eq 5b and the independently measured K_1 and K_2 values. From
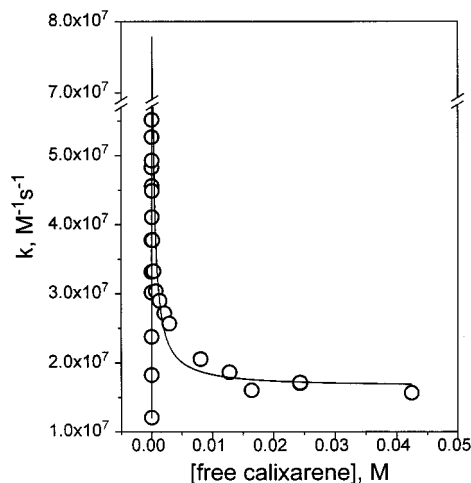
Figure 2. TMAFc$^{2+/+}$ self-exchange rate constant vs free calixarene concentration. Solid line is a best fit to eq 5b.

the fit, $k_a = 1.2 \times 10^7$ M^{-1} s^{-1} (fixed by the initial point), $k_b = 1.3 \times 10^8$ M^{-1} s^{-1}, and $k_c = 1.6 \times 10^7$ M^{-1} s^{-1}.[12,13]

The roughly 10-fold rate preference for eq 4b (electron transfer coupled to host transfer) versus eq 4c or 4a (electron transfer only) contrasts with much larger rate *inhibitions* when ET is coupled to either β-cyclodextrin or crown ether host transfer.[2,3] Two factors appear to be important. First, the degree of oxidation-state dependence of the guest/host association constant is much smaller for 1^{n-}/TMAFc$^{2+/+}$ than for either β-cyclodextrin/TMAFc$^{2+/+}$ or the ammine ruthenium/crown ether system(s).[14] We have previously noted that when self-exchange occurs sequentially via slow electron transfer and rapid host transfer, the observed rate should be attenuated by an isolated "redox asymmetry factor" equaling either [K(ox)/K(red)]$^{1/2}$ (if K(ox) < K(red)) or [K(red)/K(ox)]$^{1/2}$ (if K(ox) > K(red)).[2] Thus, for the cyclodextrin and crown systems, rather large attenuation effects are both observed and expected. With the calixarene, however, the redox asymmetry factor is small (ca. 0.4) and apparently offset by other factors. The second important factor is the opposite charges carried by the free guests and the guest/host assembly. This circumstance should lead to attractive interactions and an enhanced ET "precursor complex" formation constant for reaction 4b, but repulsive interactions between reactants in eqs 4a and 4c. These effects obviously should be mitigated to some extent by the inert electrolyte—yet not completely eliminated. In any case, they appear to be large enough to more than offset the anticipated (small) redox asymmetry effect and to induce a net acceleration of the exchange kinetics.

Finally, it is somewhat surprising that the reactivity of the fully encapsulated reactants and products (k_c) is so similar to that for the free species—despite the potential for either (1) inhibition of electronic coupling (rate deceleration) or (2) diminution of solvent reorganizational effects (rate acceleration). Conceivably both could be occurring, leading to little net rate effect. On the other hand, given the enormous differences in

(12) Equation 8 was solved for [1^{n-}] using Mathcad Plus (Mathsoft, Inc., 1994).

(13) We neglect in our analysis any possible changes in k_a, k_b, or k_c with changes in ionic strength (changes in calixarene concentration).

(14) The data in Figure 2 were fit to eq 5b by using Microcal Origin 2.8 (Microcal Software, Inc., 1993).

(15) The similarity of K_1 and K_2 likely reflects compensating effects. Electrostatic interactions clearly should enhance calix[6]arene-*p*-sulfonate association with both TMAFc^{2+} and TMAFc$^+$, but should be more important for the former. Hydrophobic interactions also should contribute to association with both TMAFc^{2+} and TMAFc$^+$, but should be more important for the latter.

ionic strength between the solutions containing the smallest and largest amounts of calixarene, perhaps little significance should be attached to the similarities or dissimilarities in reactivity for the free vs fully encapsulated species.

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