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A thermodynamic study of the electron transfer chain catalyzed substitution of triphenylphosphine for iodide on $CpFe(CO)_2I$

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Abstract

The thermodynamic parameters governing the electron transfer chain catalyzed substitution of triphenylphosphine for iodide on $CpFe(CO)_2I$ have been studied. The reaction is driven by the much higher stability of the triphenylphosphine complex relative to the iodide complex, and proceeds to completion even though the electron transfer which propagates the catalytic chain is endergonic. The standard reduction potential of $CpFe(CO)_2I$ is -1.64 V vs. Fc^+/Fc, while that of $CpFe(CO)_2(PPh_3)^+$ is -1.59 V. Nevertheless, the association constant for triphenylphosphine with the 17-electron $CpFe(CO)_2$ fragment is 4×10^5 times that for iodide ($\log K_P = 1.9 \pm 1.9$, $\log K_I = -3.7 \pm 1.9$). The rate of the reaction is accelerated enormously by reduction of the iodide complex, which allows the substitution to proceed through the more labile 17/19-electron complexes. The contrast between the π-basicity of iodide and the π-acidity of triphenylphosphine is proposed to be responsible for the favored complexation of triphenylphosphine by the relatively electron-rich $CpFe(CO)_2$ fragment. The application of redox catalysis and redox equilibration to the study of such 17/19e equilibria shows great promise for obtaining these difficult-to-measure formation constants.

Keywords: Electron-transfer; Catalysis; Iron; Substitution; Reduction

1. Introduction

The reaction of FpX ($Fp = CpFe(CO)_2$; X = Cl, Br, I) with PR_3 (R = Ph and/or Me) to yield $Fp(PR_3)^+$ has been shown to proceed through an electron transfer chain (ETC) catalysis mechanism [1]. We would like to address in this report the thermodynamics of this reaction, in particular the standard reduction potentials and the formation constants of the complexes involved. The net reaction which will be the focus of this study is the substitution of PPh_3 for I^-, Eq. (1) (K_{ex}).

$$FpI + PPh_3 \overset{K_{ex}}{\rightleftharpoons} Fp(PPh_3)^+ + I^- \quad (1)$$

This reaction is initiated by strong reducing agents and proceeds quickly to completion. Thus, the equilibrium constant heavily favors the species on the right side of Eq. (1). However, the thermal reaction in the absence of reducing agents is quite slow, so that the mixture on the left is kinetically stable for long periods at room temperature.

The mechanism of the ETC catalyzed reaction has been proposed to involve the reactions shown in Eqs. (2)–(5) [1].

$$FpI + e^- \overset{E^o_I}{\rightleftharpoons} FpI^- \quad (2)$$

$$FpI^- \overset{1/K_I}{\rightleftharpoons} Fp + I^- \quad (3)$$

$$Fp + PPh_3 \overset{K_P}{\rightleftharpoons} Fp(PPh_3) \quad (4)$$

$$Fp(PPh_3) \overset{-E^o_P}{\rightleftharpoons} Fp(PPh_3)^+ + e^- \quad (5)$$

The above reactions include two electron transfers, each characterized by a standard reduction potential, and two complexation equilibria, each characterized by a formation constant. The overall driving force for Eq.

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(1) is determined by the sum of the driving forces for these four reactions.

$$\Delta G_{\mathrm{ex}} = -RT\ln K_{\mathrm{ex}} = nF\left(E^{\mathrm{o}}_{\mathrm{P}} - E^{\mathrm{o}}_{\mathrm{I}}\right) - RT\ln\frac{K_{\mathrm{P}}}{K_{\mathrm{I}}} \qquad (8)$$

The purpose of the work reported here is to separate the factors involved and determine their relative importance to the overall reaction. In particular, we wished to examine the importance of the electron transfers relative to the formation constants. Our intuition was that electron transfer alone would favor the reactants in Eq. (1), so that there must be a strong preference for coordination to Fp of PPh_3 over iodide to drive the catalytic substitution in the observed direction.

The reaction under study is closely related to that reported by Pevear et al. [2]. They studied the ETC catalyzed substitution of various P- and As-donor ligands, including PPh_3, for CO on $Fp(CO)^+$. The mechanism of the substitutions of $Fp(CO)^+$ is exactly the same as that above, but there is a very important difference between $Fp(CO)^+$ and FpI that has a great impact on the study of the reactions of these two compounds. The $Fp(CO)^+$ complex is reduced electrochemically at a peak potential of −1.10 V vs. Fc^+/Fc [2], while the peak potential for the reduction of FpI is −1.62 V. This difference has two consequences. First, the reduction of their substitution product with PPh_3, $Fp(PPh_3)^+$, occurs at a peak potential of −1.53 V, which is negative of the $Fp(CO)^+$ reduction but positive of the FpI reduction. Thus in the electrochemically initiated substitution of $Fp(CO)^+$ it is possible to observe separate peaks by cyclic voltammetry for the reactant and product complexes. With FpI, however, a separate peak for $Fp(PPh_3)^+$ would not be observed by cyclic voltammetry and thus any substitution initiated by electrochemical reduction would not be evident. Second, assuming that the standard reduction potentials have the same relative magnitudes as the cyclic voltammetric peak potentials, the standard potential for the reduction of $Fp(PPh_3)^+$ will be more negative than that of $Fp(CO)^+$ but more positive than that of FpI. It is generally accepted that a necessary condition for efficient reductively initiated ETC catalyzed substitution reactions is that the departing ligand must be replaced by a better electron donor so that E^{o} of the substitution product is more negative than that of the reactant [2]. In this way, the homogeneous reduction of reactant by the reduced form of the product, e.g., Eq. (2) + Eq. (5), is spontaneous and serves to propagate the catalytic substitution. This condition is met for the substitution of PPh_3 for CO on $Fp(CO)^+$, but not for the reaction with FpI. If the standard potential of FpI is indeed more negative than that of $Fp(PPh_3)^+$, then this system will be a rare example of an ETC reaction involving an endergonic electron-transfer propagation step.

2. Experimental

2.1. Reagents

The $CpFe(CO)_2I$ (FpI) and $[CpFe(CO)_2]_2$ (Fp_2) were obtained from Aldrich and used as received. The $[CpFe(CO)_2(PPh_3)]PF_6$ was prepared by reaction of FpI with PPh_3 in tetrahydrofuran catalyzed by Cp^*_2Mn, followed by reaction with $[Bu_4N]PF_6$ in aqueous acetone. The $DQ(BF_4)_2$ (DQ^{2+} = 1,1′-ethylene-2,2′-bipyridinium) was prepared by reaction of 2,2′-bipyridine with ethylene dibromide according to the literature procedure [3], followed by reaction with $NaBF_4$ in water. The dichloromethane was dried with CaH_2 and distilled under nitrogen before use. The supporting electrolyte for electrochemical experiments, $[Bu_4N]PF_6$, was obtained from Southwestern Analytical Chemicals and was dried under vacuum before use. All other reagents were obtained commercially and were used as received.

2.2. Instrumentation

IR spectra were obtained using a Mattson Instruments Cygnus 100 FTIR and a cell with CaF_2 windows separated by a 0.1 mm spacer. Cyclic voltammetry and controlled potential electrolyses were performed using a Bioanalytical Systems BAS 100B/W electrochemical analyzer. Solutions contained approximately 0.1 M $[Bu_4N]PF_6$ supporting electrolyte. Conventional cyclic voltammetry was done using a 0.5 mm Pt disc working electrode, Pt wire auxiliary electrode, and Ag/AgCl reference electrode. For fast scan cyclic voltammetry and steady state voltammetry, a BAS low current module and a 10 μm Pt disc working electrode were used. Controlled potential electrolyses were performed using a BAS PWR-3 power module, 25 × 25 mm platinum foil working and auxiliary electrodes, and a silver wire quasi-reference electrode. All potentials are expressed relative to the formal potential of the ferrocenium–ferrocene couple (Fc^+/Fc), which we measure as approximately +0.45 V vs. Ag/AgCl.

2.3. General methods

2.3.1. Redox catalysis

Redox catalysis experiments were performed with the substrates FpI and $[Fp(PPh_3)]PF_6$ and the mediators 2,7-dinitro-9-fluorenone (DNF), 4-nitropyridine-*N*-oxide (NPO), 4-nitrobenzonitrile (NBN), 3,5-dinitrobenzonitrile (DNBN), and tris(dibenzoylmethanato)iron ($Fe(DBM)_3$). For each substrate/mediator combination, cyclic voltammetry was performed under argon using a variety of concentrations and scan rates, typically 1 or 2×10^{-3} M mediator with concentrations of substrate sufficient to observe redox catalysis (ranging from 2 to

40×10^{-3} M) at scan rates between 0.1 and 10 V s^{-1}. The increases in the peak currents of the mediators in the presence of the substrates were used in conjunction with published working curves [4] to calculate rate constants for the forward electron transfer between mediator and substrate. Reported values represent the averages of between five and 20 measurements for each combination.

2.3.2. Redox equilibration

Redox equilibration experiments were performed by adding known amounts of the appropriate reagents to a Schlenk flask wrapped in aluminum foil to exclude light, then evacuating the flask and filling with argon, and finally adding freshly distilled CH_2Cl_2 via a gastight syringe. The $Fp(PPh_3)^+/Fp_2$ equilibrium was approached from one direction by reacting 10×10^{-3} M $Fp(PPh_3)^+$ and 10 or 20×10^{-3} M Cp_2Cr or Cp_2^*Ni and from the other direction by reacting 4.0×10^{-3} M Fp_2, 8.0×10^{-3} M PPh_3, and 6.0×10^{-3} M Cp_2Cr^+ or 5.0×10^{-3} M Fp_2, 10×10^{-3} M PPh_3, and 9.0×10^{-3} M $Cp_2^*Ni^+$. Because of the low solubility of $DQ(BF_4)_2$ (vide infra), the FpI/Fp_2 equilibrium was studied by reacting 2.5 or 5.0×10^{-3} M Fp_2 and 5.0 or 10×10^{-3} M $[Bu_4N]I$ in a saturated solution of $DQ(BF_4)_2$ (ca. 1×10^{-6} M). IR spectroscopy was used to monitor the progress of all reactions and to quantitate the equilibrium concentrations of Fp_2 (at 1955 cm^{-1}) and FpI (at 2040 cm^{-1}) or $Fp(PPh_3)^+$ (at 2057 cm^{-1}). Calibration curves were constructed with known concentrations of the three compounds and were linear between 1 and 10×10^{-3} M. The time required to reach equilibrium varied between 3 and 30 h, depending upon the specific system under investigation. The Cp_2Cr^+ and $Cp_2^*Ni^+$ were prepared by controlled potential electrolysis and used in situ in the electrochemical cell. All reactions were carried out under argon.

3. Results and discussion

3.1. Initial estimate of K_{ex}

The overall equilibrium constant, K_{ex}, for the substitution of PPh_3 for I^- on FpI, Eq. (1), was initially estimated by combining 10×10^{-3} M FpI, 10×10^{-3} M PPh_3, and 3.0 M $[Bu_4N]I$ in CH_2Cl_2 and adding a small amount of Cp_2^*Mn to catalyze the equilibration [1]. Even with such a large excess of iodide the reaction went essentially to completion. However, based upon the observation by IR of a very small shoulder for FpI at 2040 cm^{-1} and by comparison with authentic mixtures of FpI and $Fp(PPh_3)^+$, it could be estimated that no more than 1×10^{-3} M FpI remained after equilibrium had been established, implying concentrations of $PPh_3 \leq 1 \times 10^{-3}$ M, $Fp(PPh_3)^+ \geq 9 \times 10^{-3}$ M, and $I^- = 3.0$ M by mass balance. Using these concentrations to estimate the value of the equilibrium constant gives $K_{ex} \geq 3 \times 10^4$. This equilibrium constant corresponds to a net free energy change of -6 kcal mol^{-1}.

3.2. Electrochemical reduction of FpI and $Fp(PPh_3)^+$

In order to understand the contribution of the electron transfers to the net free energy change in the catalytic substitution reaction, it was necessary to know the standard reduction potentials of the two Fp complexes, so their electrochemistry was studied by cyclic voltammetry (CV). The iodide complex, FpI, is irreversibly reduced in CH_2Cl_2 at a platinum disc electrode at a peak potential of -1.62 V vs. Fc^+/Fc at 0.2 V s^{-1} (Fig. 1). The chemical irreversibility of the reductions of Fp–halide complexes has been established to be the result of rapid dissociation of the halide following electron transfer [5–7]. The formation of I^- from FpI was confirmed by the observation of two oxidation peaks on the reverse CV scan at ca. 0.0 and $+0.1$ V, corresponding to the two-step oxidation of iodide to triiodide and then iodine typically observed in nonaqueous solvents [8].

The other initial product of the reduction of Fp–halide complexes is expected to be Fp, which may react chemically with the electrode (in the case of Hg [5–7]), be further reduced to Fp^-, or dimerize to Fp_2. At platinum electrodes only the latter two options are available. The ligand dissociation in Eq. (3) occurs so quickly that the Fp is formed in the immediate vicinity of the electrode, and at the potentials necessary for reduction of FpI the Fp is capable of being immediately reduced to the Fp^- anion, Eq. (6) ($E^o_{Fp} = -1.27$ V [9]).

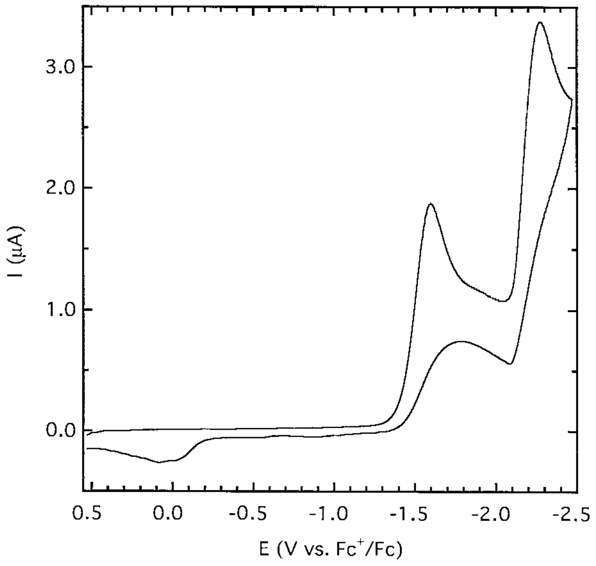

Fig. 1. Cyclic voltammogram of 2×10^{-3} M FpI in $CH_2Cl_2/[Bu_4N]PF_6$ (0.1 M) at a Pt disc electrode at 0.2 V s^{-1}.

The Fp^- anion is known to react rapidly with FpI to yield the dimer Fp_2, Eq. (7) [5,10].

$$\mathrm{Fp} + e^- \overset{E^{\circ}_{\mathrm{Fp}}}{\rightleftharpoons} \mathrm{Fp}^- \tag{6}$$

$$\mathrm{Fp}^- + \mathrm{FpI} \rightarrow \mathrm{Fp}_2 + \mathrm{I}^- \tag{7}$$

The Fp formed in the reaction shown in Eq. (3) may also dimerize directly, Eq. (9):

$$2\mathrm{Fp} \overset{K_{\mathrm{D}}}{\rightleftharpoons} \mathrm{Fp}_2 \tag{9}$$

The value of K_D has been estimated to be 2.5×10^{18} M^{-1} [9] with the forward rate constant being diffusion-controlled ($\geq 10^9$ M^{-1} s^{-1} in cyclohexane and benzene [11,12]). However, Amatore et al. have demonstrated both theoretically and experimentally that even for species which dimerize this rapidly, dimerization cannot compete effectively with reduction for reducible species formed near an electrode at a potential negative of the species' reduction potential [13,14]. Thus, the reaction in Eq. (9) is not believed to contribute significantly to the mechanism of the electrochemical reduction of FpI.

Regardless of whether the initially formed Fp undergoes further electron transfer or dimerization, the only organometallic product expected from the electrochemical reduction of FpI is Fp_2. This was confirmed by the observation of a second irreversible reduction in the CV of FpI at a peak potential of -2.24 V, matching that of known Fp_2 under the same conditions. The production of Fp_2 via a net one-electron process was also confirmed by bulk electrolysis of FpI, which consumed approximately 1.0 F mol^{-1} and yielded a solution exhibiting the IR spectrum of Fp_2 ($\nu_{CO} = 1996$, 1955, 1774 cm^{-1}). Thus, the electrochemical reduction of FpI in CH_2Cl_2 may be described by reactions $2 + 3$ and $6 + 7$.

The rapid chemical reaction following electron transfer to FpI makes it difficult to determine the standard potential of the FpI reduction, E°_{I}. We have examined the CV of FpI in CH_2Cl_2 at a 10 μm diameter platinum microelectrode at scan rates as high as 300 V s^{-1} and temperatures as low as -50 °C without observing any reverse peak for the re-oxidation of FpI^-. Therefore, its standard potential was not accessible by direct electrochemical methods.

The direct electrochemical reduction of $Fp(PPh_3)^+$ is very similar to that of FpI. Cyclic voltammetry in CH_2Cl_2 at a platinum disc electrode displayed a chemically irreversible reduction at a peak potential of -1.53 V vs. Fc^+/Fc (at 0.2 V s^{-1}). A second cathodic peak at -2.24 V confirms the production of Fp_2 and an anodic peak at $+0.95$ V on the reverse scan matches that observed for PPh_3 alone. Thus, the mechanism of the electrochemical reduction of $Fp(PPh_3)^+$ is most likely identical to that proposed for FpI. The less negative peak potential for the reduction of this complex, which is the substitution product in the reaction of FpI with PPh_3, is the opposite of what was observed in the ETC catalyzed substitution of PPh_3 for CO on $Fp(CO)^+$ [2]. This would prevent the direct electrochemical observation of the catalyzed substitution reaction under consideration.

3.3. *Redox catalysis of the reductions of FpI and* $Fp(PPh_3)^+$

The use of redox catalysis (mediated electron transfer) has become an accepted method for determining standard reduction potentials when rapid follow-up chemical reactions make them otherwise inaccessible [4,14–18]. The cyclic voltammetry of a mediator (P) with a chemically and electrochemically reversible electron transfer of known standard reduction potential is observed in the presence of the substrate (i.e., FpL^z). If the standard reduction potential of the mediator is less extreme than that of the substrate, cross electron transfer will occur at a rate which depends upon the difference between the two standard reduction potentials, Eq. (10) + Eq. (11).

$$\mathrm{P} + e^- \overset{E^{\circ}_{\mathrm{Med}}}{\rightleftharpoons} \mathrm{Q} \tag{10}$$

$$\mathrm{Q} + \mathrm{FpL}^{z} \overset{k_{+}}{\rightleftharpoons} \mathrm{P} + \mathrm{FpL}^{z-1} \tag{11}$$

The rate constant of the forward electron transfer in Eq. (11), k_+, can be determined by measuring the increase in the cyclic voltammetric peak current of P in the presence of substrate and applying published working curves [4]. Fig. 2 shows example cyclic voltammograms for the mediator DNF in the absence and pres-

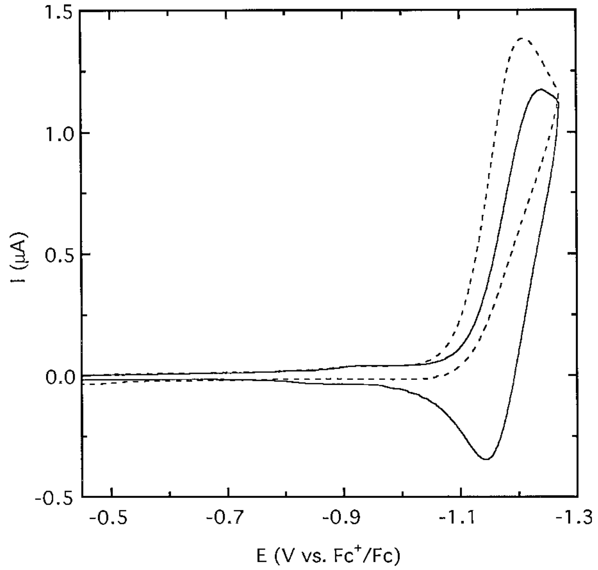

Fig. 2. Cyclic voltammograms of 1×10^{-3} M DNF in CH_2Cl_2/[Bu_4N]PF_6 (0.1 M) at a Pt disc electrode at 0.2 V s^{-1}: (————) alone; (----) in the presence of 4×10^{-3} M FpI.

Table 1
Forward rate constants (k_+) for mediated reductions of FpI and $Fp(PPh_3)^+$

Mediator[a]	E^o_{Med} (V vs. Fc^+/Fc)	$\log k_+^b$	
		FpI	$Fp(PPh_3)^+$
DNBN	−1.09	1.24 ± 0.06	1.7 ± 0.1
$Fe(DBM)_3$	−1.11	1.47 ± 0.04	2.11 ± 0.06
DNF	−1.18	2.62 ± 0.09	3.27 ± 0.09
NPO	−1.22	3.28 ± 0.09	3.87 ± 0.06
NBN	−1.27	3.80 ± 0.08[c]	4.3 ± 0.1[c]

[a] See Section 2.3.1 for abbreviations.
[b] Average ± standard deviation.
[c] Data excluded from E^o determinations.

ence of the substrate FpI, demonstrating the increase in the cathodic peak current of DNF observed when mediation takes place. [1] For mediator potentials in the 'counter diffusion' controlled region (such that the back electron transfer of Eq. (11) is diffusion limited) and for substrates for which the rate of the follow-up chemical reaction, e.g., the forward reaction of Eq. (3), greatly exceeds k_+, a plot of k_+ vs. E^o_{Med} will be linear with a slope near $-1/59$ mV^{-1} $(F/2.303RT)$. The standard potential for the substrate is then taken as the intersection of this line with the diffusion limited rate constant for the solvent, k_{diff}.

Table 1 and Fig. 3 present results for the redox-catalyzed reductions of FpI and $Fp(PPh_3)^+$ by a series of mediators. Excluding the data obtained with NBN, both compounds yielded the expected linear relationships with the lines being nearly parallel and having slopes of $-1/63$ mV^{-1} for FpI and $-1/60$ mV^{-1} for $Fp(PPh_3)^+$. The mediator NBN had the most negative standard potential and the values of k_+ determined for its mediated reduction of both FpI and $Fp(PPh_3)^+$ deviated significantly from the linear relationships between E^o_{Med} and k_+ established by the other four mediators. The reason for this deviation is most likely that NBN lies in the 'activation' controlled region of the k_+ vs. E^o_{Med} plot, where a slope of $-\alpha F/2.303RT$ would be expected [14–18]. The data obtained with NBN were thus excluded from the determination of the E^o values. The value of k_{diff} was calculated to be 1×10^{10} M^{-1} s^{-1} [19,20], though this result is subject to some uncertainty [14], leading to some uncertainty in the standard reduction potentials. Treatment of the data using 1×10^{10} for k_{diff} with an uncertainty in log k_{diff} of ±0.5 yields $E^o_I = -1.64 \pm 0.03$ V for FpI and $E^o_P = -1.59 \pm 0.03$ V for $Fp(PPh_3)^+$. It should be noted that the uncertainties in these numbers are not critical to the present analysis since it is the difference in standard potentials that will be of importance to ΔG_{ex}. Regardless of the value used for k_{diff}, this difference is equal to 50 mV, with the cationic $Fp(PPh_3)^+$ being easier to reduce.

3.4. Formation constants of FpI^- and $Fp(PPh_3)$

Once the standard reduction potentials of the 18e FpL^z complexes were known, the formation constants of the 19e FpL^{z-1} complexes could be estimated through the use of a thermodynamic cycle and the redox equilibration method [9]. In this method, an equilibrium is established between FpL^z and Fp_2 by means of a suitable redox agent (RA). The individual reactions, Eqs. (12)–(15), and the net redox equilibrium, Eq. (16), are as follows:

$$RA \overset{-E^o_{RA}}{\rightleftharpoons} RA^+ + e^- \qquad (12)$$

$$FpL^z + e^- \overset{E^o_L}{\rightleftharpoons} FpL^{z-1} \qquad (13)$$

$$FpL^{z-1} \overset{1/K_L}{\rightleftharpoons} Fp + L^{z-1} \qquad (14)$$

$$Fp \rightleftharpoons \frac{1}{2} Fp_2 \qquad (15)$$

$$FpL^z + RA \overset{K}{\rightleftharpoons} \frac{1}{2} Fp_2 + L^{z-1} + RA^+ \qquad (16)$$

A suitable redox agent will position the equilibrium in Eq. (16) at a point where measurable concentrations

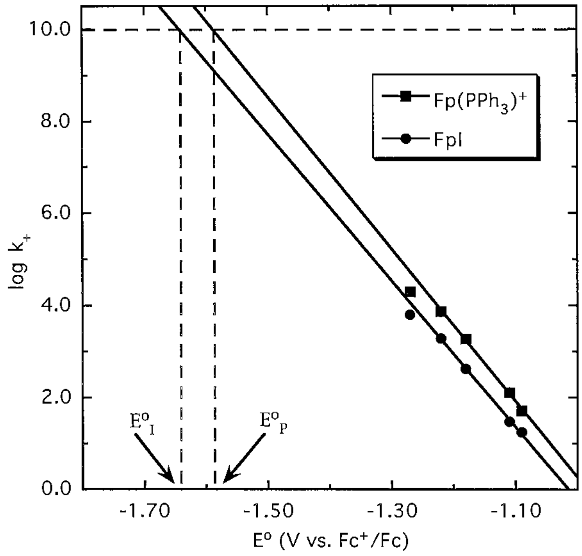

Fig. 3. Log of forward rate constant for mediated reduction (k_+) vs. E^o_{Med} and the determination of E^o values. ■, $Fp(PPh_3)^+$, $E^o_P = -1.59$ V; ●, FpI, $E^o_I = -1.64$ V. NBN data at −1.27 V were excluded from the linear regressions.

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[1] These voltammograms were successfully simulated using the program DigiSim 2.0 incorporating all standard potentials and reactions herein reported as well as a slow pseudo-first-order decomposition of the DNF radical anion a second-order chemical reaction between it and FpI in the mediated CV.

of both FpL^z and Fp_2 are present. These concentrations may be determined by an appropriate spectroscopic technique, such as IR absorbance. The concentrations of RA and RA^+ are then established by mass balance, and the equilibrium constant is calculated. Once the equilibrium constant for the reaction in Eq. (16) is known, its free energy change may be related to those of the reactions in Eqs. (12)–(15) as follows:

$$-RT\ln K = nF(E^{o}_{RA} - E^{o}_{L}) + \Delta G_{15} + RT\ln K_{L} \qquad (17)$$

The free energy change for the reaction in Eq. (15) is taken as -12.5 ± 2.5 kcal mol^{-1}, one half the value for the metal–metal bond formation in Fp_2 as reported by Pugh and Meyer [9]. Thus all the terms are known except K_L, which may then be calculated.

Two organometallic redox agents, Cp_2Cr ($E^o = -1.10$ V) and Cp_2^*Ni ($E^o = -1.15$ V), rapidly and cleanly established equilibrium for the reaction in Eq. (16) beginning with mixtures of either $Fp(PPh_3)^+$ and RA or Fp_2 and electrochemically generated RA^+. Thus, for $Fp(PPh_3)^+$ we were able to measure the equilibrium constant of the reaction in Eq. (16) for two mediators with equilibrium approached from both directions. The resulting equilibrium constants were 0.09 ± 0.04 for Cp_2Cr and 0.58 ± 0.06 for Cp_2^*Ni. Substituting these values into Eq. (17) gives $\log K_P = 1.9 \pm 1.9$ with Cp_2Cr and $\log K_P = 2.0 \pm 1.9$ with Cp_2^*Ni. It should be noted that by far the largest source of uncertainty in these results is the ± 2.5 kcal mol^{-1} uncertainty in the free energy change for the reaction in Eq. (15). While the large degree of uncertainty in K_P is disappointing, we can note that this result is in reasonable agreement with that reported for the binding of a single phosphine group of dppe to the Fp fragment, $K_{dppe} = 0.9$ [21].

It proved very difficult to find a suitable redox agent for FpI. However, DQ^{2+} (1,1′-ethylene-2,2′-bipyridinium [9], $E^o = -0.64$ V), despite its low solubility in CH_2Cl_2, did establish a measurable equilibrium when added to mixtures of Fp_2 and I^-. The concentration of a saturated solution of $DQ(BF_4)_2$ in CH_2Cl_2 was estimated to be approximately 1×10^{-6} M by steady-state voltammetry at a 10 μm diameter platinum microelectrode by comparison with a known concentration of ferrocene. Using this value, the concentrations of FpI and Fp_2 determined by IR, and mass balance to determine the other concentrations gave an approximate value for K of 1×10^{-4}. Given the large uncertainty in ΔG_{15} noted above, this value is likely adequate for the purpose of estimating K_I. Substituting the known quantities into Eq. (17) gives a value for $\log K_I$ of -3.7 ± 1.9.

Thus, using the redox equilibration method we have obtained estimates of the two 19e complex formation constants. While their individual values are subject to a large degree of uncertainty, it should be noted that the uncertainty in ΔG_{15} which contributes most of the uncertainty in the formation constants will affect both to the same extent. Thus, the ratio of the formation constants, which is the thermodynamic parameter that is actually relevant to the present study, should be considerably more certain. This ratio, K_P/K_I, should be very close to 4×10^5. Substituting this value into the Eq. (8), along with the standard reduction potentials of the 18e complexes determined by the redox catalysis method, gives $\Delta G_{ex} = -6.5$ kcal mol^{-1}. This free energy change corresponds to an equilibrium constant $K_{ex} = 6 \times 10^4$, which is in excellent agreement with the preliminary estimate of $K_{ex} \geq 3 \times 10^4$.

4. Conclusions

The redox catalysis method has been used to determine the standard reduction potentials of the complexes FpI ($E^o_I = -1.64 \pm 0.03$ V) and $Fp(PPh_3)^+$ ($E^o_P = -1.59 \pm 0.03$ V). The less negative standard potential of the PPh_3 complex, also reflected in a less negative peak potential in cyclic voltammetry, prevents direct electrochemical observation of the electron transfer chain catalyzed substitution reaction. The 50 mV difference in standard reduction potentials also makes the electron-transfer propagation of the catalyzed substitution thermodynamically uphill. However, the substitution of PPh_3 for iodide on FpI is driven by the energetically more favorable coordination of PPh_3 to the Fp moiety. The redox equilibration method has been used to obtain estimates of the formation constants of the 19e complexes, showing that in the 17e/19e manifold in which the catalyzed substitution reaction occurs, their ratio, K_P/K_I, is 4×10^5. The individual values for the formation constants are subject to considerable uncertainty due to uncertainty in the free energy change for dimerization of Fp. These values were found to be $\log K_P = 1.9 \pm 1.9$ and $\log K_I = -3.7 \pm 1.9$.

We believe that the work reported here represents the first example of the application of the combination of redox catalysis and redox equilibration to the determination of formation constants for 19e transition metal organometallic complexes. Evidence continues to accumulate pointing to the importance of these odd-electron species in many stoichiometric and catalytic processes [18,22–24]. Therefore, the determination of such formation constants is an important contribution to the fundamental understanding of organometallic reaction mechanisms. For the reaction which is the subject of the present study, the much more favorable interaction of PPh_3 with the metal center provides the driving force for the substitution. Our present speculation is that the π-acidity of PPh_3, in contrast to the π-basicity of iodide, is responsible for the preference of the relatively electron-rich Fp fragment for PPh_3 over iodide. Work is currently under way to explore this hypothesis, to improve the reliability of the formation constant measurements, and to extend the general technique to other organometallic systems.

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