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Competition between Homogeneous and Heterogeneous Electron-Transfer Pathways in an Electrochemical Square Scheme†

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Abstract: The reduction of an equilibrated isomeric mixture of CpCo(1,3-C_8H_8) (1,3) and CpCo(1,5-C_8H_8) (1,5) to their radical anions proceeds by a square scheme mechanism. The cyclic voltammetric peak heights for the cathodic waves are dependent on analyte concentration. This is shown to arise from the influence of the homogeneous cross-reaction $(1,3)^- + 1,5 \rightleftharpoons 1,3 + (1,5)^-$ near the electrode surface. Theoretical voltammograms simulated by the fast quasi-explicit finite difference method are in agreement with the experimental voltammograms over a range of concentrations and scan rates. A lower limit for the rate of isomerization of $[CpCo(1,5\text{-}C_8H_8)]^-$ to $[CpCo(1,3\text{-}C_8H_8)]^-$ is $2 \times 10^5\ s^{-1}$, 2 orders of magnitude higher than previous estimates. Theoretical investigations show that the coupling of the cross-reaction with the rapid $(1,5)^-$ to $(1,3)^-$ isomerization favors the homogeneous redox pathway. Analogies are made to electron-transfer-catalyzed reactions. This is thought to be the first voltammetric quantitation of the solution electron-transfer pathway for square schemes with the reactants initially at equilibrium.

Introduction

The "square scheme" (Scheme 1) is important in describing redox reactions coupled with structural or other chemical changes.[1–3] Electrochemical techniques have been used to our advantage to detect square schemes; the level of existing theory is generally adequate to quantify these systems.[4–6] One aspect of this redox mechanism that has received only cursory attention, however, namely that of homogeneous cross-reactions involving square scheme members, is the focus of this paper.

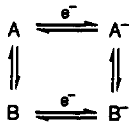
In addition to the heterogeneous electron-transfer (ET) reactions of eqs 1 and 2 occurring at the electrode surface in Scheme 1, the solution electron-transfer (SET) reaction of eq 3 is recognized as an alternate pathway for the ET reactions.[3b,4–9]

$$A + e^- \rightleftharpoons A^- \qquad (1)$$

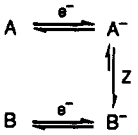
$$B + e^- \rightleftharpoons B^- \qquad (2)$$

$$A^- + B \rightleftharpoons B^- + A \qquad (3)$$

Scheme 1



Scheme 2



Under most circumstances, however, a preference for either the homogeneous route of eq 3 or the heterogeneous route of eqs 1 and 2 cannot be easily distinguished by experiment.[4,7,10] If the chemical system remains at equilibrium, the SET reaction has no effect on the electrochemical response of a square scheme system.[4] It is not surprising, therefore, that there is little if any evidence that SET reactions may affect voltammetric responses for square schemes when the reactants are present at their equilibrium concentrations under the initial reaction conditions.

On the other hand, a dramatic confirmation of SET reactions is reported for related mechanisms in which conversion between A^- and B^- (or A and B) is triggered by another reagent, Z (see the near-square scheme of Scheme 2), or when B is a separate species added to the solution for the purpose of accelerating ET reactions of A and A^-. These strategies are the bases of phenomena such as ET-catalyzed substitutions[11–15] and homogeneous redox catalysis.[16] Authoritative reviews of these mechanisms have appeared,[10,17,18] and we defer discussion of the parallels between this literature and our present observations

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† Structural Consequences of Electron-Transfer Reactions. 27. Part 26: Atwood, C. G.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5310.

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[9] Yeh, L.-S. R.; Bard, A. J. *J. Electroanal. Chem.* **1976**, *70*, 157.

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[14] Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *106*, 3771.

[15] Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1140.

[16] Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.

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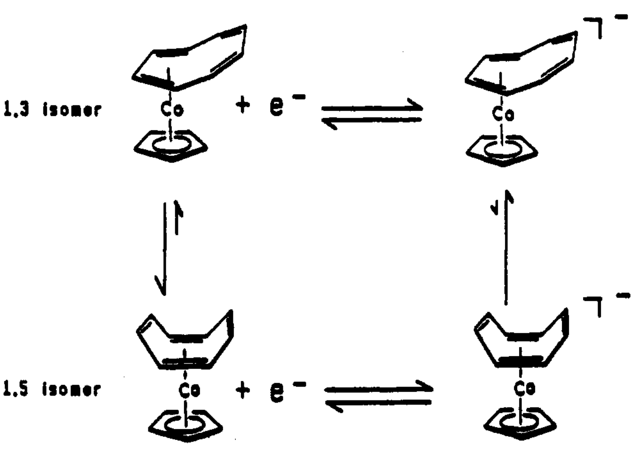
Scheme 3

$$\begin{tikzcd}
1,3 + e^- \arrow[r, shift left, "E^{\circ\prime}\,1,3 = -2.27"] \arrow[d, shift left, "k_{f(0)}"] & (1,3)^- \arrow[l, shift left] \arrow[d, shift left, "k_{f(-)}"] \\
1,5 + e^- \arrow[r, shift left, "E^{\circ\prime}\,1,5 = -2.51"] \arrow[u, shift left, "k_{b(0)}"] & (1,5)^- \arrow[l, shift left] \arrow[u, shift left, "k_{b(-)}"]
\end{tikzcd}$$

until later in this paper. For now, it is important to note that such observations have only been made when the reactants were originally present under nonequilibrium conditions, i.e., in a metastable state.

We were therefore surprised to find that a classical square scheme at equilibrium, about which we had written several papers, may prefer the homogeneous reaction route under favorable experimental conditions (concentration of analyte and electrochemical time scale). The SET effect is sufficient to affect cyclic voltammetry (CV) peak heights leading, if undetected, to errors in calculation of equilibrium constants and interconversion rates of square scheme members; indeed, in extreme cases, the presence of a predominant isomer might be missed.

The chemical system in question is that of CpCo(η^4-C_8H_8), its one-electron reduction product CpCo(η^4-C_8H_8)$^-$, and the two structural isomers of these compounds, interrelated through Scheme 3.[19] The cyclooctatetraene (COT) ring may adopt either a tub form (the 1,5-isomer) or the chair form (the 1,3-isomer).



Estimates for most of the thermodynamic and kinetic parameters of this square scheme were published earlier (Table 1).

In the process of using cyclic voltammetry (CV) to measure the interconversion rates of the neutral isomers, troublesome mismatches between theory and experiment were obtained, in a limited range of scan rates, under the assumption of purely heterogeneous ET processes. The possible role of the cross-reaction of eq 4 was then suggested by a significant concentration

$$(1,3)^- + 1,5 \underset{k_b(\text{cross})}{\overset{k_f(\text{cross})}{\rightleftharpoons}} 1,3 + (1,5)^- \tag{4}$$

dependence of the voltammetric response. Theoretical simulations confirm and quantify this hypothesis. Excellent agreement is obtained with CV measurements on both CpCo(C_8H_8) and its C_5 ring-permethylated analogue Cp*Co(C_8H_8), Cp* = η^5-C_5Me_5. The results not only verify the role of the SET reaction but also give new information about the rate of the cyclooctatetraene tub to chair isomerization rate in the 19-electron anions, (C_5R_5)Co(C_8H_8)$^-$.

Table 1. Literature Values for Reactions in Scheme 1 at 298 K

(a) Electron Transfer Reactions

isomer	$E°$ (V)	$k°$ [a] cm s^{-1}	α	ref
1,3	−2.27	0.28	0.61	19c
1,5	−2.51	0.06	0.4	19c

(b) Isomerizations

charge	K_{eq} = [1,5]/[1,3]	k_f (s^{-1})	k_b (s^{-1})	ref
neutral	K(0) = 3.26	$k_{f(0)} < 1$	$k_{b(0)} < 1$	19b,d
anion	K(−) = 4.3 × 10^{-4}	$k_{f(-)} = 0.9$	$k_{b(-)} = 2 \times 10^3$	19c

[a] Data obtained with the Hg working electrode.

Experimental Section

General Procedure. All manipulations of the cobalt complexes were accomplished under an atmosphere of dinitrogen (Schlenk techniques in preparations, drybox techniques in electrochemistry).

Materials. CpCo(C_8H_8) and Cp*Co(C_8H_8) were prepared by literature methods[20] and checked for purity by ^{1}H-NMR and electrochemistry. The purification of CpCo(C_8H_8) was accomplished by vacuum sublimation (300 K, 3 mT), and that of Cp*Co(C_8H_8), by column chromatography on neutral activity II alumina (hexanes). Reduction of the hexane eluant and cooling to 250 K yielded brown crystals. Both cobalt complexes were stored at 250 K under N_2.

Electrochemistry. *N,N*-Dimethylformamide (DMF), obtained from Burdick and Jackson, contained no electrochemically detectable impurities and was used as received, except for drying over Linde 4-Å molecular sieves. Tetrabutylammonium hexafluorophosphate, [Bu_4N][PF_6], was the supporting electrolyte at concentrations of 0.1 or 0.2 M. Potentials in this paper are referred to the ferrocene (Fc)/ferrocenium couple.[21] The experimental reference electrode was the aqueous SCE, against which Fc had a potential of +0.45 V in DMF/0.1 M [Bu_4N][PF_6]. It was housed close to the working electrode in a luggin probe.[22]

Pt was the working electrode material. For scan rates below 1 V/s, a 3.25-mm radius disk (Corning Glass Works) was used, and above this scan rate, a 247-μm disk was employed, made by sealing Pt wire (Goodfellow Metals) into soft glass. Electrode pretreatment consisted of rinsing with acetone, polishing with 0.25-μm Metadi II diamond paste on a Buehler microcloth, rinsing with water, and drying under N_2. A temperature of 313 (±1) K was maintained in all CV experiments by immersion of the voltammetry cell in a heptane bath, which was heated by a Nichrome wire encased in glass and controlled by a variable transformer. Data were recorded on a Nicolet 4094C digital oscilloscope interfaced to a Princeton Applied Research Model 173/175 potentiostat system. Charging current elimination was accomplished by acquiring voltammograms from blank solutions of DMF/[Bu_4N][PF_6] and subtracting them from scans of the analyte. The procedure utilized a computer program that performed point by point subtraction of the blank currents from the analyte currents at each digitized potential. Experimental data were transferred from the Nicolet scope to a Swan XT10 computer, on which the subtractions and data smoothing were performed.

Theoretical Calculations. Digital simulations involved three different approaches. A few pilot runs using a modified explicit finite difference (EFD) approach[23] were followed by extensive use of the fast quasi-explicit finite difference (FQEFD)[24] methodology, and finally some work utilizing the fast implicit finite difference (FIFD)[25] technique was done. Three different computational resources were employed, including a Swan 386SX personal computer, the University of Vermont's VAX 8530 mainframe,

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(18) Andrieux, C. P.; Saveant, J.-M. In *Investigations of Rates and Mechanisms*, 4th ed.; Bernasconi, C. F., Ed.; John Wiley and Sons: New York, 1986; Vol. 6, Part 2, p 305.

(19) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787. (c) Grzeszczuk, M.; Smith, D. E.; Geiger, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 1772. (d) Geiger, W. E.; Gennett, T.; Grzeszczuk, M.; Lane, G. A.; Moraczewski, J.; Salzer, A.; Smith, D. E. *J. Am. Chem. Soc.* **1986**, *108*, 7454. (e) Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314.

(20) CpCo(C_8H_8): ref 19a (a modification of the original procedure in Fritz, H. P.; Keller, H. *Z. Naturforsch.* **1961**, *16b*, 348). Cp*Co(C_8H_8): Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 273.

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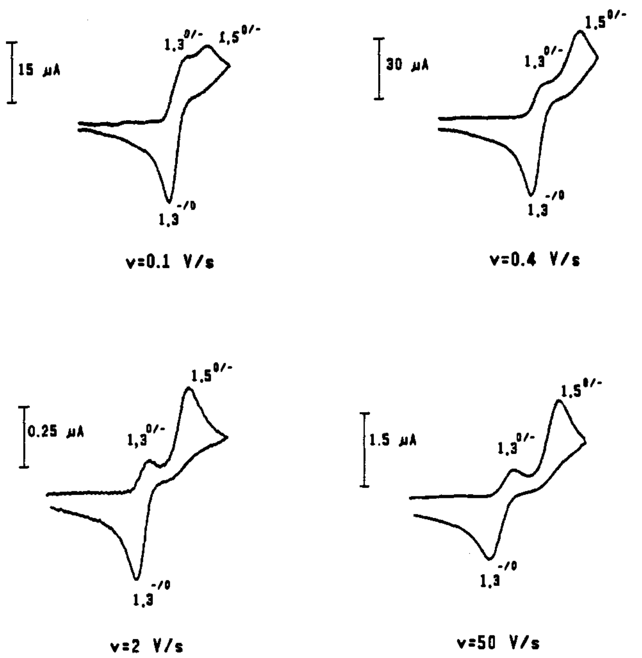

Figure 1. CV traces, after background subtraction, of $CpCo(C_8H_8)$ (0.4 mM) in DMF/0.1 M $[Bu_4N][PF_6]$ at $T = 313$ K at Pt electrodes (radius = 3.25 mm for $v < 1$ V/s, $r = 247$ μm for $v > 1$ V/s, in all experiments). Scan rates and current sensitivities are shown. All CV scans proceed from −1.5 V to lower potentials; the text should be consulted for peak potential values.

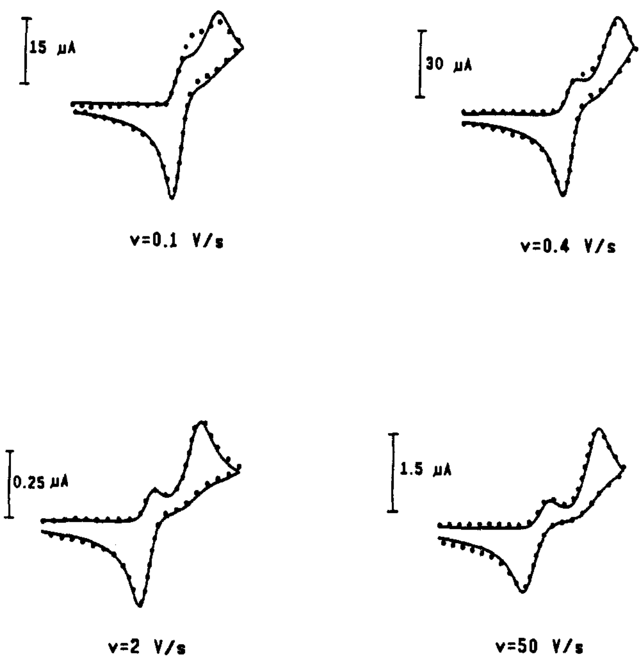

Figure 2. Circles: reproduction of experimental data of Figure 1. Solid lines: best fit for digital simulation results *not* including the SET cross-reaction of eq 4.

and an IBM 3090 at the Cornell National Supercomputer Facility, used remotely from UVM through Internet.

Results

General Description of Square Scheme Parameters. The salient general features of this system are as follows.[19] (1) The $E°'$ value of the chair isomer ($E°'_{1,3}$) is 240 mV positive of that ($E°'_{1,5}$) of the tub isomer. (2) The interconversion rates of the neutral isomers are slow, but those of the anions are fast (on the electrochemical time scale). (3) The thermodynamically favored forms in the two different oxidation states are the 1,5 isomer for the *neutral* complexes and the 1,3 isomer for the *anions*. (4) Both heterogeneous ET reactions are reasonably rapid, with reported values (at Hg) of $k°_{1,3} = 0.28$ cm/s and $k°_{1,5} = 0.06$ cm/s.[19c,d]

Overview of Voltammetric Responses. Figure 1 displays typical data at different scan rates. The traces are qualitatively easy to understand. At high sweep rates (>10 V/s, lower right), the isomerization of the neutral complexes is "frozen" and the two cathodic peak currents reflect the equilibrium amounts of the minor (1,3) and major (1,5) isomers, the latter undergoing reduction at the more negative potential. The single anodic peak arises from oxidation of the 1,3 anion, the bulk of which is furnished by the rapid, quantitative, isomerization of the 19-electron anion, $CpCo(1,5\text{-}C_8H_8)^-$, to $CpCo(1,3\text{-}C_8H_8)^-$.

The changes seen at lower sweep rates are manifested in the relative heights of the 1,3 and 1,5 cathodic waves. At sufficiently slow sweep rates, there is adequate time for the neutral 1,3 isomer, partially electrolyzed as the potential sweeps through $E°'_{1,3}$, to be replenished by conversion from the neutral 1,5 isomer with which it is in equilibrium (at the rate $k_{b(0)}$). This "extra" 1,3 isomer is reduced as it is formed, enhancing the first cathodic peak at the expense of the second.

The relative heights of the cathodic waves depend on $K(0)$ (eq 5, 3.26 at 298 K[19a]), $k_{b(0)}$, and v (sweep rate), analogous to the behavior of a CE mechanism, in which a chemical reaction (the neutral isomerization reaction) preceeds the ET of the 1,3 isomer.[26]

$$K(0) = [1,5]/[1,3] = k_{f(0)}/k_{b(0)} \qquad (5)$$

The $K(0)$ value is measured from the high scan rate data. Therefore $k_{f(0)}$ and $k_{b(0)}$ are accessible at low v through analysis of the cathodic peak currents, the relative values of which are altered by participation of the isomerization reaction (eq 6):

$$1,3 \underset{k_{f(0)}}{\overset{k_{b(0)}}{\rightleftharpoons}} 1,5 \qquad (6)$$

When digital simulations of this system were attempted using a strictly heterogeneous square scheme, no value of $k_{b(0)}$ was found which adequately accounted for all changes in cathodic peak currents. If good agreement was found for data at moderate v (e.g., 0.4–1 V/s), that value of $k_{b(0)}$ produced serious differences with experiment at lower v; the experimental current for the 1,3 isomer then *exceeded* the calculated amount (see Figure 2), and the mismatches were monotonically worse at decreasing v.

Recognition of the Role of the Cross-Reaction. Subsequent measurements showed that the relative heights of the two cathodic peaks were dependent on analyte concentration. Figure 3 displays the striking increases (at $v = 0.2$ V/s) in the ratio of the 1,3 to 1,5 waves as the formal concentration of $CpCo(C_8H_8)$ is increased by a factor of 10. This is explicable in terms of eq 4, the only second-order reaction expected to contribute to the mechanism. The very rapid isomerization of the 1,5 anion to the 1,3 anion keeps eq 4 from attaining equilibrium, the removal of the former producing a left-to-right stress, resulting in an enhanced concentration of the neutral 1,3 isomer in the electrode reaction layer.

A few digital simulations employing the EFD method and *including* the SET cross-reaction of eq 4 showed the desired effect but were impractical owing to excessively long computation times.[27] In the EFD method, computation times are proportional

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[26] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; pp 442–450.

[27] Typical digital simulation times for a single CV for the Co system using various methods: (a) EFD method on UVM mainframe computer, 24 h; (b) FQEFD method on personal 386SX computer, 45 min, on UVM mainframe, 6 min, and on Cornell Supercomputer, 30 s; (c) FIFD method on 386SX personal computer, 30 s.

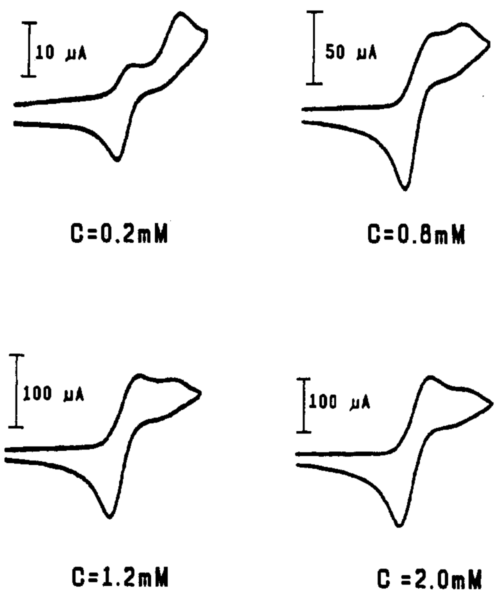

Figure 3. Raw CV traces of $CpCo(C_8H_8)$ in DMF/0.2 M $[Bu_4N][PF_6]$ at $T = 313$ K at various concentrations (shown) and $v = 0.2$ V/s.

to the sum of the simulator homogeneous rate constants.[28] At this time, however, Feldberg had developed the FQEFD algorithm, in which computation times were proportional to the one-fourth root of the rate constants, lowering computation times dramatically[27] and allowing us to proceed efficiently.[29]

Obtaining Quantitative Agreement between Theory and Experiment. Inclusion of the SET reaction in the FQEFD simulator program produced excellent fits between theory and experiment at two different concentrations over a range of scan rates. The values of $E^{\circ\prime}_{1,3}$, $E^{\circ\prime}_{1,5}$, and D_0 were taken from earlier literature;[19] equal diffusion coefficients were assumed for reactants and products. The α values may be considered as 0.50 ± 0.1. The k° values are somewhat below those previously reported[19] owing to the fact that the current values were obtained at Pt, in contrast to the earlier results at Hg. The value of K(cross) is fixed by the difference between the two $E^{\circ\prime}$ values (eq 7):

$$K(\text{cross}) = K(-)/K(0) = \exp[(F/RT)(E^{\circ\prime}_{1,5} - E^{\circ\prime}_{1,3})] \quad (7)$$

where

$$K(-) = [(1,5)^-]/[(1,3)^-] = k_f(-)/k_b(-) \quad (8)$$

Results are presented in Figures 4 and 5 and in Table 2. Simulator fits of data at the two concentrations were approached separately; the values listed in Table 2 were kept constant within a concentration set. There was generally good agreement between the parameters of the two sets of fits; to facilitate discussion, we use the average values given in Table 2.

Rates of Isomerization Reactions. The original targets of our study, namely the isomerization rates of the neutral isomers, are measured as $k_{f(0)} = 1.6$ s^{-1} and $k_{b(0)} = 0.4$ s^{-1} at 313 K. The value of $K(0)$, 3.9, suggests that the previously reported value of 3.3 at 298 K, attained by graphical analysis of the cathodic peaks, is low, since a higher temperature should result in a lower equilibrium constant.

One of the most interesting results concerns the isomerization rate of the 1,5 anion. This was previously measured by high frequency AC polarography as 2×10^3 s^{-1}.[19c] The present results show that value to be low by at least 2 orders of magnitude, for a value of $k_{b(-)} > 1.8 \times 10^5$ s^{-1} was required to fit the observed data. Simulations with $k_{b(-)}$ below this value were inconsistent with experiment, and those in excess had no further effect on the calculated trace; therefore, $k_{b(-)}$ is quoted as a lower limit.

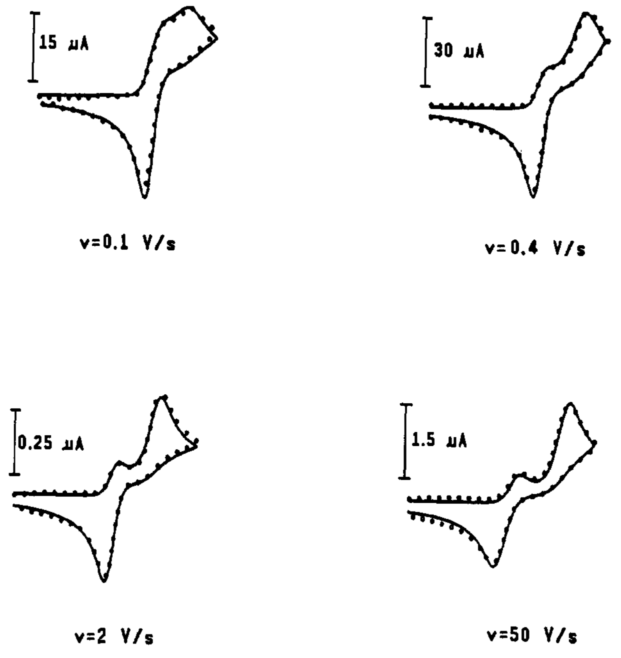

Figure 4. Comparison of experiment (circles) and theory *including* the SET reaction (solid lines). Experiment: reproduction of Figure 1 (concentration = 0.4 mM). Theory: using the FQEFD method and parameters of Table 2, left column.

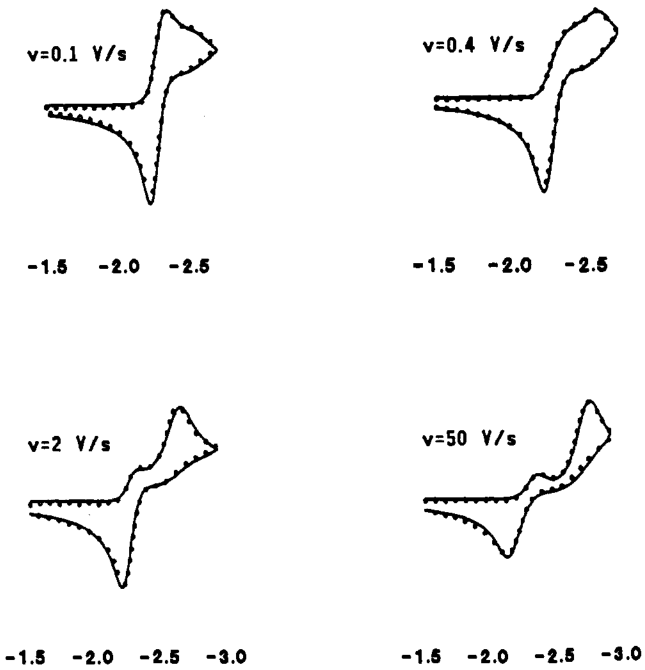

Figure 5. Comparison of experiment and theory, as in Figure 4. Experiment: concentration 1.0 mM in $CpCo(C_8H_8)$, background-subtracted data. Theory: parameters of Table 2, middle column.

Rate constants are also obtained for the SET reaction of eq 4. The value of $k_{b(\text{cross})}$, 4.6×10^8 M^{-1} s^{-1}, is close to a diffusion-controlled rate, appropriate for an outer-sphere ET reaction.

Studies of the C_5Me_5 Analogue, $Cp^*Co(\eta^4\text{-}C_8H_8)$. This structural analogue of $CpCo(C_8H_8)$, in which the cyclopentadienyl ring is permethylated, displays qualitatively similar square scheme reductive behavior.[19a,d] Two quantitative differences made it an attractive candidate to study in comparison to its C_5H_5 analogue. First, the separation of the $E^{\circ\prime}$ values is slightly higher, with $\Delta E^{\circ\prime} = 310$ mV compared to 240 mV for $CpCo(C_8H_8)$. This alters the equilibrium constant of the SET reaction [K(cross) =

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(28) Feldberg, S. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; Vol. 3, p 199.

(29) This program was made available to us through the generosity of D. H. Evans and S. W. Feldberg.

Table 2. Simulation Parameters Used for Fits with Experiment for $CpCo(C_8H_8)$ (Figures 4 and 5)

$CpCo(C_8H_8)$, 0.4 mM	$CpCo(C_8H_8)$, 1.0 mM	parameter
−2.27	−2.27	$E^{\circ\prime}_{1,3}$ (V)
−2.51	−2.51	$E^{\circ\prime}_{1,5}$ (V)
240	240	$\Delta E^{\circ\prime}$ (mV)
0.54	0.54	$\alpha_{1,3}$
0.50	0.46	$\alpha_{1,5}$
9.1×10^{-6}	9.1×10^{-6}	D_0 (cm s^{-2})
6.0×10^{-2}	4.2×10^{-2}	$k^{\circ}_{1,3}$ (cm s^{-1})[a]
5.8×10^{-3}	4.2×10^{-3}	$k^{\circ}_{1,5}$ (cm s^{-1})[a]
3.6	4.3	K(0)
0.4	0.4	$k_{b(0)}$ (s^{-1})
4.7×10^{-4}	5.7×10^{-4}	K(−)
$>2.0 \times 10^{5}$	$>1.6 \times 10^{5}$	$k_{b(-)}$ (s^{-1})
1.3×10^{-4}	1.3×10^{-4}	K(cross)
4.0×10^{4}	8.2×10^{4}	$k_{f(cross)}$ $(M\ s)^{-1}$
3.0×10^{8}	6.2×10^{8}	$k_{b(cross)}$ $(M\ s)^{-1}$

[a] Data obtained at the Pt working electrode, in contrast with the Hg electrode in ref 19 and Table 1.

1.3×10^{-4} for the C_5H_5 system and 1.0×10^{-5} for the C_5Me_5 system at 313 K]. Second, the isomerization of the neutral isomers is even slower than that of the Cp analogue. Earlier work estimated $k_{b(0)}$ as 4×10^{-4} s^{-1} at 313 K by monitoring the relative peak currents of the two isomers after dissolving an isomerically pure 1,5 sample.[30] Since this rate constant suggests a half-life of over 10 min, it can safely be assumed that the neutral isomerization reaction of eq 6 plays no role in experiments on a CV time scale. Therefore, any scan rate dependence of the relative heights of the two cathodic peaks *must* arise strictly from the cross-reaction.

The SET effects are again seen in the $Cp^*Co(C_8H_8)$ system (Figure 6). As anticipated from the larger $\Delta E^{\circ\prime}$, however, the effect is less prominent and requires higher concentrations (for the same v) to observe. With a concentration of 2.2 mM, scan rates below 0.4 V/s are required to see the onset of the homogeneous reaction pathway. Fits between theory and experiment are shown in Figure 6. It was difficult to account precisely for the background currents in this system. Addition of the $Cp^*Co(C_8H_8)$ analyte seemed to affect the background currents and lead to inaccuracies in baseline subtraction. This is responsible for the baseline mismatches seen in the slowest scan experiments. Table 3 gives the pertinent parameters coming out of the CV simulation fits of the 2.2 mM experiment.

Once again, it was necessary to invoke a very rapid isomerization of the 1,5 anion, with a lower limit of $k_{b(-)}$ of 1.5×10^5 s^{-1} for the reaction $Cp^*Co(1,5\text{-}C_8H_8)^- \rightarrow Cp^*Co(1,3\text{-}C_8H_8)^-$. The other parameters of the system are also consistent with those found for $CpCo(C_8H_8)$ (Table 3). Note that the value of $K(0)$ for $Cp^*Co(C_8H_8)$, 1.9, is significantly less than those reported earlier (4.6 and 2.1 at 298 K and 370 K, respectively).[19d] This is presumably because the present experiments allowed a more lengthy period for the isomers to equilibrate.

Discussion

It is instructive to consider why the conditions under which the SET reaction becomes important in the CV responses of a square scheme mechanism had not been previously recognized. We then point out analogies to other electrochemical mechanisms to aid in the qualitative understanding of the effect.

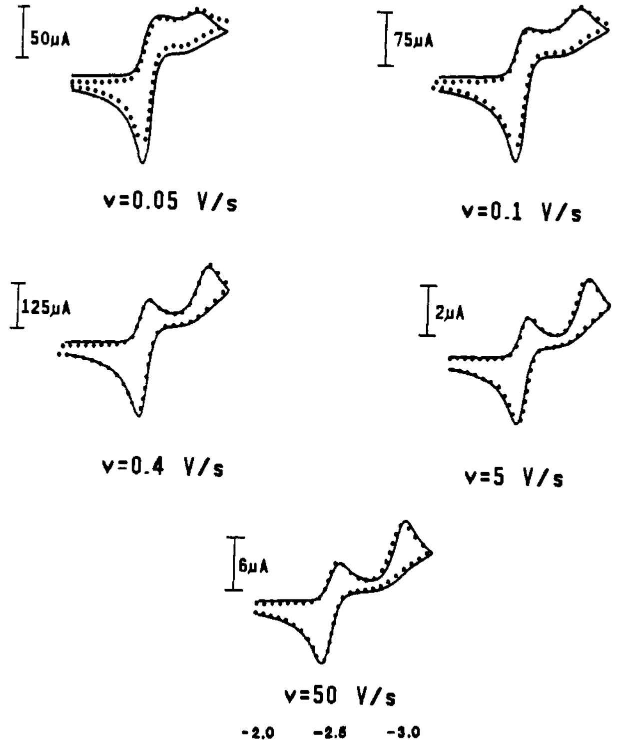

Figure 6. Comparison of experiment (circles) and theory (solid lines) for $Cp^*Co(C_8H_8)$. Experiment: concentration = 2.2 mM, in DMF/0.3 M $[Bu_4N][PF_6]$, T = 313 K. Theory: using the FQEFD method and parameters of Table 3.

Table 3. Comparison of Final Square Scheme Parameters for $CpCo(C_8H_8)$ and $Cp^*Co(C_8H_8)$[a]

$CpCo(C_8H_8)$	$Cp^*Co(C_8H_8)$	parameter
−2.27	−2.48	$E^{\circ\prime}_{1,3}$ (V)
−2.51	−2.79	$E^{\circ\prime}_{1,5}$ (V)
240	310	$\Delta E^{\circ\prime}$ (mV)
0.54	0.50	$\alpha_{1,3}$
0.48	0.55	$\alpha_{1,5}$
9.1×10^{-6}	3.0×10^{-6}	D_0 (cm s^{-2})
5.1×10^{-2}	7.9×10^{-2}	$k^{\circ}_{1,3}$ (cm s^{-1})[b]
5.0×10^{-3}	1.8×10^{-3}	$k^{\circ}_{1,5}$ (cm s^{-1})[b]
3.95	1.9	K(0)
0.4	4×10^{-4} (est)	$k_{b(0)}$ (s^{-1})
5.2×10^{-4}	2.0×10^{-5}	K(−)
$>1.8 \times 10^{5}$	$>1.5 \times 10^{5}$	$k_{b(-)}$ (s^{-1})
1.3×10^{-4}	1.0×10^{-5}	K(cross)
6.1×10^{4}	2.0×10^{3}	$k_{f(cross)}$ $(M\ s)^{-1}$
4.6×10^{8}	1.9×10^{8}	$k_{b(cross)}$ $(M\ s)^{-1}$

[a] Data for $CpCo(C_8H_8)$ are taken as the average of two experiments in Table 2. [b] Data obtained at the Pt working electrode, in contrast with the Hg electrode in ref 19 and Table 1.

Earlier theoretical work on square schemes recognized the presence of the thermodynamically mandated cross-reaction[4–7] but did not find the conditions under which it would become an effective alternative to the direct heterogeneous ET. Lerke et al.[7] specifically showed that, when the interconversion rates of products A^- and B^- and reactants A and B are equal, there is no significant effect of the cross-reaction on the CV trace. It is the combination of slow interconversion of reactants and fast interconversion of products, we believe, that makes the influence of the cross-reaction so striking in the case of the $CpCo(C_8H_8)$ system.

This combination of slow reactant isomerization and very fast product isomerization allows the system to take on certain characteristics analogous to those of ECE systems, for which SET effects may be vivid.[11–15,32] An ECE mechanism requires a thermodynamically unstable reactant (A, or a set of reactants) which is blocked from proceeding to its stable form (B) by a small

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(30) When crystals of $Cp^*Co(C_8H_8)$ are dissolved, only the resonances of the 1,5 isomer are observed initially.[19d] Voltammetry shows only the cathodic peak for the 1,5 isomer when scans are initiated immediately after dissolution of the solid. The cathodic peak for the 1,3 isomer grows in as time progresses, until equilibrium is reached. We generally waited over 1.5 h for solutions at 313 K to reach this point, whereupon the data such as those shown in Figure 6 were obtained.

(31) The smallest value of $k_{f(cross)}$ found to induce effects from the cross reaction was 4×10^2 M^{-1} s^{-1} when $k_{b(-)} > 3 \times 10^3$ s^{-1} and $\Delta E^{\circ\prime}$ = 300 mV.

value of $k_{f(0)}$ (Scheme 1). Reduction of A to A^-, followed by conversion of A^- to B^-, provides the reagents necessary for the SET reaction of eq 3 to proceed and equilibration of A and B to occur near the electrode. The conversion from A^- to B^- may be direct[33,34] or through the action of an added reagent.[11-15,32] If $E^{\circ\prime}{}_B$ is more positive than $E^{\circ\prime}{}_A$, and if the kinetics of the reactions are fast, the voltammetry wave for B may almost entirely replace that of A, even though the latter is the compound present in the bulk of solution. This scenario is found in ET-catalyzed isomerization and substitution reactions.[10]

The $CpCo(C_8H_8)$ system differs from the above in that it lies initially at equilibrium and is perturbed only during the potential scan, as E_{appl} nears $E^{\circ\prime}{}_{1,3}$ ($E^{\circ\prime}{}_A$) and A is removed (as A^-). The system remains thermodynamically unsettled owing to the fact that $k_{b(0)}$ is too small to allow for sufficient B → A (1,5 → 1,3) interconversion to make up for the electrolytic loss of A. Although the SET reaction (eq 3) provides a route for replenishment of A, the equilibrium constant is unfavorable, minimizing the effectiveness of this route. It is the rapid B^- to A^- isomerization that is key to providing the left-to-right stress (eqs 3, 4) that allows the SET to furnish additional A (1,3) to the electrode. Of course, the reduction of additional A to A^- at nearly a diffusion-controlled rate at this E_{appl} assures that the solution kinetics determine the ultimate amount of current at the peak potential of A.

The above model rationalizes why the SET influence is so noticeable when the anion isomerization rates are fast. In this model, the SET reaction is seen to *catalyze the conversion of 1,5 (B) to 1,3 (A)* at the electrode. An alternate model views the SET as *catalyzing conversion of 1,5 (B) to (1,5)⁻ (B⁻)*; inspection of eq 3 suggests either is valid. The latter, however, aids rationalization of why the SET effect is predicted to be larger when the heterogeneous ET rate of B, $k^\circ{}_{1,5}$, is low. Here, we turn for an analogy to the well-understood mechanism of homogeneous redox catalysis,[16-18] which normally involves irreversible reduction of B with formation of product(s) Z (eq 9).

$$B + e^- \rightleftharpoons B^- \rightarrow Z \qquad (9)$$

A promoter, P, having an $E^{\circ\prime}$ somewhat positive of that of B, is added to the solution. When P is reduced to P^-, the SET reaction of eq 10 is set up, but this homogeneous reaction would

$$B + P^- \rightleftharpoons B^- + P \qquad (10)$$

have no effect on the voltammetry were it to remain in equilibrium. The rapid removal of B^- (as Z) allows the SET reaction to proceed left to right in spite of an unfavorable K_{eq}, resulting in re-formation of P and reduction of B to B^- (eq 11):

$$\begin{tikzcd} P^- + B \arrow[r, shift left, Rightarrow, no head] & B^- \arrow[d] + P \\ & Z \end{tikzcd} \qquad (11)$$

The most telling characteristic of this system is an enhanced cathodic current for P. In the Co system, the 1,3 isomer plays the role of the promoter P in that it has a significantly more rapid heterogeneous ET rate than does the 1,5 isomer (B). From this viewpoint, the 1,3 isomer of the Co system behaves as an isomerization redox catalyst, with the $(1,5)^- \rightarrow (1,3)^-$ isomerization replacing the $B^- \rightarrow Z$ reaction.

Conclusions

The present work constitutes verification that homogeneous cross-reactions may have a profound effect on the shapes of cyclic voltammograms for square scheme mechanisms with the reactants at equilibrium. The SET effect can be seen for a system combining slow interconversions in one oxidation state with very rapid interconversions in the other oxidation state. Given the vast differences in reactivities common to compounds in different oxidation states,[1,2,35,36] it is probable that other examples of favored SET routes will be unearthed. We suggest that investigators of square scheme redox processes routinely test the concentration dependence of the electrochemical responses in order to probe the possible relevance of the homogeneous cross-reaction.

One significant benefit of the "square scheme with SET" analysis is the possibility of probing very fast isomerization rates. The present data show that the published[19c] isomerization rate for $[CpCo(1,5\text{-}C_8H_8)]^-$ to $[CpCo(1,3\text{-}C_8H_8)]^-$, ca. $2 \times 10^3\ s^{-1}$, is too low by at least 2 orders of magnitude. This pushes the lifetime of the COT tub-shaped anion below several microseconds. This estimate would be very difficult to obtain directly by CV, even with very fast sweep ultramicroelectrode technology,[37] owing to the electrochemical irreversibility of the $[CpCo(1,5\text{-}C_8H_8)]^{0/-}$ couple at high v.

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Supplementary Material Available: Digital simulations were performed in order to more broadly explore the combinations of square scheme parameters that might elicit observable SET effects. Text discussing these findings is available (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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