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Solution Electron-Transfer Reactions in Organic and Organometallic Electrochemistry

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Contents

The overall electrochemical oxidation and reduction reactions of organic and organometallic molecules often comprise complex sequences of electrochemical and chemical steps. In the shorthand notation now universally used, an electrochemical step is designated with the identifier E and is defined as a step involving loss or gain of an electron at the electrode–solution interface. Chemical steps, designated with the letter C, can in principle be surface chemical reactions involving adsorbed species (surface or heterogeneous reactions) or they can take place in solution among diffusing reactants (volume or homogeneous reactions). Most investigators have concentrated on the latter type of chemical steps, and this review will include only homogeneous chemical reactions.

The types of chemical reactions that are encountered as steps in organic and organometallic electrode reactions are extremely diverse. A given reaction can be protonation or deprotonation, bond cleavage, complexation or decomplexation, ligand exchange, nucleophilic or electrophilic attack, polymerization, isomerization, or conformational change. For example, the reduction of a quinone to the hydroquinone in a proton-donating medium requires two E steps and two C steps, the latter being protonations. Designating the quinone as Q, one can write a substantial number of possible reaction sequences. However, for benzoquinone, it has been shown[1,2] that only three reaction sequences are of importance, a CECE process in acidic media (pH < 2), an ECEC sequence at pH > 7, and an ECCE reaction at intermediate pH.

$$Q \rightarrow HQ^+ \rightarrow HQ^{\bullet} \rightarrow H_2Q^{\bullet+} \rightarrow H_2Q \quad (CECE) \qquad (1)$$

$$Q \rightarrow Q^{\bullet-} \rightarrow HQ^{\bullet} \rightarrow H_2Q^{\bullet+} \rightarrow H_2Q \quad (ECCE) \qquad (2)$$

$$Q \rightarrow Q^{\bullet-} \rightarrow HQ^{\bullet} \rightarrow HQ^- \rightarrow H_2Q \quad (ECEC) \qquad (3)$$

The coexistence of the reactant and various intermediates in the layer of solution close to the electrode surface leads to the possibility of perhaps the simplest of all of the homogeneous chemical reactions, an electron-transfer reaction. These *solution electron-transfer* (*SET*) *reactions* are the subject of this review. For example, in the ECEC scheme mentioned above, it is almost always the case that the neutral radical, $HQ^{\bullet}$, formed by protonation of the anion radical, is capable of being reduced by the anion radical itself.

$$HQ^{\bullet} + Q^{\bullet-} \rightarrow HQ^- + Q$$

Thus, under certain circumstances, reduction of $HQ^{\bullet}$ in solution (C step) is essentially the exclusive route, completely dominating the direct reduction of $HQ^{\bullet}$ at the electrode (E step).

It was in the context of the ECE family of reactions that the importance of SET reactions was first demonstrated. The concept was introduced by Hawley and Feldberg,[3,4] and Savéant and co-workers developed the theory in its most complete form.[5-7] In the last decade, SET reactions have been considered as steps in a variety of electrode reaction schemes, and in some cases they exert a dramatic influence on the current–potential–time response. The most frequently employed experimental techniques are the various types of voltammetry, so this review will concentrate upon the

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effects of SET reactions in voltammetry.

I. The E Reaction

Here a reactant forms product in the simplest of all reactions, a one-electron step with neither partner significantly adsorbed. (Sample reactions will be written as reductions with uncharged reactants in this paper. Extension to oxidations and ionic reactants is straightforward. In addition, species initially present in solution (reactants) will be italicized.)

$$A + e^- = A^- \qquad (4)$$

The only possible SET reaction is the self-exchange reaction ($A + A^- = A^- + A$), which can have no effect on the voltammetric response.

There is a growing recognition that reactions that appear to be simple E reactions may, in fact, involve significant structural changes so that chemical steps (e.g., conformational interconversion) will need to be included.[8,9] In such cases, SET reactions may play a role. (See more under section VI, Square Schemes.)

II. The $E(E)_mE$ Reaction (m = 0, 1, 2, ...)

The existence of a second electron-transfer step (EE reaction) immediately introduces the possibility of a disproportionation/comproportionation SET reaction (eq 6). Depending on the standard potentials for the

$$A + e^- = A^-; \qquad A^- + e^- = A^{2-} \qquad (5)$$

$$A^{2-} + A = 2A^- \qquad (6)$$

two electron-transfer steps, equilibrium in eq 6 will favor either A^{2-} and A (disproportionation) or A^- (comproportionation). Usually, this SET reaction is very fast so, for example, in the case where comproportionation is favored and the potential is maintained at a value where A is reduced to A^{2-}, the layer of solution near the electrode will contain substantial concentrations of $A^{\bullet-}$ formed by reaction of A^{2-} diffusing away from the electrode and encountering A diffusing toward the electrode. In view of the substantial amount of redox activity taking place in the reaction–diffusion layer, it is natural to assume that the SET (eq 6) will exert a pronounced effect on the voltammetric response. However, this expectation is unfounded, at least for the case of reversible electrode reactions, equal diffusion coefficients, and semiinfinite linear diffusion, where it has been shown that eq 6 can have absolutely no effect on the voltammetric response.[10] The basis of this remarkable result is that the SET does not change the average oxidation state of species in the reaction–diffusion layer so the current is not affected as it arises from the oxidation or reduction of this entire population of species. The proof is easily extended to $m > 0$.

By contrast, techniques that measure directly the concentrations of species in solution near the electrode are very sensitive to the occurrence of the SET. In fact, an early application of spectroelectrochemistry was the measurement of the rates of comproportionation in an EE scheme.[11]

When one or more of the three restrictions cited above is relaxed, the SET reaction will influence the voltammetric response. In the context of cyclic voltammetry, the effect of eq 6 is most easily detected in calculated voltammograms when substantial differences among the diffusion coefficients are invoked while maintaining reversibility of the electrode reactions.[12] However, the diffusion coefficients of the three related species in an EE scheme are likely to be similar so this effect will be infrequently encountered in real chemical systems. When one or both of the heterogeneous electron-transfer reactions is slow, the inclusion of the SET (eq 6) can be crucial in matching experiment and theory.[13,14]

$E(E)_mE$ schemes, either alone or as a part of a more complex scheme, are frequently encountered.[15-38] The EE reduction of tetraphenylethylene in dimethylformamide was investigated by the Fourier transform faradaic admittance method.[28] Under the conditions of the experiment the standard potentials for the neutral/anion radical and anion radical/dianion couples are very similar and the second couple is quasi-reversible. It was found that eq 6 must be included in the model in order to account satisfactorily for the data. The disproportionation rate constant was 1×10^8 M^{-1} s^{-1}.

The reduction of 3,8-dimethyl-2-methoxyazocine also proceeds by an EE scheme with closely spaced standard potentials.[25] In this case, it is the first step of reduction that has a small electron-transfer rate constant. In order to fit the experimental cyclic voltammograms by digital simulation, it was necessary to include the SET reaction (eq 6). Similar conclusions were drawn in studies of the EE reduction of cyclooctatetraene,[24,36] which features a sluggish first step of reduction that has been attributed to a change in structure on going from the tub-shaped neutral to the more planar anion radical.

In the reactions cited above, the effect of the SET reaction on the voltammetric response is fairly subtle, as it produces only small changes in the shape and position of the current–potential curve. A much more striking effect was discovered by Pierce and Geiger[22] in their study of a bis-arene complex of ruthenium, $(\eta^6\text{-}C_6Me_6)_2Ru^{2+}$. This compound, M^{2+}, undergoes an EE reduction in acetonitrile in which the formal potential for the second step (M^+/M) is slightly positive of that of the first (M^{2+}/M^+). More importantly, the standard heterogeneous electron-transfer rate constant for the second step is quite small so, even at moderate scan rates, the cyclic voltammograms feature a relatively reversible first step and a highly irreversible second step of reduction (Figure 1). The overall reduction is accompanied by a significant structural change, a modification of the bonding of one of the arene ligands from η^6 to η^4, and it is thought that this structural change is associated with the transfer of the second electron, explaining the relatively small rate constant for the second step.

In the voltammogram shown in Figure 1, reduction peaks I and II correspond to the first and second steps of reduction, respectively. Anodic peak III, however, arises from the oxidation of the cation to the dicationic starting material. The oxidation of the neutral compound to the cation does not occur until the potential has returned to the region of anodic peak IV. Of course, at this potential the cation is immediately oxidized to the dication as the potential is positive of peak III! Here, the SET reaction is crucial to the ultimate appearance of the voltammogram. The size of peak IV depends strongly on the rate of the SET reaction. If the rate of eq 6 were large in this case, peak IV would

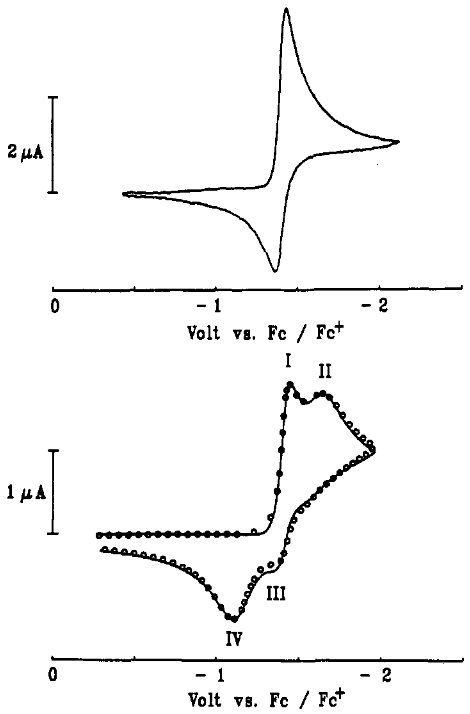


Figure 1. Cyclic voltammograms of $[(\eta^6\text{-}C_6Me_6)_2Ru][BF_4]_2$ in CH_3CN/0.5 M Bu_4NPF_6 at a platinum electrode (T = 298 K): (top) scan rate = 0.2 V/s, concentration = 2.73×10^{-4} M, area of platinum bead ca. 1 mm^2; (bottom) scan rate = 10 V/s, concentration = 1.31×10^{-3} M, Pt disk (radius = 238 µm); circles = experimental values, line = values calculated by digital simulation. Reprinted from ref 22; copyright 1989 American Chemical Society.

be entirely absent as M would instead be oxidized by the sequence of eqs 7 and 8. The best fit of digital

$$M + M^{2+} \rightarrow 2M^{+} \qquad (7)$$

$$M^{+} \rightarrow M^{2+} + e^{-} \qquad (8)$$

simulation to the experimental data was obtained with a rate constant of 2.7×10^4 M^{-1} s^{-1}. This is a relatively small value for an SET reaction but it is quite plausible because the same structural change that causes the second heterogeneous electron transfer to be sluggish must also occur in the SET reaction.

III. Mixtures of Reactants

$$A + e^{-} = A^{-} \qquad (9)$$

$$B + e^{-} = B^{-} \qquad (10)$$

$$A^{-} + B = A + B^{-} \qquad (11)$$

Two components are postulated to be present in solution, and they may be reduced at the electrode with the same or different formal potentials. Once again, it can be shown[40,41] that for reversible electrode reactions, identical diffusion coefficients, and linear diffusion, SET reaction 11 can have no influence on the response for any kind of voltammetry.

The effects of SET reaction 11 were investigated at an early stage by ac polarography.[42-46] More recently, theory has been presented for constant-potential experiments wherein the diffusion coefficients of A and B are quite different.[47] An experimental investigation of the reduction of mixtures of 4-nitrotoluene (A) and cobalt(II) tetraphenylporphyrin (B) employed chronoamperometry and cyclic voltammetry. The diffusion coefficient of the smaller A was about 3 times that of B. In this case, A is reduced at more negative potentials than B so eq 11 tends to proceed from left to right. When the potential in chronoamperometry is maintained at a value where A is reduced, the electron-transfer coupling of diffusional pathways causes an enhancement of the current over what would be seen in the absence of eq 11. Similarly, in cyclic voltammetry the second reduction peak is larger than would be obtained without the electron-transfer coupling provided by eq 11. The effect of unequal diffusion coefficients has also been noted in the context of homogeneous redox catalysis.[48]

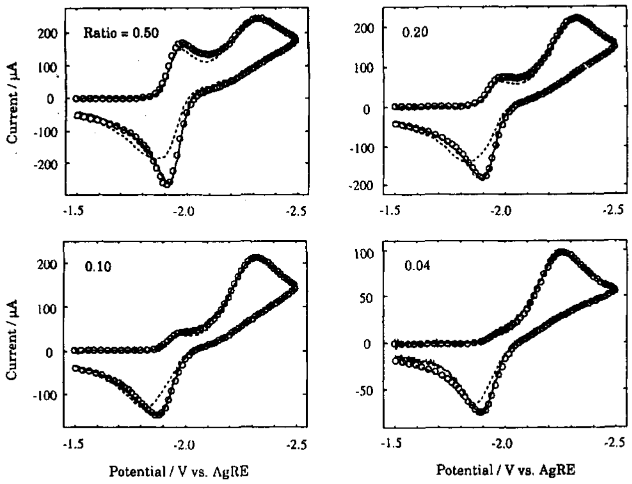


Figure 2. Homogeneous redox catalysis of the reduction of 2-methyl-2-nitropropane by terephthalonitrile (mercury electrode, 0.10 M Bu_4NClO_4 in acetonitrile). Continuous line = experimental curve; points = digital simulations; dashed line = digital simulations without SET reaction 11. "Ratio" is the ratio of catalyst (terephthalonitrile) to substrate (2-methyl-2-nitropropane) concentrations. Concentration of 2-methyl-2-nitropropane was 1.32 mM. The scan rate was 50 V/s except for ratio = 0.10, where it was 10 V/s. T = 298 K. Reprinted from ref 49; copyright 1989 Elsevier Sequoia S.A.

When one or both of the couples is less than reversible, the SET can affect the voltammetric response. This result has been characterized in terms of the isopotential points seen in a series of mixtures of reactants, A and B, where the total concentration is maintained constant.[41] The SET (eq 11) causes the isopotential points to defocus.

When the formal potentials of the two couples are similar and the standard heterogeneous electron-transfer rate constants are much different, the SET reaction provides a route for catlysis of the more sluggish electrode reaction by the more facile couple.[49] Figure 2 illustrates the effect for mixtures of terephthalonitrile (A) and 2-methyl-2-nitropropane (B) studied by cyclic voltammetry using a hanging mercury drop electrode in acetonitrile. The formal potential for terephthalonitrile is −1.993 V vs the Ag^+/Ag reference electrode and the standard rate constant for the neutral/radical anion couple is large so essentially reversible behavior is seen. On the other hand, 2-methyl-2-nitropropane has a similar formal potential, −2.034 V, but a much smaller standard rate constant, 4.2×10^{-3} cm/s.

Terephthalonitrile is reduced near its formal potential, producing a peak at −2.0 V, whereas the peak for direct reduction of 2-methyl-2-nitropropane is displaced by about 0.4 V negative of its formal potential due to the sluggish electron-transfer kinetics. However, indirect reduction of 2-methyl-2-nitropropane, B, can occur by reduction of A to $A^{\bullet -}$, followed by SET reaction 11 that reduces B and regenerates A, which, in turn, can be reduced at the electrode. This process produces added current at the first peak. The dashed curves in Figure 2 indicate the current that would be seen in the absence of the SET reaction. Because the reverse of eq 11 is faster than the forward reaction in this case, the catalytic effect is even more pronounced on the return sweep. Thus, under these conditions, the SET reaction can affect the voltammetric response quite substantially, and from the data the rate constants for the SET can be evaluated.[49]

Other examples of this phenomenon have involved catalysis of the kinetically sluggish electrode reactions of biomolecules by small-molecule catalysts.[50-52]

IV. Homogeneous Redox Catalysis

As mentioned in the previous section, SET reactions are encountered whenever mixtures of reactants are studied but the effect on the voltammetric response is usually small. In particular, if the formal potential for reduction of B is considerably negative of that for A, the SET reaction will be unfavored and no indirect reduction of B will occur at the potential where A is reduced. An important exception arises when B^- undergoes a fast and essentially irreversible reaction (eq 15) that removes this species, allowing the thermodynamically uphill SET reaction to proceed. Thus, the overall process for reduction of B to P can be more favorable than reduction of A, because $E°_{B,P} = E°_{B,B^-} + (RT/F) \ln (1 + K_{15})$.

$$A + e^- = A^- \qquad (12)$$

$$B + e^- = B^- \qquad (13)$$

$$B + A^- = B^- + A \qquad (14)$$

$$B^- = P \qquad K_{15} \gg 1 \qquad (15)$$

This raises the question of why direct reduction of B does not occur at the electrode. Direct reduction is inherently less efficient than the catalyzed process, causing a substantial overpotential for reduction of B. Thus, the sequence of eqs 12, 14, and 15 constitutes a catalysis by redox couple A/A^- of a sluggish electrode reaction, the reduction of B to P. Hence the name *redox catalysis*, with the descriptor *homogeneous* indicating catalysis in solution rather than on the electrode surface.[53-102]

An early and quite representative example is the reduction of halobenzenes and halopyridines.[62] The simplified reaction scheme can be represented by eqs 16–20. Also of importance are hydrogen atom abstraction reactions of the aryl radicals formed in eq 18.

$$A + e^- = A^- \qquad (16)$$

$$ArX + A^- = ArX^- + A \qquad (17)$$

$$ArX^- = Ar^\bullet + X^- \qquad (18)$$

$$Ar^\bullet + A^- = Ar^- + A \qquad (19)$$

$$Ar^- + HS = ArH + S^- \qquad (20)$$

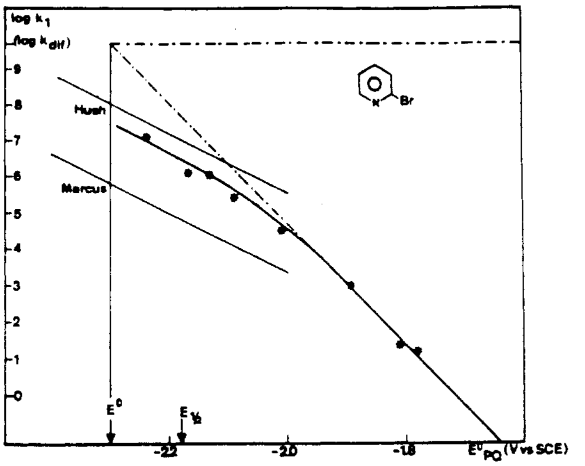


Figure 3. Rate constants for forward reaction 17 (here labeled k_1) vs standard potentials of various catalyst couples, reaction 16 (here labeled $E°_{PQ}$). $E°$ is the value of the standard potential for substrate reduction (2-bromopyridine) obtained by extrapolation to the diffusion-limited rate constant, k_{dif}. $E_{1/2}$ is the observed irreversible half-wave potential for reduction of 2-bromopyridine. Experiments conducted with 0.1 M Bu_4NI in dimethylformamide at a hanging mercury drop electrode; T = 295 K. Reprinted from ref 62; copyright 1979 American Chemical Society.

Andrieux et al.[62] used a variety of aromatic and heteroaromatic compounds as catalysts (species A) and were able to demonstrate efficient catalytic reduction of the aryl halide at potentials several tenths of a volt less negative than required for the direct electrochemical reduction.

In addition to reducing the potential required to reduce the aryl halide, homogeneous redox catalysis also provided information about the properties of the postulated ArX^- intermediates. For many of the compounds investigated, the cleavage of halide from the radical anion is so fast that the rate-determining step becomes forward reaction 17, the SET reaction. By measuring the enhancement of the current for reduction of catalyst A in the presence of ArX, the rate constant for the SET can be evaluated. Figure 3 illustrates data for catalytic reduction of 2-bromopyridine using a series of catalysts with varying reversible formal potential, $E°_{A,A^-}$.

The rate constant for the SET reaction is largest for those catalysts with negative formal potential. The plot of log k_{17} vs $E°_{A,A^-}$ shows a region with slope of −59 mV. This is indicative of the fact that the rate constant for the reverse SET reaction, k_{-17}, is at the diffusion-controlled limit for these catalysts. As illustrated in Figure 3, extrapolation of this portion of the plot to the diffusion-controlled limit allows evaluation of the reversible formal potential for the ArX/ArX^- couple, a quantity that is very difficult to obtain by other methods.[62]

In addition, under favorable conditions it is possible to extract the rate constant for cleavage of halide from the intermediate radical anions, even when their lifetime is of the order of nanoseconds.[63,66] Homogeneous redox catalysis allows the measurement of rate constants several orders of magnitude greater than by direct electrochemical methods.[103]

Theory for homogeneous redox catalysis is well developed.[53-60] Applications to catalytic oxidation have also appeared[82,92,94,95,101] and autocatalysis has been observed.[68,79] Sometimes there is a competition between electron transfer by the catalyst and addition of intermediates to the catalyst.[60,77] The action of the catalyst can be through an "inner-sphere" reaction[70,96] as well as the more normal outer-sphere electron transfer. The irreversible step in the overall scheme can be ring opening,[81,83,87] coupling,[78] or isomerization.[98,99]

V. ECE Reactions

As mentioned in the introduction, it was in the context of ECE schemes that the importance of SET reactions was first realized. A generalized ECE scheme is given in eqs 21 and 22. In eq 21, the chemical step is implied to be a structural change from an A-type structure (conformer or isomer) to a B-type structure. The charges on the species are included to provide an accounting for changes in the state of oxidation. Most frequently, however, the chemical step is a pseudo-first-order process in which A^- reacts with a reagent in excess, e.g., a proton donor and, typically, B^- is more easily reduced than A. Depending upon the nature of the chemical system being investigated, the chemical step can be any of a wide variety of types of reactions.

$$\begin{tikzcd} A \arrow[r, shift left, "e^-"] & A^- \arrow[l, shift left] \arrow[d] & \\ & B^- \arrow[r, shift left, "e^-"] & B^{2-} \arrow[l, shift left] \end{tikzcd} \qquad (21)$$

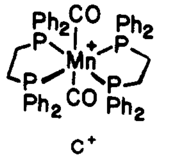
$$A^- + B^- \rightleftharpoons A + B^{2-} \qquad (22)$$

When the reaction proceeds by eq 21, B^- is reduced at the electrode surface and the scheme is designated as ECE. On the other hand, B^- may be formed in solution and be reduced by A^- before it can reach the electrode to be reduced. This SET reaction is formally a disproportionation in that A^- and B^- are at the same oxidation state. Hence, the scheme is usually termed a DISP reaction, specifically DISP1 if the SET reaction is fast so that the chemical step in eq 21 is rate determining.

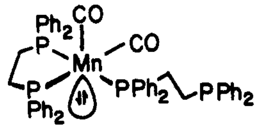
The theory for ECE schemes, including SET reactions, is well developed,[5-7,104,107] including an important series of papers pertaining to the conditions of preparative-scale electrolyses.[109-115] Examples of reported types of chemical reactions are protonations,[116,123,134-136] deprotonations,[128,133] structural changes,[126,127,131] and cleavage of halide from anion radicals.[120]

In many cases it is difficult to determine whether a reaction is proceeding by a pure ECE scheme (eq 21) or via a DISP scheme involving SET reaction 22 as both schemes result in the two-electron reduction of A to B^{2-}. The calculated voltammetric responses for the two reaction pathways are in most cases extremely similar.

However, under certain circumstances, quite striking differences are predicted[4] and observed. An interesting recent example is afforded by the work of Kuchynka and Kochi,[125] who studied the reduction of *trans*-$Mn(CO)_2(\eta^2\text{-DPPE})_2^+$ (C^+, where DPPE is 1,2-bis(diphenylphosphino)ethane) in tetrahydrofuran. C^+ (closed) is reduced in an overall two-electron process to produce the anion O^- (open) in which one end of the one of the DPPE ligands has been extruded, forming a ring-opened structure. An experimental multicycle voltammogram of 5 mM C^+ at 500 mV/s is shown in Figure 4. The most unusual feature seen in this voltammogram is the "curve crossing" near −1.5 to −1.6 V where, on each positive-going half-cycle, reduction current occurs at potentials less negative than the primary reduction peak. The reaction is postulated to occur by an ECE–DISP scheme wherein the closed-ring reactant, C^+, is reduced to C, which opens quickly ($k > 4 \times 10^6\ s^{-1}$), giving neutral O. This species in turn is more easily reduced than C^+, completing the ECE sequence.



C⁺



O⁻

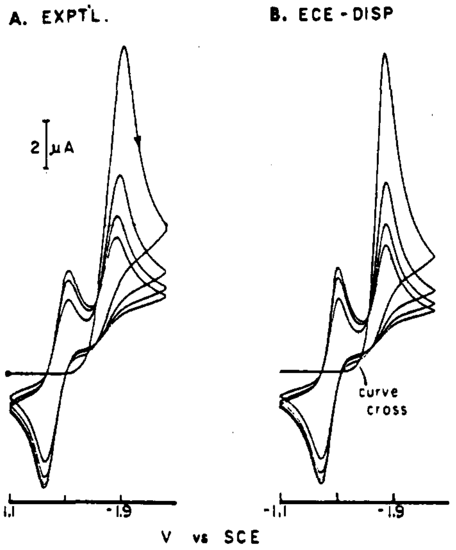


Figure 4. (A) Initial negative scan (four cycle) cyclic voltammogram of 5×10^{-3} M [*trans*-$Mn(CO)_2(\eta^2\text{-DPPE})_2$][$PF_6$] (DPPE = 1,2-bis(diphenylphosphino)ethane) in 0.3 M Bu_4NClO_4/tetrahydrofuran at a platinum electrode at 500 mV/s. (B) Digital simulation based on eqs 23 and 24. Reprinted from ref 125; copyright 1988 American Chemical Society.

$$\begin{tikzcd} C^+ \arrow[r, shift left, "e^-"] & C \arrow[l, shift left] \arrow[d] & \\ & O \arrow[r, shift left, "e^-"] & O^- \arrow[l, shift left] \end{tikzcd} \qquad (23)$$

$$C^+ + O^- \rightleftharpoons C + O \qquad (24)$$

However, digital simulations according to the pure ECE scheme (eq 23) do not reproduce the curve crossing that is seen in the experimental curves (Figure 4). Instead, it is necessary to include the SET reaction 24. Though this reaction is not thermodynamically favored, it is driven by the rapid conversion of C to O so, effectively, eq 24 can be considered as $C^+ + O^- \rightarrow 2O$. When eq 24 is included in the simulation program, not only is the curve-crossing phenomenon accurately reproduced but other features also match the experimental voltammograms, including the more rapid reduction in the height of the primary reduction peak in successive cycles and the appearance of the pair of isopotential points at slightly different potentials.

The reason that inclusion of the SET reaction can account for the cathodic current seen positive of the primary reduction peak (curve crossing) is that in the pure ECE scheme, any O that could be reduced there must arise via the reduction of C^+, i.e., $C^+ \rightarrow C \rightarrow O$. However, C^+ cannot be reduced at potentials positive of the primary reduction peak. The SET reaction provides a way for C^+ to react with the ultimate product O^- to produce O that can be reduced in this potential range.

Examples of other ECE-type schemes in which curve crossing is seen have been discovered, including examples with organic[24,128,129] and organometallic[24,130,132] reactants. Fit of the data by simulation with inclusion of the SET reaction has been achieved in many cases.[24,129,130,132] It should be noted that the necessity of an SET reaction for observation of curve crossing was demonstrated in the early work of Feldberg.[4] In some of the cases cited above,[129,130,132] the ECE process is actually a part of a larger scheme, an extended square, ladder, or fence scheme, and other examples of curve crossing will be mentioned in later sections when these more complex schemes are discussed.

VI. Square Schemes

The term was apparently introduced by Jacq[143] ("schema carré") in the context of electron-transfer reactions with associated protonations. In its simplest form, it is a four-member scheme where reactant A is reduced to A^-, which can react by some chemical step to produce B^-. In the case of the square scheme,

$$\begin{tikzcd} A \arrow[r, shift left, "e^-"] \arrow[d, shift left] & A^- \arrow[l, shift left] \arrow[d, shift left] \\ B \arrow[u, shift left] \arrow[r, shift left, "e^-"] & B^- \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd} \qquad (25)$$

$$A + B^- \rightleftharpoons A^- + B \qquad (26)$$

however, B^- participates in an electrode reaction with its oxidized form, B, rather than being further reduced as in an ECE-type reaction. The SET reaction that interconnects these four species is eq 26 and, potentially, it can play a significant role in the electrochemical reduction of A.

In an important series of papers,[144-156] Laviron has analyzed square schemes (and extended versions) for cases where the species are adsorbed, where thin-layer conditions prevail, and for certain cases with normal diffusion of reactants. A significant conclusion of this work[156] is that the SET reaction (eq 26) can have no effect when the chemical steps are at equilibrium. This is because the separate maintenance of equilibrium between A and B and between A^- and B^- guarantees that eq 26 is at its equilibrium condition irrespective of whether the SET reaction itself is fast or slow. When the chemical steps are at equilibrium, the system behaves as a single-electron-transfer reaction connecting equilibrating A/B with equilibrating A^-/B^-.

When the chemical steps are not at equilibrium, a number of situations arise in which the SET reaction can play a significant, even crucial, role. The nature of the voltammetric response depends in a critical manner upon the relative values of E°_{A,A^-} and E°_{B,B^-}. In the case where B is more easily reduced than A ($E^\circ_{B,B^-} - E^\circ_{A,A^-} > 0$), the reduction of A proceeds by a simple EC process leading to B^- (assuming that $K^-_{AB} \gg 1$). In this case, the equilibrium state of SET reaction 26 lies to the left. Its influence is negligible because there is no B in solution to react with A^- in the reverse of eq 26. It is only on the return sweep in cyclic voltammetry that the SET reaction can occur because B^- is oxidized to B. This type of reaction is usually called an *electron-transfer-induced reaction.*

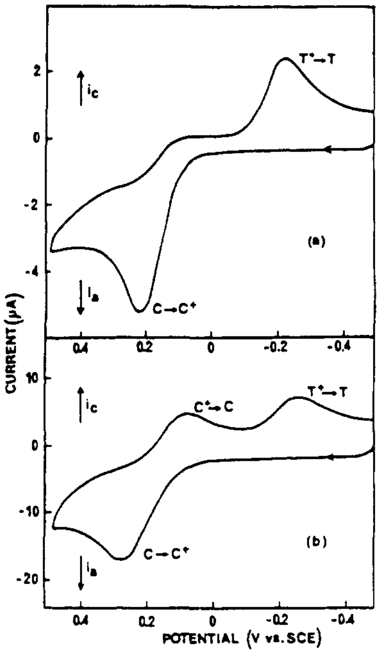


Figure 5. Voltammograms of 5×10^{-3} M *cis*-W(CO)$_2$(DPPE)$_2$ (form C) in 0.2 M Bu_4NClO_4/dimethylformamide at a platinum disk electrode (radius = 62.5 μm). T designates the trans isomer. (a) 100 V/s. (b) 1000 V/s. Reprinted from ref 157; copyright 1987 American Chemical Society.

Some of the most interesting examples of square schemes may be found in electron-transfer-induced isomerization. A recent example has been provided by Vallat et al.,[157] who reinvestigated a system discovered by Bond et al.[158] Cyclic voltammograms for oxidation of *cis*-W(CO)$_2$(DPPE)$_2$, C, in dimethylformamide are shown in Figure 5. (Once again, the example is an oxidation reaction while the general formulation is in terms of reductions. The appropriate mental inversion must be made.) In this case, the cis form is favored in the neutral complex whereas trans predominates at equilibrium in the cations. Upon oxidation at +0.2 V, C forms short-lived C^+ that rapidly isomerizes to T^+. Consequently, no peak for the reduction of C^+ to C is detected on the reverse sweep at scan rates less than 250 V/s. Instead, the reverse sweep features a single prominent peak for reduction of T^+ to T. At scan rates greater than 250 V/s, a peak for reduction of C^+ to C grows in (Figure 5). In this case, a complete analysis was achieved, including evaluation of the reversible potentials, equilibrium constants for the chemical steps, and rate constants for the chemical steps. As mentioned above, the SET reaction has little influence and could be neglected in the analysis.[157]

Some of the most dramatic effects in the square scheme are encountered when B is more difficult to reduce than A ($E^\circ_{B,B^-} - E^\circ_{A,A^-} < 0$). In this case, at the potential where A is reduced, the B^- formed from A^- can be oxidized to B, either at the electrode or via SET reaction 26. When this is the case, B is actually the thermodynamically more stable form; i.e., A is metastable. The conversion of A to B is catalyzed by electron transfer and, because the combination of $A^- \rightarrow B^-$

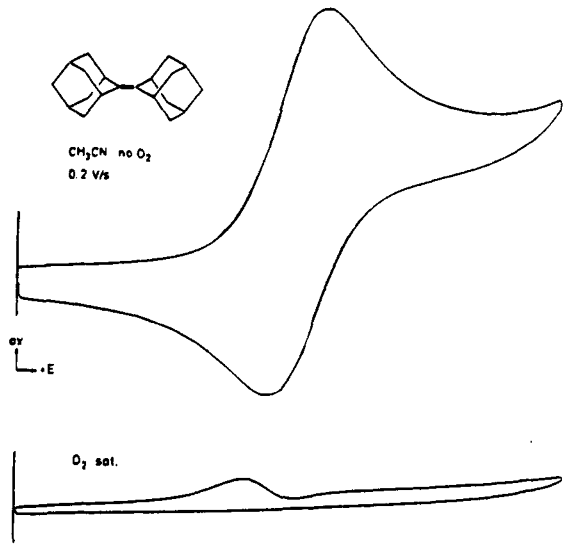
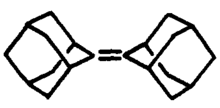


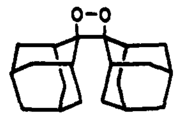
Figure 6. Cyclic voltammograms of adamantylideneadamantane in 0.1 M Bu_4NClO_4/acetonitrile at 200 mV/s. Note that increasingly positive potentials are plotted to the right and anodic currents are directed upward. Potential range: +1.15 (left) to +1.75 V (right) vs SCE. Top: no oxygen. Bottom: oxygen-saturated solution. Reprinted from ref 161; copyright 1981 American Chemical Society.

and the reverse of eq 26 constitutes a chain reaction, it is termed *electron-transfer chain catalysis* (ETC).

In electrochemistry this type of square scheme was first discovered by Feldberg and Jeftic[159] in their study of the reduction of $Cr(CN)_6^{3-}$ in aqueous alkaline solution. An early example from organometallic electrochemistry involved isomerization of carbene complexes.[160] An illustrative case from organic electrochemistry is the oxidation of adamantylideneadamantane (1) in the presence of dioxygen.[161-163] In Figure 6 are shown cyclic voltammograms for oxidation of 1 in the absence and presence of dioxygen. In solutions free of dioxygen, 1 is oxidized to the relatively stable cation radical, 1^+. However, in solutions saturated with dioxygen (1 atm), a dramatic change in the voltammetric response occurs. The oxidation peak almost disappears and it shows a curious current minimum just positive of the residual peak. Either electrolysis[162] of 1 in the presence of dioxygen or treatment with a small amount of oxidant (NO^+ or tris(*p*-bromophenyl)amine radical cation) results in the production of dioxetane 2 by an ETC process. The electrode reaction has been formulated to include eqs 27–30. The SET reaction 30 is exothermic



1



2

$$1 = 1^+ + e^- \qquad E^{\circ\prime} = 1.62 \text{ V vs SCE} \tag{27}$$

$$O_2 + 1^+ \rightarrow 2^+ \tag{28}$$

$$2^+ + e^- = 2 \qquad E^{\circ\prime} = 2.29 \text{ V} \tag{29}$$

$$1 + 2^+ \rightarrow 1^+ + 2 \tag{30}$$

by 0.67 V and probably proceeds at rates near the diffusion-controlled limit. The rate-determining step, eq 28, is only moderately fast, and the catalytic effect is largely absent at scan rates exceeding 10 V/s.[163] 2^+ is unstable and its decomposition constitutes a chain termination reaction. Digital simulations show that SET reaction 30 is required to account for the zero current crossing seen at slow scan rates.[163]

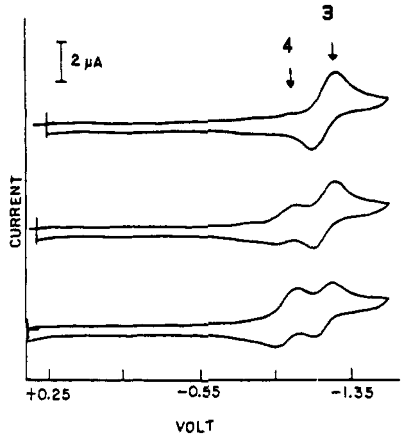
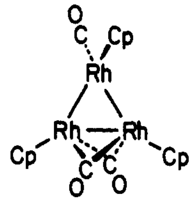


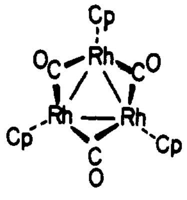
Figure 7. Cyclic voltammograms of 3.5 × 10^{-4} M C_s-form $Cp_3Rh_3(\mu_2\text{-}CO)_2(CO)$ (3) (Cp = η^5-C_5H_5) in tetrahydrofuran as a function of initial potential: +0.25 V (top), +0.30 V (middle), and +0.35 V (bottom). Conditions: T = 298 K, v = 0.20 V/s. The small feature at ca. +0.30 V is due to an impurity. Reprinted from ref 164; copyright 1989 American Chemical Society.

The ETC oxygenation of 1 discussed above causes the voltammetric oxidation peak to be very small and allows complete reaction of 1 by electrolysis with very small coulometric *n* values.[162] The transformation is catalyzed by the electrode so that when the potential is maintained at a value where the olefin is oxidized, 1 is rapidly converted to 2 in the solution adjacent to the electrode surface. When both the chemical step and the SET reaction are very fast, the voltammetric peak virtually disappears.

A fascinating example of this phenomenon was discovered by Mevs and Geiger[164] in their study of trirhodium clusters 3 and 4 (Cp is η^5-C_5H_5). Of the two forms, 4 is the more stable. Both isomers are reduced to stable anions that do not isomerize but oxidation of solutions of 3 leads to rapid ETC isomerization to 4. The process is so rapid that absolutely no oxidation peak for 3 could be detected even at a scan rate of 100 V/s! These authors conclude that the rate constant for $3^+ \rightarrow 4^+$ must exceed 10^5 s^{-1}. As no oxidation peak could be observed, an ingenious indirect method was used to estimate the potential for $3^+ + e^- = 3$.



3



4

Voltammetric reduction of a solution of 3 reveals a single peak when the initial potential is negative of about +0.1 V vs SCE. However, when the initial potential is more positive, the voltammograms reveal a peak for reduction of 4 (Figure 7). Thus, the reductive voltammograms provide a means of monitoring the oxidative ETC isomerization. By using a fast sweep rate that effectively "freezes" the reaction–diffusion layer, the cathodic peak height for 4 was measured after

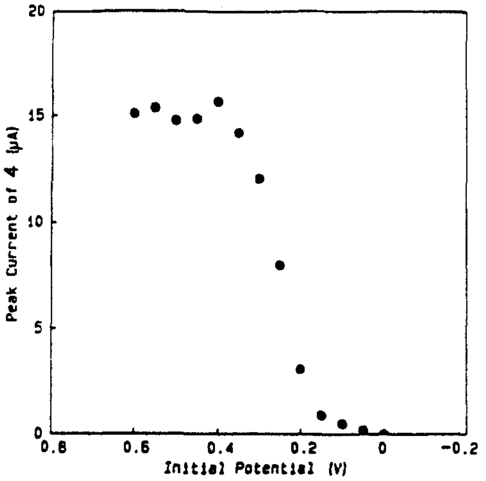


Figure 8. Plot of the corrected current height of the reduction wave of C_{3v}-form $Cp_3Rh_3(\mu_2\text{-}CO)_3$ (**4**) obtained from cyclic voltammograms of ca. 3×10^{-4} M **3** in tetrahydrofuran using different initial potentials after 15-s application of initial potential (T = 298 K, v = 10 V/s). The current height is corrected for the amount of isomer **4** generated in scans with initial potentials positive of the $E_{1/2}$ value of **3**. Reprinted from ref 164; copyright 1989 American Chemical Society.

holding the potential for 15 s at a series of initial potentials. The plot of the data resembles a steady-state voltammogram (Figure 8) from which the value of the formal potential for the $3^+/3$ couple was estimated to be +0.25 V.

Isomerization reactions are frequently encountered components of square schemes.[165-175] Various theoretical treatments have been given,[176-181] most of which do not include the SET cross reaction. A digital simulation technique is usually applied when the SET reaction must be considered.

A very important and widely studied class of reactions can properly be considered as partial square schemes, viz., the *electrochemically catalyzed aromatic substitution reactions*.[182-204] These processes are often called $S_{RN}1$ reactions, i.e., nucleophilic substitution via radical intermediates.

Retaining for the moment our "A,B" notation, we may distinguish two types of the electrochemical substitution reactions (eq 31). Here it is to be remembered

$$\begin{tikzcd}
A \arrow[r, shift left, "e^-"] & A^- \arrow[l, shift left] \arrow[d, shift left] & & A \arrow[r, shift left, "e^-"] & A^- \arrow[l, shift left] \arrow[d, shift left] \\
B \arrow[r, shift left, "e^-"] & B^- \arrow[l, shift left] \arrow[u, shift left] & & & B^- \arrow[u, shift left]
\end{tikzcd} \qquad (31)$$

that the chemical step(s) connecting A^- and B^- accomplish the replacement of one substituent on the aromatic substrate A by another. On the left side of eq 31, B is more difficult to reduce than A ($E^\circ_{A,A^-} - E^\circ_{B,B^-} > 0$) so B^-, once formed, is oxidized to B, resulting in the *electron-transfer-catalyzed substitution* on A giving B. B^- is oxidized to B either at the electrode or by an SET reaction, $B^- + A \rightarrow B + A^-$. Putting it another way, nucleophilic displacement on substrate A to give B is thermodynamically favorable and the electrode catalyzes the reaction.

In the case where B is more easily reduced than A ($E^\circ_{A,A^-} - E^\circ_{B,B^-} < 0$), the reaction is the noncatalyzed substitution (right side of eq 31) on substrate A. Here reducing equivalents are needed to achieve the substitution producing B^-, which must be oxidized subsequently to B to complete the transformation. Such noncatalyzed substitutions are less common than their catalytic counterparts[184,193] though one of the earliest examples, substitution of iodine on iodonitrobenzenes by cyanide or nitrite,[182] was of this type.

A recent and representative example of electron-transfer-catalyzed substitution may be found in the work of Amatore et al.,[198] who investigated the 2-nitropropane anion as a nucleophile in $S_{RN}1$ substitution during reduction of PhI or $4\text{-}BrC_6H_4COPh$. With the former as an example, the reactions are eqs 32–37.

$$PhI + e^- = PhI^{\bullet -} \tag{32}$$

$$PhI^{\bullet -} \rightarrow Ph^\bullet + I^- \tag{33}$$

$$Ph^\bullet + (CH_3)_2C{=}NO_2^- = Ph(CH_3)_2C\text{-}NO_2^{\bullet -} \tag{34}$$

$$Ph(CH_3)_2C\text{-}NO_2^{\bullet -} = Ph(CH_3)_2C^\bullet + NO_2^- \tag{35}$$

$$Ph(CH_3)_2C^\bullet \rightarrow \text{products} \tag{36}$$

$$Ph(CH_3)_2C\text{-}NO_2^{\bullet -} = Ph(CH_3)_2C\text{-}NO_2 + e^- \tag{37}$$

The interesting variation observed in this system is that the normal product of substitution, α-nitrocumene, is a minor product due to facile loss of nitrite from the anion radical (eq 35).[205] The principal products derive from the cumyl radical so a kind of double substitution has occurred, i.e., replacement of iodine on the aromatic and displacement of nitrite from the nitronate nucleophile.

Other nucleophiles that have been employed include thiolates,[183,191] cyanide,[184,191,193,197] diethyl phosphite,[187] phenoxide,[199,200] and anions of β-dicarbonyl or β-cyanocarbonyl compounds.[203]

Though often discussed as a separate class of reaction, the *electron-transfer-catalyzed* and *electron-transfer-induced ligand substitution reactions* are strictly analogous to the above nucleophilic substitutions. The first example of such a reaction was apparently the electron-transfer-catalyzed substitution of cyanide by hydroxide ligand during reduction of $Cr(CN)_6^{3-}$.[159] A decade passed before other such reactions were discovered and a flurry of activity ensued.[206-227]

The reactions are usually initiated by disruption of a substitutionally inert 18-electron mononuclear organometallic complex by oxidation or reduction to 17- or 19-electron species, respectively. For example, manganese carbonyls of general formula $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2L$, i.e., ML) have been shown to undergo ligand substitution by the reaction sequence in eqs 38–41.

$$ML = ML^+ + e^- \tag{38}$$

$$ML^+ + L' = ML'^+ + L \tag{39}$$

$$ML'^+ + e^- = ML' \tag{40}$$

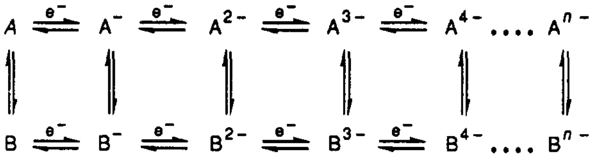
$$ML'^+ + ML = ML' + ML^+ \tag{41}$$

Here L = MeCN, pyridine, THF, Me_2SO, etc. and L′ = PPh_3, $PMePh_2$, PPh_2OMe, $P(OPh)_3$, $CNCMe_3$, and $AsPh_3$.[207-212] As with aromatic nucleophilic substitution, the electron-transfer-catalyzed reaction occurs because the exchange of ligands ($ML + L' \rightarrow ML' + L$) is thermodynamically favored. Oxidation to the substitutionally labile 17-electron cation radical provides a low-energy pathway around the kinetic barrier that hinders the thermally activated substitution in the neutral complex.

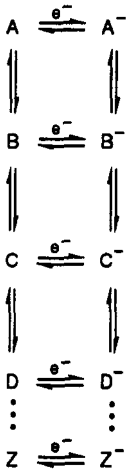
As mentioned above, other such reactions are initiated by reduction[206,213,215–219,222] to form labile anions. Substitution in metal clusters has also been studied.[215–217,219,226,227]

VII. Extended Square Schemes (Fences, Ladders, etc.)

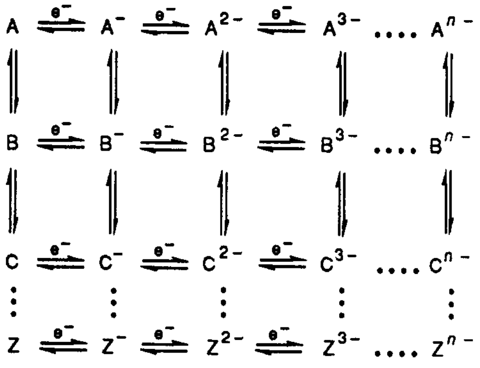
For systems that involve more than two states of oxidation and/or more than two structural classifications, extended square schemes must be considered. These include the *fence scheme* (eq 42), the *ladder scheme* (eq 43), or, to generalize, *mesh schemes* (eq 44).



(42)



(43)



(44)

Numerous SET reactions among the components of these schemes are possible, and they may play a crucial role in determining the voltammetric response.

The electrochemical behavior of substituted bianthrones, dixanthylene, and lucigenin has been discussed in terms of fences with up to five oxidation states (i.e., five pickets).[26,27,29–35,37,38,98,99] These molecules are all highly hindered and can in principle adjust to the hindrance by adopting doubly folded (A) or twisted (B) structures. Voltammetric identification of B structures from the dication to the dianion has been reported,[31] whereas only A and A⁻ are well supported in the A series.[31,38,228]

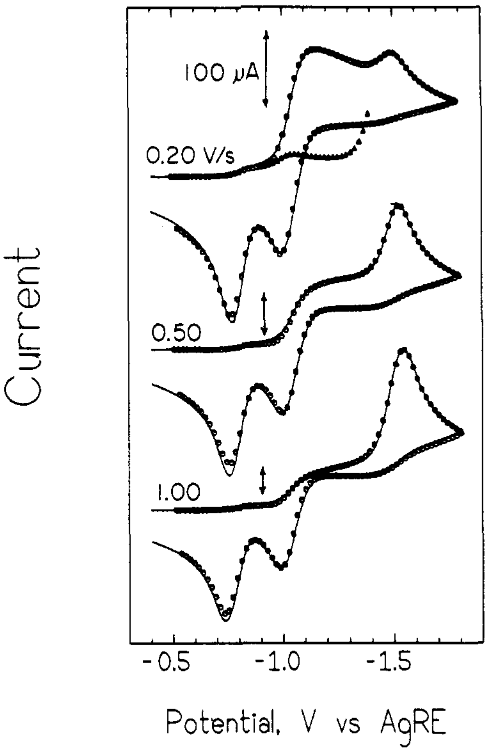
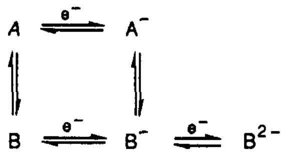


Figure 9. Cyclic voltammograms of 1.64 mM bianthrone in 0.10 M Et_4NClO_4/benzonitrile at a platinum disk electrode (area = 0.38 cm²). T = 353 K. Curves: background-corrected voltammograms. Circles: digital simulations using eqs 45 and 46. Triangles: simulation in which SET reaction 46 has been omitted. Reprinted from ref 33; copyright 1984 Elsevier Sequoia S.A.

Studies in the bianthrone series have demonstrated the importance of SET reactions. One of the more impressive effects is seen upon reduction of bianthrone at elevated temperatures.[33] The section of the fence scheme that must be considered is shown in eq 45. At



(45)

room temperature, the pathway along the fence is A → A⁻ → B⁻ → B²⁻ (an ECE scheme) for reduction and B²⁻ → B⁻ → B → A for oxidation.[27,29,31,35,228] At room temperature, this ECE process produces a single irreversible process at about −1.5 V (cf. Figure 9, 1.00 V/s). Here SET reaction 46 has a small but detectable effect in

$$B^{2-} + B = 2B^{-} \qquad (46)$$

voltammetry[29,30,32] and a very significant effect on UV-vis absorption spectroelectrochemistry where absorbance due to B was monitored.[29,30]

At higher temperatures, the rate of conversion of A to B becomes important,[33] opening up the pathway A → B → B⁻ → B²⁻ for reduction. As may be seen in Figure 9, additional reduction current occurs between −1 and −1.4 V, prior to the main reduction peak, and the relative magnitude of this current increases as the scan rate is lowered. It is noteworthy that the largest growth in cathodic current occurs near the potential for reduction of B⁻ to B²⁻ (−1.0 V, Figure 9). This is a vivid demonstration of the importance of SET reaction 46, which accomplishes an electron-transfer-induced isom-

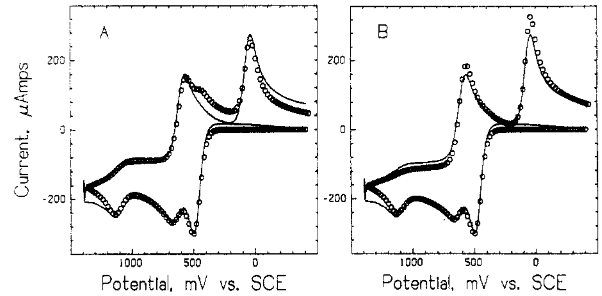


Figure 10. Comparison of digital simulation (points) with experimental cyclic voltammogram of 0.95 mM $Mn_2(\mu\text{-}SMe)_2(\mu\text{-}CO)(PMe_3)_2(CO)_4$ in 0.10 M Bu_4NClO_4/acetonitrile at a platinum disk electrode (radius = 0.125 cm) at 50 V/s. (A) Simulation without SET reaction 52. (B) Simulation including SET reaction 52. Reprinted from ref 229; copyright 1988 American Chemical Society.

erization of A in solution near the electrode by the sequence of eqs 47–50. The reaction scheme has au-

$$A = B \tag{47}$$

$$B + e^- = B^- \tag{48}$$

$$B^- + e^- = B^{2-} \tag{49}$$

$$B^{2-} + B = 2B^- \tag{50}$$

tocatalytic character; the current rises with time in constant-potential experiments as the concentration of chain-carrier B^{2-} builds up in the diffusion–reaction layer. The points in Figure 9 correspond to digital simulations that were fit to the experimental voltammetric curves. These fits are unusual in that no adjustable parameters were used. The standard potentials, equilibrium constants, and rate constants were all evaluated in separate experiments, and SET reaction 50 was treated as a fast equilibrium.[33]

An analogous behavior was noted on oxidation of dixanthylene at elevated temperature.[37] Here, however, the SET reaction was partially rate limiting due to the unusually low concentration of the B form of dixanthylene present in these solutions.

A related case of an SET reaction being important in a partial fence scheme is found in the oxidation of $Mn(\mu\text{-}SMe)_2(\mu\text{-}CO)(PMe_3)_2(CO)_4$ in acetonitrile.[229] Here, the neutral reactant contains a bridging carbonyl in addition to the two thiolate bridges (T, tribridged). The cation undergoes attack by solvent, resulting in the opening of the CO bridge giving a species with CO residing on one manganese center and CH_3CN on the other (D^+, dibridged). D^+ is oxidized in a subsequent step to the dibridged dication, D^{2+}. At fast scan rates, T^+ can be detected before opening by its oxidation to T^{2+}, which rapidly opens to D^{2+} (+1200 mV, Figure 10). Reduction on the return scan occurs by the sequence $D^{2+} \rightarrow D^+ \rightarrow D \rightarrow T$.

$$\begin{tikzcd}
(T^{2+}) \arrow[r, leftrightharpoons, "e^-"] \arrow[d] & T^+ \arrow[r, leftrightharpoons, "e^-"] \arrow[d] & T \\
D^{2+} \arrow[r, leftrightharpoons, "e^-"] & D^+ \arrow[r, leftrightharpoons, "e^-"] & D \arrow[u]
\end{tikzcd} \tag{51}$$

Thus the oxidation is of the ECE type and it is necessary to include the SET reaction 52, formally a disproportionation (cf. ECE reactions, section V).

$$D^+ + T^+ = D^{2+} + T \tag{52}$$

The importance of eq 52 can be judged by comparing the simulations (points) in Figure 10A and 10B. In the former, SET reaction 52 has been ignored and an additional reduction peak is predicted at 500 mV, where T^+ would be reduced to T. Inclusion of the SET reaction in the simulation (Figure 10B) eliminates this peak to produce better agreement with experiment. Fundamentally, this change occurs because eq 52 provides a route for the removal of T^+.

Scheme 51 is actually an ECE oxidation scheme with the added member D that converts it to a partial fence. The presence of D is noted only in the third half-cycle in fast-scan experiments, where the process $D \rightarrow D^+$ is detected at about +100 mV.[229]

Another partial fence scheme was investigated by Nelsen et al.,[230] who studied the oxidation of a bis-bicyclic tetraalkylhydrazine. The behavior is complex, but it may be represented in simplified form by eq 53.

$$\begin{tikzcd}
S^{2+} \arrow[r, leftrightharpoons, "e^-"] \arrow[d, leftrightharpoons] & S^+ \arrow[r, leftrightharpoons, "e^-"] \arrow[d, leftrightharpoons] & S \arrow[d, leftrightharpoons] \\
A^{2+} \arrow[r, leftrightharpoons, "e^-"] & A^+ \arrow[r, leftrightharpoons, "e^-"] & A, A'
\end{tikzcd} \tag{53}$$

The S structures feature a syn arrangement while A denotes anti. (A and A′ are shown because both of these rapidly interconverting conformers of the neutral hydrazine lead to the anti cation radical.) The voltammetry of an equilibrium mixture of S, A, and A′ conformers shows a single oxidation peak forming a 1.45:1 mixture of S^+ and A^+. At more positive potentials, two closely spaced peaks are seen for oxidation of the two cations to the corresponding dications. The relative heights of these two latter peaks are dependent on scan rate as the ratio of S^+ to A^+ approaches the equilibrium value of 0.08. Direct conversion of S^+ to A^+ is too slow to affect the cyclic voltammetric results. Instead, the isomerization is effected by SET reaction 54 that provides a low-energy pathway for the process.

$$A + S^+ = A^+ + S \tag{54}$$

Ladder schemes (eq 43) are probably less common than fences owing to the improbability that the various structurally related species (A, B, C, ...) will have sufficiently different electrochemical behavior to allow voltammetric resolution. Indeed, the reduction of $Co(dien)_2^{3+}$ (dien = diethylenetriamine) has been interpreted in terms of the reduction of the three isomers (unsymmetrical facial, symmetrical facial, and meridional) to the corresponding Co(II) complexes.[231,232] This corresponds formally to a three-rung ladder scheme but the available evidence suggests that resolution of the three electrode reactions will not be practical.

Nevertheless, it would be unwise to dismiss the possibility of the emergence of a ladder scheme in the electrochemical reactions of metal complexes, perhaps at reduced temperatures where structural changes are sluggish and with ligands featuring unusual steric effects.

Earlier in this review we enumerated the various types of chemical processes subtended within the C notation. The E steps are of a single character, but combined with the numerous types of C steps, a dazzling array of fence schemes, ladder schemes, and mesh schemes are possible. Whenever the C steps are not too fast, so that appreciable concentrations of reactants and products can exist, then SET reactions must be considered. Many times, thankfully, their influence is muted. Nevertheless, as I hope has been forcefully demonstrated above, their occurrence can be so disruptive as to upend our conventional expectations of the course of an electrode reaction. When this happens, the investigator is left with the difficult but rewarding task of deciphering their enigmatic role in the redox process.

VIII. Epilogue

If one's net is cast widely enough, a large fraction of chemical processes will be found to involve SET reactions. Thus it should not astonish anyone that the present review ignores some important areas. Much of the present structure of analysis of complex reaction schemes was developed in an earlier review.[233] Electron-transfer reactions in organic[234] and organometallic[235] chemistry have been discussed elsewhere and specific discussions of the importance of SET reactions in electrochemically catalyzed aromatic substitution[186] and ligand exchange[214] have appeared. Finally, it should be noted that the phenomenon of electrogenerated chemiluminescence depends in a fundamental way on the existence of SET reactions. This topic has been reviewed[236] and continues to receive attention.[237]

Acknowledgments. The support of the National Science Foundation (Grant CHE-8722764) is gratefully acknowledged. Eric Engelman, Susan Lerke, Janet Rühl, Diane Smith, and William Strohben assisted in the review of the literature.

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