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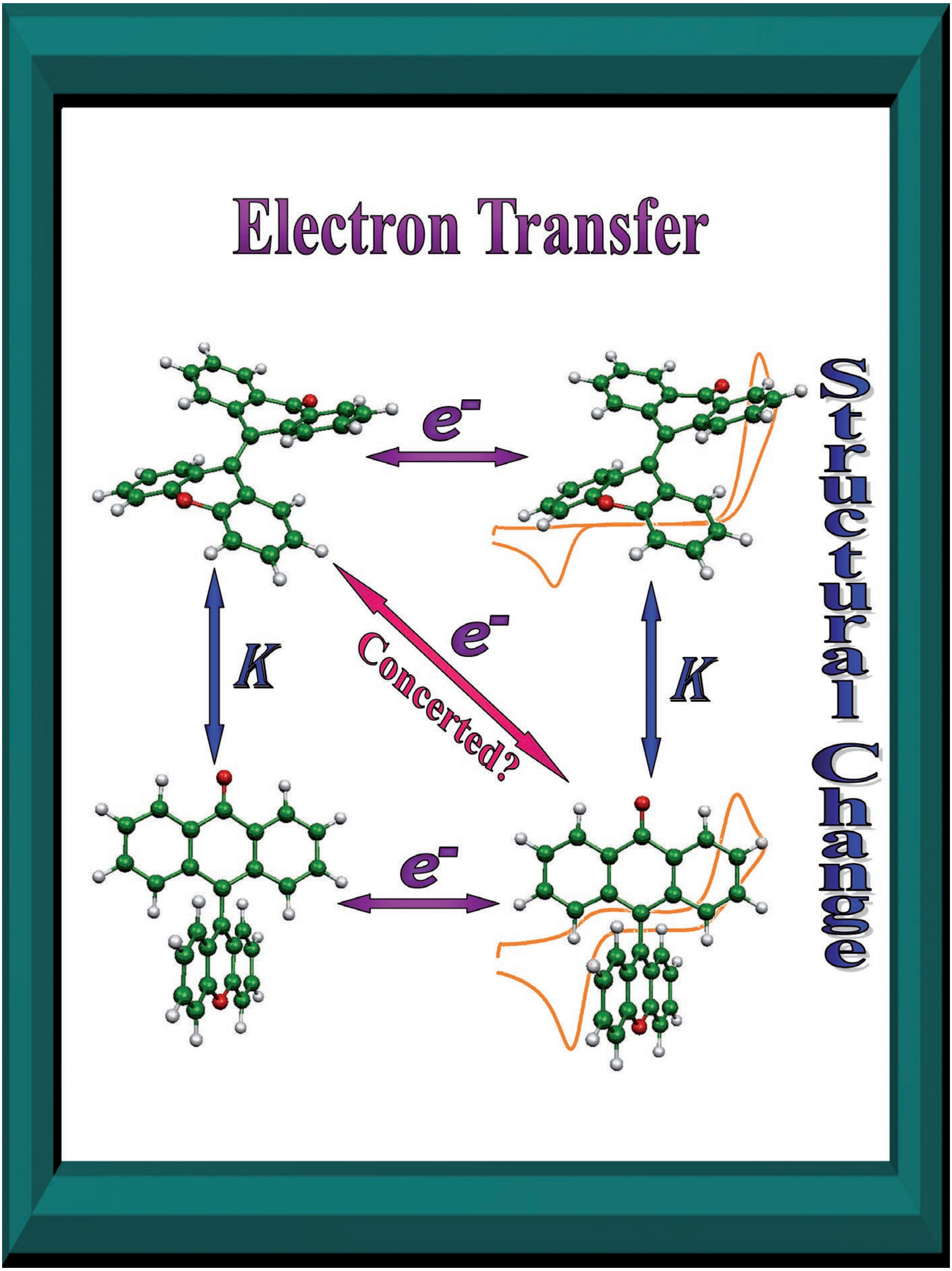


Electron Transfer and Structural Change: Distinguishing Concerted and Two-Step Processes

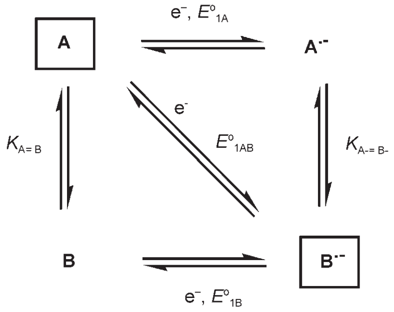
Norma A. Macías-Ruvalcaba[b] and Dennis H. Evans*[a]

Abstract: In electron-transfer reactions accompanied by structural changes, the structural change can be concerted with electron transfer or can occur in a separate reaction either preceding or following the electron-transfer step. In this paper we discuss ways of distinguishing concerted reactions from the latter two-step type. Included are recent examples in which no intermediates have been detected in the reactions, thus precluding the direct assignment to the two-step category. In these cases, other means are used to build support for the two-step mechanism with respect to the concerted process. These include an example of structural change preceding electron transfer, a demonstration that the current models of concerted reactions cannot fit the voltammetric data, and a case in which an independent measure of the inner reorganization energy was used to show that the reaction could not be a concerted electron transfer and structural change.

Keywords: conformational change • electron transfer • electron-transfer kinetics • isomerization

Introduction

Electron-transfer reactions in molecular systems are inevitably accompanied by changes in structure. These changes will be highlighted by considering two extremes. In one extreme, the changes are relatively minor in character, involving small changes in bond lengths and bond angles on going from reactant to product (concerted electron transfer and structural change).[1] At the other extreme, the structural changes are enormous, involving as they do large changes in the overall shape of the molecule. These structural changes correspond to isomerizations or conformational changes (two-step electron transfer and structural change). This classification is illustrated in Scheme 1, in which the reactant is indicated by the enclosed A, A$^{\bullet-}$ is the product in a "reactant-like" structure, B is the reactant in a "product-like" structure, and the enclosed B$^{\bullet-}$ is the product in its preferred structure. The source of electrons in Scheme 1 is an electrode, but it could equally as well be a solution-phase electron donor. Also the entire scheme can be easily reversed as necessary, such that the reactant is oxidized (loses an electron) to form the product.



Scheme 1. Square scheme showing the concerted (diagonal reaction)and two-step mechanisms of electron transfer (horizontal reactions) and structural change (vertical reactions).[14]

In Scheme 1, the reaction involving concerted electron transfer and structural change is depicted along the diagonal, A + e$^-\rightleftarrows$B$^{\bullet-}$. Here the minor structural differences between A and B$^{\bullet-}$ can be considered to occur through molecular vibrations that carry the reactant to a transition state of intermediate structure in which electron transfer occurs. The product then relaxes to its preferred structure.

For such reactions, this structural change is a key parameter in the widely used Marcus theory of electron transfer. The energy required to adjust the nuclear coordinates of the

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[a] Prof. D. H. Evans
Department of Chemistry, University of Arizona
Tucson, AZ 85721 (USA)
Fax: (+1) 520-621-8407
E-mail: dhevans@email.arizona.edu

[b] Prof. Titular N. A. Macías-Ruvalcaba
Facultad de Química
Universidad Nacional Autónoma de México
México, D. F. 04510 (México)

reactant to the values corresponding to the product is called the inner reorganization energy, λ_i. The contribution of the inner reorganization to the aforementioned transition state energy is approximately one-fourth λ_i. Also relevant is the outer reorganization energy, λ_o, which corresponds to reorganization of solvent molecules surrounding the reactant. The inner and outer reorganization energies are combined to give the total reorganization energy, λ, in order to estimate the transition-state energy for the electron-transfer reaction. The above description is for electrode reactions; a slightly different formulation applies to electron transfer between two solution-phase species.

So, in general, for the concerted electron transfer and structural change, when large energies must be expended to bring about the structural change (large inner reorganization energy), the transition state energy will be high and the electrochemical electron-transfer rate constant will be correspondingly smaller. Small rate constants constitute the experimental signature of concerted electron transfer and structural change with large reorganization energies.

Returning to Scheme 1, two-step electron transfer and structural change can in principle proceed with electron transfer preceding structural change (upper horizontal reaction; right-side vertical reaction) or vice versa (left-side vertical reaction; lower horizontal reaction). In either case, there is an intermediate along the reaction pathway ($A^{\bullet -}$ or B, respectively), and hence the overall reaction is not concerted, but is a two-step electron transfer and structural change. Considering first electron transfer followed by structural change, vibrational activation of A leads not to a transition state for conversion to $B^{\bullet -}$, but rather to $A^{\bullet -}$, a product requiring more modest structural change than for formation of $B^{\bullet -}$. Thus, $A+e^- \rightleftarrows A^{\bullet -}$ is considered to be a concerted electron transfer with structural change. So, in this case, $A^{\bullet -}$ is a true intermediate which converts to the more stable $B^{\bullet -}$ in a chemical step (isomerization or conformational change) following electron transfer.

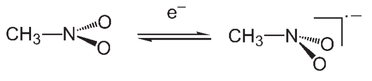
It is tempting to describe the reactant in a concerted reaction, $A+e^- \rightleftarrows B^{\bullet -}$, as being vibrationally competent to reach the transition state and, in a two-step reaction ($A+e^- \rightleftarrows A^{\bullet -}$; $A^{\bullet -} \rightleftarrows B^{\bullet -}$), A is vibrationally incompetent to achieve the rather substantial change in structure that is required to proceed directly to $B^{\bullet -}$. Instead, the electron-transfer reaction proceeds by the less demanding $A+e^- \rightleftarrows A^{\bullet -}$ with most of the structural change as a subsequent chemical step. In the majority of cases in which two-step reactions have been convincingly demonstrated, they proceed by this electron-transfer/structural change pathway.

As mentioned earlier, it is also possible that structural change will precede electron transfer. This route ($A \rightleftarrows B$; $B+e^- \rightleftarrows B^{\bullet -}$) is perhaps not so common, but it can be found when the $A \rightleftarrows B$ reaction is sufficiently facile and the B form is more easily reduced than the A form (i.e., E°_{1B} is less negative than E°_{1A}). This latter requirement, $E^{\circ}_{1B}-E^{\circ}_{1A}>0$, is encountered in many examples of structural changes associated with electron transfer. Once again, the concerted reaction ($A+e^- \rightleftarrows B^{\bullet -}$) is prevented by the inability of A to reach a transition state corresponding to the substantial structural change needed to reach $B^{\bullet -}$. To the extent that species B is available, the electron transfer will involve the structurally less demanding $B+e^- \rightleftarrows B^{\bullet -}$ reaction, that is, most of the structural change occurs prior to the electron-transfer reaction. It is not uncommon to find that the current is governed at least in part by the rate at which B is formed, $A \rightarrow B$.

Concerted Electron Transfer and Structural Change

The operational definition of a concerted reaction is one in which reactants proceed to products without formation of a reaction intermediate. This negative definition means that one cannot prove that a reaction is concerted, only that it is not by detecting an intermediate. Thus, the term concerted electron transfer and structural change must be assigned on an a priori basis. That is, if the structures of reactant and product are connected through well-defined vibrations and if this structural change does not allow identifiable intermediate states, the reaction is a priori assigned as concerted.

A simple example will illustrate the point. The redox reactions of many octahedral metal complexes are considered to be concerted, with little room for contradiction.[2,3] In these reactions the structural change is almost entirely defined by a change in the metal–ligand bond lengths and the M–L symmetrical breathing mode smoothly connects the structures at the two oxidation states of the metal with no identifiable intermediate being possible between the two forms. A similar situation may be found in the reduction of nitroalkanes, of which nitromethane (**1**) is the simplest example.[4] The most notable change in structure accompanying reduction of the neutral compound to the radical anion is a change in geometry at nitrogen: planar in the neutral compound to pyramidal in the radical anion (Scheme 2).



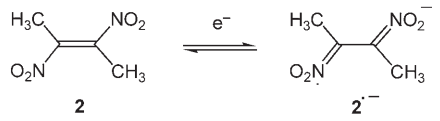
1 **1**$^{\bullet -}$

Scheme 2.

These two structures are connected by an out-of-plane bending vibration and there again is no identifiable intermediate along the path between reactant and product—another concerted electron transfer and structural change.

A slightly more complex example involves *trans*-2,3-dinitro-2-butene (**2**).[5] In the neutral compound, calculations show that the nitro groups are planar, but are turned out of the plane of the butene (≈50°), and there is no twisting about the central double bond (CCCC dihedral angle ≈180°). By contrast, in the radical anion the nitro groups are still planar, but less turned (≈10°), while some twisting about the former double bond is predicted (CCCC dihedral angle ≈150°). There are also significant changes in alkene

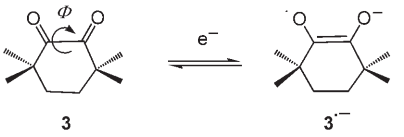
CC bond length as well as the NC bonds. These changes in structural features continue on going from radical anion to dianion (Scheme 3).



Scheme 3.

In the case of **2** one cannot associate most of the structural change with a single vibration. However, a DFT vibrational analysis of both the neutral compound and radical anion reveals that there are several normal modes involving turning of the nitro groups and twisting of the alkene bond that should provide competence in reaching the transition state for electron transfer. Thus it is highly likely that reduction of **2** to its radical anion is another example of a concerted electron transfer and structural change in that no intermediate along the reaction path can be identified.

A still more complex example is provided by 3,3,6,6-tetramethyl-1,2-cyclohexanedione (**3**).[6] Here, the six-membered ring favors an O-C-C-O dihedral angle of about 60° in the neutral compound. However, the radical anion possesses some C–C double-bond character (as shown in Scheme 4) causing the O-C-C-O dihedral angle to close down to about 5°.

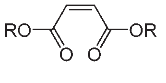


Scheme 4.

There are also other significant changes in bond length (particularly in the diketone functionality) and bond angles (mainly in the ring conformation). Is it possible to proceed from the structure of the neutral compound to that of the radical anion through a vibrationally accessible transition state and thus have a concerted reaction? Our DFT calculations of the structure of the neutral compound reveal that it possesses a chair structure, while that of the radical anion resembles the structure of cyclohexene.[7] Examination of the normal vibrational modes of both the neutral compound and radical anion reveal numerous motions that in combination could bring about movement from either form to a transition state of intermediate structure. A calculation search for intermediates failed leaving one with the impression that the reduction of **3** may well be another example of concerted electron transfer and structural change.

Two-Step Mechanism: Structural Change Following Electron Transfer

On the other extreme there are numerous examples of reactions in which the structural change follows electron transfer. In such reactions an intermediate ($A^{\bullet -}$) is detected by electrochemistry or spectroscopy and the rate of conversion of $A^{\bullet -}$ to $B^{\bullet -}$ can be measured. Two early examples are the reduction of dialkyl maleates, **4**,[8,9] and *cis*-stilbene, **5**.[10,11]



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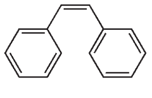

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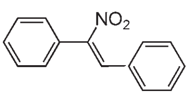
Here, the *cis* isomers are reduced to *cisoid* radical anions in what is thought to be a concerted electron transfer and structural change, with the latter being of a minor nature, both reactant and product featuring the *cis* configuration. Most of the structural change at the stage of the radical anion takes place in the purely chemical step of *cisoid/transoid* isomerization. The half-life of $5^{\bullet -}$ is long enough (>1 s) to allow it to be readily detected.[10,11]

Since the *transoid* radical anion of stilbene is strongly favored over the *cisoid* isomer ($K_{A^{\bullet -}\rightleftarrows B^{\bullet -}} > 1$; Scheme 1), it turns out that direct reduction of A to $B^{\bullet -}$ (diagonal reaction in Scheme 1) will be thermodynamically favored compared to initial reduction of A to $A^{\bullet -}$, that is, E°_{1AB} is more positive than E°_{1A}. Why then does the reaction not proceed by the concerted electron transfer and structural change represented by $A + e^{-} \rightleftarrows B^{\bullet -}$? The answer is that the free energy of activation of this electron-transfer reaction must be sufficiently high so as not to allow reaction to occur by this path before the potential reaches a value at which A is reduced to the high-energy intermediate, $A^{\bullet -}$. This large free energy of activation must include a major contribution from the substantial λ_i associated with the *cis*-to-*trans* structural change.

For other compounds, the rate of the $A^{\bullet -} \rightleftarrows B^{\bullet -}$ reaction is much larger than for *cis*-stilbene, making it difficult to detect the intermediate $A^{\bullet -}$. For example, the rate constants for isomerization of the radical anions of **6** and **7** have been estimated to be of the order of $10^{5}\,s^{-1}$ by voltammetric studies.[12,13] In addition to the rather large rates of isomerization, the similarity of E°_{1A} and E°_{1B} in the cases of **6** and **7** also makes difficult the unambiguous detection of the intermediate. Nevertheless, these reactions can be assigned with



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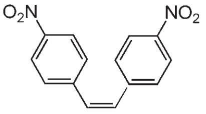

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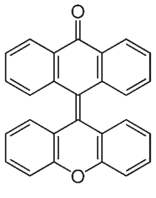
confidence to be two-step processes, electron transfer followed by structural change.

Structural Change that Precedes Electron Transfer: Detecting the Intermediate



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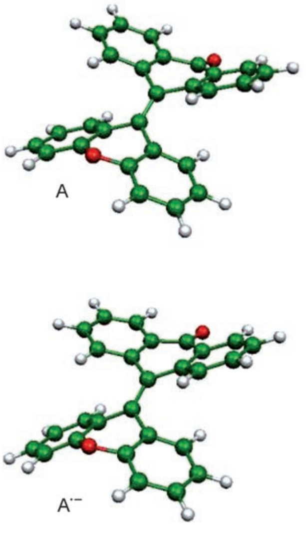


Figure 1. Optimized structures of xanthylideneanthrone (**8**) for the two minimum energy structures found for the neutral compounds A and B, and for the radical anions $A^{\bullet-}$ and $B^{\bullet-}$.[14]

As mentioned above, it is also possible that the preferred reaction pathway under certain conditions will involve a structural change preceding electron transfer. As an illustration of such a reaction, consider xanthylideneanthrone, **8**.[14] This thermochromic compound exists in two forms, the low-temperature A form and the high-temperature B form (Figure 1). The A structure is a doubly folded structure, which avoids steric interaction between ring hydrogen atoms on the anthrone and xanthene ring systems. The B form prevents these same interactions by twisting one ring system with respect to the other and allowing planarity of each to be achieved. The energy of the B form is about 3 kcal mol^{-1} larger than the A form.

The radical anion of **8** also exists in two forms, $A^{\bullet-}$ and $B^{\bullet-}$, the structures of which are very similar to their neutral counterparts (Figure 1). However, in this case $B^{\bullet-}$ is the lower energy form, calculated to be 17 kcal mol^{-1} below $A^{\bullet-}$. Hence, A should be reduced to $B^{\bullet-}$. The questions is whether the reaction is a two-step process with structural change following electron transfer ($A+e^- \rightleftarrows A^{\bullet-}$; $A^{\bullet-} \rightleftarrows B^{\bullet-}$), a two-step process with structural change preceding electron transfer ($A \rightleftarrows B$; $B+e^- \rightleftarrows B^{\bullet-}$), or a concerted electron transfer and structural change ($A+e^- \rightleftarrows B^{\bullet-}$).

In the case of **8**, one sees both types of two-step reactions depending upon conditions. The concerted electron transfer and structural change is never competitive with these two-step reactions. Figures 2 and 3 show voltammograms of **8** obtained in *N*,*N*-dimethylformamide with a glassy carbon electrode.[15] The initial negative-going sweep in Figure 2 reveals an irreversible reduction peak near −1.7 V. This peak is assigned to the two-step reduction mechanism, $A+e^- \rightleftarrows A^{\bullet-}$; $A^{\bullet-} \rightleftarrows B^{\bullet-}$, that is, electron transfer followed by structural change. While the intermediate $A^{\bullet-}$ was not detected in these experiments, the internally consistent analysis of all of the voltammetric data strongly supports its existence, a conclusion also supported by calculation (Figure 1). On the return sweep, an oxidation peak, far removed from the initial reduction peak, is observed. This peak is assigned to the reaction $B^{\bullet-} \rightleftarrows B+e^-$ followed by isomerization of B to the stable, low temperature form, A. As the B→A reaction is not particularly fast, one can readily see a peak for reduction of B in two-cycle experiments (not shown).

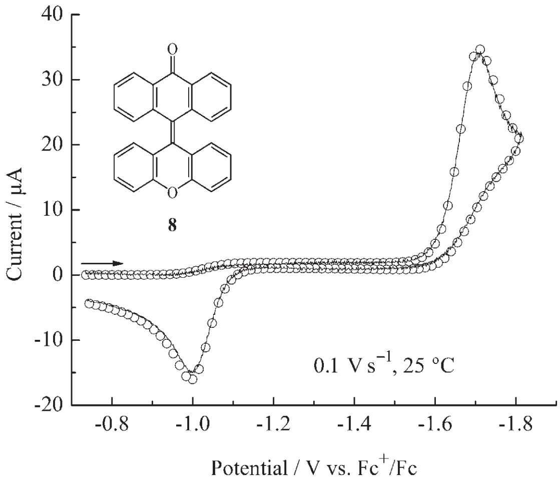


Figure 2. Voltammogram (solid curve) of 2.40 mM xanthylideneanthrone (**8**); ○: simulation according to Scheme 1.[14]

Careful examination of Figure 2 reveals a very small rise in current on the initial negative-going scan near −1.0 V that reaches a plateau value of about 2 µA before the onset of the main peak for reduction of A. This current starting near −1.0 V is assigned to the reduction of the B form. The interpretation was assisted by the independent determination of the thermochromic equilibrium constant, $K_{A \rightleftarrows B}$, from spectroscopic studies, which indicated that less than 0.5 % of **8** exists in the B form under the conditions of Figure 2 (25 °C). Thus, the plateau current in Figure 2 is a kinetic current, which is controlled by the rate at which A can be converted to B. The current is much too large to be due solely to the diffusion of the equilibrium concentration of B that exists in solution.

This interpretation is supported by Figure 3, obtained at 82 °C, at which $K_{A\rightleftarrows B} = 0.011$. Here, the plateau current has grown to about 20 % of the total reduction current. Again, the equilibrium amount of B, about 1 %, is much too small to account for this large plateau current (though green coloration due to B is visible to the eye). Rather, the large kinetic current plateau is due to much larger rate constants for the A-to-B conversion. The points in Figure 3 are from a simulation that includes the known value of $K_{A\rightleftarrows B}$ and an adjustable value of $k_{A\rightleftarrows B}$ ($26\,s^{-1}$) to achieve a fit to the experimental data. This voltammetric behavior is a classic example of a CE mechanism, a chemical reaction ($A\rightleftarrows B$) preceding an electrode reaction ($B + e^- \rightleftarrows B^{\bullet -}$).[16b]

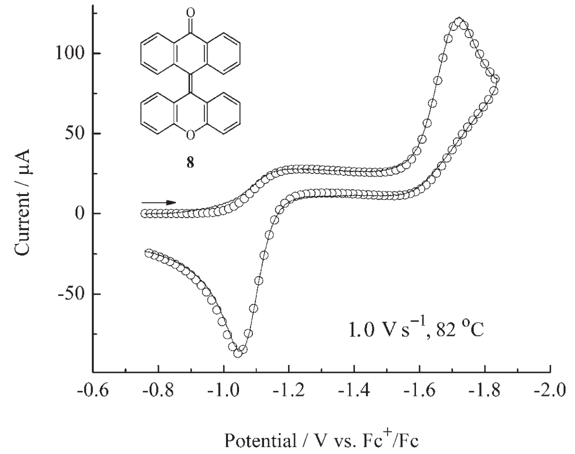
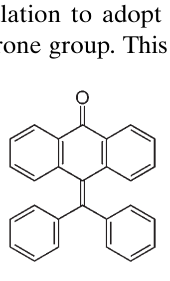


Figure 3. Voltammogram (solid curve) of 2.40 mm xanthylideneanthrone (**8**); ○: simulation according to Scheme 1.[14]

Thus, at low temperatures most of the reaction proceeds by the two-step mechanism of electron transfer followed by structural change, while at high temperatures the two-step mechanism of structural change followed by electron transfer begins to prevail.

Inference of a Two-Step Mechanism from Analysis of Voltammetric Peak Shapes

Compound **9** (10-(diphenylmethylene)anthrone) bears some similarity to **8**. In this case, however, neutral **9** does not exist in two different forms.[14] Only an A form with folded anthrone unit was found experimentally and by calculation. Similarly, the radical anion was found by experiment and calculation to adopt a twisted form, $B^{\bullet -}$, featuring a planar anthrone group. This lack of identifiable intermediates (B or $A^{\bullet -}$) would appear to make this reduction an ideal candidate for a concerted electron transfer and structural change, $A + e^- \rightleftarrows B^{\bullet -}$. However, there are some doubts including the possibility that the molecule may not be vibrationally competent to reach a transition state for the large structural change that is required.



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In this case, as in others cited earlier, it was not possible to detect by voltammetry any intermediates in the one-electron reduction of **9**, for example, an A-like radical anion or a B-like neutral compound. The voltammetry at all scan rates studied shows a relatively reversible one-electron reduction process. An example is shown in Figure 4, which is taken from a collection of voltammograms at each of eleven scan rates from 0.1 to 30 V s⁻¹ and five temperatures between −8 and 25 °C.[14] The conclusions to be drawn were found to be adequate to explain all of these voltammograms.

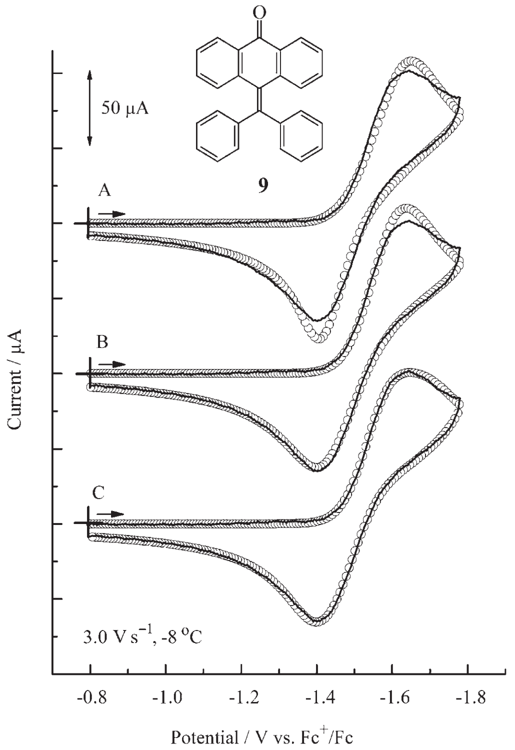


Figure 4. Voltammogram (solid curve) of 2.17 mm 10-(diphenylmethylene)anthrone (**9**); simulations (○): A) Butler–Volmer formulation of electron-transfer kinetics. B) Marcus formulation with α from Equation (3). C) Square Scheme 1.[14]

In Figure 4A, the points represent the best-fit using the classical Butler–Volmer electron-transfer rate law, which considers the reaction $A + e^- \rightleftarrows B^{\bullet -}$ to be a concerted electron transfer and structural change.[16c] The rate constants, k_f and k_b, for the Butler–Volmer formulation are given by Equations (1) and (2), in which k_s, the standard electron-transfer rate constant, and α, the electron-transfer coefficient, are the parameters, along with the standard potential, that can be adjusted.

$$k_f = k_s \exp\left[-\frac{\alpha F}{RT}(E - E^\circ)\right] \tag{1}$$

$$k_b = k_s \exp\left[-\frac{(1-\alpha)F}{RT}(E-E^\circ)\right] \tag{2}$$

It is clear that the Butler–Volmer formulation of a concerted electron transfer and structural change is unable to account for the experimental data. The simulation produces curves that are considerably too sharp in both the cathodic and anodic peak regions. It should be emphasized that these same deficiencies exist for fits at all of the scan rates and temperatures that were studied.

Curve B of Figure 4 represents the best fit that can be achieved by a more modern treatment of electron-transfer kinetics, the Marcus theory, in which the electron-transfer coefficient is not regarded as being a constant. Rather, α is predicted to vary with potential according to Equation (3),[16c] in which λ is the total reorganization energy that was discussed earlier.

$$\alpha = {}^1\!/_2 + \frac{F(E-E^\circ)}{2\lambda} \tag{3}$$

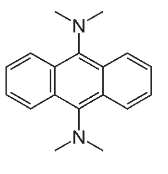
One can see in Figure 4B that the fit in the anodic peak region is much improved, but the cathodic peak region is scarcely different from the fit obtained with Butler–Volmer kinetics. In addition to the fact that simulations using Equation (3) do not provide an adequate match of the data, there is another troubling result: the required reorganization energy, which ranges from 0.21 to 0.27 eV, is unreasonably small, being one-half or less of the reorganization energies for other organic electron-transfer reactions.

Thus the two most commonly used models of electron-transfer kinetics are not able to account for the voltammetric data for **9**. It is clear from both experiment and calculation that a substantial structural change accompanies the reduction, $A + e^- \rightleftarrows B^{\bullet-}$. However, we cannot successfully interpret the data as a single step, concerted electron transfer and structural change. It is possible that a refined model of electron-transfer kinetics might be successful. A clue may be taken from the successful treatment of concerted electron transfer and bond cleavage.[19] Here the distinctly anharmonic Morse curve is incorporated in the model. Such a departure from invoking equal parabolas for reactant and product as in Marcus theory may possibly prove successful for the case of structural change concerted with electron transfer. Nevertheless, in the absence of such a model we feel compelled to conclude that the reaction actually follows a two-step mechanism, structural change either following or preceding electron transfer.

Simulation C of Figure 4 is a fit based on the two-step mechanism as presented in Scheme 1. Clearly the agreement between simulation and experiment is excellent and similar fits were obtained at all the other scan rates and temperatures. Under the conditions of Figure 4, the simulation parameter values correspond to a mixed pathway through Scheme 1, involving both structural change preceding and following electron transfer.[14] However, the major reduction pathway is $A + e^- \rightarrow A^{\bullet-}$; $A^{\bullet-} \rightarrow B^{\bullet-}$ whereas the oxidation tends to follow the route $B^{\bullet-} \rightarrow B + e^-$; $B \rightarrow A$.[17] (For an illustration of the relative importance of the two pathways in various portions of the voltammogram, see Figure 9 of reference [14]). Of course in this case we have no experimental or computational information about the identities of the postulated intermediates. Also, it should not be surprising that good fits were obtained using the square scheme (Scheme 1) in view of the abundance of adjustable parameters compared to the one-step mechanism. Thus, it is not so much the agreement of simulation and experiment for the two-step mechanism that prompts us to conclude that the reaction is not concerted. Rather, it is the failure of electron-transfer models for a concerted reaction to provide an acceptable agreement.

Inference of a Two-Step Mechanism Based on Independent Measurement of the Inner Reorganization Energy

The oxidation of 9,10-bis(dimethylamino)anthracene (**10**) is unusual in several respects (Figure 5).[20] First, there is a single oxidation and a single reduction peak, but the height of these peaks corresponds to overall two-electron processes. The oxidation proceeds from the neutral diamine to its radical cation and then to the dication and the reduction involves the reverse sequence. The two-electron stoichiometry of the oxidation is supported by controlled potential coulometry.[20]



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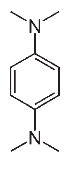

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The fact that there is a single oxidation peak suggests that the standard potentials for the two steps of oxidation must be very similar so that the two oxidation steps are merged into one. In fact, the initial analysis of the data[21] suggested that the potentials were inverted, that is, E_1° (for formation

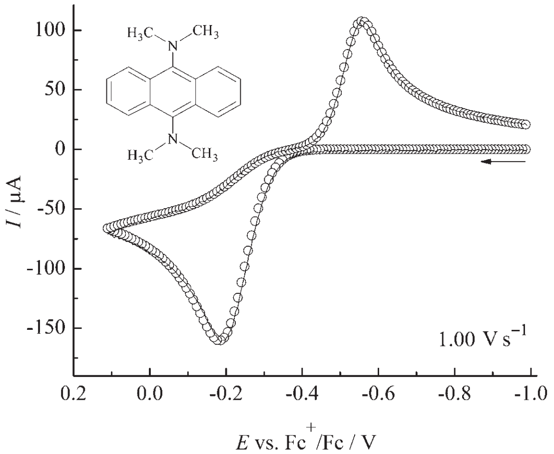
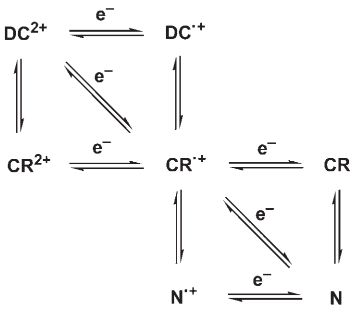


Figure 5. Cyclic voltammogram of 1.34 mM 9,10-bis(dimethylamino)anthracene (**10**). Temperature: 298 K. Full curve: background-corrected experimental voltammogram; ○: simulation according to Scheme 5.[20]

of the radical cation) was actually more positive than E_2° (corresponding to the radical cation/dication couple). Such potential inversion is usually associated with the occurrence of significant structural changes.[22]

Another feature of Figure 5 is the fact that the anodic and cathodic peak potentials are separated by almost 0.4 V. At first glance, this is suggestive of rather small standard electron-transfer rate constants for the reactions.[16a] By contrast, reactions with large rate constants will have differences in peak potentials approaching 58 mV for a one-electron process or 29 mV for a two-electron reaction with strong potential inversion.[16a] Thus, the original analysis of this reaction assumed that the rate constants were rather small in order to account for the large separation in peak potentials.[21]

The data could be well accounted for by two concerted reactions (electron-transfer with structural change) represented by the diagonal reactions in the conjoined square schemes in Scheme 5. Here N denotes structures that resemble the structure of neutral **10**, CR those that resemble the structure of the radical cation, and DC those that resemble the structure of the dication. The best-fit parameter values are, for the first couple, $\mathrm{CR}^{\bullet+} + e^- \rightleftarrows \mathrm{N}$, $E_1^{\circ} = -0.26$ V vs. ferrocene, $k_{s,1} = 0.0054\ \mathrm{cm\,s^{-1}}$, $\alpha_1 = 0.40$ and for $\mathrm{DC}^{2+} + e^- \rightleftarrows \mathrm{CR}^{\bullet+}$, $E_2^{\circ} = -0.46$ V vs. ferrocene, $k_{s,2} = 0.0011\ \mathrm{cm\,s^{-1}}$, $\alpha_2 = 0.85$. Note that these parameter values correspond to 0.20 V potential inversion and fairly small k_s values.



Scheme 5. Conjoined square schemes showing the concerted and two-step electron-transfer mechanisms for a two-electron process.[20]

Substantial structural changes accompany the oxidation of **10**. Calculated structures of the three oxidation states of the diamine are shown in Figure 6. The neutral compound (a) features a planar anthracene unit and two dimethylamino groups, each pyramidal at nitrogen, turned out of the plane of the anthracene. Two isomers of the radical cation were found. The first (b) has the dimethylamino groups partially turned into the plane with accompanying distortion of the anthracene. The second (b′), which is of similar energy, is a folded structure with a boat-like central six-membered ring and the dimethylamino groups directed to the same side of the anthracene moiety. The dication (c) also adopts this folded structure with the extent of folding being more severe than in the radical cation.

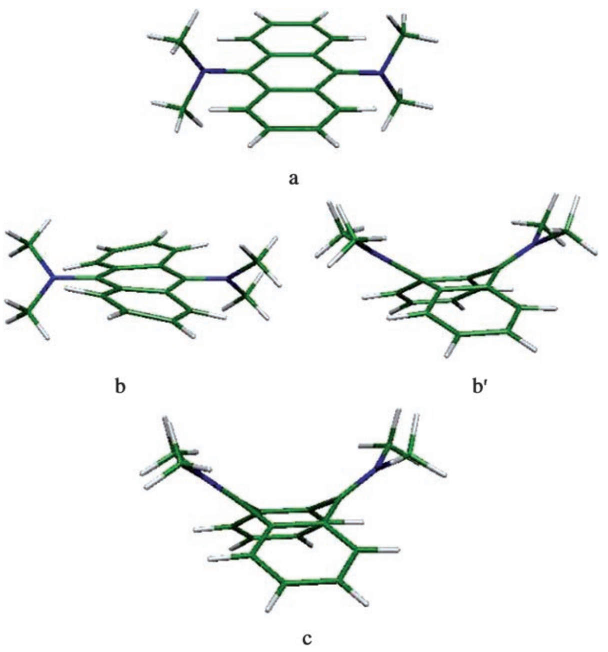


Figure 6. [20] Optimized structures of the neutral compound (a), radical cation (b and b′) and dication (c) of 9,10-bis(dimethylamino)anthracene (**10**).

Thus a consistent description of the electron-transfer reactions was achieved. The oxidation involves substantial structural changes (though there is uncertainty concerning the preferred structure of the radical cation) and these structural changes induce potential inversion. Also, the same structural changes bring about large values of the inner reorganization energies thus explaining the small values of the electron-transfer rate constants.

This explanation requires that the inner reorganization energy for the $\mathrm{CR}^{\bullet+} + e^- \rightleftarrows \mathrm{N}$ reaction be unusually large, larger than, for example, the same reaction for *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (**11**), which has a very large rate constant for the same reaction.[21] The technique of gas-phase photoelectron spectroscopy (PES) allows for an independent measure of the inner reorganization energy. In the experiment an incident photon causes ejection of an electron from (inter alia) the HOMO of the molecule. The most probable event is the vertical ionization that forms the cation with the structure of the neutral precursor species. However, transitions to cation structures of lower energy, though not as probable, are seen to occur and, ideally, the onset energy for the PES will represent ionization to the lowest energy form of the cation, its equilibrium structure. Thus, this transition is an adiabatic transition, from the equilibrium structure of the neutral compound to the equilibrium structure of the cation. The difference between the vertical ionization energy and the adiabatic ionization energy is the gas-phase inner reorganization energy of the cation. Though a rigorous analysis of the PES spectra is more complicated, the above discussion captures the essence of this method of evaluating inner reorganization energies.[20]

Using PES, the inner reorganization energy for **11** was found to be 0.72 eV. The spectrum of **10** consists of a low ionization energy band that does not avail itself to quantitative analysis. However, from the width of the band one qualitative conclusion is clear: the inner reorganization energy for **10** is certainly not greater than for **11**; in fact, it is likely to be smaller.[20]

Thus a key element in the interpretation of the voltammetric data for **10** has been lost. The small electron-transfer rate constants cannot be due to an abnormally large inner reorganization energy for this compound. However, the assumption of concerted electron transfer and structural change requires small rate constants (large reorganization energies). We are led to the conclusion that the reactions cannot be concerted, but must be two-step reactions with structural change either preceding or following electron transfer.

This scheme is represented by the conjoined square schemes in Scheme 5. Now there are four electron-transfer reactions (horizontal) and four solution-phase chemical reactions (vertical). The points in Figure 5 represent a simulation of the voltammogram based on Scheme 5. The same parameter values were found to provide good fits for scan rates from 0.1 to 30 $\mathrm{V\,s^{-1}}$. The data and summary of simulation parameter values can be found elsewhere,[20] but one notable improvement will be emphasized: instead of aberrant values of transfer coefficients like $\alpha_2 = 0.85$ (see above) from the analysis according to the concerted mechanism, the two-step mechanism accommodates comfortably normal transfer coefficients indistinguishable from one-half.

Once again, we prefer not to promote the two-step mechanism based on the ability to obtain good fits of simulation to experimental parameters. Such agreement is not unexpected in view of the ample number of adjustable parameters. Rather, the concerted mechanism can be rejected because it requires, contrary to experiment, a large value of the inner reorganization energy.

Summary

Electron transfer in molecular systems inevitably involves some change in structure. When the structural change is small and no intermediates can be identified along the path of structural change, the reaction is deemed a priori to be a concerted electron transfer and structural change. When larger structural changes are involved, the occurrence of two-step processes can sometimes be proved through the detection of intermediates, by either direct electrochemical or spectroscopic identification. In one cited example, the reduction of 10-(diphenylmethylene)anthrone, the occurrence of a two-step reaction mechanism was inferred by the failure of available kinetic models for concerted electron transfer and structural change to account for the voltammetric data. Assumption of a two-step mechanism provided good agreement of calculation with experiment. Finally, in the case of the oxidation of 9,10-bis(dimethylamino)anthracene, analysis of the data according to the concerted model produced small values of the electron-transfer rate constants, which implied that the substantial structural changes that were involved had produced a large value of the inner reorganization energy. However, photoelectron spectroscopic data showed that the inner reorganization energy was not abnormally large, but instead was equal to or smaller than that for compounds which have much larger electron-transfer rate constants. Thus the two-step mechanism of structural change preceding or following electron transfer is strongly indicated in this case.

When electron transfer is associated with substantial structural change, it can be difficult to distinguish two-step and concerted reactions. However, by use of a number of different approaches progress is being made in this area.

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[1] A comment is in order about what is meant by a concerted electron transfer and structural change. Due to Franck–Condon restrictions, such a reaction cannot involve simultaneous transfer of the electron and changes in the nuclear coordinates. Rather, the concerted reaction involves reorganization of the reactant and solvent to a transition state configuration between reactant and product states with rapid electron transfer occurring at this point followed by further changes in nuclear configuration to reach the solvated product structure.

[2] J. M. Hale in *Reactions of Molecules at Electrodes* (Ed.: N. S. Hush), Wiley, New York, **1971**, pp. 229–257.

[3] J. T. Hupp, M. J. Weaver, *J. Phys. Chem.* **1985**, *89*, 2795–2804.

[4] C. Kraiya, P. Singh, D. H. Evans, *J. Electroanal. Chem.* **2004**, *563*, 203–212.

[5] M. W. Lehmann, P. Singh, D. H. Evans, *J. Electroanal. Chem.* **2003**, *549*, 137–143.

[6] B. Brielbeck, J. C. Rühl, D. H. Evans, *J. Am. Chem. Soc.* **1993**, *115*, 11898–11905.

[7] N. A. Macías-Ruvalcaba, D. H. Evans, unpublished results, **2007**.

[8] A. J. Bard, V. J. Puglisi, J. V. Kenkel, A. Lomax, *Faraday Discuss. Chem. Soc.* **1973**, *56*, 353–366.

[9] L.-S. R. Yeh, A. J. Bard, *J. Electrochem. Soc.* **1977**, *124*, 189–195.

[10] R. Dietz, M. E. Peover, *Discuss. Faraday Soc.* **1968**, *45*, 154–166.

[11] B. S. Jensen, R. Lines, P. Pagsberg, V. D. Parker, *Acta Chem. Scand. Ser. B* **1977**, *31*, 707–710.

[12] Somewhat unexpectedly, for both the neutral and radical anion of α-nitrostilbene, it is the isomer with the two phenyl groups *cis* to one another that is the more stable form: C. Kraiya, P. Singh, Z. V. Todres, D. H. Evans, *J. Electroanal. Chem.* **2004**, *563*, 171–180.

[13] N. A. Macías-Ruvalcaba, J. P. Telo, D. H. Evans, *J. Electroanal. Chem.* **2007**, *600*, 294–302.

[14] N. A. Macías-Ruvalcaba, D. H. Evans, *J. Phys. Chem. B* **2006**, *110*, 24786–24795.

[15] In the technique of cyclic voltammetry, a stationary working electrode is placed in a solution containing a high concentration of supporting electrolyte (to conduct charge through solution) and a low concentration (of the order of millimolar) of electroactive reactant. The solution is purged of dissolved air and is allowed to become quiescent. Then, the potential of the working electrode (with respect to a reference electrode) is caused to change linearly with time until a convenient switching potential is reached after which the direction of potential scan is reversed and the potential is returned (typically)

to its initial value. The information content is in the resulting current-potential curve that is called a voltammogram. The principal experimental variables are the rate of change of potential (scan rate), substrate concentration, and temperature. For a discussion of the principles of the method, see reference [16a].

[16] a) A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, Chapter 6; b) A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, Chapter 12; c) A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, Chapter 3.

[17] As pointed out elsewhere,[18] the fact that the reaction pathway for reduction ($A+e^- \rightleftarrows A^{\bullet -}$; $A^{\bullet -} \rightleftarrows B^{\bullet -}$) differs from the pathway for oxidation ($B^{\bullet -} \rightleftarrows B+e^-$; $A \rightleftarrows B$) might appear to be a violation of the principle of microscopic reversibility. However, the electrons involved in the reduction (near -1.7 V; Figure 1) are from different energy states in the electrode than those involved in the oxidation (near -1.0 V) so the forward and reverse reactions are fundamentally different. Therefore, there is no violation of microscopic reversibility. In fact, the reduction and oxidation reactions could follow exactly opposite pathways ($A+e^- \rightleftarrows A^{\bullet -}$; $A^{\bullet -} \rightleftarrows B^{\bullet -}$ and $B^{\bullet -} \rightleftarrows A^{\bullet -}$; $A^{\bullet -} \rightleftarrows A+e^-$) so long as the kinetics of the $A^{\bullet -} \rightleftarrows B^{\bullet -}$ reaction are sufficiently facile. By the same token, as is about to be discussed, the reduction reaction could proceed by the pathway, $A \rightleftarrows B$; $B+e^- \rightleftarrows B^{\bullet -}$, and the oxidation by the reverse, $B^{\bullet -} \rightleftarrows B+e^-$; $B \rightleftarrows A$, depending again on the kinetics of the chemical step, $A \rightleftarrows B$.

[18] J.-M. Savéant, *Elements of Molecular and Biomolecular Electrochemistry*, Wiley-Interscience, New York, **2006**, p. 95.

[19] a) J.-M. Savéant, *J. Am. Chem. Soc.* **1987**, *109*, 6788–6795; b) J.-M. Savéant, *Acc. Chem. Res.* **1993**, *26*, 455–461; c) C. Costentin, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **2004**, *126*, 16834–16840.

[20] N. E. Gruhn, N. A. Macías-Ruvalcaba, D. H. Evans, *J. Phys. Chem. A* **2006**, *110*, 5650–5655.

[21] K. Hu, D. H. Evans, *J. Electroanal. Chem.* **1997**, *423*, 29–35.

[22] For a recent example of potential inversion and extensive references, see N. A. Macías-Ruvalcaba, D. H. Evans, *J. Phys. Chem. B* **2006**, *110*, 5155–5160.