

One-Electron and Two-Electron Transfers in Electrochemistry and Homogeneous Solution Reactions

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One-Electron and Two-Electron Transfers in Electrochemistry and Homogeneous Solution Reactions

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Dennis H. Evans is Professor of Chemistry at the University of Arizona, where he has been since 2004. Before that he was, for 18 years, Professor of Chemistry at the University of Delaware, and before that, he spent a total of 20 years at the University of Wisconsin—Madison, leaving there with the title of Meloche-Bascom Professor of Chemistry. His research and that of his students has been reported in over 200 publications. The central focus of his research has been the study of the mechanisms of complex, multistep electrode reactions of organic and organometallic systems.

because that single electron transfer is situated fairly close to the solvent breakdown potential so that second or subsequent electron transfers are masked. However, in many instances two separate electron-transfer reactions can be detected with the normal pattern being that addition or removal of the second electron occurs with greater difficulty than the first. In many of these cases, but not all, the molecule contains two identical electroactive groups, an example being the reduction of dinitroaromatics such as 1,4-dinitrobenzene.

As any practitioner in this field is quite aware, the product of one or both of these electron-transfer reactions may undergo reactions that will affect the overall process in interesting ways. These reactions can be self-reactions (e.g., dimerization), reactions with the substrate (e.g., parent-child reactions), or most commonly reactions with components of the medium (solvent or electrolyte). The characterization of these coupled chemical reactions will not be included in this review which instead will concentrate on the electron transfers themselves.

Our focus will be upon the electrode as a donor or acceptor of electrons to/from a solution-phase substrate. In some cases, however, the thermal reactions of two solution-phase species, an electron acceptor and an electron donor, provide interesting parallels to the electrode reactions and these will be discussed in the course of the review. Photoinduced electron transfer between solution-phase species will not be reviewed.

1. Introduction

Certainly one of the first topics to come to mind on seeing the term “molecular electrochemistry” is the subject of electron-transfer reactions. In most cases, a multistep electrode reaction will be initiated by an electron-transfer step, either gain or loss of an electron. The product of that reaction will subsequently participate in chemical and electrochemical reactions leading finally to the end product of the reaction. Thus, an understanding of electron transfer is basic to the entire field of molecular electrochemistry.

For a majority of electrode reactions of organic and organometallic species, only a single oxidation or reduction is encountered within the accessible potential range of the solvent/electrolyte medium that is chosen. This is often

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There will be two principal questions that will be emphasized in our review of single-electron reactions. The first of these is thermodynamic in nature: What are the factors that govern the standard potential for the oxidation or reduction? The second is a kinetic question: What are the factors that determine the rates of the heterogeneous or homogeneous electron-transfer reactions? Both of these questions possess a rich history of prolonged investigation by many scientists, but at the same time, both questions continue to be actively scrutinized and the objective of this review is to expose the reader to the latest results in these areas.

As mentioned above, in the cases of systems that contain two identical electroactive groups and undergo two oxidation or reduction reactions, the typical observation is that addition or removal of the second electron occurs with greater difficulty than the first. The separation between the two standard potentials is quite variable, ranging from about 0.1 V to over 1 V. The separation is mainly due to electrostatic factors. For a reduction of a neutral molecule, for example, the second reduction is more difficult because an electron is being added to a species that already bears a negative charge whereas in the first reduction the reactant is neutral. This situation is called "normal ordering of potentials".

For organic and organometallic systems, there are a number of cases in which the difference between the two potentials is very small such that in voltammetry the two electron-transfer reactions produce a single voltammetric peak. These are examples of "potential compression". In fact, in some instances the sign of the difference in potentials is reversed with it being less difficult to add or remove the second electron than the first. Such a situation has been called "potential inversion", and at first glance, this result seems to contradict the electrostatic argument offered above. However, another factor, structural change associated with one or both of the electron transfers, is at work and is usually the factor responsible for potential inversion.

When potential inversion exists, a consequence is that the product of the first electron transfer is unstable with respect to disproportionation to the original reactant and the two-electron product. As the extent of potential inversion increases, the energy of the intermediate becomes so large that its concentration is negligible during the oxidation or reduction and, consequently, the reaction is purely a two-electron process from a thermodynamic point of view. In such a case, the number of electrons appearing in the Nernst equation for the reaction is two.

This limiting behavior is well-known in aqueous inorganic electrochemistry where such overall reactions as $M^{2+}(aq) + 2 e^- \rightleftharpoons M(s)$ ($M = Cu, Zn, Cd, Pb$, e.g.) behave as pure two-electron reactions with the caveat that the appropriate Nernst expression be used recognizing that $M(s)$ is not a freely diffusing product. (Here, Cu is an intermediate case where the energy of Cu^I in noncomplexing media is such that the concentration of Cu^I will be significant during the reduction of Cu^{II}). In recent years a number of examples of this limiting two-electron behavior have been found in organic and organometallic cases as well.

As alluded to above, those cases with strong potential inversion (addition or removal of the second electron being much easier than the first) correspond to intermediate oxidation states of very high energy. In such cases, it is natural to ask whether the intermediate actually exists; that is, are the processes concerted two-electron reactions?

Though the area is somewhat murky, we will review what has been said about the subject and indicate the conditions under which concerted two-electron processes are likely to be possible.

This last topic involves the mechanism of electron transfer and this subject will be encountered in the discussion of both one-electron and two-electron processes. For one-electron reactions, the theoretical basis for the electron-transfer kinetics is well developed. The Marcus theory of electron transfer is widely applied. It describes an activation Gibbs energy of the reaction which comprises two parts, the contribution from the outer reorganization energy (reorganization of solvent surrounding the reactant) and from the inner reorganization energy (reorganization of the reactant through changes in bond lengths and bond angles). We will review aspects of this topic with emphasis on the relationship of the outer reorganization energy to solvation energies and to the identification of those relatively rare systems in which the inner reorganization energy is significant. The final factor governing the magnitude of the electron-transfer rate constant is the pre-exponential factor, which indeed has been thoroughly developed in the last 25 years. However, this topic is beyond the scope of the present review.

Electron-transfer kinetics in two-electron reactions is a topic normally treated by considering each one-electron transfer separately. Here the emphasis of the review will be focused on the individual steps in two-electron transfers with potential inversion and the possible role of the inner reorganization energy in explaining the electron-transfer rate constants that can be extracted from the data.

Of necessity, this review is far from comprehensive. However, it is hoped that the wide scope of the topics covered and an integrative style of presentation will offer some significant benefits to the reader.

2. One-Electron Reactions

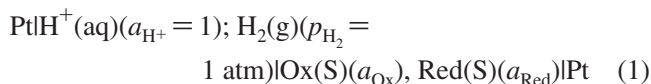
2.1. Standard Potential for One-Electron Reactions

The reduction and oxidation potentials of a myriad of compounds, mainly organic, have been measured and tabulated.¹⁻⁴ Many of the results are for reversible couples from which it is possible to obtain estimates of the standard (or formal) potentials. There are several levels of understanding these potentials. First, compounds can be grouped in classes, depending on the molecular structure, that will have standard potentials that fall in a certain range. Examples would be, for reductions, quinones or nitroaromatics, and for oxidations, triarylaminines or tetraalkylhydrazines.

A second, more detailed understanding would be based on a specific molecular property, usually electron affinity for reductions and ionization energy for oxidations. Of course, these gas-phase properties are only qualitatively relevant to the standard potentials which are measured for solution-phase species. There are two key quantities that are required to move from the gas-phase quantities to the solution-phase electrode potential: the solvation energies of the participants in the redox couple and a term accounting for the difference in energy of the electron in the gas-phase (vacuum actually) compared to the metal in the reference electrode.

2.1.1. Fundamentals

The conventional reference electrode is the normal (or standard) hydrogen electrode (NHE), almost exclusively used in water, which is assigned a potential of zero. The schematic of a cell with the NHE(aq) as reference and the Ox/Red couple in solvent, S, as the second redox couple is shown as 1.



The cell voltage (right side minus left side) is given by eq 2 where $E^\circ_{\text{Ox/Red}}$ is

$$E_{\text{cell}} = E_{\text{Ox/Red}} - E_{\text{NHE(aq)}} + E_j = E^\circ_{\text{Ox/Red}} + \frac{RT}{F} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}} + E_j \quad (2)$$

the standard potential of the Ox/Red couple and E_j is the liquid junction potential between aqueous NHE and the solvent/electrolyte containing ox and red. When ox and red are in their standard states ($a_{\text{Ox}} = a_{\text{Red}} = 1$), the cell voltage is simply

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ox/Red}} + E_j \quad (3)$$

based on $E_{\text{NHE(aq)}} \equiv 0$. Here E°_{cell} is the measured cell voltage when all species are in their standard states.

Now, assume that Ox and Red are also in an aqueous solution. The conventional cell reaction associated with cell 1 is



and the standard Gibbs energy change for the cell reaction is

$$\Delta G^\circ_{\text{cell}} = \Delta G^\circ_{\text{H}^+(\text{aq})} + \Delta G^\circ_{\text{Red}(\text{aq})} - 1/2\Delta G^\circ_{\text{H}_2(\text{g})} - \Delta G^\circ_{\text{Ox}(\text{aq})} = -FE^\circ_{\text{cell}} \quad (5)$$

where ΔG°_i is the conventional standard Gibbs energy of formation of species i .

By convention, $\Delta G^\circ_{\text{H}_2(\text{g})} = 0$ and also the conventional ionic scale of free energies states that $\Delta G^\circ_{\text{H}^+(\text{aq})} = 0$. Using these values, equation 5 becomes 6.

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ox/Red}}(\text{vs. NHE}) = (1/F)(\Delta G^\circ_{\text{Ox}(\text{aq})} - \Delta G^\circ_{\text{Red}(\text{aq})}) \quad (6)$$

Thus, in aqueous solution, all that is needed to compute $E^\circ_{\text{Ox/Red}}$ (vs NHE) are the conventional standard free energies of formation of the redox partners. In aqueous solution, these standard free energies are available for many species, both ionic and neutral.⁵ The fact that these are conventional rather than absolute free energies is unimportant so long as we express the potential vs NHE with the convention that $E_{\text{NHE}(\text{aq})} \equiv 0$.

The only caveat is that the measured cell voltage, E°_{cell} , contains the liquid junction potential between the NHE and the solution containing Ox and Red. In a few instances, it is possible to design cells in which the liquid junction potential is negligible. In other cases, E_j can be estimated.

In fact, in practical laboratory measurements a secondary reference electrode is used, a reference whose potential vs NHE(aq) is well-known, +0.2412 for the (KCl) saturated calomel electrode or +0.197 for the saturated silver/silver

chloride electrode, to give two examples.⁶ The presence of saturated KCl in these electrodes leads to sharply reduced values of E_j .

The situation is quite different when one turns to non-aqueous solvents (S in cell 1). First, the nonaqueous hydrogen electrode is seldom used in these solvents, at least those of greatest interest in molecular electrochemistry (acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, methylene chloride, and tetrahydrofuran). Thus, there has been no development of conventional standard free energies of formation in these solvents and the procedures described above for water as solvent are inapplicable.

Instead, absolute standard free energies of Ox and Red are used. Values for these, or, more specifically, values for differences in standard free energies, can be obtained in various ways, for example from the standard Gibbs energy of attachment of electrons to Ox (ΔG°_a) in the gas phase plus model calculations of standard free energies of solvation. However, in order to compute $E^\circ_{\text{Ox/Red}}(\text{S})$ vs NHE(aq), for example, an absolute value of $E_{\text{NHE}(\text{aq})}$ is needed to replace the conventional value of zero. Among other things, this absolute potential will take into account the difference in energy of the electron in vacuum and the electron in the electrode metal of the NHE (aq).

The subject of an absolute potential for NHE (aq) has been thoroughly investigated but no absolutely rigorous way of ascertaining its value is available. Parsons⁷ reviewed the literature and suggested that the best available value was -4.44 ± 0.05 V, and the same value was recommended by Trasatti.^{8a} (The experimental determination of this quantity has been discussed by Fawcett.^{8b} Recent theoretical evaluation of the absolute Gibbs energy of hydration of the proton has resulted in a proposed value of -4.28 eV. See section 2.1.3). This quantity must be added to the difference in absolute standard free energies of Ox and Red to obtain $E^\circ_{\text{Ox,Red}(\text{S})}$ with respect to NHE (aq) as in eq 7

$$FE^\circ_{\text{Ox/Red}(\text{S})} \text{ vs NHE (aq)} = \Delta G^\circ_{\text{Ox}(\text{S})} - \Delta G^\circ_{\text{Red}(\text{S})} - 4.44 \text{ eV} \quad (7)$$

where the standard free energies are now absolute values.

As an illustration, consider the standard Gibbs energy of attachment of an electron to Ox, as measured in the gas phase

$$\Delta G^\circ_a = \Delta G^\circ_{\text{Red}(\text{g})} - \Delta G^\circ_{\text{Ox}(\text{g})} \quad (8)$$

the electron considered to be at zero energy.

The standard Gibbs energy of the species in solution is, for example

$$\Delta G^\circ_{\text{Ox}(\text{S})} = \Delta G^\circ_{\text{Ox}(\text{g})} + \Delta G^\circ_{\text{solv,Ox}} \quad (9)$$

Putting eq 9 (and another for $\Delta G^\circ_{\text{Red}(\text{S})}$) in eq 8 and rearranging gives

$$\Delta G^\circ_{\text{Ox}(\text{S})} - \Delta G^\circ_{\text{Red}(\text{S})} = -\Delta G^\circ_a + (\Delta G^\circ_{\text{solv,Ox}} - \Delta G^\circ_{\text{solv,Red}}) \quad (10)$$

which, when combined with eq 7 gives

$$FE^\circ_{\text{Ox/Red}(\text{S})} \text{ vs NHE (aq)} = -\Delta G^\circ_a + (\Delta G^\circ_{\text{solv,Ox}} - \Delta G^\circ_{\text{solv,Red}}) - 4.44 \text{ eV} \quad (11)$$

Equation 11 allows one to take measured free energies of attachment and calculated solvation energies and obtain the standard potential for the Ox/Red couple in solvent S vs NHE (aq). For predictions with respect to other reference electrodes, all that is needed is the potential of that reference vs

NHE (aq). This includes aqueous reference electrodes or such electrodes as Ag (s)|0.01 M AgNO₃(CH₃CN), widely used in experiments with various dipolar aprotic solvents, or the ferrocenium ion/ferrocene couple as a reference. In some cases, authors prefer to express the constant in eq 11 in terms of the desired reference. For example, the constant is -4.68 V for potentials referred to SCE (aq).

Equation 11 is the favored method of converting theoretically derived $\Delta G^\circ_{i(S)}$ to potentials vs a given reference (see below).

An alternative use of eq 11 is to obtain estimates of the difference in solvation energies of Ox and Red, $\Delta G^\circ_{\text{solv.Ox}} - \Delta G^\circ_{\text{solv.Red}}$, from measured ΔG°_a and $E^\circ_{\text{Ox/Red(S)}}$. Since one of the redox partners is often a neutral species whose solvation energy is small, these differences in solvation energies can be taken as good estimates of the solvation energy of the ionic partner (see below).

It is easy to forget the liquid-junction potential that exists between the reference electrode and the test solution, eqs 2 and 3. No matter what reference electrode is selected for use in the laboratory, there is some point where potentials with respect to that reference must be converted to potentials vs an aqueous reference. It is impossible to assess the severity of this problem. In practice, E_j is typically neglected.

Although eq 11 is couched in terms of the Gibbs energy of electron attachment, ionization energies can be used as well, by replacing ΔG°_a by ΔG°_i where the latter is a Gibbs energy of ionization. In practice, these free energies are usually not available and they are replaced by electron affinities and ionization energies, respectively, with the attendant introduction of small errors. Some free energies of electron attachment and ionization are available through gas-phase ion–molecule equilibria.⁹ For a similar treatment of the above ideas see ref 10.

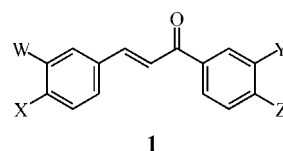
2.1.2. Correlations with Molecular Properties

The application of linear Gibbs energy relationships, most notably the Hammett equation, was found to be very powerful in interpreting the reversible and irreversible potentials of classes of compounds as a function of the substituents on the molecule. The early work is summarized in the monograph by Zuman¹¹ and the subject continues to be the topic of additional applications and refinements^{12–21} as well as reviews.²²

Early applications of theory were based on the Hückel molecular orbital theory and extensions.²³ Here, HOMO energies were correlated with oxidation potentials because, according to Koopmans' theorem, the HOMO energy is equal to the ionization energy (but opposite in sign). Also, LUMO energies were correlated with reduction potentials of, for example, aromatic hydrocarbons. The theoretical methods have been refined resulting in improved correlations.²⁴ Such correlations ignore the solvation energy terms and implicitly assume that there is a linear correlation between LUMO energies and electron affinity, EA.

It would be better to compute, for example, the difference in energy between gas-phase Ox and gas-phase Red and correlate that with electrode potentials. Such was done at an early date by Dewar and Trinajstić²⁵ who used semiempirical MO methods to obtain such differences for a series of twenty-five quinone/hydroquinone couples. As theoretical methods have improved, so have such correlations. For example, Hicks et al.²⁶ correlated EA (which is the difference in energy between the neutral and the anion radical), computed by DFT

methods, with one-electron reduction potentials of various mono-, di-, tri-, and tetrasubstituted chalcones, **1**. The correlation of potentials of 29 monosubstituted chalcones (training set) vs their EA (calculated at the B3LYP/61-G* level) gave a correlation coefficient of 0.969 and a slope of 0.374. Remarkably, the same correlation line was found to fit the data for an additional 72 di-, tri-, and tetrasubstituted chalcones. If the calculated EA are close to the true values, the fact that the slope is 0.374 rather than unity must mean that the magnitude of the solvation energy terms decreases linearly with increasing EA, a trend that was found earlier for reduction of a series of substituted nitrobenzenes.²⁷ The direction of this trend can be rationalized by noting that high-EA compounds will produce anion radicals with the charge more tightly bound and thus less available for solvation interactions.



This last study²⁷ is an example of the use of eq 11 for the determination of $\Delta G^\circ_{\text{solv.Ox}} - \Delta G^\circ_{\text{solv.Red}}$ by use of measured reversible reduction potentials and experimental EA. Compounds studied included 22 nitrobenzenes and 9 quinones and the results were used inter alia for correlations of solvation energies with rate constants for the self-exchange reactions of the neutral/anion radical systems. For a similar set of data on quinones, see ref 28.

In another example, gas-phase free energies of electron-transfer reactions among various bis(arene)metals were determined by electron-transfer equilibrium measurements. By reference to a compound, bis(benzene)chromium, whose Gibbs energy of ionization is known, absolute free energies of ionization of ten ($\eta^5\text{-C}_5\text{H}_5$)₂M and ($\eta^5\text{-C}_5(\text{CH}_3)_5$)₂M compounds were determined and from those and eq 11, $\Delta G^\circ_{(\text{cation, CH}_3\text{CN})} - \Delta G^\circ_{(\text{neutral, CH}_3\text{CN})}$ were obtained.²⁹

Likewise, Nelsen, Rumack, and Meot-Ner³⁰ measured gas-phase electron-transfer equilibrium constants for 35 pairs of tetraalkylhydrazines and their cation radicals. From these and the corresponding standard potentials for the cation radical/neutral couples, the authors determined values of $\Delta G^\circ_{(\text{cation, CH}_3\text{CN})} - \Delta G^\circ_{(\text{neutral, CH}_3\text{CN})}$, relative to that of tetramethylhydrazine⁺⁰ as reference, for 30 compounds. The values ranged from -0.3 to $+7.0$ kcal/mol (1 kcal = 4.1840 kJ). These relative solvation energies were discussed in terms of the structures of the various tetraalkylhydrazines.

A recent example of correlation of calculated (DFT) gas-phase EA with reduction potentials for a series of quinone/quinone anion radical couples in aqueous solution found for the one-electron process a slope of 0.93 or 1.04 depending on the computational method. The potential spanned over 0.3 V and the result suggests that the solvation energy terms are more nearly constant for this series of compounds.³¹

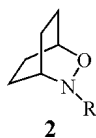
As mentioned earlier, potentials for oxidation of neutrals to cations are expected to correlate with IP whereas potentials for reduction of neutrals to anions should correlate with EA. Both types of correlation were studied by Wayner, Sim, and Dannenberg,³² who examined a number of substituted benzyl radicals. The potentials were not those of reversible processes but were argued to be fairly close to the reversible values. The plot of oxidation potential vs calculated (AM1) IP was

linear with a slope of 1.03 and the slope of the reduction potential/calculated EA plot was 1.04. This is one of the few cases where close-to-unity slopes have been found signifying that the solvation terms for both benzyl cations and benzyl anions are constant among the various substituted benzylys that were studied.

Other standard potential-IP or -EA correlations gave slopes of 1.17 for E° -EA for quinones (the slope was lower for halogenated quinones),²⁸ 0.71 for E° -IP for aromatic hydrocarbons (trifluoroacetic acid solvent),³³ 0.85 for E° -IP for aromatic hydrocarbons (DMF),³⁴ 0.66 for E° -IP for secondary bicyclic peroxides (CH_3CN)³⁵ wherein the same slope was found for aromatic hydrocarbons and alkyl benzenes (data from literature), 0.5 for E° -EA for disubstituted 1,2,4,5-tetrazines (CH_3CN),³⁶ 0.7 for E° -EA for aromatic hydrocarbons (25% dioxane/75% water; reversible potentials?),³⁷ and 0.96 for E° -EA for polypyridinic compounds.³⁸

Interestingly, linear correlation of the one-electron reduction potentials of a series of tris(β -diketonato)ruthenium(III) complexes with IP has been found.³⁹ This surprising result was explained by the fact that these were open-shell compounds in which the electron is inserted into the HOMO rather than the LUMO as with closed-shell species.

In some instances, the correlations of reversible oxidation potentials with vertical IP, the most readily measured quantity, are very poor. The vertical ionization potential is the energy required to remove an electron from the neutral species to form the cation with the same structure. The most striking example of this behavior was found with tetraalkylhydrazines which undergo a very large change in structure upon oxidation.⁴⁰ This serves as a reminder that, since the electrode reaction proceeds from the equilibrated structure of the neutral to the equilibrated structure of the cation, it is the adiabatic ionization potential that should be used in correlations. For the hydrazines, the difference between the vertical and adiabatic ionization energies can be very large (1.0–1.5 eV) and it does not correlate with ionization energy leading to the poor correlations between oxidation potential and vertical ionization potential. Similar poor correlation between oxidation potential and vertical ionization energy was reported for 3-substituted 2-oxa-3-azabicyclo[2.2.2]octane derivatives, **2**, an observation again attributed to large differences between vertical and adiabatic ionization energies (Figure 1).⁴¹



Adiabatic ionization energies for a large set of tetraalkylhydrazines were later obtained by gas-phase electron-transfer equilibrium studies³⁰ and correlation of the reversible oxidation potential vs the adiabatic ionization energy was linear ($R^2 = 0.75$; 31 compounds; plotted by the present author) with a slope of 0.69, much like the correlations of potential vs vertical ionization energy found in cases where no large structural changes accompany oxidation.

As mentioned earlier, the fact that plots of both oxidation potential-ionization energy and reduction potential-electron affinity are relatively linear with slopes typically less than unity signifies that the solvation energy of ions decreases with either increasing ionization energy or electron affinity. Qualitative explanations of this behavior have been offered.²⁸ In view of the success of modern methods of calculation of

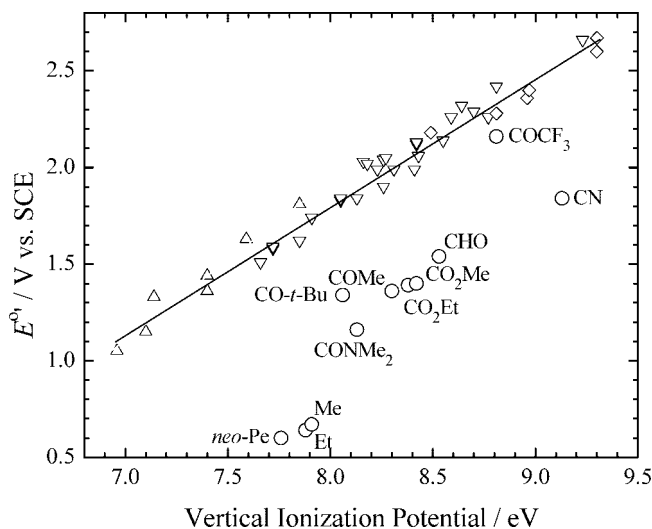


Figure 1. Plots of E° vs vertical IP. The triangles correspond to fused-ring aromatic hydrocarbons, the inverted triangles to alkylated benzenes, and the diamonds to bicyclic peroxides.³⁵ The circles show data for **2** with **R** as indicated. Reprinted with permission from ref 41, Copyright American Chemical Society, 1987. Figure redrafted by author.

solvation energies, attention to these less-than-unity slopes by computational methods would be welcome.

Such methods have been applied to the interpretation of solvation energies of ions extracted from standard potentials and ionization energies or electron affinities. Of particular interest is the polarizable continuum model which has been applied to a number of systems with some success.^{42–46} An interesting outcome of the method was the detection of coordination of a molecule of solvent (acetonitrile) to arylselenonium ions, signified by large deviations between experimental and calculated solvation energies if the coordinated solvent molecule is not included in the solvation calculations.⁴⁴ The more common application of models of solvation is in the full theoretical calculation of standard potentials.

2.1.3. Calculation of Standard Potentials

Recently there have appeared examples of the complete theoretical prediction of the reversible potentials for the Ox/Red couple. This requires the computation of the gas-phase structures of Ox and Red and then the free energies of these species. This is then followed by computation of the solvation energies of Ox and Red usually using methods based on a dielectric continuum model of the solvent, though some more sophisticated treatments have been used.

The solvation energy calculation is inherently more difficult for water as a solvent in view of the chemical interactions that exist between water and solutes and among water molecules. Nevertheless, we will begin with calculations of standard potentials in water as they represent the most sophisticated treatment of the solvent and because of the practical importance of redox processes in water, both from a technological and biological perspective.

There are at least two ways of computing the standard potential for $\text{Ox} + e^- \rightleftharpoons \text{Red}$. In the first, a full cell reaction is considered (as in reaction 4) such that computation of the free energies of the aqueous species in both half-reactions will allow $E^\circ_{\text{Ox/Red(aq)}}$ to be computed with respect to the other half-reaction, the NHE in the case of reaction 4 (see eq 5). Of course, once the free energies of $\text{H}_2(\text{g})$ and $\text{H}^+(\text{aq})$ have

Table 1. Comparison of Calculated⁶¹ and Experimental Standard Potentials for Some Organic Couples in Acetonitrile^a

couple	E° vs Fc (calc)/V	E° vs Fc (exp)/V	reference (exp)	$ E^\circ(\text{calc}) - E^\circ(\text{exp}) /\text{V}$
anthracene(0/1-) (3)	-2.563	-2.401	27	0.162
benzophenone(0/1-) (4)	-2.247	-2.219	27	0.028
nitrobenzene(0/1-) (5)	-1.408	-1.540	27	0.132
TCNQ(0/1-) (6)	-0.092	-0.197	62	0.105
		-0.226 ^b	62	0.134
TCNQ(1-/2-)	-0.802	-0.747	62	0.055
		-0.811 ^b	62	0.009

^a Solvent: acetonitrile (except for the calculated potential for anthracene which was in DMF); Electrolyte for experimental: 0.10 M Bu₄NPF₆ (except for TCNQ (7,7,8,8-tetracyanoquinodimethane) which was 0.07 M Me₄NPF₆). 298 K. ^b Extrapolated to infinite dilution (both organic couple and ferrocene).

been determined, they may be used again and again for the calculation of $E^\circ_{\text{Ox/Red(aq)}}$ for many different Ox/Red couples by focusing only on the computation of the free energies of Ox and Red for each new couple.

A second way is to compute the absolute standard potential of NHE(aq) which, when combined with free energies of Ox and Red, will provide $E^\circ_{\text{Ox/Red(aq)}}$ via eq 11 (where it is recognized that for specific cases where one partner is neutral ΔG°_a is simply the Gibbs energy of Red minus that of Ox (Red being an anion) and ΔG°_i is the same (Ox being a cation)). Computing the absolute standard potential of NHE(aq) reduces to the problem of finding the absolute solvation energy of the proton in water, as the free energies of the other species are accurately known. Kelly et al.⁴⁷ applied the cluster-pair approximation to obtain the Gibbs energy of aqution of the proton and found -265.9 kcal/mol, in agreement with earlier results.⁴⁸

This leads to a value of -4.28 eV to be used^{49,50} in eq 11. This proposed value, which falls outside the estimated error on the earlier evaluation (-4.44 ± 0.05 eV), will lead to a 3.7 kcal/mol difference in quantities evaluated from experimental data, such as solvation energy differences between Ox and Red.^{27,28,42-44} The same methods have been applied to compute the absolute value of the NHE(solvent) for methanol, acetonitrile and dimethyl sulfoxide (-4.34, -4.48, and -3.92 eV, respectively).⁵¹ Absolute free energies of solvation of a variety of cations and ions were also computed in water⁴⁷ and the other solvents.⁵¹

These and other methods have been applied for computation of the standard potentials (aqueous) of Ru³⁺/Ru²⁺,^{49,52,53} Cu²⁺/Cu⁺,⁵⁴ Ag²⁺/Ag⁺,^{54,55} MnO₄⁻/MnO₄²⁻,⁵⁶ RuO₄⁻/RuO₄²⁻,⁵⁶ and Fe³⁺/Fe²⁺ and Mn³⁺/Mn²⁺,⁵⁷ with reasonable accuracies. The validity of comparison of computed with experimental potentials is enhanced by the fact that most but not all of the experimental values have been extrapolated to infinite dilution so that they are not contaminated by activity effects (finite ionic strength) or hydrolysis of highly charged cations such as Fe³⁺. In the determination of $E^\circ_{\text{Fe}^{3+},\text{Fe}^{2+}}$, corrections were required for the hydrolysis (apparent acid dissociation) of Fe³⁺ as well as the activity coefficients of Fe³⁺, Fe²⁺, and H⁺ in order to obtain accurate extrapolations to infinite dilution.⁵⁸ As we shall see, infinite dilution potentials are seldom available for the solvents widely used in molecular electrochemistry.

Oxidation potentials of organic systems in aqueous media have also been computed.⁵⁹ In a theoretical study of 21 mono- and disubstituted anilines, good agreement was found between calculated and experimental oxidation potentials (absolute potential of NHE(aq) taken as -4.44 eV; mean unsigned difference between experimental and calculated equal 0.09 V for one of the theoretical methods). However, the experimental results⁶⁰ were half-wave potentials for the

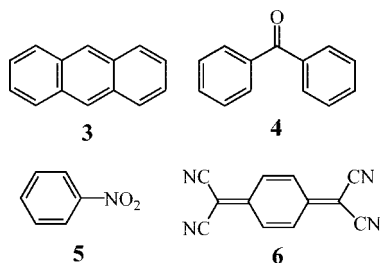
admittedly irreversible oxidation of the anilines in acetate buffer, 50:50 by volume water/2-propanol (not purely aqueous). The experimental potentials are likely to differ from the desired reversible one-electron oxidation potentials casting doubt on the validity of the correlation that was carried out.

Computations of standard potentials in nonaqueous solvents have also been conducted. For example, Baik and Friesner⁶¹ computed potentials for anthracene(0/1-), azobenzene(0/1-), benzophenone(0/1-), nitrobenzene(0/1-), TCNQ(0/1- and 1-/2-), tetrathiafulvalene(1+/0) and 14 metallocenes in acetonitrile. The authors used -4.43 V in eq 11 but ultimately expressed their calculated potentials vs SCE(aq) (Note, however, an apparent error in sign of the potential of SCE(aq) vs NHE(aq)). A dielectric continuum model of solvation was employed along with DFT calculations. Best agreement between calculation and experiment was obtained using the cc-pVTZ(-f)++ level of DFT, but the degree of agreement was less than satisfactory. In view of the fact that it is common practice to refer measured potentials to the standard potential of the ferrocenium/ferrocene couple (Fc reference), it is interesting to compare differences in the computed potentials that Baik and Friesner found for ferrocene and the various organics with experimental values referred to ferrocene. Such a comparison is made for a few compounds in Table 1.

One can see that comparison of calculated and experimental potentials vs ferrocene shows fairly good agreement with a mean unsigned error for all entries of 0.09 V. This is not smaller than the error found for these compounds when the potentials are referred to SCE(aq)⁶¹ which indirectly supports the validity of the absolute value of the NHE(aq) that was used, -4.43 V.⁶¹ Thus, with the present level of sophistication, there is no practical value in comparing calculated and experimental potentials referred to ferrocene (or some other reference in the solvent being studied). However, comparison to ferrocene is fundamentally superior as it almost completely obviates the difficulty with the unknown liquid junction potential that inevitably exists when potentials in a solvent like acetonitrile are referred to an aqueous reference electrode (cf. Equation 2 and 3). As the accuracy of the calculational methods improves so as to approach the accuracy in the experimental determinations (~5 mV), comparisons vs ferrocene in the solvent being studied will be preferred.

Another interesting comparison involves the two experimental potentials for each TCNQ couple reported in Table 1.⁶² One is for the TCNQ and ferrocene couples measured in 0.07 M Me₄NPF₆ and the other is for the TCNQ couple referred to ferrocene but with each potential extrapolated to infinite dilution. The difference, 0.029 V for the 0/1- couple and 0.064 V for the 1-/2- couple, is principally due to activity

effects, though ion pairing can be at play as well (no ion pairing could be detected in the TCNQ system with Me_4N^+ as counterion).⁶² Calculations are traditionally conducted on isolated species so that activity is ignored. So, as the accuracy of calculations approaches ~ 50 mV, either activity effects should be included in the calculations or comparisons should be made with infinite dilution experimental potentials. Unfortunately, there are few reports of the latter for non-aqueous solvents.^{62–65}



Direct comparison with ferrocene was employed by Felton et al.⁶⁶ for calculations of standard potentials in acetonitrile while Greco et al.⁶⁷ referred their calculated potentials to SCE(aq). Both groups were investigating synthetic analogs of the active site of iron-only hydrogenases. Fu et al.⁶⁸ calculated standard potentials for 270 simple organic reactions involving anions, cations, and neutral radicals for acetonitrile as solvent. These authors used -4.44 eV as the absolute potential of NHE(aq) to make their comparisons and they found an average error of 0.17 V upon comparing theoretical and experimental quantities. It should be noted that very few of the experimental measurements were for reversible electrode reactions. In a slightly different approach, Namazian and Norouzi⁶⁹ computed standard potentials in dimethyl sulfoxide solvent for the one-electron reductions of ten quinones. The values were referred to the standard potential for 1,4-naphthoquinone neutral/anion radical couple whose experimental value allowed expression of the calculated values vs SCE(aq). The average rms deviation between experiment and calculation was 0.143 V.

As mention has been made of the use of the standard potential of the ferrocenium/ferrocene couple in a given solvent as a reference potential against which measured standard potentials are reported,⁷⁰ some comment is in order concerning this procedure. The suggestion of this couple as reference dates to 1960 with the study of Koeppe et al.⁷¹ but it was much later that it began to be used in practice.⁷² Finally, in 1984 its use in this regard became, along with the bis(benzene)chromium(1+/0) couple, an official recommendation of the IUPAC.^{73,74} Remarkably, the over one-volt difference in the standard potentials for these two couples was constant for 22 solvents with the largest deviation being 40 mV.^{73,74}

What is the significance of using ferrocene as a reference potential against which to report experimental potentials? It is easier to state what it is not. The ferrocene couple is not an absolute standard whose potential is independent of the identity of the solvent. The aforementioned constancy of the difference between the potentials of the ferrocene and bis(benzene)chromium couples simply means that the relative solvation energies of the four participants in the two couples is independent of solvent, an observation that is not too surprising considering the identical charge types and similar sizes of those partici-

pants. The use of ferrocene as standard is principally a procedure that provides easily measured and quite reproducible values of reported standard potentials for various couples measured in a given solvent. There is no uncertainty associated with irreproducible liquid junction potentials when employing an aqueous reference electrode. The ferrocene potential is either measured by voltammetry under the same conditions as the study in question or, in some cases, ferrocene is added to the test solution as an internal standard. The standard potential is taken as the average of the anodic and cathodic peak potential as obtained by cyclic voltammetry. The procedure is very accurate but large uncompensated resistances must be avoided as the absolute magnitude of the error of the anodic peak is larger than that of the cathodic peak so the IR error is larger for the former meaning that the errors do not quite cancel when taking the average.

More recently, Noviantri, et al.⁷⁵ convincingly demonstrated that the solvent dependence of the standard potential of decamethylferrocene was smaller than either that of pentamethylferrocene or ferrocene when measured in 29 solvents. Thus, decamethylferrocene was recommended as a superior reference compound. However and of course, this does not mean that the decamethylferrocene potential is independent of solvent, only that its dependence is smaller than the other reference compounds.

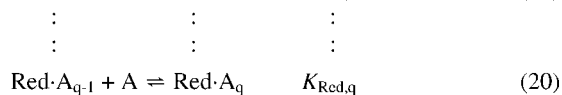
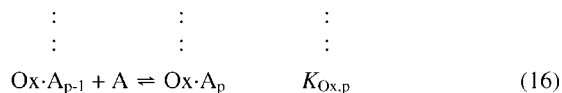
2.1.4. Effect of Additives on Observed Potentials

There are many examples of cases where potentials are affected by often small quantities of a substance that is added to the solution. For example, a common observation is that the potential required to reduce a compound in a nonaqueous medium is significantly less negative when the solvent is not completely anhydrous. This is attributed to association of the anionic product of the electrode reaction with the hydrogen-bond donor, water.

Consider reaction 12 in which it will be assumed that the oxidized and reduced



forms can associate with additive A in a series of reactions, 13–20.



Furthermore, overall formation constants are defined as $\beta_{\text{Ox},i} = K_{\text{Ox},1}K_{\text{Ox},2}\cdots K_{\text{Ox},i}$ and $\beta_{\text{Red},i} = K_{\text{Red},1}K_{\text{Red},2}\cdots K_{\text{Red},i}$.

The observed standard potential in the presence of the additive, E°_{app} , is given by

$$E^\circ_{\text{app}} = E^\circ_{\text{Ox/Red}} + \frac{RT}{F} \ln \frac{\theta_{\text{Ox}}}{\theta_{\text{Red}}} \quad (21)$$

where θ_{Ox} and θ_{Red} indicate the fraction of all of the Ox species that exist as free Ox and the fraction of all of the Red species that exist as free Red. These fractions are given by

$$\theta_{\text{Ox}} = \frac{1}{1 + \beta_{\text{Ox},1}[A] + \beta_{\text{Ox},2}[A]^2 + \cdots + \beta_{\text{Ox},p}[A]^p} \quad (22)$$

$$\theta_{\text{Red}} = \frac{1}{1 + \beta_{\text{Red},1}[A] + \beta_{\text{Red},2}[A]^2 + \cdots + \beta_{\text{Red},q}[A]^q} \quad (23)$$

These expressions may be traced to DeFord and Hume,⁷⁶ who applied them to metal–ligand equilibria (Ox and Red being two different oxidation states of a metal and A being a ligand). Such applications were abundant as were those of the formally equivalent case of organic reactants and A being the proton. Additional cases have involved organic reactants whose anions undergo ion pairing with metal ions (A). None of these applications will be reviewed here except for a few recent cases of ions interacting with host molecules. Instead, we will focus on cases of hydrogen bonding between the additive and a component of the redox reaction.

In all applications, E°_{app} is studied as a function of the concentration of the additive A. It is noteworthy that there are no restrictions on the concentration of A but it is essential to be able to evaluate [A] at the electrode surface under the conditions where E°_{app} is measured, usually at the half-wave potential of a voltammetric experiment. This is a difficult but not impossible task if [A] is small and it is normally avoided by using high concentrations of A, say $[A] > 10[\text{Ox}]$, so that the concentration of A at the electrode surface is close to its value in the bulk solution.

An unstated requirement for the validity of eqs 21–23 is that the association reactions 13–20 be rapid and reversible on the time scale of the technique used to determine E°_{app} . For hydrogen-bonding reactions, this requirement will always be met under normal experimental conditions. With metal–ligand complexation reactions, however, this is not always the case. In fact, some complexes are sufficiently inert that no voltammetric experiment is slow enough to guarantee that equilibrium is maintained. In this regard, it should be mentioned that eqs 21–23 can also be applied when E°_{app} is determined in the potentiometric titration of Ox with a reducing titrant. In such a case, E°_{app} is the measured potential at the half-titrated point. With this technique, even rather sluggish equilibrium processes can be characterized.

The greatest level of recent activity in this area has been the study of additives that are hydrogen-bond donors with Red being an anion radical or dianion. Here the appropriate expressions have been developed and presented anew.^{77,78} In many cases, eqs 21–23 have been simplified by considering that only certain complexes exist over a given range of [A]. When Ox is a neutral molecule such as a quinone, all complexes of Ox with a hydrogen-bond donor can usually but not always⁷⁷ be ignored. In addition, one can assume (and then test the assumption) that only certain species of the anion radical are formed, say the free anion and the 2:1 complex of alcohol:anion radical.⁷⁷ In other cases, a very

simple expression is used wherein only one complex is assumed to exist, say $\text{Red}\cdot\text{A}_k$, and the value of k is ascertained from the data.⁷⁹ When nonintegral values of k are encountered, the assumption of only one complex being present is probably invalid.

Interactions of hydrogen-bond donors with quinone anion radicals and dianions have been widely studied.^{77,79–95} The work has been reviewed.⁹⁶ Most of the donors that have been studied are alcohols but benzoic acid⁸⁹ and some amides⁹¹ have also been studied. When the hydrogen-bond donor is a sufficiently strong acid, transition to proton transfer to the anion radical is seen.^{89,92}

In the case of hydroxylic donors, the interaction with the anion radical is significantly weaker than that seen with the dianion. In many cases, the effect on the first reduction process is so small that it is ignored but useful studies of association of the anion radicals with the donor have been reported.^{77,79,93,97} The quinone dianion not only forms hydrogen-bonded complexes more avidly, there is evidence for a number of different complexes containing a progressively larger number of donor molecules.⁷⁹ For example, for some *p*-benzoquinone dianions in acetonitrile, up to four methanol molecules can be associated⁷⁷ while in dimethyl sulfoxide, complexation of up to six molecules has been reported.⁸⁸ In most cases, the maximum concentration of the hydrogen-bond donor is 1 M or less where self-association of the donor can probably be neglected (the equations assume that the donor is completely monomeric). Also, as the concentration of donor becomes large, part of the observed shift in E°_{app} may be due to changes in the liquid junction potential between the test solution and the reference electrode. In some work, attempts are made to correct for these changes in liquid junction potential.⁸⁸

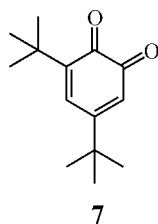
The conclusion that multiple donor molecules (up to six) are complexed with the dianion is based on the improved fits of plots of E°_{app} vs $\log[A]$ that are obtained by including all of the indicated formation constants compared to, for example, fits with no more than four or five molecules of A. There is no doubt that improved fits are found, but there is some doubt about the conclusion that specific 6:1, 5:1, 4:1, etc. complexes are formed. In fact, nonspecific interactions (changes in solvation) with the dianion provide a more conservative and perhaps better description.⁹⁸ For example, the solvation energy of 1,4-benzoquinone anion radical is larger²⁷ in methanol solvent compared to acetonitrile by 8 kcal/mol (0.35 V) and the solvation energies of the dianion should differ in the same direction but probably to a larger degree. Hence, it is at least a viable alternative to interpret the shifts upon addition of methanol to an acetonitrile solution as changes in the solvation energy of the anions, $\Delta\Delta G^\circ_{\text{solv}}$, as [A] increases. This alternative expression would take the form

$$E^\circ_{2,\text{app}} = E^\circ_2 - F(\Delta\Delta G^\circ_{2,\text{solv}} - \Delta\Delta G^\circ_{1,\text{solv}}) \quad (24)$$

where the subscript 2 in the potentials refers to the anion radical/dianion potential and the subscripts 1 and 2 in solvation energies refer to the anion radical and dianion, respectively.

To illustrate the uncertainties in assignment of specific complexes, consider the complexation of the anion radical of 3,5-di-*tert*-butyl-1,2-benzoquinone, **7**, by water. In the first study⁹⁷ where additions of up to 1 M water to acetonitrile were carried out, the fit of E°_{app} vs $[\text{H}_2\text{O}]$ was improved when both 1:1 and 2:1 complexes were included whereas in a later

study,⁹³ limited to 0.10 M water, the data could be adequately accounted for by considering only a 1:1 complex. Of course, the effects of higher complexes become more evident as the concentration of additive increases.

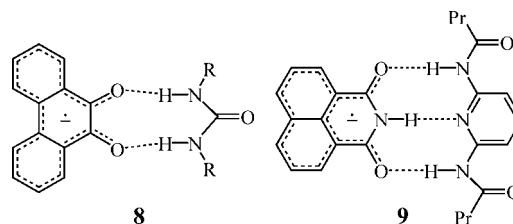


With the same quinone, and using 2,2,2-trifluoroethanol (TFE) as additive, very strong interactions between the anion radical and TFE were found ($K_{\text{Red},1} = 143 \text{ M}^{-1}$; $K_{\text{Red},2} = 42 \text{ M}^{-1}$), but the results are complicated in an interesting way by the intervention of proton transfer from TFE to the anion radical.⁹⁹ The evaluation of $K_{\text{Red},1}$ and $K_{\text{Red},2}$ was based mainly on the shift in the first reduction peak, just as seen for cases uncomplicated by proton transfer. In fact, it was in the analysis of the kinetics of proton transfer that it became necessary to invoke the formation of a very small amount of an intermediate 3:1 complex, $K_{\text{Red},3} \sim 0.1 \text{ M}^{-1}$. In short, the data were interpreted in terms of the proton transfer occurring within the 3:1 complex.

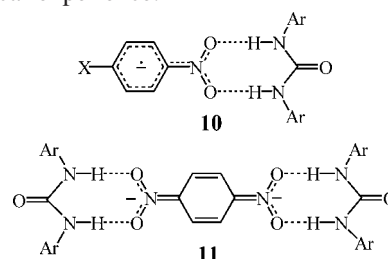
In the study of the mechanism of the reduction of dioxygen in the presence of water, 2-propanol and methanol, the shift in the first reduction potential ($\text{O}_2 + e^- \rightleftharpoons \text{O}_2^{\cdot-}$) indicated some formation of a 1:1 and a 2:1 complex with the first and third of these additives.^{100,101} By contrast, a kinetic analysis of the second, irreversible process, reduction of superoxide to hydrogen peroxide anion ($\text{O}_2^{\cdot-} + \text{H}_2\text{O} + e^- \rightleftharpoons \text{HO}_2^- + \text{OH}^-$), required the invocation of, in addition, a 3:1 and 4:1 complex. Reasonable chain-like structures were suggested for these higher complexes.¹⁰² So, not only thermodynamics but kinetics as well can provide evidence for the formation of complexes of this type.

Nevertheless, the evidence for higher complexes is quite indirect, so that ample circumspection should be exercised in this area. All of this serves as a reminder that electrochemistry can provide only inferences about structure. Spectroscopic tools give less ambiguous information about structure.

In a few instances, the structural characteristics of the quinone anion radical (or other hydrogen-bond acceptor) and the additive strongly suggest the structure of the complex. For example, 1:1 complexes of 9,10-phenanthrenequinone anion radical with various ureas (**8**) or 1,8-naphthalimide anion radical with diamidopyridines (**9**) are reasonably formulated as shown based on formation of hydrogen bonds facilitated by the structures of the two partners.^{80,85} These complexes feature two-point and three-point hydrogen-bonding, respectively, with the geometrical arrangement of the donor and acceptor groups being well designed for maximum interaction. Here, the structure of a hypothetical 2:1 complex is not easily imagined and no such complex was found.



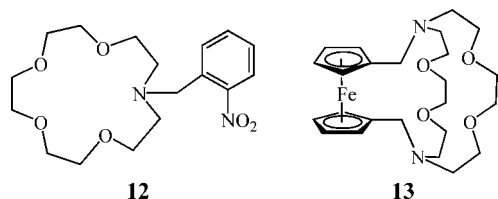
Similarly, and for analogous reasons, 1:1 complexes between the anion radicals of *p*-substituted nitrobenzenes and arylureas, **10**, are favored without detectable amounts of 2:1 or other complexes.¹⁰³ However, the dianion of 1,4-dinitrobenzene forms both a 1:1 and a 2:1 complex with diarylureas, **11**, another example of structure-directed hydrogen-bond complexation.¹⁰⁴ Nevertheless, it must be remembered that these structures are not known with certainty but are inferred from the electrochemical results and chemical experience.



A very similar situation is encountered with what have been called “redox-switchable ligands” such as **12** and **13**. These feature the crown ligands aza-15-crown-5 (**12**) and diaza-18-crown-6 (**13**) each attached to a redox center, nitrophenyl and ferrocene, respectively. For example, **12** will complex sodium ions in acetonitrile by way of its crown function.¹⁰⁵ By the same token, the ligand undergoes a reversible one-electron reduction process due to the nitrophenyl group. However, upon reduction of the ligand to form its anion radical, the affinity for sodium ions increases resulting in a ten thousand-fold increase of the formation constant. As a consequence, in the presence of less than stoichiometric amounts of sodium ion, a new reduction peak appears prior to the main peak for **12**, and this peak grows in height until one equivalent of sodium is present, after which its height is constant. Under these conditions, the overall electrode reaction is $\text{Na}^+ \cdot \mathbf{12} + e^- \rightleftharpoons \text{Na}^+ \cdot \mathbf{12}^{\cdot-}$ and, because of the relatively strong binding, only the term involving the 1:1 complexes of oxidized and reduced ligand is important in eqs 21–23, which reduce to eq 24. This equation predicts, as observed experimentally, that the new process will be displaced in the positive direction from the potential due to reduction of the free ligand.

$$E_{\text{app}}^{\circ} = E_{\text{OxRed}}^{\circ} + \frac{RT}{F} \ln \frac{\beta_{\text{Red},1}}{\beta_{\text{Ox},1}} \quad (24)$$

The opposite behavior is seen with **13** where the ligand with neutral ferrocene binds monocations quite strongly but, upon oxidation, the ferrocenium-containing ligand binds the cations more weakly resulting in a peak appearing after (more positive than) the main oxidation peak of the ligand when studied in the presence of cation (see ref 106 which also contains a review of many other “redox-switchable ligands”).



2.2. Aspects of Electron-Transfer Kinetics for One-Electron Reactions

The activity in this area has been intense and we will restrict ourselves to discussions of three areas: evidence for nonadiabatic reactions, correlations of self-exchange rate constants with solvation energies, and studies of systems with significant inner reorganization energies.

Equation 25 is based on a transition-state formalism of heterogeneous electron-transfer kinetics.¹⁰⁷ Here, k_s is the standard rate constant for the outersphere electrode reaction $\text{Ox} + e^- \rightleftharpoons \text{Red}$, κ is the electronic transmission coefficient, K_p is the equilibrium constant for the encounter complex of the reactant with the electrode, ν_n is the nuclear barrier crossing frequency, and ΔG^* is the Gibbs energy of activation for the electrode reaction. The transmission coefficient is close to unity for an adiabatic reaction and less than unity (sometimes much less than) for a nonadiabatic reaction. For adiabatic reactions, the value of $K_p\nu_n$ is 10^3 – 10^4 cm/s near room temperature.

$$k_s = \kappa K_p \nu_n \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (25)$$

The Gibbs energy of activation is in turn related to the inner (λ_i) and outer (λ_o) reorganization energies by eq 26.

$$\Delta G^* = \frac{\lambda}{4} = \frac{\lambda_i + \lambda_o}{4} \quad (26)$$

The inner reorganization energy involves internal reorganization of the reactant molecule to reach the transition state (changes in bond lengths and bond angles) while the outer reorganization energy is due to the reorganization of the solvent molecules around the reactant. The most commonly used expression for evaluating λ_o is eq 27.

$$\lambda_o = \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{a_0} - \frac{1}{R}\right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s}\right) = \frac{e^2}{8\pi\epsilon_0 a_0} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s}\right) \quad (27)$$

Here e is the elementary charge, ϵ_0 is the permittivity of free space, a_0 is the radius of the reactant (assumed spherical), R is the distance from the center of the reactant to its image charge in the electrode, ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent.¹⁰⁸ Often, the term involving the image charge is neglected giving the expression shown on the right of eq 27.

2.2.1. Measurement of Electron-Transfer Rate Constants

The measurement of the standard potential of a simple electrode reaction is relatively straightforward at least in cases where both partners in the couple are stable species. However, the measurement of the standard electron-transfer rate constant, k_s , though deceptively simple in appearance, is fraught with difficulties. For our generic reaction $\text{Ox} + e^- \rightleftharpoons \text{Red}$, the most obvious approach is to determine the difference between the anodic and cathodic peak potentials, $\Delta E_p = E_{p,a} - E_{p,c}$ which equals ~ 58 mV at 298 K (with a

slight dependence on switching potential) for the case of fully reversible behavior (very large k_s). For smaller values of k_s , ΔE_p will exceed 58 mV and its value will increase with increasing scan rate. Values of ΔE_p vs a characteristic kinetic parameter, ψ , have been tabulated^{109a} which provides a simple means for the rapid determination of k_s (eq 28).

$$\psi = \left(\frac{D_{\text{Ox}}}{D_{\text{Red}}}\right)^{\alpha/2} \frac{k_s}{\sqrt{\pi\sigma D_{\text{Ox}}}} \quad (28)$$

where D_{Ox} and D_{Red} are the diffusion coefficients and $\sigma = \nu F/RT$ where ν is the scan rate. Thus, measured values of ΔE_p can be converted to ψ values which in turn allow extraction of k_s , knowing D_{Ox} , D_{Red} , and ν .

Some restrictions apply. The method is based on the assumption that electron-transfer kinetics are described by the Butler–Volmer formalism, that α (the electron-transfer coefficient) is 0.5, the switching potential is 141 mV past the reversible $E_{1/2}$, and the temperature is 298 K.^{109a} Lack of strict adherence to most of these factors will lead to only minor errors but there is one experimental problem that can be severe: incomplete compensation of solution resistance. The theoretical results contain no effects of solution IR drop.^{109a}

Measurement error will be low at relatively low scan rates (where currents and IR errors are low) and where ΔE_p differs significantly from its reversible limit, ~ 58 mV. For example, a value of ΔE_p near 100 mV will be obtained at 1 V/s if $k_s = 0.02$ cm/s. However, the same peak separation will require 100 V/s (with possibly significant IR error due to the larger current) when $k_s = 0.20$ cm/s. Thus, careful instrumental compensation of solution resistance or proper correction during data analysis is required to obtain results uncontaminated by the effects of solution resistance. The direction of the error is always such that the apparent value of k_s is smaller than the true value. (For a discussion of resistance compensation and many other topics see ref ^{109b}).

The existence of these and other errors has cast a shadow over published measurements of k_s by cyclic voltammetry. It is clear that reliable values can be obtained using electrodes of ordinary size, with careful attention to the effects of solution resistance, for k_s values up to about 0.5–1.0 cm/s.^{98,110–112} By turning to microelectrodes, with their inherently smaller IR errors, values up to about 3 cm/s have been reported.¹¹³ In most of this work, reliance is not based entirely on ΔE_p but on simulation of the entire voltammogram, often with inclusion of residual uncompensated resistance in the simulations.

AC methods have found greater favor among researchers for the measurement of large values of k_s ^{114–116} in part because the uncompensated solution resistance can be evaluated from the experimental data themselves. Another technique is convolution potential sweep voltammetry which has also been applied to moderately fast reactions.¹¹⁷ Scanning electrochemical microscopy has been employed for the measurement of large values of k_s and recently, by use of extremely small platinum electrodes (radius: 0.4–400 nm) the range of measurements has been extended: 7.7–11.6 cm/s for ferrocene oxidation and 1.0–1.2 cm/s for reduction of TCNQ (**6**), both in acetonitrile.¹¹⁸

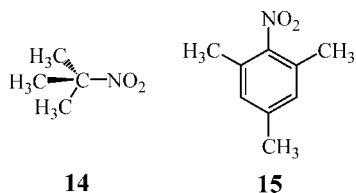
In spite of these various techniques for the accurate measurement of k_s , surveys of published values can be quite dismaying. A striking example is a survey of the literature on the determination of the rate constant for ferrocene oxidation in acetonitrile, at platinum electrodes and temper-

atures near 298 K.¹⁰⁷ The values of k_s that were reported ranged from 0.019 to 220 cm/s, over 4 orders of magnitude variation! Although there are sound reasons for rejecting the outliers, and a value around 4 cm/s was thought to be the most accurate,¹⁰⁷ this survey makes it clear that reports of large values of k_s should be considered with due circumspection.

To be fair, ferrocene oxidation is an example of a reaction with a rather large rate constant, difficult to measure accurately. In fact, there are very few simple electron transfer reactions of organic compounds that are inherently slow so that accurate measurement of k_s is usually problematic.

2.2.2. Nonadiabatic Heterogeneous Electron-Transfer Reactions

Most electron transfer reactions are thought to be adiabatic ($\kappa = 1$, eq 25). For example, the reduction reactions of 20 aromatic systems, assumed to be adiabatic, displayed k_s values from 0.4 to 5 cm/s in DMF at mercury corresponding to an average reorganization energy (the inner reorganization energy assumed to be negligible) of 15.6 kcal/mol.¹¹⁴ Nitrobenzenes and derivatives fall into this class, but the early work by Peover and Powell¹¹⁹ demonstrated that the rate constants for one-electron reduction of nitroalkanes and nitrobenzenes bearing two ortho methyl groups had k_s values ranging from 0.009 for 2-methyl-2-nitropropane (**14**) to 0.28 cm/s for nitromesitylene (**15**) in DMF at mercury with Bu₄NI as electrolyte. Numerous studies of these and other compounds followed^{98,115–117,120–122} with part of the emphasis being on the study of the potential dependence of the transfer coefficient, α .



Although k_s for **14** in acetonitrile with Et₄NClO₄ electrolyte is 0.037 cm/s (slightly on the low side), it decreases markedly to 0.0041 cm/s on going to Bu₄NClO₄ and to 6.5×10^{-4} cm/s for Hp₄NClO₄ (Hp $\equiv n$ -C₇H₁₅).^{98,112,121} Thus, increasing the size of the cation of the electrolyte results in about a 50-fold change in k_s . Even larger effects (factors >100) were seen for nitromethane, nitroethane, and 2-nitropropane. A similar marked dependence of k_s on cation size was seen for the first step of reduction of cyclooctatetraene.¹²³ Also, a weaker cation effect was seen with some 1,2-diketones.⁹⁸

The source of these cation effects on k_s of nitroalkanes cannot involve changes in the outer or inner reorganization energies as the reactant remains the same, only the cation of the electrolyte changes. Attention was focused on the preexponential factor in eq 25, in particular the value of κ . The compounds are reduced at rather negative potentials where the surface charge density on the metal of the electrode is quite high. Consequently, the surface concentration of cations is very high, a factor that is augmented by specific adsorption, at least in the case of the larger cations. If it is postulated that a dense, liquid-like film is formed on the electrode, and that the film separates the reactant from the electrode surface, then it is reasonable that the electronic coupling between the reactant and the electrode will become very weak and the reaction will become nonadiabatic, $\kappa <$

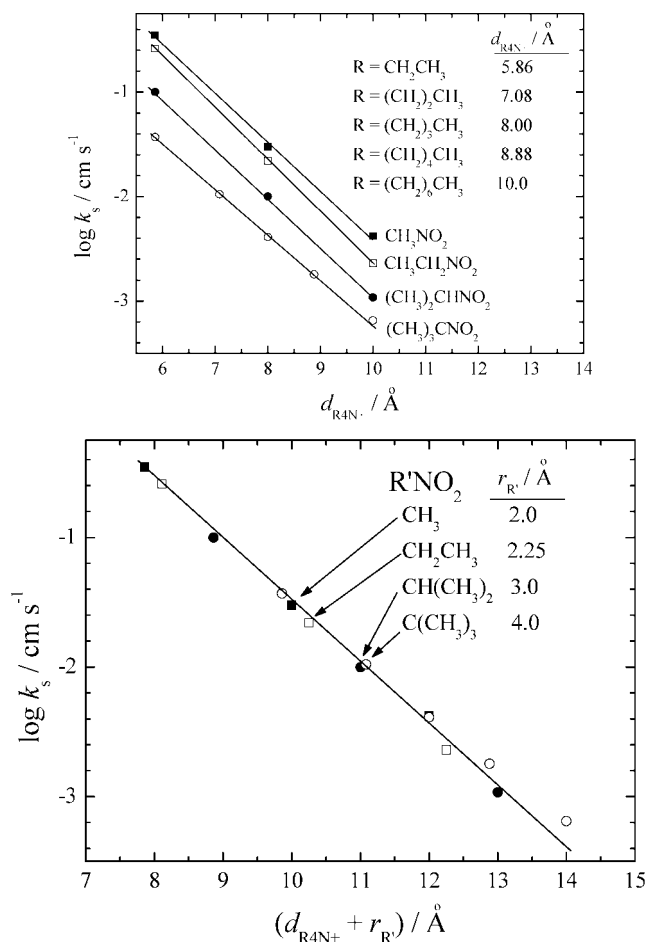


Figure 2. Standard electron-transfer rate constants for four nitroalkanes, R'NO₂, obtained in acetonitrile containing 0.10 M R₄NClO₄ at a hanging mercury drop electrode. (a) Data for different cations, R₄N⁺, of the electrolyte plotted vs the hydrodynamic diameter of R₄N⁺. (b) Data from part (a) plotted vs the sum of the hydrodynamic diameter of R₄N⁺ and the radius of R'. Reprinted with permission from Reference 116, Copyright Elsevier, 2004.

1. Studies of the temperature dependence of k_s for nitroethane with Et₄NClO₄ and Hp₄NClO₄ gave preexponential factors of 1.5×10^4 cm/s for the former but only 330 cm/s for the latter.¹¹² The result for the tetraethylammonium ion in the electrolyte is in the normal range for an adiabatic reaction but the result for tetra-*n*-heptylammonium ion is indicative of significant nonadiabatic character.

Another way of expressing the same idea is to consider the distance required for electron tunneling from the electrode to the reactant situated at a distance approximately equal to the diameter of the cation of the electrolyte. The rate constant is expected to decrease exponentially with tunneling distance¹²⁴ and Figure 2a shows plots of $\log k_s$ vs the diameter of the cation for all four nitroalkanes.¹¹⁶ Linear relationships are found and the slope gives an average inverse exponential decay constant of 0.93 \AA^{-1} , close to values seen in other electron tunneling problems.

The same behavior and explanation was offered by Fawcett et al.¹²⁵ for the reduction of **15** in propylene carbonate and by Fawcett and Fedurco¹²⁶ for benzophenone (**4**) in acetonitrile with various tetraalkylammonium salts.

Not explained in the data of the Figure 2a, is the significant difference in k_s , for any given electrolyte, for the four nitroalkanes, with the values being largest for nitromethane and smallest for 2-methyl-2-nitropropane. Part of this dif-

ference could also be a change in tunneling distance with the average distance from the electrode surface of the nitro group (the electron acceptor) of the tumbling molecules of the larger alkanes being larger than for the smaller alkanes. This effect is illustrated in Figure 2b, where a distance, designated as r_R' , has been added to the diameter of the electrolyte cation such as to bring all of the points to a single line. These values of r_R' are reasonably close to the radii of the alkyl groups in the nitroalkanes suggesting that at least part of the effect of the structure of the nitroalkane on k_s may be due to this distance effect.¹¹⁶ However, it should be noted that the smallest distance from electrode to the nitro group will be largely independent of the size of R' and, since rotational diffusion of small molecules is fast, such an effect on the rate constant is likely to be small. Hamman et al.¹²⁷ found that electron-transfer rate constants for $[\text{Os}(\text{R}_2\text{bpy})_3]^{3+/2+}$ ($\text{R}_2\text{bpy} = 4,4'$ -dialkyl-2,2'-bipyridyl) were quite sensitive to the size of R , being about fifty times smaller for $R = \text{tert-C}_4\text{H}_9$ than for $R = \text{CH}_3$, an effect again attributed to an increase in the electron-transfer distance. In this case, however, the symmetrical nature of the reactant means that the metal center is situated farther from the electrode for $\text{tert-C}_4\text{H}_9$ compared to CH_3 irrespective of reactant orientation.

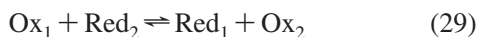
However, it is also true that calculated values of the inner reorganization energy are larger for 2-methyl-2-nitropropane compared to nitromethane, so this factor also contributes to the differences in k_s among the nitroalkanes (see section 2.2.4).

Nonadiabatic electron transfer and distance effects have been more definitively demonstrated for redox molecules attached to gold surfaces by variable length organized thiol monolayers.¹²⁸ Nevertheless, it is interesting that identical effects were detected at an early date with unattached spacers (tetraalkylammonium ions) and diffusing reactants, as discussed above.

2.2.3. Correlation of Self-Exchange Rate Constants with Solvation Energies

As stated earlier, most electron-transfer reactions are thought to be adiabatic or nearly so. In such cases, variation of the rate constant from one system to another can be traced to changes in the reorganization energies and often the reorganization energy is dominated by the outer reorganization, the changes in the internal structure of the reactant being of a minor nature.

The rate constants of self-exchange reactions can be measured by a number of techniques including line broadening in electron paramagnetic resonance spectroscopy experiments. Such a reaction is shown as reaction 29 (in which the subscript is an index to distinguish the two molecules that are involved) and the



outer reorganization energy is given by eq 30 where a_o is the common radius of Ox and Red and d is the distance between Ox and Red when electron transfer

$$\lambda_0 = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{a_o} - \frac{1}{d} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) = \frac{e^2}{8\pi\epsilon_0 a_o} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \quad (30)$$

occurs ($d = 2a_o$).¹⁰⁸ It is important to recognize that in this case reorganization of solvent around two molecules is considered, not just one molecule as in the electrode reaction.

It has been known for some time that there exists a good linear correlation between $\log k_{\text{ex}}$ and the solvation energy of the anion for Ox being neutral and Red being an anion radical.²⁷ The following will rationalize that behavior and provide a prediction for the slope of such plots.

The Born equation for the Gibbs energy of solvation of the anion is given by eq 30.^{129a} This is known to be an inadequate expression for the solvation energy^{129b}

$$\Delta G_{\text{solv}}^\circ = -\frac{e^2}{8\pi\epsilon_0 a_o} \left(1 - \frac{1}{\epsilon_s} \right) \quad (31)$$

but it is based on the same approach used for derivation of λ_0 and it is possible that some cancelation of the limitations will occur when eq 31 is combined with eq 30 to give eq 32 where the factor of 2 arises because λ_0 includes contributions from reorganization of two reactant molecules.

$$\lambda_0 = -2\Delta G_{\text{solv}}^\circ \left(\frac{\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s}}{1 - \frac{1}{\epsilon_s}} \right) \quad (32)$$

Now we write the expression for the rate constant (where Z_{ex} is the preexponential factor).

$$k_{\text{ex}} = Z_{\text{ex}} \exp\left(-\frac{\lambda_0}{4RT}\right) = Z_{\text{ex}} \exp\left(-\frac{2\Delta G_{\text{solv}}^\circ}{4RT}\right) \left(\frac{\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s}}{1 - \frac{1}{\epsilon_s}} \right) \quad (33)$$

$$\log k_{\text{ex}} = \log Z_{\text{ex}} + \frac{2\Delta G_{\text{solv}}^\circ}{2.303(4RT)} \left(\frac{\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s}}{1 - \frac{1}{\epsilon_s}} \right) = \log Z_{\text{ex}} + 0.174\Delta G_{\text{solv}}^\circ \quad (34)$$

The predicted slope of the plot of $\log k_{\text{ex}}$ vs $\Delta G_{\text{solv}}^\circ$, 0.174 (kcal/mol)⁻¹, pertains to the dielectric properties of DMF and 298 K. The validity of this treatment depends on Z_{ex} being constant for the compounds being studied and the inner reorganization energy being negligible, i.e., $\lambda = \lambda_o$.

Data for 16 aromatic neutral/anion radical reactions are presented in Figure 3, where the data from ref²⁷ have been augmented by later sources.¹³⁰⁻¹³² The solvation energies are $\Delta\Delta G_{\text{solv}}^\circ = \Delta G_{\text{solv,Red}}^\circ - \Delta G_{\text{solv,Ox}}^\circ$ where the solvation Gibbs energy of the neutral has been considered to be negligible compared to that of the anion radical. Linear regression gives 0.153 (kcal/mol)⁻¹ for the slope with a standard deviation of 0.015 (kcal/mol)⁻¹. This result is 12% lower than the prediction of eq 34 which appears to be reasonable agreement in view of the approximations required in the derivation.

This treatment provides a simple conceptual link between measured self-exchange rate constants and measured solvation energies which should be of value in the consideration of the factors at work in governing the rates of solution-phase electron-transfer reactions.

Another interesting example of solution-phase electron-transfer rate measurements can be found in the study of cross reactions involving mainly the neutral/ cation couples of hydrazines but numerous other redox species as well.¹³³⁻¹³⁶ The cross reaction between the A and B systems is

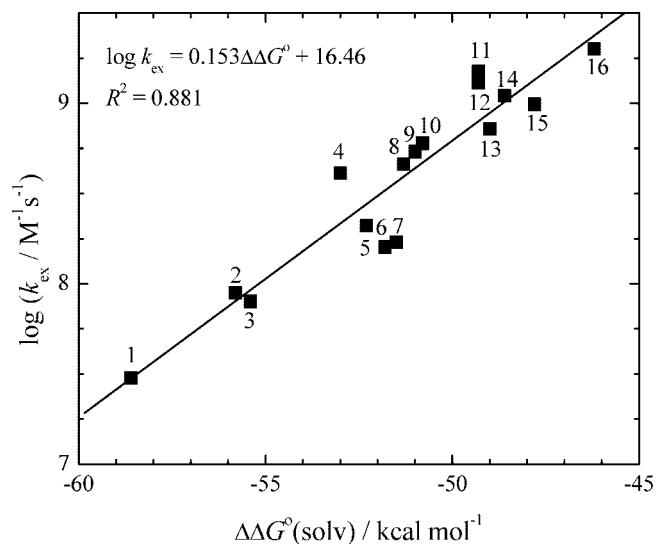


Figure 3. Logarithm of the self-exchange rate constant vs the difference in Gibbs energy of solvation of anion radical and neutral for 16 reactions of aromatic compounds in DMF. Compounds: **1**: nitrobenzene; **2**: 3-chloronitrobenzene; **3**: 4-chloronitrobenzene; **4**: 1,4-benzoquinone; **5**: benzophenone; **6**: 3,5-dichloronitrobenzene; **7**: 3-cyanonitrobenzene; **8**: 1,4-naphthoquinone; **9**: 9,10-anthraquinone; **10**: 1,3-dinitrobenzene; **11**: anthracene; **12**: 1,4-diacetylbenzene; **13**: 1,4-dinitrobenzene; **14**: 9,10-diphenylanthracene; **15**: 1,2-dicyanobenzene; **16**: 1,4-dicyanobenzene.



The couples are chosen such that reaction 35 proceeds left-to-right and the rate constant is determined by appropriate means, mainly stopped-flow techniques for fast reactions. The expression for the cross reaction rate constant is¹³⁴

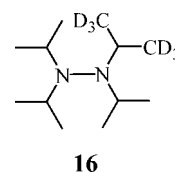
$$k_{AB} = \sqrt{k_{AA}k_{BB}K_{AB}f_{AB}} \quad (36)$$

$$\ln f_{AB} = \frac{(\ln K_{AB})^2}{4 \ln(k_{AA}k_{BB}/Z^2)} \quad (37)$$

Here k_{AB} is the forward rate constant of reaction 35, k_{AA} and k_{BB} are the self-exchange rate constants for the A and B couples, respectively, K_{AB} is the equilibrium constant of reaction 35 and Z is the preexponential factor. Equations 36 and 37 afford a relatively simple means of computing the self-exchange rate constant of couple A, k_{AA} , knowing k_{BB} and K_{AB} . The last quantity can be obtained from the standard potentials of the A and B couples. By studying the A couple in cross reactions with various B, it is possible to find values of k_{AA} that provide the best fit to the above relationships. A total of 72 couples were analyzed on the basis of 206 cross reactions to provide values of k_{AA} ranging from 4.5×10^{-4} to $1.6 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$.¹³⁶

Equations 36 and 37 require that the cross reactions be adiabatic electron transfers but most of those studied are clearly nonadiabatic so the success of the application to predict k_{AA} values is surprising. Yet the correlations provide $k_{AA} = 2.7 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ for tetraisopropylhydrazine which is identical to the experimental value, $3.0 (\pm 0.3) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, measured directly by NMR through loss of the deuterium label in the neutral by equilibration of **16** with unlabeled cation.¹³⁷ The very small self-exchange rate constant is presumably associated with a substantial inner reorganization energy combined with a high degree of nonadiabaticity due to weak overlap between the reactants that possess bulky isopropyl substituents. After this brief

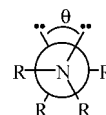
foray into solution-phase electron-transfer reactions, we will return to the kinetics of electrode reactions.



2.2.4. Electrode Reactions with Significant Inner Reorganization Energies

As mentioned earlier, the majority of organic electrode reactions that have been studied feature reorganization energies that are dominated by the outer reorganization energy. The inner reorganization energy is of minor importance because of the relatively small changes in bond lengths and angles that occur upon oxidation or reduction of the compound. This is particularly true of aromatic systems and there has been a natural bias favoring the study of such reactions as they usually react at moderate potentials that are well separated from the background discharge.

The tetraalkylhydrazines are prime examples of systems with significant inner reorganization energies. The most important contributor to the inner reorganization energy is the change in the lone pair-lone pair dihedral angle, θ . The nitrogen atoms are significantly pyramidal and a value of θ near 90° is preferred in the neutral hydrazines.



However, removal of an electron to form the cation results in a three-electron π bond between the nitrogens, a closing of θ toward 0° (or 180°) and flattening at the nitrogens. This expectation of $\theta \sim 90^\circ$ is approximately realized for $R = \text{alkyl}$.¹³⁵ The measured activation energy for self-exchange in these compounds is 17–22 kcal/mol.

The reversibility of the electrode reactions for hydrazine oxidation is strongly dependent on the composition of the working electrode, with $k_{s,\text{app}}$ increasing in the order glassy carbon < platinum < gold < mercury for 1,1-dimethyl-2,2-dibenzylhydrazine in acetonitrile.¹³⁸ Such differences suggest that the reactions are not true outer-sphere processes at some of the surfaces and that some specific interaction with reactants and the electrode surface is occurring. Thus, there is not likely to be a simple relationship between $k_{s,\text{app}}$ and the reorganization energy, which has a large inner component in these compounds.

Nevertheless, studies of tetraisopropylhydrazine, **16** (undeuterated), and tetracyclohexylhydrazine at gold electrodes in acetonitrile did show quasireversible behavior with apparent k_s values in the range of 0.02–0.10 at 298 K¹³⁹ certainly not unusually small as would be expected for a reaction with a large reorganization energy.

Up to this point, we have considered electron transfer reactions to occur in a single step, characterized by a value of k_s and α , the electron transfer coefficient. Thus, any internal reorganization that is required occurs in the same step as the electron transfer. This is not to say that the electron transfer and the changes in nuclear coordinates occur simultaneously for this would violate the Franck–Condon

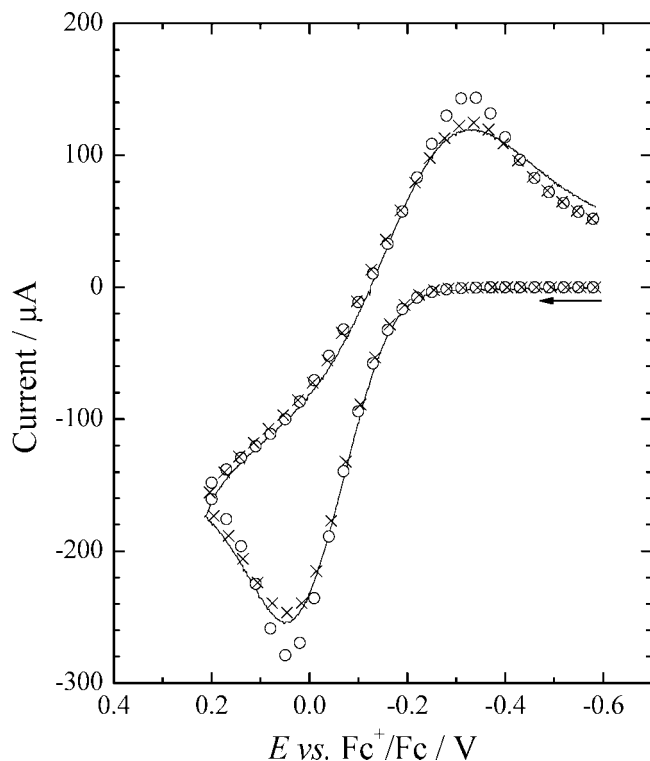


Figure 4. Background-corrected cyclic voltammogram (full curve) of 0.99 mM **16** (undeuterated) at a gold electrode in 0.10 M Bu₄NPF₆/acetonitrile. 15 °C and 20 V/s. Simulations: (O) one-step mechanism; (X) two-step mechanism. See ref 139 for simulation parameters. Reprinted with permission from ref 139, Copyright Elsevier (2000).

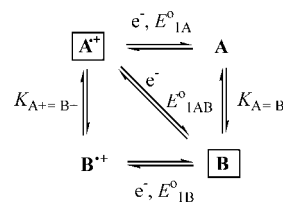
principle. Rather, changes in nuclear coordinates occur to reach the transition state for electron transfer and after electron transfer the product relaxes to its preferred structure. So in this sense, the electron transfer and the structural change are concerted.

With this in mind, attempts were made to fit the electrochemical results for solutions of **16**, tetracyclohexylhydrazine and their corresponding radical cation salts (which can be isolated for these two hydrazines) according to this concerted one-step mechanism. A typical voltammogram is shown in Figure 4 for **16** at 15 °C and 20 V/s (full curve) along with a simulation for the one-step mechanism (open circles).¹³⁹ The simulation is based on the best-fit parameter values from simulations for scan rates from 0.2 to 40 V/s. Clearly, the best-fit simulation shows significant deviations from experiment. Similar failings were noted for five other temperatures from -15 to +50 °C.

Concluding that the one-step mechanism cannot account for the data, a two-step mechanism was considered. In such a mechanism, most of the structural change occurs in a separate chemical step (conformational change) before and/or after the electron transfer. The simplest version of such a mechanism is the square scheme as shown in general form in Scheme 1.

For the case under consideration, A^{•+} and B^{•+} correspond to two different conformations of the cation radical with A^{•+} being the dominant form. Similarly, A and B are two different conformations of the neutral hydrazine with B being the dominant form. Also indicated are equilibrium constants connecting the various forms. The corresponding rate constants are not shown. Electron transfer involving conformations of similar structure are shown by the upper and

Scheme 1



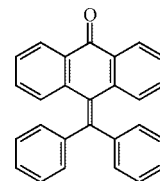
lower horizontal reactions. The one-step reaction, which cannot explain the results (Figure 4), is shown as the diagonal. It connects B to A^{•+}, structural change and electron transfer in a single step.

Simulation according to square scheme 1 afforded an improved fit of the experimental data (X in Figure 4). Furthermore, the same set of simulation parameter values was found to fit adequately all scan rates from 0.2 to 40 V/s. Similar agreement was found for five other temperatures and for studies of solutions of the cation radical salt of **16**. The only serious breakdown was the fact that the electron transfer rate constants required to fit the data of the cation radical were significantly smaller than those used for the neutral hydrazine. A similarly successful analysis was obtained for tetracyclohexylhydrazine and its cation radical.¹³⁹

Thus, in this case a reaction with a known large inner reorganization energy does not occur via a concerted pathway, but rather follows a two-step mechanism with electron transfer both following and preceding the structural change. The square scheme is probably too simple to account fully for the behavior of these compounds. Computational studies¹³⁸ of **16** reveal that there are two conformations within 2.2 kcal/mol of the lowest energy conformation. Although this energy difference is approximately what was assumed in the simulations,¹³⁹ the square scheme includes not three, but only two forms of the neutral hydrazine.

Thus, the effects of large inner reorganization energies for the hydrazines are not seen directly. Rather, there is a change of mechanism such that the structural reorganization occurs as a chemical step preceding or following electron transfer.

A similar behavior was found for **17**, 10-diphenylmethyleneanthrone.^{140,141}



17

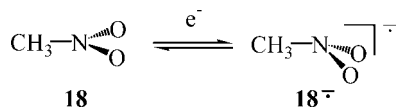
This molecule undergoes a quasireversible one-electron reduction, and Scheme 1 was found to accommodate the data adequately (with A^{•+} and B^{•+} replaced by A and B; A and B replaced by A^{•-} and B^{•-}). A calculational search found only two different forms of the neutral and anion radical indicating that the square scheme should be an adequate description of the reaction. In this case, like the hydrazines, calculations show that the reorganization energy on going from the preferred form of the neutral, A, to the more stable form of the anion radical, B^{•-}, would be very large, possibly explaining the quasireversible nature of the reaction. However, simulations according to the one-step reaction (diagonal of Scheme 1) failed to account for the voltammetric data and simulations according to the two-step square scheme were required. So, once again, the system responds to a high inner

reorganization energy, not by following the one-step mechanism with a very small rate constant, but by proceeding by the kinetically favorable two-step square scheme.

Another example of a one-electron oxidation following the square scheme is the oxidation of $W(\eta^5-C_5(CH_3)_5)(CH_3)_4$, which adopts two structures, a square-pyramidal (SP) structure along with a pseudo trigonal bipyramid (TBP). Oxidation proceeds from the favored square-pyramidal neutral compound to a cation of similar structure (SP \rightarrow SP $^+$) followed by rapid isomerization to the favored form of the cation, the pseudo trigonal bipyramid structure (SP $^+$ \rightarrow TBP $^+$).¹⁴² Again, the reaction does not occur by the diagonal reaction, concerted electron transfer and structural change, because the reorganization energy for the diagonal reaction is so large that its overpotential is large enough that the initial electron transfer enters the square scheme instead.

One must proceed to systems in which there are no conceivable intermediates on the pathway from reactants to products to be certain that the reactions proceed by concerted electron-transfer and structural change, rather than by a two-step pathway with a well-defined chemical intermediate. The reductions of nitroalkanes, of which **14** and nitromethane, **18**, are examples, will illustrate the point.

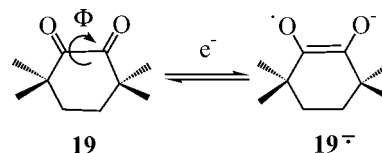
The nitro group is strictly planar in the neutral compounds but significant pyramidalization occurs upon formation of the anion radical.^{116,141} Furthermore, this change in geometry, along with other smaller structural changes, result in large calculated (DFT) inner reorganizations for nitromethane (16.6 kcal/mol) and these increase significantly as the alkyl group increases in size reaching 19.9 kcal/mol for **14**. This is sufficient to explain the differences in k_s between **14** and **18** but caution must be exercised as these are calculated reorganization energies. More importantly, examination of the normal modes of vibration of both **18** and **18 $^{\cdot-}$** shows that there is a prominent out-of-plane bending mode in each so that the molecule is able to reach the transition state for electron transfer through its vibrations and thus is likely to undergo a one-step electron transfer with structural change being concerted with electron transfer.



Another example of reactions with substantial structural changes are alkyl radical/anion couples. For example, both the benzyl radical and benzyl anion are found to be planar species contrasted with *n*-butyl radical (planar at the radical center) and *n*-butyl anion (pyramidal).¹⁴³ This is one of the reasons that the measured reorganization energy for the former reaction is 20 ± 5 kcal/mol, whereas it is much larger, 50 ± 10 kcal/mol, for the purely aliphatic system. Again, it is likely that specific vibrational modes are available to bring reactants to the transition state for electron transfer without the possibility of a chemical intermediate.

A somewhat more complex example is found with cyclohexane-1,2-dione, **19**. Here calculations show that there is a substantial change in the O–C–C–O dihedral angle, ϕ , upon reduction.^{141,144} The angle changes from about 60° in the neutral diketone to around 5° in the anion radical. In this case there is a significant difference in the measured values of k_s which can be traced to the contribution of this structural change to a significant inner reorganization energy, though calculations for **19** and its five-, seven-, and eight-membered ring analogs do not produce changes in inner reorganization energies that are quite large enough to explain

the trend for the four compounds. More importantly, however, vibrational analysis again reveals that **19** is vibrationally competent to reach a reasonable transition state suggesting that the electron transfer is again a one-step process.

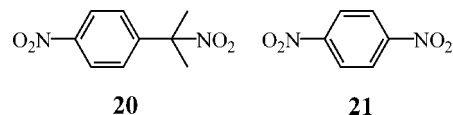


Another example of a reaction with a significant inner reorganization energy is the reduction of disulfides in which the anion radical has a substantially elongated sulfur–sulfur bond.^{145–147} In other cases, such as the tetraalkylhydrazines, simple means of obtaining theoretical inner reorganization energies have been introduced.^{134,136,148} For these systems, the inner reorganization energies are large. Attention has also been directed to the calculation of the smaller reorganization energies associated with aromatic systems.^{149–155} In some cases, larger inner reorganization energies are inferred from the structural changes determined experimentally.¹⁵⁶

Other systems with real or apparent large inner reorganization energies are encountered in two-electron reactions, particularly in the case of potential inversion as described later in section 3.

3. Two-Electron Reactions

As mentioned earlier, a given molecule can accept not one but two electrons depending on the molecular structure and the functional groups that are present. For example, there can be two different functional groups that will give rise to reduction steps occurring at two resolvable potentials as in α,p -dinitrocumene, **20**,¹⁵⁷ which contains two different kinds of electroactive nitro groups. By contrast, the nitro groups in **21** are equivalent so that one might expect that each would be reduced at the same potential. This is definitely not the case as we shall see in the next section. For molecules of appropriate structure, the insertion (or removal) of three-, four-, five-, or six-electrons can be detected. An example, would be the stepwise six-electron reduction¹⁵⁸ of C_{60} and C_{70} or the six-(or more) electron reduction of certain polyoxometalate anions.¹⁵⁹



3.1. Difference in Standard Potentials

Our focus will be upon two-electron reactions in those cases, like **21**, which contain two identical electrophores or are otherwise symmetric species. A class of molecules of fundamental significance is the aromatic hydrocarbons, A, whose reduction reactions are given by reactions 38 and 39.



In cases where the reversible standard potentials have been measured, it is found that E°_2 is ca. 0.5–0.8 V more negative than E°_1 . This is easily understood as an electrostatic effect reflecting the fact that it is more difficult to insert an electron into the negatively charged anion radical than it is to reduce

the neutral molecule. In fact, the difference in standard potentials is expected to be 4–5 V when gas-phase species are considered. This large effect, originally termed the electron-repulsion energy,¹⁶⁰ was predicted quite some time ago based on simple molecular orbital calculations.¹²³ Kubota et al.¹⁶¹ used CNDO/2 calculations for the same purpose and Evans and Hu¹⁶² applied the AM1 semiempirical method to aromatic hydrocarbons and a number of other systems, including **21** for which the gas-phase difference in potentials was found to be 4.59 V.

It has long been recognized that solvation energies tend to compress these large gas-phase potential differences to the much smaller values seen in solution with the effect being accounted for with moderate success by Born solvation energies (see section 2.2.3). The effect of solvation is most easily seen in the energetics of disproportionation reaction 40, whose equilibrium constant and standard Gibbs energy change are related to the difference in standard potentials through eq 41.



$$\ln K_{\text{disp}} = -\frac{\Delta G^{\circ}_{\text{disp}}}{RT} = -\frac{F}{RT}(E^{\circ}_1 - E^{\circ}_2) \quad (41)$$

For the cases just discussed, $E^{\circ}_1 - E^{\circ}_2 \sim +4-5$ V in the gas phase, becoming +0.5 to 0.8 V in solution. Each of these values corresponds to a disfavored disproportionation reaction ($K_{\text{disp}} < 1$) but the reaction is less disfavored in solution. This is caused by the fact that the solvation energy of ions depends approximately on the square of the charge number so that the solvation energy of the dianion is four times that of the anion radical and the solvation energy of the neutral is quite small and can be neglected. Therefore, even the primitive Born model predicts the direction and approximate degree of potential compression on going from the gas phase to solution.

Recently, more powerful theoretical methods (DFT, B3LYP, and 6-311+G*) have been applied for the calculation of the energies of the three species in the disproportionation reaction and the solvation energies have been evaluated using the polarized continuum model (PCM).^{163,164} The calculations also included ion pairing between the cation of the supporting electrolyte and A^{2-} and this effect, though significant, was far less important than the solvation energies. A particularly striking illustration of these effects may be seen in Figure 5.¹⁶³ Here, the hypothetical gas-phase voltammogram for anthracene, **3**, is shown (curve B) based on the calculated potential difference, $E^{\circ}_1 - E^{\circ}_2 = 4.187$ V. The addition of the solvation energies brings the separation down to 0.876 V (curve C) and the ion-pairing effect reduces it by another 42 mV to 0.834 V (curve D). Figure 5 illustrates the main point of the paper in a vivid fashion: ~98% of the potential compression on going from gas phase to solution is due to solvation with ion pairing playing a minor role.¹⁶³ The work has been extended to other cations of the supporting electrolyte¹⁶⁴ and the conclusions are similar.

Very similar conclusions were drawn by Macías-Ruvalcaba and Evans, who found the experimental $E^{\circ}_1 - E^{\circ}_2$ for solvation only (no ion-pairing; infinite dilution value) and compared it with DFT-computed gas-phase $E^{\circ}_1 - E^{\circ}_2$ for 1,4-dinitrobenzene, **21**, and 2,5-dimethyl-1,4-dinitrobenzene, **22**.⁶⁴ Similar studies with 7,7,8,8-tetracyanoquinodimethane, **6**, found negligible ion pairing between its dianion and tetramethylammonium ion in acetonitrile.⁶²

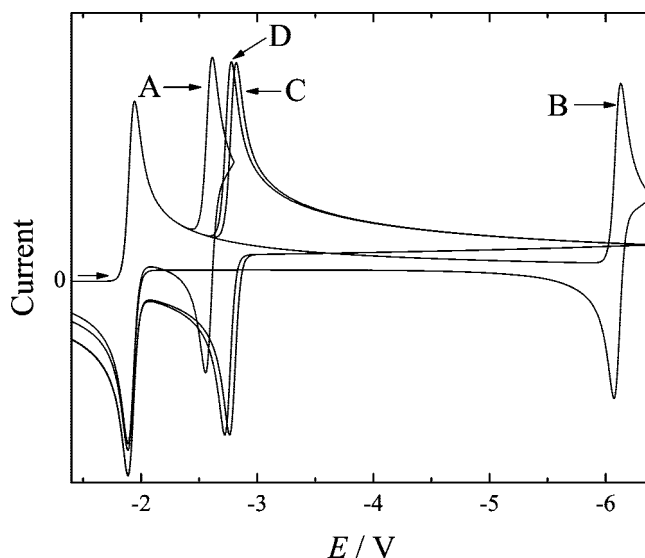


Figure 5. ¹⁶³ Cyclic voltammograms of anthracene, **3**. (A) Experimental voltammogram for *N,N*-dimethylformamide with 0.10 M tetraethylammonium iodide at 284 K ($E^{\circ}_1 = -1.915$ V; $E^{\circ}_2 = -2.585$ V vs SCE (aq)). (B) Hypothetical voltammogram in absence of solvent, $E^{\circ}_2 = -6.102$ V. (C) Computed voltammogram in solution without electrolyte (no ion-pairing), $E^{\circ}_2 = -2.791$ V. (D) Computed voltammogram in solution with 0.10 M tetraethylammonium ion, $E^{\circ}_2 = -2.749$ V. Reprinted with permission from ref.¹⁶³ Copyright Elsevier, 2005.

3.1.1. Normal Ordering of Potentials


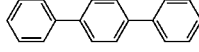

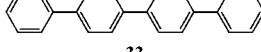
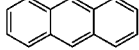
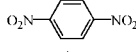
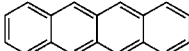
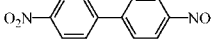
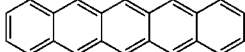
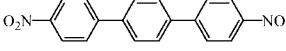
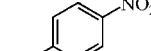
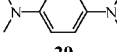
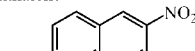
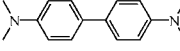
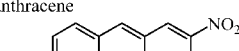
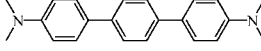
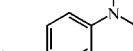

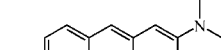
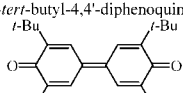

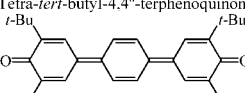
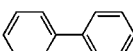
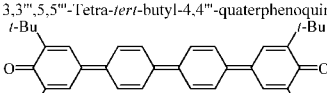
The situation in which $E^{\circ}_1 - E^{\circ}_2$ is positive (for reductions) or negative (for oxidations) has been called normal ordering of potentials¹⁶² which state of affairs is characterized by the addition or removal of the second electron occurring with more difficulty than the first. As can be seen with the example of anthracene, where $E^{\circ}_1 - E^{\circ}_2 = 0.834$ in DMF, the aromatic hydrocarbons feature a rather large difference in standard potentials. Other examples are given in Table 2, compounds **3** and **23–26**, benzene through pentacene. These linearly benzannulated aromatic hydrocarbons have large values of $E^{\circ}_1 - E^{\circ}_2$ that decrease about 0.5 V along the series. This decrease is due to a substantial decrease in the gas-phase Gibbs energy of disproportionation brought about by the increasing size of the molecules (electron repulsion energy: the electrons are confined in larger boxes)^{160,162,164} that is partially offset by decreases in the solvation energy (equation 31). This behavior is expected for those cases in which the charge on the anion radical and dianion is largely delocalized over the molecule. A similar trend is seen for polyphenyls, **22**, **31–33** (Table 2).

Somewhat different behavior is seen for conjugated systems containing two identical electrophores. Here, the charge in the ion radical is still largely delocalized but for the doubly charged ion the charge tends to be localized on the electroactive groups.

This tendency, first discussed by Hapiot et al.¹⁷⁸ in connection with the two-electron reactions of some carotenoids, is illustrated for the diions of **28**, **30**, and **35**.

As shown there¹⁷⁸ with a simple argument based on the Born model of solvation, for any effective radius of the localized charge, r_{loc} (the electrophoric group), that is smaller than the radius of the delocalized charge, r_{deloc} (the entire molecule), there will be a larger net solvation energy term that will lead to stronger compression of standard potentials or even potential inversion.¹⁷⁸ Thus, in Table 2, for **24**

Table 2. Difference in Standard Potentials^a

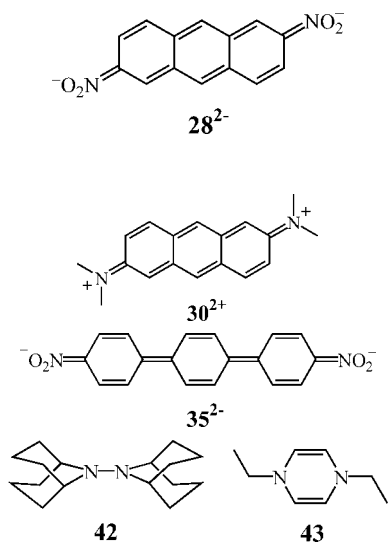
Compound	$E^{\circ}_1 - E^{\circ}_2 / \text{V}$, experimental (calculated)	Reference ^c	Compound	$E^{\circ}_1 - E^{\circ}_2 / \text{V}$, experimental (calculated)	Reference ^c
Benzene  23	(1.065)	164	<i>p</i> -Terphenyl  32	0.30	165
Naphthalene  24	(0.990)	164	<i>p</i> -Quaterphenyl  33	0.175	165
Anthracene  3	(0.876) 0.755 0.74 0.68 0.60	164 161 167 166 165	1,4-Dinitrobenzene  21	0.332	64
Tetracene  25	0.65 0.66 0.60	161 167 165	4,4'-Dinitrobiphenyl  34	0.067	168
Pentacene  26	0.585	161	4,4''-Dinitroterphenyl  35	-0 (?)	171
1,4-Dinitrobenzene  21	0.332	64	1,4-bis(Dimethylamino)benzene  29	-0.60	169
2,6-Dinitronaphthalene  27	0.199	168	4,4'-bis(Dimethylamino)biphenyl  36	-0.195	172
2,6-Dinitroanthracene  28	0.137	168	4,4''-bis(Dimethylamino)terphenyl  37	-0 ^b	173
1,4-bis(Dimethylamino)benzene  29	-0.60	169	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone  38	0.78	174
2,6-bis(Dimethylamino)anthracene  30	-0.13	170	3,3',5,5'-Tetra- <i>tert</i> -butyl-4,4'-diphenylquinone  39	0.37 0.494	175 176
Benzene  23	(1.065)	164	3,3'',5,5''-Tetra- <i>tert</i> -butyl-4,4''-terphenylquinone  40	0.227	176
Biphenyl  31	0.50	165	3,3''',5,5''''-Tetra- <i>tert</i> -butyl-4,4''''-quaterphenylquinone ^d  41	0.080	177

^a Neutral/anion radical (E°_1) and anion radical/dianion (E°_2) couples except for **29**, **30**, **36**, and **37** which are for cation radical/neutral (E°_1) and dication/cation radical (E°_2) couples. ^b Potentiometric titration in aqueous solution (pH = 1.8) produces a single, two-electron titration curve. ^c Reference and experimental conditions: 64: DMF, 0.10 M Bu₄NPF₆, 298 K. 161: DMF, 0.10 M Pr₄NClO₄, 298 K. 164: Calculated (not experimental), acetonitrile, no electrolyte, 298 K. 165: Dimethylamine solvent, 0.10 M Bu₄NBr, Range: 233 to 213 K. 166: DMF, Et₄NI, 284 K. 167: DMF, 0.008 M Me₄NI, 263 K. 168: DMF, 0.10 M Bu₄NPF₆, 298 K. 169: Acetonitrile, 0.10 M Bu₄NPF₆, 295 K. 170: CH₂Cl₂, 0.50 M Bu₄NPF₆, 294 K. 171: DMF, Bu₄NClO₄, Temperature: not specified. 172: Conditions not specified. 173: Aqueous, pH 1.8, 293 K. 174: Acetonitrile, 0.10 M Bu₄NPF₆, 298 K. 175: Acetonitrile, 0.10 M Bu₄NBF₄, room temperature. 176: Pyridine, 0.10 M Bu₄NPF₆, room temperature. 177: Pyridine, 0.10 M Bu₄NBF₄, Temperature: not specified. ^d Interestingly, **41** exists in a thermal equilibrium between a diradical and the quinoid structure shown.¹⁷⁷

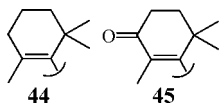
(delocalized charge on ions), one finds $E^{\circ}_1 - E^{\circ}_2$ averaging about 0.7 V, whereas for **28** (localized charge on dianion), there is a significant decrease of $E^{\circ}_1 - E^{\circ}_2$ to 0.14 V (decrease of 13 kcal/mol). Similar changes are seen in the

bis(dimethylamino) compounds (**29**, **30**, **36**, and **37**), dinitropolyphenyls (**21**, **34**, and **35**) and polyphenoquinones (**38**–**41**).

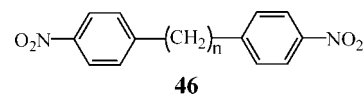
Thus, for species with two identical electrophores, the size of the molecule and degree of localization of charge in the diion, are two of the most important factors governing $E_1^\circ - E_2^\circ$, as illustrated by $E_1^\circ - E_2^\circ = 1.19$ V for oxidation of **42**¹⁷⁹ and 1.06 V for **43**.¹⁸⁰ The charges on the dication of the former are formally located on adjacent nitrogen atoms whereas they are separated by a slightly larger distance in **43**.¹⁸¹ It would be interesting to be able to obtain the standard potentials for $O_2/O_2^{\cdot-}$ and the $O_2^{\cdot-}/O_2^{2-}$ couples, where the charge is unquestionably localized on only two atoms. However, the second step of reduction of dioxygen is always irreversible.¹⁰¹



At the other extreme, certain carotenoids¹⁷⁸ have electrophores (**44** and **45**) that are separated by 18-carbon polyene or monoene-polyene chains and, in the cases where charge localization in the doubly charged ions is predicted, the compression in potentials is so strong that potential inversion results. A significant feature of these results is the ability to explain, based on the solvation argument given above, the fact that the same compound shows inversion in, say, the reduction potentials but does not have potential inversion upon oxidation.¹⁷⁸



The molecules discussed so far feature electrophores that are formally conjugated with one another along with a certain degree of rigidity. Conjugation can be removed by use of a polymethylene chain as in **46**. Here each nitrophenyl group acts independently of the other, that is, the charge on the ions is localized on the nitrophenyl groups. As there is no conjugative interaction, the values of $E_1^\circ - E_2^\circ$ fall off rapidly with increasing n : 72.4 mV for $n = 1$; 63.2 mV for $n = 2$; 38.4 mV for $n = 3$ and 41.2 mV for $n = 4$, all at 20 °C in DMF. As the electrophores are identical, in the limit of no interaction (large n), $E_1^\circ - E_2^\circ$ approaches the statistical limit of $(RT/F)\ln 4$ or 35.0 mV at 20 °C.¹⁸² Note that the case of $n = 0$ (4,4'-dintriobiphenyl, **34**) is not a member of this same family as some conjugation has been restored. In cases where a conjugated linker is present, the $(RT/F)\ln 4$ limit does not apply and values of $E_1^\circ - E_2^\circ$ less than this amount can be encountered. Even potential inversion can occur as with the carotenoids.¹⁷⁸



3.1.2. Medium Effects on Normal Ordering of Potentials

We consider again reduction reactions 38 and 39.



The equation relating the standard potential and free energies of gas-phase species in a redox reaction along with the solvation energies is eq 11, which has been extended

$$FE_{\text{Ox/Red}}^\circ \text{ (S) vs NHE (aq)} = -\Delta G_a^\circ + (\Delta G_{\text{solv,Ox}}^\circ - \Delta G_{\text{solv,Red}}^\circ) - 4.44 \text{ eV} \quad (11)$$

to include Gibbs energy changes due to ion pairing, $\Delta G_{\text{ip,Ox,CA(S)}}^\circ$ and $\Delta G_{\text{ip,Red,CA(S)}}^\circ$. S refers to the specific solvent being considered and CA is the electrolyte, C^+A^- .

Equation 11 can be applied to reactions 38 and 39 to obtain $E_1^\circ - E_2^\circ$ (eq 42).

$$E_1^\circ - E_2^\circ = \frac{1}{F} [(\Delta G_{\text{A(g)}}^\circ + \Delta G_{\text{A2-(g)}}^\circ - 2\Delta G_{\text{A-(g)}}^\circ) + (\Delta G_{\text{solv,A(S)}}^\circ + \Delta G_{\text{solv,A2-(S)}}^\circ - 2\Delta G_{\text{solv,A-(S)}}^\circ) + (\Delta G_{\text{ip,A,C+(S)}}^\circ + \Delta G_{\text{ip,A2-,C+(S)}}^\circ - 2\Delta G_{\text{ip,A-,C+(S)}}^\circ)] \quad (42)$$

In the case of reduction reactions 38 and 39, the ion pairing refers to interactions of the cation of the electrolyte with the two anionic species in the redox reactions. A very useful feature of eq 41 is the lack of dependence on the constant, -4.44 eV, in eq 11. As discussed in section 2.1.2, prediction of standard potentials for single electron-transfer reactions depends on accurate knowledge of this constant. For $E_1^\circ - E_2^\circ$, such knowledge is not required. The experimental potentials for one-electron reactions are often referred to the potential of ferrocene, measured in the same solvent, and interpretation of such potentials in terms of solvent properties is based on the implicit assumption that the solvation energies of ferrocene and ferrocenium ion (and also ion pairing involving ferrocenium) are independent of the identity of the solvent.¹⁸³ In such cases, as mentioned earlier, it is often found that the reduction potentials (neutral to anion radicals) correlate linearly with solvent acceptor number such that high acceptor number solvents shift the potential in the positive direction (stabilization of the anion radical). Similarly, oxidation to form cation radicals from neutral substrates, often features potentials that correlate linearly with solvent donor number.¹⁸³ It is wise to remember that the magnitude of the slope (and conceivably even its sign) may be affected by the variation of the solvation energies of the ferrocene species with changes in solvent. This is not a problem when studying the solvent dependence of $E_1^\circ - E_2^\circ$ because the potential of the reference electrode cancels upon taking the difference in the observed standard potentials.

In spite of these advantages, there have not been many studies of $E_1^\circ - E_2^\circ$ vs the properties of the medium. A recent example is the study of two organometallic systems, one which undergoes stepwise two-electron oxidation and the other which shows both reduction and oxidation.¹⁸⁴ The authors studied eleven different solvents each with up to ten different electrolytes. As many low dielectric constant solvents were used, some of the data are affected by the

intertwined workings of both solvation and ion pairing so this paper will be discussed later when we consider ion pairing effects.

In one case known to this author, a pure solvation effect on $E^{\circ}_1 - E^{\circ}_2$ has been reported.⁶⁴ Here, $E^{\circ}_1 - E^{\circ}_2$ was determined at infinite dilution (no ion pairing or effects of activity coefficients) for reduction of 1,4-dinitrobenzene, **21**, giving 0.254 V in acetonitrile and 0.390 V in DMF, both determined at 298 K. The only factor not considered was differences in diffusion coefficients of the neutral, anion radical and dianion which is relevant because the potentials were measured by cyclic voltammetry.⁷⁰ This could change the results by 5–10 mV. With only two solvents, the most that can be concluded is that the two infinite-dilution values of $E^{\circ}_1 - E^{\circ}_2$ change as expected if solvation of the dianion and anion radical is stronger in the solvent with the larger acceptor number, acetonitrile in this case (AN = 18.9 for acetonitrile; 16.0 for DMF). An infinite-dilution value of $E^{\circ}_1 - E^{\circ}_2$ of +0.585 V for TCNQ, **6**, was determined in acetonitrile, a result that includes a correction for differences in diffusion coefficients (8 mV),⁶² but only one solvent was studied.

An example of a study involving many different substrates and solvents is that of Sasaki et al.¹⁸⁵ who studied the reduction of 13 *para*-quinones in 6 different aprotic solvents. The work was conducted with careful attention to the reversibility of the neutral/anion radical and anion radical/dianion couples as well as the dryness of the solvents (<0.8 mM water) and temperature control (298 K).

The authors discussed a number of different features of the data including the increase in solvation energy of the anion radical with increasingly negative values of E°_1 , behavior noted by several previous authors (and mentioned in Section 2.1.2). (“Increasing” solvation energies means that they are becoming more negative). If the solvation energy of the dianion also increases with increasingly negative E°_1 and if the rate of increase is more than twice that of the anion radical, $E^{\circ}_1 - E^{\circ}_2$ must decrease with increasingly negative E°_1 (eq 41). This would be the case, for example, if the solvation energies followed the Born equation wherein the solvation energy of the dianion would be four times that of the anion radical. A plot of $E^{\circ}_1 - E^{\circ}_2$ vs E°_1 is shown in Figure 6 for ten quinones in three of the six solvents. The general decrease of $E^{\circ}_1 - E^{\circ}_2$ with more negative E°_1 is clearly evident in Figure 6. The data for the other three solvents follow a similar trend. They were omitted for clarity.

Thus the compression of $E^{\circ}_1 - E^{\circ}_2$ with increasingly negative E°_1 shows that the solvation of the dianion is more than twice as sensitive as that of the anion radical toward changes in E°_1 . The dependence on solvent properties is less clear. In a very approximate way we can say that $E^{\circ}_1 - E^{\circ}_2$ is largest for DMF, DMSO, and dimethylacetamide (DMF results plotted in Figure 6), intermediate for acetonitrile and butyronitrile (acetonitrile plotted) and smallest for propylene carbonate. The solvents are all rather polar so ion pairing is not expected to be dominant, though some may be occurring between the dianions and tetraethylammonium ion from the electrolyte.

A more recent example of a large series of compounds is the work of Shamsipur et al.¹⁸⁶ who studied the reduction of 33 anthraquinone derivatives but in only one solvent, acetonitrile. A plot analogous to Figure 6 is shown in Figure 7. Six derivatives with reactive substituents (bromomethyl, dibromomethyl and allyl) were removed from the data set.

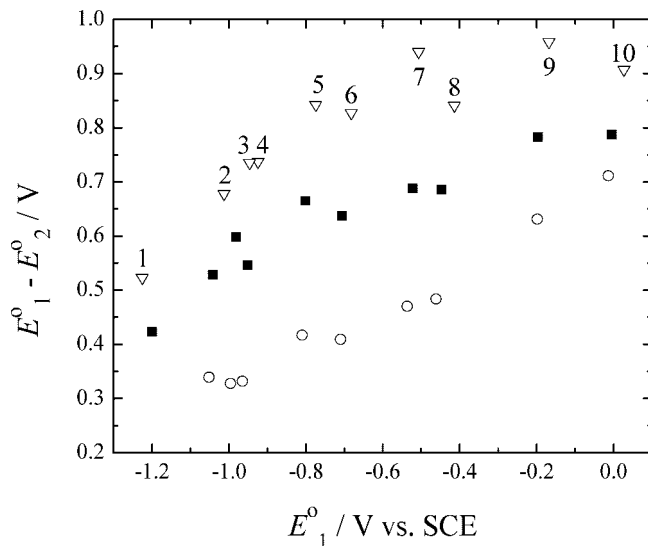


Figure 6. $E^{\circ}_1 - E^{\circ}_2$ vs E°_1 for reduction of quinones in three different solvents: Triangles: DMF; full squares: acetonitrile; circles: propylene carbonate. 1: 1,4-diamino-9,10-anthraquinone; 2: 1-amino-9,10-anthraquinone; 3: 2-methyl-9,10-anthraquinone; 4: 9,10-anthraquinone; 5: 2-methyl-1,4-naphthoquinone; 6: 1,4-naphthoquinone; 7: 1,4-benzoquinone; 8: 2,3-dichloro-1,4-naphthoquinone; 9: 2,5-dichloro-1,4-benzoquinone; 10: 2,3,5,6-tetrachloro-1,4-benzoquinone. Data from reference 185. The saturated calomel electrode was prepared in each solvent. For ambiguities about compound assignment, see original reference.

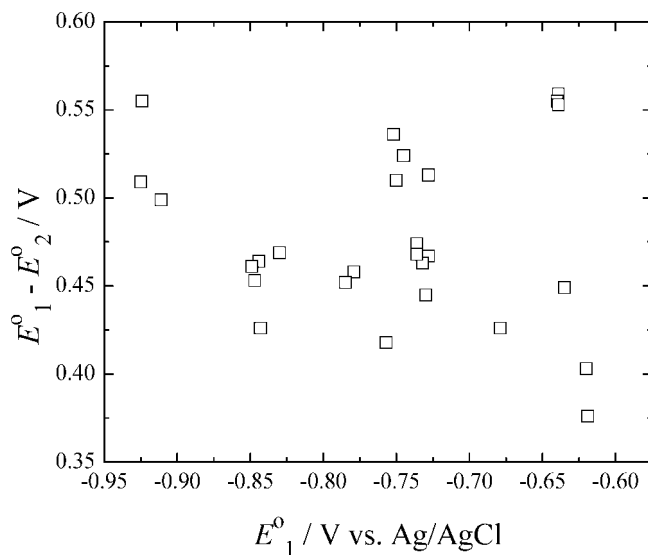


Figure 7. $E^{\circ}_1 - E^{\circ}_2$ vs E°_1 for reduction of 9,10-anthraquinone derivatives in acetonitrile. The Ag/AgCl reference electrode was prepared in acetonitrile. Data from ref 186, which may be consulted for identification of compounds. Linear regression: $E^{\circ}_1 - E^{\circ}_2 = -(0.0642)E^{\circ}_1 + 0.429$ ($R^2 = 0.015$).

There is much more scatter in the data compared to that seen in Figure 6 but this is partly due to the narrow range of E°_1 (0.3 V), the range being controlled by the fact that all compounds were derivatives of anthraquinone. No significant correlation is seen in Figure 6. This may possibly be due to the fact that all but five of the quinones whose data are plotted in Figure 7 are 2-hydroxy-9,10-anthraquinones and it is known that such derivatives behave differently from other quinones due to internal hydrogen bonding or actual proton transfer from the hydroxyl group to quinoidal oxygen in the anionic forms. Another contributor may be variable amounts of water present in the separate experiments for the

33 quinones. Unlike the authors of ref 185, these workers do not report the water content in the acetonitrile that was used. Thus the tendency for $E^{\circ}_1 - E^{\circ}_2$ to increase as E°_1 moves in the positive direction is not a general phenomenon, or it is at least masked by the scatter in the results of Figure 7.

As indicated in eq 41, another factor that will affect $E^{\circ}_1 - E^{\circ}_2$ will be ion pairing between ionic forms of the redox system and the ions of the electrolyte. In an example relevant to the systems just discussed, Rüssel and Jaenicke¹⁸⁷ determined the formation constant for the ion pairing of tetraalkylammonium ions with the dianion of 1,4-benzoquinone in acetonitrile and found values of $K_f = 8.1 \times 10^4 \text{ M}^{-1}$ for tetramethylammonium ion, 5.9×10^3 for tetraethylammonium and 48 for tetrabutylammonium ion. These values may not be highly accurate, based as they are on measurements at a single concentration of electrolyte, but they provide a rough idea of the magnitude of the ion pairing effect. In accordance with the work of other authors, no ion pairing between the anion radical of 1,4-benzoquinone and tetraalkylammonium ions was detected. In a study involving a variety of electrolyte concentrations, formation constants were reported for tetraalkylammonium ions with the dianion of 1,4-dinitrobenzene, **20**, and that of 2,5-dimethyl-1,4-dinitrobenzene with tetraalkylammonium ions⁶⁴ and no ion pairing of any sort was detected for the anions of TCNQ, **6**, and tetramethylammonium ions in acetonitrile.⁶² This last result is consistent with ion pair formation constants correlating with the potential required to form the ion, with smaller constants being associated with easily reduced substrates, an often observed but seldom mentioned trend.

Though it is true that no detectable ion pairing occurs between anion radicals and tetraalkylammonium ions, the same cannot be said for metal cations. A recently reported example is ion-pair formation between the anion radical and dianion of 1,3,5,7-cyclooctatetraene and lithium ions in tetrahydrofuran.¹⁸⁸

In principle, the effect of ion pairing between tetraalkylammonium ions and anionic participants in the electrode reaction can be so severe that potential inversion can be seen, i.e. the formal potential for the second reduction is positive of that of the first, $E^{\circ'}_1 - E^{\circ'}_2 < 0$. For the reduction reactions 38 and 39, the associated ion pairing equilibria are



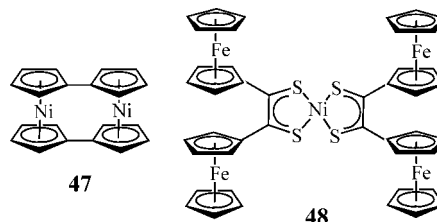
Using the same principles as in eqs 21–23, we obtain eq 46 for the difference in formal potentials in the presence of ion pairing.

$$E^{\circ'}_1 - E^{\circ'}_2 = E^{\circ}_1 - E^{\circ}_2 + \frac{RT}{F} \ln \left[\frac{(1 + K_{11}C_{\text{M}^+})^2}{(1 + K_{21}C_{\text{M}^+} + K_{21}K_{22}C_{\text{M}^+}^2)} \right] \quad (46)$$

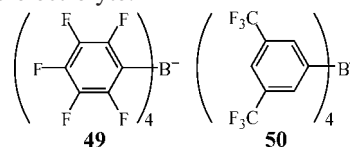
Here E°_1 and E°_2 are the standard potentials in the absence of ion pairing, and C_{M^+} is the concentration of the cation of the electrolyte. Completely analogous equations hold for ion pairing between the anion of the electrolyte and the cationic products of the oxidation of a neutral compound and for the hydrogen-bonding interactions between an additive and the anionic partners in a reduction reaction.

In any of these systems, if K_{21} is much larger than K_{11} (K_{22} is of lesser importance), potential inversion can occur within a normal range of C_{M^+} . It is common for the interaction of the cation with the dianion to be the strongest of the three so such “inversion” may occur frequently. The quotation marks are used because this is a case where the intrinsic difference in standard potentials shows normal ordering and the interaction with the medium brings about compression and finally inversion.

Returning to our theme of the interpretation of $E^{\circ}_1 - E^{\circ}_2$ in terms of properties of the medium, we examine the work of Barrière and Geiger¹⁸⁴ which involves both ion pairing and solvent effects for the two-step oxidation of nickel complex, **47**, and the oxidation (total of four electrons) or reduction (two one-electron steps) of **48**.



For the study of oxidations, this work featured the characterization of electrolytes containing weakly coordinating anions (WCA), most notably tetrakis(pentafluorophenyl)borate, **49**, and tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, **50**. The use of WCA in electrolytes offers two important advantages. Unlike the anions usually used (ClO_4^- , BF_4^- , PF_6^- , etc.), **49** and **50** are so weakly nucleophilic that sensitive cations may be isolated when using one of these anions in the electrolyte.



Also, in connection with the present discussion, the anions show very little tendency to form ion pairs with cationic species.^{184,189–197} Thus, with a more normal anion such as PF_6^- , $E^{\circ}_1 - E^{\circ}_2$ may be quite small or even close to zero for a neutral/cation radical/dication redox system due to extensive ion pairing between PF_6^- and the cations in the reaction scheme. However, with **49** or **50** the compression of $E^{\circ}_1 - E^{\circ}_2$ is eased and more normal values of the order of a few hundreds of millivolts are seen, all because of the very limited ion pairing that prevails.

These trends were amply illustrated in the studies of the oxidation of **47**.¹⁸⁴ Some very low dielectric constant solvents were used, five with values below 10. Here, strong ion pairing is expected which will result in smaller values of $E^{\circ}_1 - E^{\circ}_2$. The intrinsic value of $E^{\circ}_1 - E^{\circ}_2$ is large, owing to the fact that the two metal centers are rigidly held quite close to one another in **47**. Table 3 displays data for oxidation of **47** in dichloromethane as solvent ($\epsilon = 8.9$). The results are dominated by the extensive ion pairing that occurs in this low-dielectric-constant solvent. Competitive ion pairing must be considered, reactions 47–49, in which the electrolyte is C^+A^- and the oxidized forms of **47** are M^+ and M^{2+} .





Strong ion pairing with the substrate cations, particularly reaction 49, brings about a lowering of the magnitude of $E^{\circ}_1 - E^{\circ}_2$ and vice versa. Thus the largest separation in potentials occurs for 0.02 M [Na][**50**] (-850 mV) but the same anion in 0.10 M [NBu₄][**50**] gives $E^{\circ}_1 - E^{\circ}_2 = -744$ mV. Part of this decrease in $E^{\circ}_1 - E^{\circ}_2$ is due to the different concentrations but this is augmented by the stronger ion pairing of the electrolyte (reaction 47) that exists with the sodium-containing electrolyte compared to the electrolyte with NBu₄⁺ cations. That is, the concentration of free **50** is smaller in the sodium-containing electrolyte (self-association). The other entries in the table are for electrolytes with NBu₄⁺ (except for the bromide) and there is a steady decrease in the magnitude of $E^{\circ}_1 - E^{\circ}_2$ as the anions are changed from weakly ion pairing anions, ([NBu₄][B(C₆F₅)₄], $E^{\circ}_1 - E^{\circ}_2 = -753$ mV), to strongly ion pairing [NBu₄][Cl] (-273 mV). Generally, the smaller anions with their more localized charge interact with M⁺ and M²⁺ (reactions 44 and 45) bringing about compression in $E^{\circ}_1 - E^{\circ}_2$. The effect of ion pairing of the electrolyte operates in the opposite direction but is apparently less important than ion pairing between A⁻ and M⁺ and M²⁺.

The authors showed that the range of values of $E^{\circ}_1 - E^{\circ}_2$ encountered for the change in anion of the electrolyte from **49** and **50** differs for different solvents. For example, the range of values of $E^{\circ}_1 - E^{\circ}_2$ is smaller in DMSO, larger in THF and largest in methylene chloride. As the latter two have about the same polarity, it is not clear what solvent property is responsible for the change.

To shed light on this question, studies of the same electrolyte, [NBu₄][Cl], in various solvents were conducted (Figure 8). A good correlation was found for the solvent property, acceptor number (AN). No other successful correlations were found including correlations with donor number or dielectric constant. Again, two competing processes appear to be at work. First, the high donor number solvents have larger free energies of solvation of M⁺ and, particularly M²⁺, which should cause a reduction in the magnitude of $E^{\circ}_1 - E^{\circ}_2$. However, this factor is more than offset by the much stronger ion pairing between Cl⁻ and the substrate cations, M⁺ and M²⁺, in the low donor number solvents, causing a stronger compression of $E^{\circ}_1 - E^{\circ}_2$ in these solvents. The self-association of the electrolyte (reaction 43) is apparently less important than ion pairing between Cl⁻ and the substrate cations.

In general, the opposite type of effect is seen with reduction reactions. Compound **48** has four groups that can be oxidized (the four ferrocenyl functions) and two reduction

Table 3. $E^{\circ}_1 - E^{\circ}_2$ for Oxidation of **47** with Various Supporting Electrolytes in Methylene Chloride^{184,a}

electrolyte	$E^{\circ}_1 - E^{\circ}_2$ /mV
[Na][50] ^b	-850
[NBu ₄][49]	-753
[NBu ₄][50]	-744
[NBu ₄][B(C ₆ H ₅) ₄]	-517
[NBu ₄][PF ₆]	-480
[NBu ₄][ClO ₄]	-422
[NBu ₄][CF ₃ SO ₃]	-410
[NBu ₄][BF ₄]	-410
[NHep ₄][Br] (Hep ≡ <i>n</i> -heptyl)	-313
[NBu ₄][Cl]	-273

^a The electrolyte concentration was 0.10 M unless otherwise indicated. ^b Saturated, ~0.02 M.

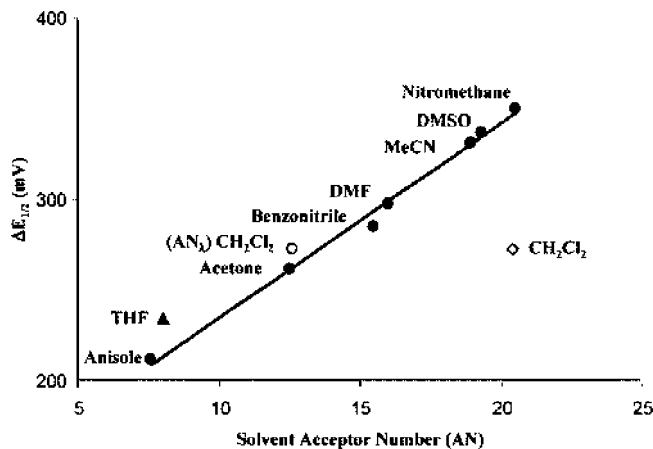


Figure 8. ¹⁸⁴ Correlation between measured $\Delta E_{1/2}$ (defined as $-(E^{\circ}_1 - E^{\circ}_2)$) for **47** in 0.10 M [NBu₄][Cl] and solvent acceptor number.¹⁸⁴ Result for THF was for [NBu₄][Br] and was not included in the regression. There are two points for CH₂Cl₂ corresponding to two different AN values from the literature. The point at AN = 20 was not used in the regression. See ref 184 for discussion of this discrepancy. Reprinted with permission from ref 184, Copyright American Chemical Society, 2006.

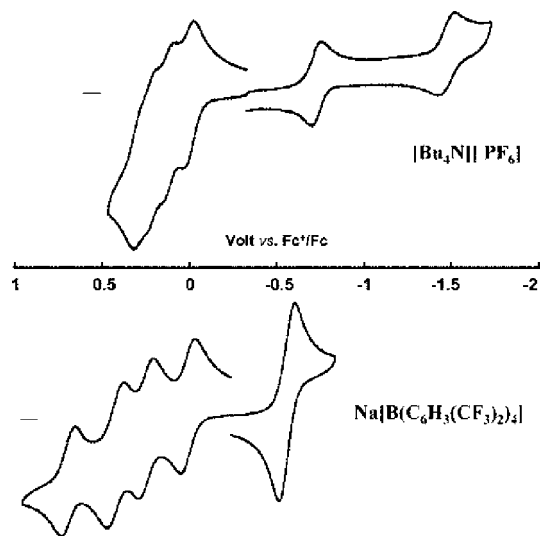


Figure 9. ¹⁸⁴ Cyclic voltammograms, 0.10 V/s for **50** in methylene chloride with 0.10 M [NBu₄][PF₆] (upper) and 0.02 M [Na][**48**] (lower). Reprinted with permission from ref 184, Copyright American Chemical Society, 2006.

steps (reduction of the nickel dithiolene). For the oxidations, larger separations in the standard potentials are seen with the WCA, **50** (Figure 9), compared to PF₆⁻, exactly as seen for the oxidation of **47**. However, reduction of the nickel dithiolene center (Figure 9) shows larger $E^{\circ}_1 - E^{\circ}_2$ for PF₆⁻ compared with **50**. The authors refer to this observation as a “mirror image” effect.

Another striking example of these effects was found in the oxidation of Rh₂(TM₄)₄²⁺ (TM₄ ≡ 2,5-diisocyno-2,5-dimethylhexane) in methylene chloride with 0.1 M tetrabutylammonium salts with various anions.¹⁹⁸ The potentials for the overall two-electron oxidation show normal ordering with $E^{\circ}_1 - E^{\circ}_2$ larger than -590 mV with **48**, a value that decreases to -187 mV with PF₆⁻. However, inversion occurs with BF₄⁻ ($+172$ mV) and ClO₄⁻ ($+191$ mV). Finally, with Cl⁻ the cation–anion interaction is so strong that $E^{\circ}_1 - E^{\circ}_2$ is estimated to be inverted more than $+354$ mV. The interactions are described as coordination rather than simply ion pairing. This investigation and others¹⁹⁹ was facilitated

by the measurement of disproportionation equilibria by infrared spectroelectrochemistry.

All of this work illustrates how the medium (solvent and electrolyte) can affect $E^{\circ}_1 - E^{\circ}_2$ both by changes in solvation energies of ionic partners in the redox couples and by ion pairing, the interaction of an ion of the electrolyte with substrate ions. An indirect effect of ion-pairing occurs through self-ion pairing of the electrolyte. The important practical consequence of these observations is that an overall two-electron reaction that shows a single peak with a given solvent and electrolyte may be induced to display two separate peaks with a proper change of the solvent and/or electrolyte. As we shall see, potential inversion is often rationalized in terms of structural changes occurring in the reactant molecule, changes that should be independent of the solvent and electrolyte. If, however, the single peak characteristic of potential inversion is partitioned into two peaks by a change in solvent and/or electrolyte, structural change cannot be of dominant importance.

$E^{\circ}_1 - E^{\circ}_2$ can also be affected by hydrogen-bonding additives, particularly in the case of the reduction of quinones, as mentioned in section 2.1.4. Compression of $E^{\circ}_1 - E^{\circ}_2$ usually occurs due to the stronger hydrogen-bonding interactions between the additive and the dianion as compared to the anion radical. Recently, the reduction of 1,4-benzoquinone and 9,10-anthraquinone-2-sulfonate has been investigated in unbuffered aqueous solutions. The most striking result of this work is that $E^{\circ}_1 - E^{\circ}_2$ for these quinones is very small in pure water, echoing earlier results of $E^{\circ}_1 - E^{\circ}_2 = +37$ mV for benzoquinone and $\sim +34$ mV for the anthraquinone sulfonate. So, the strong hydrogen-bond donor, water, brings about a large compression of $E^{\circ}_1 - E^{\circ}_2$ from about 0.7–0.8 V in dipolar aprotic solvents to about 0.04 V in water.²⁰⁰

3.1.3. Potential Inversion

As stated earlier (section 1), potential inversion with reduction reactions (38 and 39) corresponds to the case where addition of the second electron occurs with greater ease than the first, i.e., $E^{\circ}_1 - E^{\circ}_2 < 0$.



$$\ln K_{\text{dist}} = - \frac{\Delta G^{\circ}_{\text{disp}}}{RT} = - \frac{F}{RT} (E^{\circ}_1 - E^{\circ}_2) \quad (41)$$

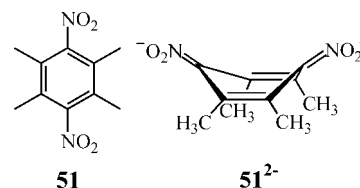
The opposite situation pertains when considering oxidations, $E^{\circ}_1 - E^{\circ}_2 > 0$.

Normal ordering of potentials corresponds, for reductions, to $E^{\circ}_1 - E^{\circ}_2 > 0$, i.e., it is more difficult to add the second electron than the first. In section 3.1.1, normal ordering was illustrated by the case of polycyclic aromatic hydrocarbons where it was shown that the extremely large and positive values of $E^{\circ}_1 - E^{\circ}_2$ expected in the gas phase (3–4 V) are ameliorated in solution by the very strong solvation of doubly charged ions compared to the singly charged ion radicals. Typical values in solution range from a few tenths volt to greater than one volt, depending on structure. With normal ordering, the ion radical is stable with respect to disproportionation, as seen in eqs 40 and 41.

As discussed in section 3.1.1, for cases where two identical electrophores are separated by a nonconjugated spacer, the values of $E^{\circ}_1 - E^{\circ}_2$ will be large for short spacers but will decrease as the spacer length increases approaching the limit of $E^{\circ}_1 - E^{\circ}_2 = (RT/F) \ln 4$, 35.6 mV at 298 K. This is indeed the lower limit and it is not possible to see potential inversion ($E^{\circ}_1 - E^{\circ}_2 < 0$) for the case of a saturated linker.

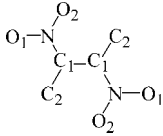
However, when a conjugated linker is used, potential inversion is sometimes seen, and this behavior has been traced to the fact that the charge on the ion radical may be highly delocalized but the charges on the doubly charged ion may be localized on the electrophores. In this case, if the effective radius of the localized charges (the electrophore) on the doubly charged ion is smaller than the radius of the delocalized charge on the ion radical (the entire molecule), the solvation energy of the diion will be increased such as to decrease the magnitude of $E^{\circ}_1 - E^{\circ}_2$ or even cause inversion. This was also discussed in section 3.1.1. Structural differences among the species (neutral, ion radical, diion) may also exert an effect.

In other cases, however, such changes in structure are undoubtedly the principal cause of potential inversion. Examples of this type were among the first cases studied, although the underlying causes of potential inversion were not understood. For example, a 1964 study of the polarographic reduction of some dinitrobenzenes showed typical normal ordering of potentials with two separate polarographic reduction waves.²⁰¹ With dinitrodurene, **51**, however, a single polarographic wave was observed whose height was double that of a single-electron reduction. We now know that this potential inversion is associated with significant changes in structure: neutral **51** features a planar durenene ring with the nitro groups turned out of its plane due to steric interaction with the methyl groups. In the dianion, the nitro groups turn into the plane which results in ring distortion giving a boat-like six-membered ring, exaggerated version shown as **51**²⁻.²⁰² Thus, the structural change is induced by a combination of electronic and steric factors. In the dianion, the formal N–C_{ring} double bond (electronic factor) would cause severe steric interaction between oxygen atoms in the nitro group and the nearby methyl groups in a planar version of the dianion. The molecule adjusts by distorting the ring into the boat form shown (steric factor).



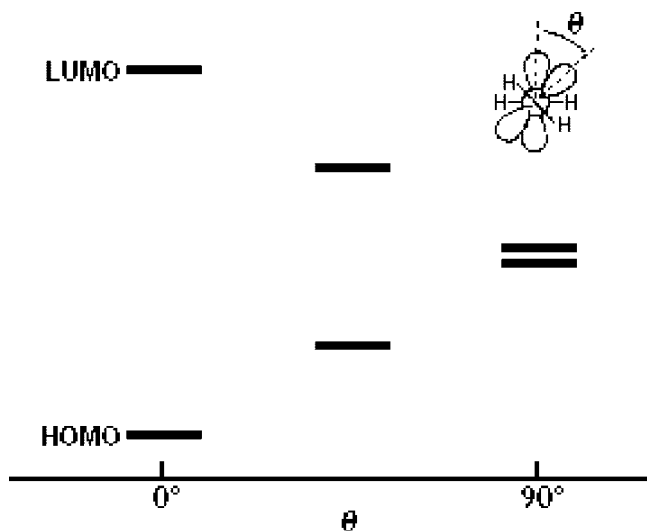
Why should such structural changes bring about potential inversion? To examine this question, we turn to one of the simplest molecules that shows potential inversion, *trans*-2,3-dinitro-2-butene, **52**. A few salient features of the calculated structures of the neutral, anion radical and dianion of **52** are shown in Table 4. None of the three forms adopts a planar structure for the N, C, and O atoms.

The steric interactions preventing planarity are not obvious, but the structural parameters in Table 4 make it clear that a planar backbone is not preferred. In the neutral the C₂C₁C₁C₂ dihedral angle is 175° but the nitro groups are significantly turned (O₁NC₁C₁ dihedral angle 129°). On going to the anion radical, twisting occurs about the central olefinic bond while

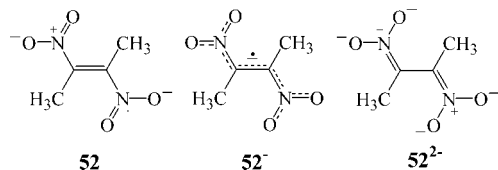
Table 4. Calculated Structures of the Neutral, Anion Radical, and Dianion of *trans*-2,3-Dinitro-2-butene, **52**^a


species	structural parameter: angle or bond length			
	dihedral angle/°		bond length/Å	
	C ₂ C ₁ C ₁ C ₂	O ₁ NC ₁ C ₁	C ₁ C ₁	NC ₁
neutral	174.6	129.3	1.34	1.49
anion radical	150.5	168.2	1.40	1.41
dianion	130.0	169.9	1.46	1.34

^a DFT with B3LYP functional using 6-31G and 6-31G+(d) basis sets.

**Figure 10.** ²⁰⁴ Qualitative variation of LUMO and HOMO energies of ethylene as a function of twist angle, θ . Reprinted with permission from ref 204, Copyright American Chemical Society, 1982.

the nitro groups tend to turn into the plane. Finally, in the dianion substantial twisting occurs between C₁ and C₁ (C₂C₁C₁C₂ dihedral angle 130°) and the nitro groups are close to coplanar with C₂C₁C₁ (O₁NC₁C₁ dihedral angle 170°). At the same time, and in accord with the resonance structures shown, the C₁C₁ bond length changes from a value typical of a double bond in the neutral to the single-bond range in the dianion. The reverse trend is seen for the NC₁ bond length.



There are several ways of understanding how these structural changes can bring about potential inversion. A very qualitative but useful explanation can be found by considering the LUMO and HOMO energies of ethylene as a function of the twist angle of the *p*-orbitals that comprise the π -bond in ethylene (Figure 10).²⁰⁴

A twist angle of 0° corresponds to undistorted ethylene while with $\theta = 90^\circ$ the two *p* orbitals do not overlap and are degenerate in energy. Partial twisting results in a decrease in LUMO energy and an increase in the HOMO energy. Now, if one considers that **52** is simply an ethylene

Table 5. Calculated Values of $\Delta G^\circ_{\text{disp}}(\text{g})$ with Optimized Geometries and with Geometries Restricted to That of the Neutral Species^a

species	$\Delta G^\circ_{\text{f}}(\text{g})/\text{kcal mol}^{-1}$	
	optimized geometry	geometry of neutral
Anthracene, 3		
neutral	+64.5	(+64.5)
anion radical	+29.2	+29.4
dianion	+104.0	+107.1
$\Delta G^\circ_{\text{disp}}(\text{g})$	+110.2	+112.8
<i>trans</i> -2,3-Dinitro-2-butene, 52		
neutral	+12.4	(+12.4)
anion radical	-54.0	-46.4
dianion	+1.0	+58.6
$\Delta G^\circ_{\text{disp}}(\text{g})$	+121.4	+163.8

^a $\Delta G^\circ_{\text{disp}}(\text{g})$ refers to the Gibbs energy change of reaction 40. Computations by AM1.

derivative, the twist angle in the neutral is $\sim 0^\circ$ (Table 4) and, upon introduction of an electron into the LUMO, the anion radical will twist until $\theta \sim 30^\circ$. The resulting lowering of the LUMO energy will make the anion radical easier to reduce, explaining qualitatively how the sterically driven/electronically allowed twisting can bring about potential inversion.

Obviously **52** is not ethylene as its reduction involves changes in several structural parameters in addition to twisting about the central double bond. Nevertheless, twisting about double bonds (or potential double bonds) is an extremely common feature of systems that show potential inversion, e.g., **51**.

A better explanation must involve the actual energies of the three species being considered, not simply the orbital energies. As an example, the gas-phase free energies of formation of the neutral, anion radical and dianion of two different systems, anthracene, **3**, and **52**, were computed. The first of these shows normal ordering of potentials and only minor changes in structure upon reduction while the second, as discussed above, shows potential inversion and substantial changes in structure on going from neutral to anion radical and then to the dianion. The results are shown in Table 5.²⁰³

As discussed in earlier sections, the values of $\Delta G^\circ_{\text{disp}}(\text{g})$ are quite positive, corresponding to a hypothetical gas-phase $E^\circ_1 - E^\circ_2$ of +4–5 V. For anthracene, $\Delta G^\circ_{\text{disp}}(\text{g}) = +110.2$ kcal/mol for the optimized structures of all three species and a similar number, +121.4 kcal/mol, was found for **52**. To see the effect of the structural change on $\Delta G^\circ_{\text{disp}}(\text{g})$, the calculations were repeated but with the structures for all three species frozen in the form of the neutral. For anthracene, where the structural changes are small, $\Delta G^\circ_{\text{disp}}(\text{g})$ changed negligibly, from +110.2 (optimized) to +112.8 (structure of the neutral) kcal/mol. By contrast, there was a large decrease in $\Delta G^\circ_{\text{disp}}(\text{g})$ for **52**, from +163.8 kcal/mol (optimized) to +121.4 kcal/mol (structure of the neutral). Thus, allowing the structural changes makes the disproportionation reaction much less unfavorable for **52** which is in the direction of achieving potential inversion in solution. A similar line of thinking has been advanced to explain the disproportionation of some hindered stilbene anion radicals.²⁰⁵

The third level of prediction of potential inversion will involve careful calculation of the solvation energies for the three species involved in the disproportionation equilibrium. These, combined with the gas-phase free energies, will give the solution-phase $\Delta G^\circ_{\text{disp}}(\text{S})$ and then solution-phase E°_1

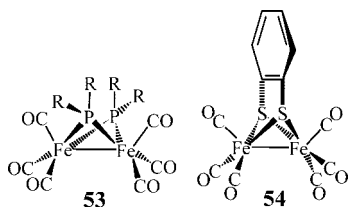
– E°_2 . These calculations, using the polarizable continuum model, are not sufficiently accurate to predict inversion.^{203,206} For **52** in 83% acetonitrile/17% water, the experimental value of $E^{\circ}_1 - E^{\circ}_2$ is -0.080 V,²⁰³ which corresponds to $\Delta G^{\circ}_{\text{disp}}(\text{S})$ of only -1.8 kcal/mol, well within the error of the calculations.

Evans and Hu¹⁶² used an empirical approach to estimate solvation energies. For example, when considering 1,4-dinitrobenzene, **21**, and dinitrodurene, **51**, these authors computed (AM1) the gas-phase free energies of disproportionation for each system, $\Delta G^{\circ}_{\text{disp}}(\text{g})$. For **20**, which shows normal ordering of potentials, the value of $E^{\circ}_1 - E^{\circ}_2$ in solution (S) was known. This allowed for the evaluation of the contribution of solvation to the change in the Gibbs energy of disproportionation on going from gas phase to solution, $\Delta G^{\circ}_{\text{disp,solv}}$ (eq 50).

$$\Delta G^{\circ}_{\text{disp}}(\text{S}) = F(E^{\circ}_1 - E^{\circ}_2) = \Delta G^{\circ}_{\text{disp}}(\text{g}) + \Delta G^{\circ}_{\text{disp,solv}} \quad (50)$$

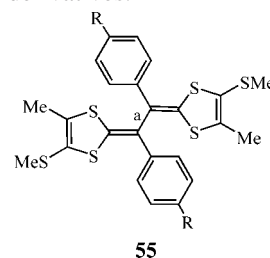
At this point, two assumptions were made. First $\Delta G^{\circ}_{\text{disp,solv}}$ was assumed to vary with the reciprocal of the radius of the species (as in the Born equation) and that radius was assumed to be the equivalent spherical radius of the species. Thus, $\Delta G^{\circ}_{\text{disp,solv}}$ obtained from calculation and experiment for **20** was used to compute $\Delta G^{\circ}_{\text{disp,solv}}$ for the somewhat larger **51**. This was combined with the computed $\Delta G^{\circ}_{\text{disp}}(\text{g})$ for **51** through eq 50 to obtain $E^{\circ}_1 - E^{\circ}_2$ for **51**, indicating potential inversion for **51**, as observed. This simple procedure was found to predict correctly the occurrence of potential inversion in seven out of ten systems that were investigated.¹⁶²

In at least two cases, computations of $\Delta G^{\circ}_{\text{disp}}(\text{g})$ by DFT methods and $\Delta G^{\circ}_{\text{disp,solv}}$ by COSMO (conductor-like screening model) have been successful in predicting potential inversion in the two-electron reduction of diiron complexes. One involved the bisphosphino-bridged complex **53** ($\text{R} = \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5$) for which calculations²⁰⁷ showed extensive inversion in full agreement with experiment.²⁰⁸ In **53** the structural change is breakage of the Fe–Fe bond and planarization of the Fe_2P_2 core. Potential inversion was also predicted by similar calculations for **54**, in agreement with experiment, but here the important structural change is cleavage of one S–Fe bond in the dianion. For both **53** and **54** the extent of inversion is too large to evaluate accurately by voltammetric experiments. However, it is clear from the voltammograms that extensive inversion occurs. Similar methods have been applied to calculation of the difference in standard potentials for the two-electron reduction of 1,3,5,7-cyclooctatetraene, where ion pairing as well as solvation were considered.²⁰⁹

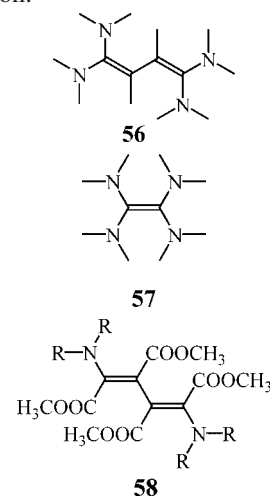


It is normally necessary to rely on computation to reveal the changes in structure that accompany the two-electron oxidation or reduction reactions in systems that display potential inversion. This is due to the fact that only one of the forms, usually the neutral species, is sufficiently stable to obtain suitable crystals for X-ray crystallography. A notable exception is found in the work of Bellec et al.²⁰⁶ who found potential inversion in the two-electron oxidation of some vinylogous tetrathiafulvalenes

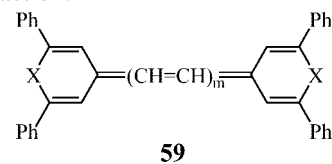
(TTF), **55** ($\text{R} = \text{H}, \text{NO}_2, \text{CN}$). A number of other related derivatives were also investigated. In this case, X-ray structures of several neutrals, cation radicals and dications in the series were available, though structures for all three oxidation states for a single molecule were not. So, in this case, experimental evidence supports the occurrence of substantial structural changes during the oxidation. The neutral molecule is twisted about central bond “a” but in the cation radical the extended TTF core becomes planar. It remains planar in the dication in which bond “a” is formally a double bond. This change in planarity appears to be the most significant structural change and is an important factor in bringing about the observed potential inversion. The extent of potential inversion is dependent upon the solvent²⁰⁶ which suggests that both structural change and solvation are at work in this case. Similar results have been seen with other vinylogous TTF derivatives.^{210–212}

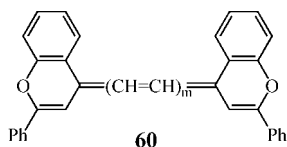


Other examples exist of cases where the principal structural change appears to be twisting about a central double bond around. Early examples are butadienes (**56** for example),²¹³ and later tetrakis(dimethylamino)ethylene (**57**)²¹⁴ and ester derivatives (**58**, $\text{R} = \text{iPr}, \text{cHx}, \text{and nPr}$)²¹⁵ all of which show potential inversion.

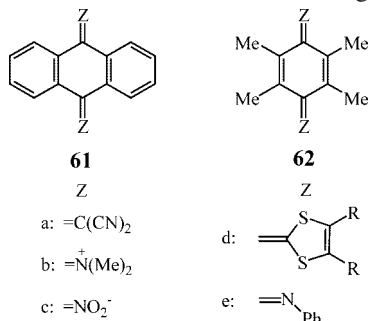


Other examples are families **59** ($\text{X} = \text{O}$ or S , $m = 4$ or 6) and **60** ($m = 4$ or 6),²¹⁶ of which several members show potential inversion. Related systems are tetraphenylethylene and derivatives, many of which display potential compression or inversion.^{217–221} Here again, the extent is dependent on solvent suggesting that both structural change and solvation effects are important. Reduction of some extended viologens also appears to occur with potential inversion in at least one step of the reaction.^{222,223}





A very rich group of compounds showing potential inversion is based on **61** and **62**. The structures shown are those in which the substituent Z is attached to the ring system via a double bond bringing about the type of distortion discussed earlier in connection with dinitrodurene. This distortion is relieved upon oxidation or reduction and all of the systems show potential inversion. By contrast, the benzene derivatives, in which steric interactions are absent, all show normal ordering of potentials.

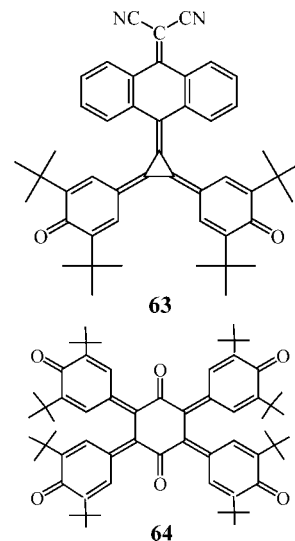


61a and **62a** have been thoroughly studied.^{224–229} Each shows potential inversion in contrast to the benzene derivative, tetracyanoquinodimethane, **6**, whose potentials are normally ordered. Of some note is the confirmation of the value of $E^{\circ}_1 - E^{\circ}_2$, obtained by voltammetry, through quantitative EPR measurements.²²⁹ In a related compound, **63**, potential inversion was seen and was again attributed to significant structural change analogous to that seen with **61a**.²³⁰ Similarly, **64** is reduced with a total of six electrons in 1-, 1-, 2-, and 2-electron steps with apparent potential inversion in the last two steps. The exact cause of potential inversion was not determined.²³¹

61b and **62b**, shown as the two-electron dicationic oxidation products of the bis(dimethylamino)arene, also show potential inversion with the added feature that the electron-transfer reactions are apparently somewhat irreversible.^{169,232} By independent determination of the reorganization energies, it was shown that this apparent irreversibility was actually due to the oxidations proceeding by two-step processes, electron transfer either preceding or following structural change.²³² Potential inversion is also seen upon two-electron oxidation of *N,N,N',N'*-tetramethyl-1,1'-naphthidine, which is structurally related to **61b**.²³³

As already mentioned, dinitroaromatics **61c** and **62c** have inverted potentials in their two-electron reduction to the dianionic forms shown.^{64,201,202,234–236}

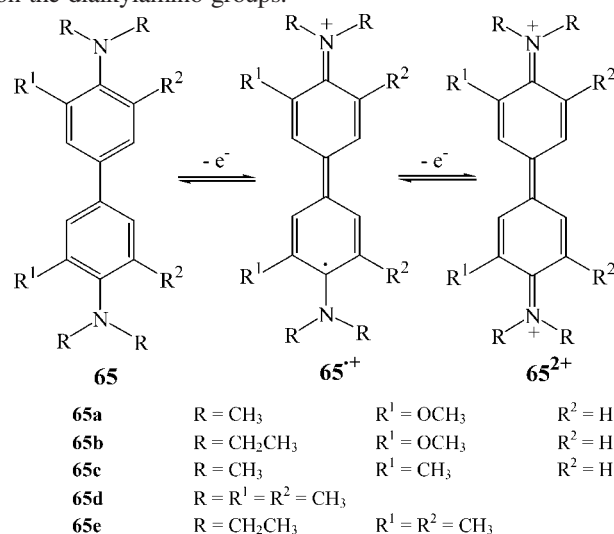
Extended tetrathiafulvalene **61d** has also been shown to undergo two-electron oxidation with potential inversion.^{237–243} This is another case where the electron-transfer reactions appeared to be somewhat sluggish but independent determination of the inner reorganization energy demonstrated that the oxidations must be two-step processes of structural change either preceding or following electron transfer as opposed to concerted electron transfer and structural change. A lower limit to the extent of potential inversion, determined by voltammetry, was confirmed by quantitative EPR measurements.²⁴³



Final examples taken from this family are **61e** and **62e**, the bis(phenylimino)arenes. In the presence of either Brønsted or Lewis acids, **61e** and **62e** undergo a single-step, two-electron reduction to the corresponding bis(phenylamino) compounds. The results are consistent with potential inversion, or at least strong potential compression.²⁴⁴

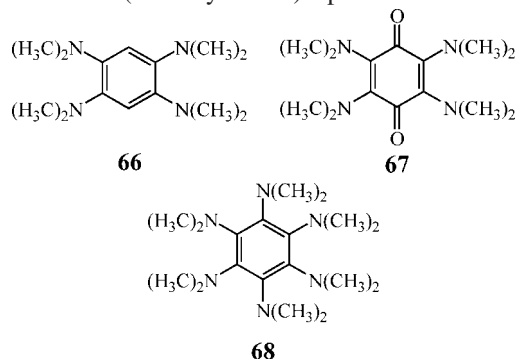
For all of the derivatives of **61** and **62**, the corresponding benzene compound shows normal ordering of potentials. Also, in either the fully oxidized or fully reduced forms, these compounds adopt a folded ring structure (like that described for dinitrodurene), with the evidence for this conclusion ranging from computational to X-ray crystallographic studies.

In a related series of compounds, a number of benzidines, **65a–e**, have been found to undergo two-electron oxidation with very similar potentials and in some cases potential inversion.^{245,246} The steric factors are admittedly small but apparently the interaction between the nitrogen alkyl groups and ring substituents is the basis of structural changes that are partially responsible for potential compression. Solvation effects are also probably at work in that the dicationic feature localized charges on the dialkylamino groups.

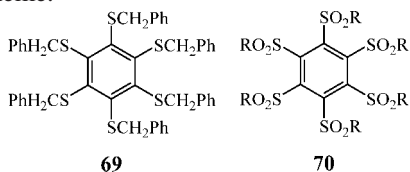


Some similar factors are seen in the oxidation of poly-(dimethylamino) benzenes. 1,2,4,5-tetrakis(dimethylamino)benzene, **66**, undergoes two-electron oxidation in a single step, signifying potential compression or inversion.²⁴⁷ In spite of a somewhat similar structure, 2,3,5,6-tetrakis(dimethylamino)-1,4-benzoquinone, **67**, undergoes stepwise oxidation to the dication.^{248,249} The heterogeneous electron-transfer

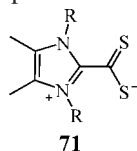
kinetics for both one-electron oxidation and one-electron reduction of **67** have been reported.²⁵⁰ Hexakis(dimethylamino)benzene, **68**, shows potential inversion in the two-electron oxidation to the dication. The reaction features unusually sluggish electron-transfer kinetics.^{251,252} Other hexaaminobenzene derivatives have been shown to be oxidized with potential inversion²⁵³ as have three of the isomeric tetrakis(dimethylamino)naphthalenes.²⁵⁴



On a somewhat similar note, Speiser and co-workers have studied hexakis(benzylthio)benzene, **69**.²⁵⁵ These authors found substantial compression of the first two oxidation potentials ($E^{\circ}_1 - E^{\circ}_2 = -23$ mV at -40 °C) and the studies were complicated by the slow decomposition of the dication. Structural changes accompanying oxidation have not been elucidated. Evaluation of $E^{\circ}_1 - E^{\circ}_2$ was aided by a type of potentiometric titration, called “fractional electrolysis”, which should be of general value in the study of potential compression and inversion.²⁵⁶ By contrast, reduction of hexakis(alkylsulfonyl)benzenes, **70** (R = Me, Et, nBu, iPr, and iBu), occurred by a single-electron step forming the anion radical. The results were affected in an interesting way by conformational changes (characterized by computation), such that the voltammetry needed to be characterized by a square scheme.²⁵⁷



Another example of potential inversion was encountered with *N,N'*-dialkyl-4,5-dimethylimidazolium-2-dithiocarboxylates, **71** (R = Me, Et, and *i*-Pr; one of several resonance structures shown).²⁵⁸ The methyl and ethyl derivative show normal ordering of reduction potentials whereas potential inversion is seen with isopropyl **71**. The structural change associated with the reduction is thought to occur mainly in the second step, in which the dithiocarboxylate group, orthogonal to the imidazolium ring in the neutral compound, turns into the plane of the ring bringing about steric interaction between sulfur atoms and the isopropyl group. So once again, structural change is postulated to be pivotal in the establishment of potential inversion.



Some of the earliest examples of potential inversion or compression derive from inorganic complexes and organometallic systems. We have already mentioned the bis(phosphino)bridged diiron complex, **53**,²⁰⁸ in connection

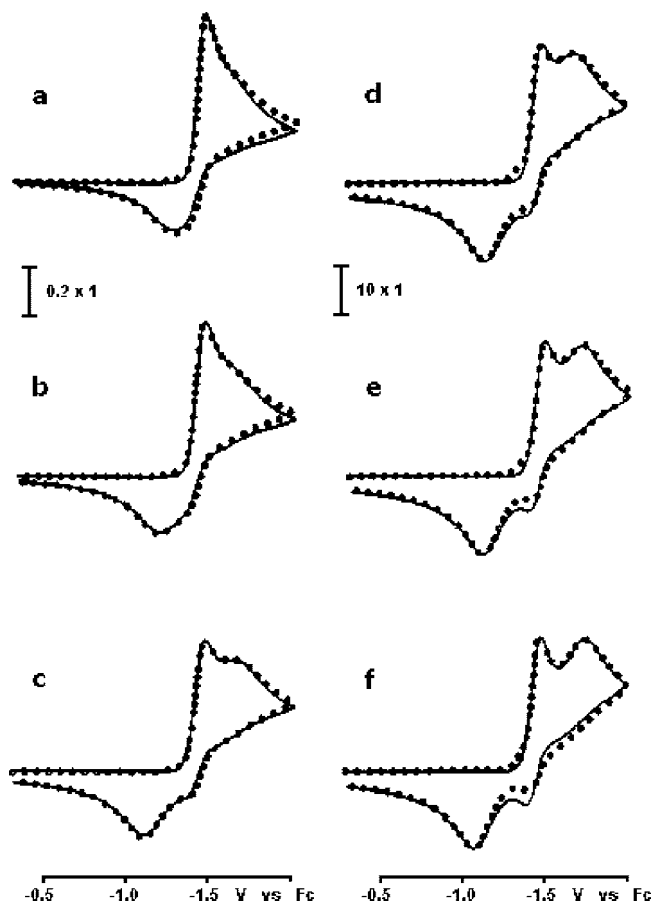
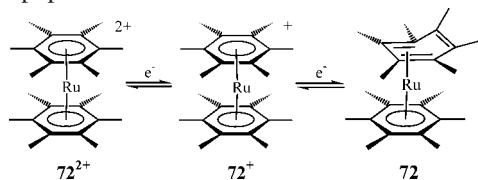


Figure 11. Digital simulations (lines) compared to experimental data (filled circles) for reduction of 72^{2+} in acetonitrile. Simulations included 30 mV of potential inversion and $k_{s,1}/k_{s,2} > 4.3 \times 10^3$. Scan rates: (a) 0.4, (b) 1.0, (c) 5.0, (d) 10, (e) 20, and (f) 50 V/s. Reprinted with permission from ref 271, Copyright American Chemical Society, 1992.

with theoretical calculation of potential inversion. In this case, the general structural change that is observed is the breakage of a metal–metal bond and flattening of the $M_2(\mu-L)_2$ core (where $\mu-L$ is a bridging ligand). This theme appears in a number of studies.^{198,199,259–266} Of particular note is the thorough kinetic and thermodynamic study of $M_2(\mu-PPh_2)_2(CO)_4^{0/2-}$ (M = Mo, W) which showed 0.17 V inversion for the Mo derivative and 0.18 V for W.²⁶⁶

In other cases, the structural change underlying potential compression or inversion is a change in hapticity of an η -bound ligand (or other change in bonding) upon oxidation or reduction.^{267–272} A very interesting illustration can be found in the reduction of bis(hexamethylbenzene)ruthenium dication, 72^{2+} , in a two-electron process with potential inversion.^{269,271} As shown, the change in hapticity is thought to occur upon reduction of the anion to the dianion (second step) and analysis of the voltammetric data indicates that the standard heterogeneous electron-transfer rate constant for the second electron transfer is much smaller than the first, consistent with the structural change being associated with the second electron transfer (large inner reorganization energy). This unusual situation underlies the unique changes seen in the cyclic voltammograms upon increasing the scan rate (Figure 11). At slow scan rates (a, 0.4 V/s), there is a single reduction peak but as the scan rate increases a new peak appears (c, 5 V/s) which grows further at the largest scan rate (f, 20 V/s). Concurrent with the growth of the second

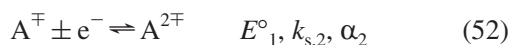
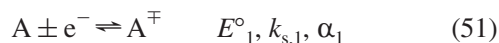
reduction peak is the development of a second, less negative, anodic peak. The second reduction peak and the second anodic peak constitute the second reduction process whose separation in peak potential becomes quite large at rapid scan rates due to the small electron-transfer rate constant for the second step. There are other unusual features in this mechanism for which referral to the original paper is recommended.²⁷¹



Other examples from inorganic systems involve different types of structural changes.^{273–280} It should be emphasized that in many cases the exact determination of whether potential inversion has occurred has not been accomplished but for all of the systems listed the potentials are at the very least strongly compressed so that only one two-electron process is resolved. Also, though some kind of structural change has been identified, the relative importance of structural change, solvation and ion pairing in bringing about the compression or inversion has seldom been evaluated.

3.2. Question of Concerted Two-Electron Transfers

In the preceding section we have discussed two-electron processes with potential inversion, that is, reactions in which removal or addition of the second electron occurs with greater ease than the first (cf. reactions 51–53).



Here, potential inversion corresponds to $E^{\circ}_1 - E^{\circ}_2 > 0$ for oxidations and $E^{\circ}_1 - E^{\circ}_2 < 0$ for reductions. When the electron-transfer kinetics are facile, the reaction will occur near the standard potential for the overall process, $E^{\circ}_{ov} = (E^{\circ}_1 + E^{\circ}_2)/2$. For example, when $E^{\circ}_1 - E^{\circ}_2$ equals -0.4 V (for a reduction), the reduction near E°_{ov} is occurring 0.2 V positive of E°_1 but 0.2 V negative of E°_2 . Thus, at the potential needed for reduction, E°_{ov} , there is a 0.2 V overvoltage for insertion of the second electron, a reaction which must therefore be very fast, so fast in fact that the question arises as to whether the two electrons might be added concertedly rather than sequentially.

This is tantamount to saying that the intermediate A^{\mp} is of too high an energy to be accessed and that reaction 53 proceeds directly without any intermediate by way of a concerted two-electron reaction. The possibility of concerted two-electron transfer reactions has been widely considered in the literature, both in theoretical treatments^{281–285} and in more phenomenological discussions^{262,286–290} and it is generally agreed that such reactions are possible.

Much of the discussion has been in terms of intermolecular^{281,282,288,291} or intramolecular^{292–294} electron-transfer reactions. In the former, the electron transfer is between acceptor A and donor D^{2-} , the reaction treated as occurring through an encounter complex as shown in reaction 54.

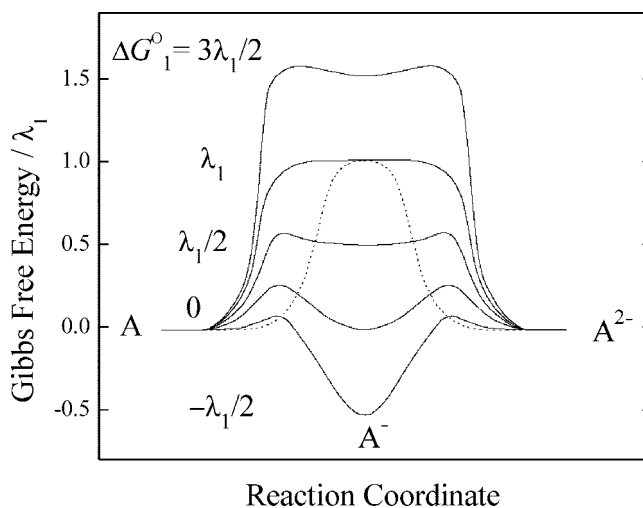
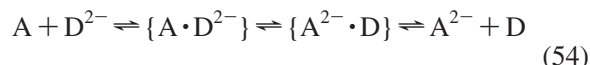


Figure 12. Diagram of Gibbs energy surface for the stepwise two-electron reaction of A with the potential being E°_{ov} (solid curves) and concerted two-electron reaction (dashed). Labeling of solid curves: $\Delta G^{\circ}_1 = -\lambda_1/2$ (normal ordering of potentials; note intermediate is stable with respect to disproportionation), $\Delta G^{\circ}_1 = 0$ (that is, $E^{\circ}_1 = E^{\circ}_2$), $\Delta G^{\circ}_1 = \lambda_1/2$, $\Delta G^{\circ}_1 = \lambda_1$, $\Delta G^{\circ}_1 = 3\lambda_1/2$ (last three values correspond to increasing degree of potential inversion; intermediate unstable with respect to disproportionation; for $\Delta G^{\circ}_1 > \lambda_1$ the energy of the intermediate exceeds the energy of the barrier for the concerted two-electron reaction). Note that barrier for concerted two-electron transfer reaction is equal to λ_1 (see text). Reaction coordinate: multidimensional changes in nuclear coordinates of the reactant and solvent coordinates on proceeding left-to-right from A to A^{\mp} and thence to $A^{2\mp}$.



For an electrochemical reaction there is formally no reactant complex. The two electrons are transferred to or from energy levels in the electrode that are close to the Fermi energy.

A useful way to discuss the possibility of concerted two-electron transfers in a phenomenological fashion is within the context of potential inversion as described in section 3.1.3. The question becomes whether or not the postulated intermediate, A^{\mp} (reactions 51–53), is so high in energy that it lies above the barrier for the concerted, two-electron reaction. This is essentially the approach taken by Gileadi.²⁹⁰ Gileadi writes that the intermediate falls ΔG°_1 above the common energy of reactants and products (for the condition corresponding to the standard potential for the electrode reaction, E°_{ov} , or self-exchange conditions for a solution-phase reaction ($D^{2-} \equiv A^{2-}$ in reaction 54)), see Figure 12. The extent of potential inversion, $E^{\circ}_1 - E^{\circ}_2$, in these terms, is $-2\Delta G^{\circ}_1/F$. The Gibbs energy barrier to the initial electron transfer, $\Delta G^{\circ,*}_1$, is given by eq 55

$$\Delta G^{\circ,*}_1 = \frac{\lambda_1}{4} \left(1 + \frac{\Delta G^{\circ}_1}{\lambda_1} \right)^2 \quad (55)$$

where λ_1 is the reorganization energy for the one-electron process. For the case where $\Delta G^{\circ}_1 = \lambda_1$, equation 55 gives $\Delta G^{\circ,*}_1 = \lambda_1$, which represents a crossing point in the analysis, as we will see. See the series of curves for various ΔG°_1 in Figure 12. As ΔG°_1 increases, the energy of the intermediate becomes larger (conditions of potential inversion) and finally it is larger than the barrier for the concerted two-electron reaction (see below). Note that, in the case of two-step reduction, it is assumed that $\lambda_1 = \lambda_2$.

The reorganization energy for the concerted, two-electron process is λ_{ov} , is given by eq 56

$$\lambda_{\text{ov}} = 4\lambda_1 = 4\lambda_{1,\text{o}} + 4\lambda_{1,\text{i}} \quad (56)$$

in which $\lambda_{1,\text{o}}$ is the one-electron outer reorganization energy and $\lambda_{1,\text{i}}$ is the one-electron inner reorganization energy. This expression is rationalized as follows. Following Fernandez et al.,²⁶² Gileadi²⁹⁰ notes that the Marcus expression for the outer reorganization energy depends on the square of the charge transferred (giving $\lambda_{\text{ov,o}} = 4\lambda_{1,\text{o}}$) and, by assuming harmonic vibrations and that changes in nuclear coordinates are equally divided between the first and second electron transfers, it follows that $\lambda_{\text{ov,i}} = 4\lambda_{1,\text{i}}$. Thus, the total reorganization energy for the concerted two-electron process is simply four times the one-electron value (equation 56) and the Gibbs energy barrier is $\Delta G^{\circ,*}_{\text{ov}} = \lambda_{\text{ov}}/4 = \lambda_1$. So, the barrier for the concerted reaction (dashed curve in Figure 12), equals that of the first step of the stepwise reaction for the case where the energy of the intermediate is higher than reactants and products by λ_1 . If the energy of the intermediate is smaller, the barrier for stepwise reduction is lower than concerted and vice versa, showing that $\Delta G^{\circ}_1 = \lambda_1$ is the crossing point between stepwise and concerted behavior, for a reaction proceeding at E°_{ov} . As the driving force of the reaction increases ($E - E^{\circ}_{\text{ov}}$ becomes negative), the concerted reaction becomes more and more favored compared to the sequential insertion of electrons.^{286,287,290} This treatment makes the additional assumption that the pre-exponential factors for both one-electron and concerted two-electron reactions are equal.

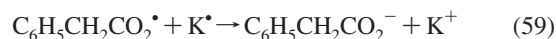
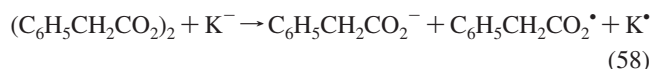
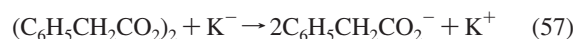
What are the requirements for the concerted two-electron reaction to have a lower barrier than that of sequential transfer of two electrons? First, it is important to realize that the reactions must be electron transfer reactions and not reactions that are coupled to chemical steps. Thus, several examples offered by Gileadi²⁹⁰ do not qualify as simple electron-transfer reactions. For example, the reduction of $\text{Ni}^{2+}(\text{aq})$ to metallic nickel²⁹⁰ involves, in addition to electron transfer, steps of deaquation and adsorption/crystallization. Similarly, the reduction of $\text{CrO}_4^{2-}(\text{aq})$ to metallic chromium²⁹⁰ involves, in addition to electron transfer, conversion of the tetrahedrally coordinated oxygen atoms in CrO_4^{2-} to OH^- (in the neutral to alkaline medium needed to stabilize CrO_4^{2-}). The overall reaction, $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Cr}(\text{s}) + 8\text{OH}^-$, obviously involves much more than electron transfer. The same can be said for the possibility of simultaneous transfer of three electrons to chromate,²⁹⁰ $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{OH})_3(\text{s}) + 5\text{OH}^-$.

One example, mentioned in passing,²⁹⁰ does seem to qualify as a two-electron reaction without coupled chemical steps. That reaction is $\text{Tl}^{3+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Tl}^+(\text{aq})$ which is studied in acidic media owing to the insolubility of thallium(III) hydroxide. Both of these ions (as well as the hypothetical intermediate, $\text{Tl}^{2+}(\text{aq})$) have filled d and f orbitals so that water molecules are not strongly coordinated indicating that the ions are probably hydrated in a facile, reversible fashion.²⁹⁵ Indeed, the self-exchange reaction has been studied and kinetic parameters extracted for the reaction.^{296,297} On the basis of these latter data and their own theoretical calculations, Zusman and Beratan concluded that the self-exchange reaction was likely to be a concerted two-electron process.²⁸² For this system, the known potentials are⁵ $E^{\circ}_{\text{Tl}^{3+}/\text{Tl}^{2+}} = +1.25$ V and $E^{\circ}_{\text{Tl}^{2+}/\text{Tl}^{+}} = -0.336$ V vs NHE. Hush²⁹⁸ has estimated for the unknown Tl^{2+} that $E^{\circ}_{\text{Tl}^{3+}/\text{Tl}^{2+}}$

$= +1.00$ V and $E^{\circ}_{\text{Tl}^{2+}/\text{Tl}^{+}} = +1.50$ V, these two values being consistent with $E^{\circ}_{\text{Tl}^{3+}/\text{Tl}^{+}} = +1.25$ V. Thus, the potentials are thought to be inverted by $E^{\circ}_1 - E^{\circ}_2 = -0.50$ V and $\Delta G^{\circ}_1 = 0.50/2 = 0.25$ eV. So, following the Gileadi analysis,²⁹⁰ if λ_1 is 0.25 eV or greater, certainly not an unusually large number, the concerted two-electron transfer in the exchange reaction will be favored, just as was concluded by Zusman and Beratan.²⁸²

In contrast, the reaction of $\text{Tl}(\text{O}_2\text{CCF}_3)_3$ with alkyl benzenes occurs by a one-electron transfer from the arene to Tl^{III} forming the intermediate Tl^{II} species.²⁹⁹

Thus, the evidence for concerted two-electron transfers is rather indirect in nature. An experimental test of the question was carried out by Perrin et al.³⁰⁰ based on an earlier suggestion of Szwarc.²⁸⁸ These authors studied reaction 57 which represents the concerted two-electron transfer reaction.



Its stepwise alternative mechanism is given in reactions 58 and 59. (Here, K^- is the potassium anion stabilized as the 18-crown-6 complex). The experimental mechanistic test was to determine if products from the intermediate phenylacetoxyl radical, $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^{\bullet}$, could be detected. If so, the reaction was considered to proceed in a stepwise fashion. Such products (toluene, bibenzyl and benzyl phenylacetate) were indeed detected leading the authors to conclude that the concerted reaction 57 was not competitive with the sequential electron transfers (reactions 58 and 59) in this case.³⁰⁰

The question remains whether two-electron electrochemical reaction systems showing potential inversion might undergo concerted two-electron transfers. For reductions with significant potential inversion, $E^{\circ}_1 - E^{\circ}_2 < 0$, introduction of the second electron is much more facile than the first so the second step of the reduction will rapidly follow the first. Could the electron transfers be concerted? A commonly accepted definition of a concerted reaction is one that occurs without intervention of an intermediate. For cases where $E^{\circ}_1 - E^{\circ}_2$ ranges from 0 up to about ∓ 0.3 V, the intermediate is usually detectable by spectroscopy. A common procedure is to prepare equimolar solutions of A and $\text{A}^{2\mp}$ and measure the amount of $\text{A}^{\bullet\mp}$ at equilibrium. The equilibrium constant of reaction 60, is given by



$\log K_i = \pm F(E^{\circ}_1 - E^{\circ}_2)/RT$ so the spectroscopic measurement of K_i affords the difference in standard potentials. The spectroscopic methods include, for example, electron paramagnetic spectroscopy²²⁹ and, for some organometallic systems, infrared measurements of CO bands.¹⁹⁹ In any case, detection of the intermediate can be taken as proof that the reactions are not concerted two-electron transfers.

For $E^{\circ}_1 - E^{\circ}_2$ greater than about ∓ 0.3 V, detection of the intermediate is difficult to achieve owing to its low concentration, $< 0.3\%$ of the initial concentrations of A and $\text{A}^{2\mp}$ being present as the ion radical. In some cases the absence of an EPR signal is used to put an upper limit on K_i , in one case concluding that $K_i \leq 10^{-16}$ (potential inversion equal to -1 V) for a phosphido-bridged diiron carbonyl complex.²⁰⁸ Though a relevant observation, the lack of an EPR

signal should not be used to derive quantitative information about the extent of potential inversion.

In this range of large potential inversions, it is reasonable to ask if the two electrons might be transferred in a concerted manner. Some guidance can be found from the conclusion, discussed above, that $\Delta G^\circ_1 = \lambda_1$ represents a crossing point between sequential electron transfers and a concerted two-electron transfer reaction. When $\Delta G^\circ_1 > \lambda_1$ the concerted reaction is favored. However, it is difficult to know the one-electron reorganization energy for a given system showing strong potential inversion. In organic systems, many cases of potential inversion involve aromatic systems and Kojima and Bard¹¹⁴ found that λ_1 in DMF for twenty aromatic neutral/anion radical couples was in the range of 0.5 to 0.8 eV. Taking the lower end of this range for λ_1 , we can say that crossover to a concerted two-electron reaction will occur when $\Delta G^\circ_1 = \lambda_1 = 0.5$ eV and, because ΔG°_1 is half the extent of potential inversion (see above), this would occur with potential inversion of -1 V for a reduction reaction. Thus, concerted two-electron transfer is likely to occur only when the extent of potential inversion is very large.

A similar conclusion was reached by Evans,²⁸⁹ who considered a related but actually quite different definition of a concerted process. Namely, he proposed that a bona fide intermediate must be able to diffusively escape from the electrode before undergoing the second electron-transfer reaction. Using the criterion of 10 \AA as the minimum distance defining an escape, it was concluded that no bona fide intermediates could be formed in a reduction if $E^\circ_1 - E^\circ_2$ was more negative than about -0.4 V. Under this condition, insertion of the first electron would be followed immediately by the second before the "intermediate" could escape, thus bringing about what is effectively a concerted two-electron process. Again, the word "concerted" means that no intermediate exists, not that the two electrons tunnel through the barrier simultaneously.²⁹⁰

So, in the cases of mild inversion (0 to about ∓ 0.3 V), the intermediate can often be detected by independent means thus ruling out a concerted process. It is only with stronger inversion that the concerted two-electron electrode reaction becomes likely.

4. Summary

This presentation has focused on the thermodynamic and kinetic aspects of one- and two-electron reactions in molecular electrochemistry. The thermodynamic features involve the standard potentials of the electron-transfer reactions and their dependence on the chemical structure of the reactants and products and the effects of the medium in which they are studied (solvent, electrolyte). There is a very strong relation, on both a theoretical and practical basis, between chemistry and electrochemistry in the study and characterization of these electron-transfer reactions.

The kinetics of the electron-transfer reactions are more difficult to interpret, in spite of abundant theoretical guidance. Nevertheless, giant strides have been made in understanding the rates of both electrode reactions and solution-phase electron-transfer reactions.

This paper has focused almost exclusively on electron-transfer that is not coupled to various chemical reactions involving reactants and products. These of course are of great importance and are keys to the many applications of electrochemistry, for example, in electrochemical synthesis. It seems likely that knowledge of the fundamentals of

electron transfer will continue to benefit our understanding of complete reactions, electron transfers plus coupled chemistry.

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- (70) The term "standard potential", $E^{\circ}_{\text{Ox/Red}}$, is customarily reserved to potentials obtained by extrapolation to infinite dilution. That is, there are no activity effects in the measurement. When measurements are made at finite ionic strength, the potential is usually called a "formal potential", $E^{\circ\prime}_{\text{Ox/Red}}$, in that it includes activity coefficients of Ox and Red, γ_{Ox} and γ_{Red} : $E^{\circ\prime}_{\text{Ox/Red}} = E^{\circ}_{\text{Ox/Red}} + (RT/nF) \ln(\gamma_{\text{Ox}}/\gamma_{\text{Red}})$. This expression is only relevant in those cases where only activity effects prevail. In some cases, there are unknown and unspecified interactions with the solvent/electrolyte (hydrogen bonding, complexation, ion pairing) that also affect the formal potential. Thus, the formal potential is simply the effective potential under given experimental conditions. Many standard potentials are determined by voltammetry. For all electroanalytical methods based on transient diffusion only (no convection) there is defined a half-wave potential, $E_{1/2}$, which is equal to the formal potential with a usually small correction term arising from differences in diffusion coefficients of Ox and Red, D_{Ox} and D_{Red} : $E_{1/2, \text{Ox/Red}} = E^{\circ\prime}_{\text{Ox/Red}} + (RT/2nF) \ln(D_{\text{Red}}/D_{\text{Ox}})$. Occasionally⁶² the diffusion coefficient term is evaluated. In this paper, standard potential, formal potential and half-wave potential will be used interchangeably unless a clear distinction is needed.
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