

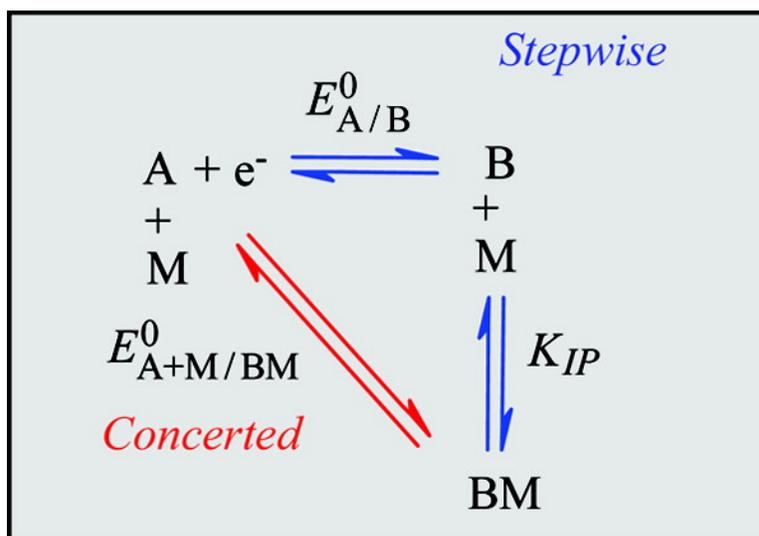
Article

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Evidence for Concerted Pathways in Ion-Pairing Coupled Electron Transfers

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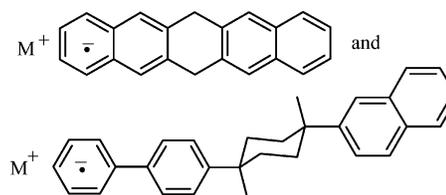
Abstract: Ion-pairing with electro-inactive metal ions may change drastically the thermodynamic and kinetic reactivity of electron transfer in chemical and biochemical processes. Besides the classical stepwise pathways (electron-transfer first, followed by ion-pairing or vice versa), ion-pairing may also occur concertedly with electron transfer. The latter pathway avoids high-energy intermediates but a key issue is that of the kinetic price to pay to benefit from this thermodynamic advantage. A model is proposed leading to activation/driving force relationships characterizing such concerted associative electron transfers for intermolecular and intramolecular homogeneous reactions and for electrochemical reactions. Contrary to previous assertions, the driving force of the reaction (defined as the opposite of the reaction standard free energy), as well as the intrinsic barrier, does not depend on the concentration of the ion-pairing agent, which simply plays the role of one of the reactants. Besides solvent and intramolecular reorganization, the energy of the bond being formed is the main component of the intrinsic barrier. Application of these considerations to reactions reported in recent literature illustrates how concerted ion-pairing electron-transfer reactions can be diagnosed and how competition between stepwise and concerted pathways can be analyzed. It provided the first experimental evidence of the viability of concerted ion-pairing electron-transfer reactions.

Introduction

The presence of ions that do not directly partake in an electron-transfer reaction may strongly affect its overall kinetics, and even their mechanism, through interactions between these ions and the reactants and/or products. Deciphering the ways in which this influence operates is important from a fundamental standpoint but also in view of the role that nonelectroactive ions are deemed to play in natural electron-transfer processes.¹

In most cases, investigations of the role of ion-pairing in the thermodynamics and kinetics of electron transfer have concerned the association of electroactive anions with an electroinactive cation, rather than the opposite arrangement. Early work² has shown that transfer of the cation in the ion pair accompanies the homogeneous electron transfer in systems where the anion radicals exist primarily as ion pairs. These systems involved anion radicals of aromatic hydrocarbons and ketones paired with alkali metal cations in ethereal solvents of low dielectric constant and large differences were found in the rate constants for exchange between an unpaired anion radical and its parent

molecule, and between a paired anion radical and its parent molecule. Theoretical considerations have allowed a discussion of the various mechanistic possibilities in systems such as those represented below^{3,4}



Nonspecific effects of electroinactive counterions on electron-transfer kinetics have attracted early attention, leading to the expression of ion–ion interaction contributions to the reorganization energy within a Debye–Hückel framework.⁵ Further refinements of the theory have then been developed.⁶ Attempts to apply these models to experimental systems have been rare.⁷ In spite of a large body of experimental data, interesting systems such as polyoxometalates have not provided real opportunities to test these theoretical approaches, because, owing to their high charges, the kinetics of electrochemical and self-exchange electron transfers is governed mostly by electrostatic work terms that blur the contribution of ion atmosphere reorganization.^{8,9,10}

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As in the homogeneous case, specific interactions involving ion-pairs strongly influence the thermodynamics and kinetics of electrochemical electron-transfer reactions.¹¹ They may also influence the mechanisms and kinetics of follow-up reactions.^{12–14} Ion-pairing is also deemed to play an important role in the thermodynamics and kinetics of electron-transfer reactions in the actively investigated room-temperature ionic liquids.^{15–18}

Ion-pairing may also influence the kinetics of reactions that are not necessarily driven by a simple electron-transfer step such as Diels–Alder reactions.¹⁹

Ion-pairing and electron transfer may be associated in a stepwise or concerted manner in the electrochemical case²⁰ as well as in homogeneous thermal or photoinduced reactions. The distinction and competition between stepwise and concerted pathways is thus an important, and so far unresolved, issue in several areas of electron-transfer chemistry and biochemistry. In spite of several experimental examples where ion-pairing was deemed important, no evidence for concerted pathways has been reported so far. This state of affairs appears to result from a lack of a reliable model describing the electron-transfer reactions that are triggered by ion-pairing. We present such a model below, focusing attention on homogeneous and electrochemical electron-transfer reactions that are coupled with ion-pairing of the electron-transfer product, *ion-pairing of the reactant being negligible*, with as a main objective the establishment of activation/driving force relationships characterizing such concerted associative electron transfers. Combination of these results with an estimation of the pre-exponential factors allows one to diagnose the occurrence of stepwise and concerted pathways and uncover the parameters that govern their competition.

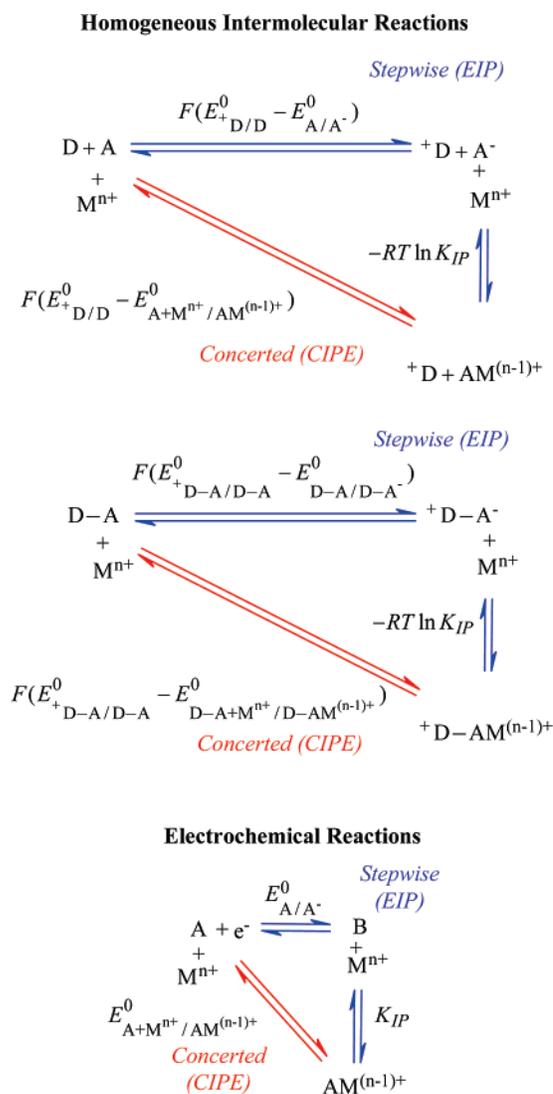
One difficulty in past attempts to rationalize the observed effects of cation addition on the kinetics of electron transfer^{19a,21} resides in the lack of a precise definition of the reaction driving force. The phrase driving force is usually connected with activation-driving force relationships such as Marcus's, the one established here in the concerted case or any other. If this is indeed the use one wants to make of the driving force concept, then it should be defined as the opposite of the reaction standard free energy, and as such referred to standard states. It is therefore independent of the reactant concentrations, in particular of the concentration of the ion-pairing agent. In past rationalizations, the driving force was instead considered as a function of the

concentration of the ion-pairing agent (according to the Nernst law) and incorporated as such in the Marcus equation for outersphere electron transfers.²¹ This approach is incorrect not only because ion-pairing-triggered electron transfer reactions are not outersphere electron transfers but also, more fundamentally, because it contravenes the basic principles of chemical equilibrium.

The next step was the search in experimental literature of examples where the diagnostic criteria we have established can be applied with a particular attention to reactions where the concerted pathway is predominant. In this connection, quite interesting examples of the effect of ion-pairing on the kinetics of electron transfer to quinones in thermal and photoinduced reactions have been reported recently.^{21a,b} As revealed by a detailed analysis of these experimental results, based on the present model of ion-pairing-triggered electron transfers, one of these series of reactions provides the first example so far of an electron transfer/concertedly triggered by ion-pairing. Analysis of an older electrochemical example¹¹ points to the stepwise character of the reaction.

Stepwise and Concerted Pathways. Theoretical Relationships. The stepwise versus concerted dichotomy is as depicted in Scheme 1. Because most experimental investigations are

Scheme 1



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concerned with ion-pairing of a reduced species by a Lewis acid, in most cases a nonelectroactive metal ion, we have considered this case in Scheme 1. The reaction scheme and the attending derivations can straightforwardly be adapted to the reverse, and more rare case, of an oxidation coupled with the reaction with a Lewis base.²² Because we focus on cases where ion-pairing of the reactant is negligible, the stepwise pathways to be considered only involve the EIP route shown in Scheme 1 with electron-transfer first, followed by ion-pairing.

Concerted Reactions. Contribution of Ion-Pairing to the Activation Barrier. The equilibrium potential of the system, or apparent standard potential, E_{ap}^0 , is a function of the concentration of ion-pairing agent, $[M]$ as represented in Figure 1, which shows the zones of stability of the various species.

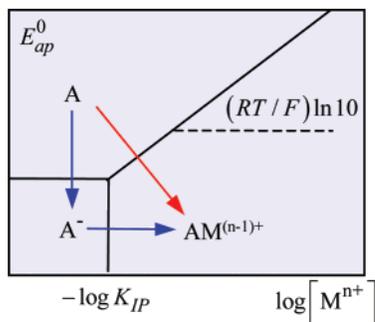


Figure 1. Zones of thermodynamic stability of the various species. Blue arrows, EIP stepwise pathway; red arrow, CIPE concerted pathway.

The equation of the oblique line is

$$\begin{aligned} E_{\text{ap}}^0 &= E_{\text{A/A}^-}^0 + \frac{RT}{F} \ln(K_{\text{IP}}[M^{n+}]) \\ &= E_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}^0 + \frac{RT}{F} \ln\left(\frac{[M^{n+}]}{[M^{n+}]^0}\right) \end{aligned} \quad (1)$$

where $E_{\text{A/A}^-}^0$ is the standard potential of the A/A^- couple and K_{IP} is the ion-pairing equilibrium constant. These two parameters define the thermodynamics of the EIP stepwise pathway, which is represented by blue arrows in Figure 1. The concerted pathway is represented by a red arrow in Figure 1. The standard potential of interest is then

$$E_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}^0 = E_{\text{A/A}^-}^0 + \frac{RT}{F} \ln(K_{\text{IP}}[M^{n+}]^0)$$

in which $[M^{n+}]^0$ is the concentration of M^{n+} at the standard state, usually 1 M. The introduction of $E_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}^0$ leads to the second expression of E_{ap}^0 in eq 1.

Homogeneous Reactions. For *intermolecular reactions* (Scheme 1), the electron is transferred from a homogeneous electron donor D, giving rise to D^+ . The reaction rate may be expressed as

$$\begin{aligned} -\frac{d[\text{A}]}{dt} &= -\frac{d[\text{D}]}{dt} = -\frac{d[\text{M}^{n+}]}{dt} = \frac{d[\text{AM}^{(n-1)+}]}{dt} = \frac{d[\text{D}^+]}{dt} \\ &= k_f [\text{A}][\text{M}^{n+}][\text{D}] - k_b [\text{AM}^{(n-1)+}][\text{D}^+] \end{aligned}$$

The driving force is defined as the opposite of the reaction standard free energy.

$$\Delta G^0 = F(E_{\text{D}^+/\text{D}}^0 - E_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}^0) \quad (2)$$

In conditions where the reaction is irreversible and in the presence of an excess of M, the reaction rate is proportional to M^{n+} . This implies a termolecular collision leading to a pre-exponential factor, $Z_{\text{ter}}^{\text{hom}}$, which is, for a 1 M reference state for M^{n+} concentrations, about 20 times smaller than the bimolecular collision factor $Z_{\text{bi}}^{\text{hom}}$, meaning that $Z_{\text{ter}}^{\text{hom}}[M^{n+}]^0$ is about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ or $Z_{\text{ter}}^{\text{hom}}$ is about $10^{10} \text{ M}^{-2} \text{ s}^{-1}$.²³

For *intramolecular reactions* (Scheme 1), the electron is transferred from one part of the molecule to the other. The reaction rate may be expressed as

$$\begin{aligned} -\frac{d[\text{D-A}]}{dt} &= -\frac{d[\text{M}^{n+}]}{dt} = \frac{d[\text{D-AM}^{(n-1)+}]}{dt} \\ &= k_f [\text{D-A}][\text{M}^{n+}] - k_b [\text{D-AM}^{(n-1)+}] \end{aligned}$$

and the reaction standard free energy is now

$$\Delta G^0 = F(E_{\text{D-A}^+/\text{D-A}}^0 - E_{\text{D-A+M}^{n+}/\text{D-AM}^{(n-1)+}}^0) \quad (3)$$

In conditions where the reaction is irreversible and in the presence of an excess of M, the reaction rate is proportional to $[M^{n+}]$. The pre-exponential factor is the classical bimolecular collision factor $Z_{\text{bi}}^{\text{hom}}$ (typically $3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$).

For *electrochemical reactions*, the current density is given by

$$\begin{aligned} \frac{I^{\text{conc}}}{F} &\approx k_{(\text{E})}^{\text{conc}} \left\{ [\text{A}]_{x=0} [\text{M}^{n+}] - [\text{AM}^{(n-1)+}]_{x=0} \times \right. \\ &\quad \left. \exp\left[\frac{F}{RT}(E - E_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}^0)\right] \right\} \end{aligned} \quad (4)$$

where I is the current density, E is the electrode potential, $k_{(\text{E})}^{\text{conc}}$ is the potential-dependent forward rate constant, and the subscript $x = 0$ indicates that the concentration is taken at the electrode surface. $[M^{n+}]$ is large enough to be considered as constant and equal to its bulk value throughout the diffusion layer. The pre-exponential factor for the concerted pathway, $Z_{\text{ter}}^{\text{el}}$, corresponds to a triple collision involving the electrode, A and M^{n+} ,

$$Z_{\text{ter}}^{\text{el}} = \nu \frac{f_{\ddagger}}{f_{\text{AM}^{n+}}^{\text{trans-x}}} K_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}} [M^{n+}]^0$$

where ν is the frequency at which the transition state collapses into products, f_{\ddagger} is the translation partition function of the transition state, $f_{\text{AM}^{n+}}^{\text{trans-x}}$ is the translation partition function of the precursor complex AM^{n+} resulting from the collision of A and M^{n+} along a direction perpendicular to the electrode surface, and $K_{\text{A+M}^{n+}/\text{AM}^{(n-1)+}}$ is the equilibrium constant corresponding to the formation of AM^{n+} from A and M^{n+} ,

$$\begin{aligned} \frac{f_{\ddagger}}{f_{\text{AM}^{n+}}^{\text{trans-x}}} &= \frac{k_B T}{h\nu} \frac{1}{\sqrt{2\pi(m_A + m_{M^{n+}})k_B T/h^2}} \\ &= \sqrt{\frac{RT}{2\pi(M_A + M_{M^{n+}})}} \end{aligned}$$

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where m s and M s are the molecular and molar masses, respectively, and

$$K_{A+M^{n+}/AM^{(n-1)+}} = \frac{Z_{bi}^{hom}}{k_B T/h}$$

For $[M^{n+}]^0 = 1 M$,²³

$$Z_{ter}^{el}[M^{n+}]^0 \approx \frac{Z^{el}}{20}$$

Typically,

$$Z_{ter}^{el}[M]^0 \approx 1.5 \times 10^3 \text{ cm/s}$$

In all three cases, activation involves solvent reorganization and a contribution of ion-pair formation. The latter factor can be derived from a Morse curve representation of the potential-energy variation upon changing the distance between the moieties of the ion pair as represented in Figure 2, similarly to the theory of dissociative electron transfer.²⁴

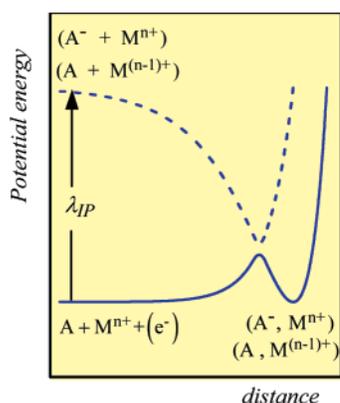


Figure 2. Electron-transfer concerted with ion-pairing. Morse curve potential-energy profiles.

Figure 2 shows a situation where the driving force is zero and represents only the contribution of ion pair formation to which solvent (λ_0) and intramolecular (λ_i) reorganization should be added:

$$\lambda^{conc} = \lambda_{IP} + \lambda_0 + \lambda_i \quad (5)$$

The product system, that is, the ion-pair, is represented by a Morse curve profile with a dissociation energy, noted λ_{IP} , and the reactant system by a purely dissociative profile equal to the repulsive part of the product system. The use of Morse curves in the modeling of bond making and breaking is suited to the case where ion-pairing is so strong that dissociation is homolytic (example in ref 20). This corresponds to a situation where, inside the solvent shell surrounding the ion-pair the oxidation potential of B is smaller than the oxidation potential of M. In the reverse case, heterolytic dissociation prevails. In spite of its resulting Coulombic character, the interaction within the ion pair may nevertheless be approximately represented by the same system of Morse curves, with however a different definition of λ_{IP} .

It follows that for homogeneous concerted reactions, the forward rate constant is given by

$$k_f^{conc} = Z^{hom} \exp\left[-\frac{\Delta G^\ddagger}{RT}\right]$$

with²⁴

$$\Delta G^\ddagger = \frac{\lambda_{IP} + \lambda_0 + \lambda_i}{4} \left(1 + \frac{\Delta G^0}{\lambda_{IP} + \lambda_0 + \lambda_i}\right)^2 \quad (6)$$

and

$$Z^{hom} = Z_{ter}^{hom} \text{ or } Z_{bi}^{hom}$$

for inter- and intramolecular reactions respectively. ΔG^0 is given by eq 2 in the first case and eq 3 in the second.

The activation-driving force relationship is therefore given by the familiar Marcus quadratic equation,²⁵ with a driving force and a reorganization energy that are independent of the concentration of the ion-pairing agent.

In the electrochemical case, eq 6 applies to each of the electrode electronic states. After summation over the electronic states and linearization,^{25,26} eq 4 becomes

$$\frac{I}{F} \approx k_S^{conc} \exp\left[-\frac{\alpha^{conc} F}{RT}(E - E_{A+M^{n+}/AM^{(n-1)+}}^0)\right] \times \left\{ [A]_{x=0}[M^{n+}] - [AM^{(n-1)+}]_{x=0} \times \exp\left[\frac{F}{RT}(E - E_{A+M^{n+}/AM^{(n-1)+}}^0)\right] \right\}$$

(α^{conc} : transfer coefficient)

with

$$k_S^{conc} = Z_{ter}^{el} \sqrt{\frac{\pi RT}{4 \lambda^{conc}}} \exp\left(-\frac{\lambda^{conc}}{4RT}\right)$$

and

$$k_{(E)}^{conc} = Z_{ter}^{el} \sqrt{\frac{\pi RT}{4 \lambda^{conc}}} \exp\left(-\frac{\lambda^{conc}}{4RT}\right) \times \exp\left[-\frac{\alpha^{conc} F}{RT}(E - E_{A+M^{n+}/AM^{(n-1)+}}^0)\right]$$

Introducing the apparent standard potential, E_{ap}^0 , defined in eq 1,

$$\begin{aligned} \frac{I}{F} &\approx k_S^{conc} [M^{n+}]^{1-\alpha^{conc}} \exp\left[-\frac{\alpha^{conc} F}{RT}(E - E_{ap}^0)\right] \times \\ &\left\{ [A]_{x=0}[M^{n+}] - [AM^{(n-1)+}]_{x=0} \exp\left[\frac{F}{RT}(E - E_{ap}^0)\right] \right\} \\ &= k_S^{ap} \exp\left[-\frac{\alpha^{conc} F}{RT}(E - E_{ap}^0)\right] \times \\ &\left\{ [A]_{x=0}[M^{n+}] - [AM^{(n-1)+}]_{x=0} \exp\left[\frac{F}{RT}(E - E_{ap}^0)\right] \right\} \end{aligned}$$

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with

$$k_S^{\text{ap,conc}} = k_S^{\text{conc}} [M^{n+}]^0 \left(\frac{[M^{n+}]}{[M^{n+}]^0} \right)^{1-\alpha^{\text{conc}}}$$

Discrimination and Competition between the Concerted and Stepwise Pathways. In the stepwise case, two situations may arise. In one of these, the ion-pairing reaction is fast in both directions and therefore remains at equilibrium during the whole course of the reaction. In the other, electron transfer is fast in both directions and acts as a pre-equilibrium toward a rate-determining ion-pairing reaction.

Homogeneous Reactions. In the first situation,

$$\begin{aligned} -\frac{d[A]}{dt} &= -\frac{d[D]}{dt} = \frac{d[A^-]}{dt} = \frac{d[D^+]}{dt} \\ &= k_f [A][D] - k_b [A^-][D^+] \end{aligned}$$

$$[A^-] = \frac{([A^-] + [AM^{(n-1)+}])}{1 + K_{IP}[M^{n+}]} \approx \frac{([A^-] + [AM^{(n-1)+}])}{K_{IP}[M^{n+}]}$$

(insofar as substantial ion-pairing effects are concerned, $K_{IP}[M^{n+}] \gg 1$).

In conditions where the reaction is irreversible, the reaction rate is therefore independent of the concentration of the ion-pairing agent, a situation that is easy to distinguish from the concerted case where the reaction rate is proportional to the concentration of the ion-pairing agent.

A second important situation arises when electron transfer is fast in both directions and acts as a pre-equilibrium toward a rate-determining ion-pairing reaction (rate constant: k_{IP}). Then,

$$\begin{aligned} -\frac{d[A]}{dt} &= -\frac{d[D]}{dt} = \frac{d[AM^{(n-1)+}]}{dt} \\ &= \frac{[A][D][M^{n+}]}{[D^+]} k_{IP} \exp\left[-\frac{F}{RT}(E_{D^+/D}^0 - E_{A/A^-}^0)\right] \end{aligned}$$

In conditions where the reaction is irreversible, the reaction rate is proportional to the concentration of the ion-pairing agent, as in the concerted case where the reaction rate is proportional to the concentration of the ion-pairing agent. A way of distinguishing the two pathways resides in the fact that the reaction rate is inversely proportional to the concentration of D^+ , which is not the case for the concerted pathway.

Electrochemical Reactions. For the stepwise EIP pathway, the current density is given, after summation over the electrode electronic states and linearization by

$$\frac{I^{\text{step}}}{F} \approx k_S^{\text{step}} \exp\left[-\frac{\alpha^{\text{step}} F}{RT}(E - E_{A/A^-}^0)\right] \times \left\{ [A]_{x=0} - [A^-]_{x=0} \exp\left[\frac{F}{RT}(E - E_{A/A^-}^0)\right] \right\}$$

(α^{step} : transfer coefficient)

In a first limit, the ion-pairing reaction is fast in both directions. As in the homogeneous case,

$$\begin{aligned} [A^-]_{x=0} &= \frac{([A^-]_{x=0} + [AM^{(n-1)+}]_{x=0})}{1 + K_{IP}[M^{n+}]} \\ &\approx \frac{([A^-]_{x=0} + [AM^{(n-1)+}]_{x=0})}{K_{IP}[M^{n+}]} \end{aligned}$$

and thus,

$$\begin{aligned} \frac{I}{F} &\approx k_S^{\text{step}} \exp\left[-\frac{\alpha^{\text{step}} F}{RT}(E - E_{A/A^-}^0)\right] \times \\ &\left\{ [A]_{x=0} - \frac{([A^-]_{x=0} + [AM^{(n-1)+}]_{x=0})}{K_{IP}[M^{n+}]} \times \right. \\ &\left. \exp\left[\frac{F}{RT}(E - E_{A/A^-}^0)\right] \right\} \end{aligned}$$

introducing the same apparent standard potential as before (eq 1)

$$\begin{aligned} \frac{I^{\text{step}}}{F} &\approx k_S^{\text{ap,step}} \exp\left[-\frac{\alpha^{\text{step}} F}{RT}(E - E_{\text{ap}}^0)\right] \times \\ &\left\{ [A]_{x=0} - ([A^-]_{x=0} + [AM^{(n-1)+}]_{x=0}) \exp\left[\frac{F}{RT}(E - E_{\text{ap}}^0)\right] \right\} \end{aligned}$$

with

$$\begin{aligned} k_S^{\text{ap,step}} &= \frac{k_S^{\text{step}}}{(K_{IP}[M^{n+}])^{\alpha^{\text{step}}}} \\ &= \frac{Z^{\text{el}}}{(K_{IP}[M^{n+}])^{\alpha^{\text{step}}}} \sqrt{\frac{\pi RT}{4 \lambda^{\text{step}}}} \exp\left(-\frac{\lambda^{\text{step}}}{4RT}\right) \end{aligned}$$

(λ^{step} : reorganization energy for the initial electron-transfer step)

The variations of the apparent standard rate constant, k_S^{ap} , with the concentration of ion-pairing agent thus provide an easy diagnosis of the concerted and stepwise mechanisms. With $\alpha^{\text{step}} \approx \alpha^{\text{conc}} \approx 0.5$, k_S^{ap} increases as $\sqrt{[M^{n+}]}$ in the first case and decrease as $1/\sqrt{[M^{n+}]}$ in the second. Equivalently, the forward rate constant increases as $[M^{n+}]$ in the first case and is independent of $[M^{n+}]$ in the second. In cases where the overall reaction is irreversible, the cyclic voltammetric peak is expected to vary by $(RT/2\alpha F) \ln 10$ by decade $[M^{n+}]$, that is, ca. 60 mV at 298 K for the concerted pathway and is independent of $[M^{n+}]$ in the stepwise case.

In a second limiting situation, electron transfer is fast in both directions and acts as a pre-equilibrium toward a rate-determining ion-pairing reaction. The cyclic voltammetric peak potential is then expected to vary by $(RT/2F) \ln 10$, that is, ca. 30 mV at 298 K, by decade of $[M^{n+}]$. The peak width is also half of what it is in the concerted case.

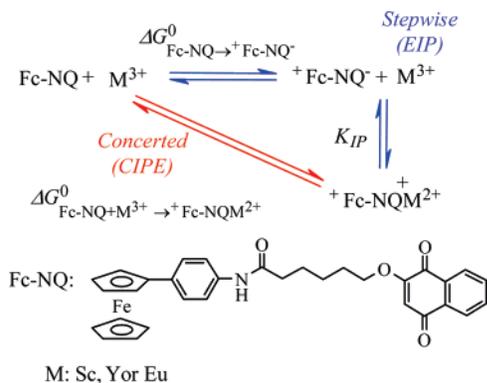
The various expressions that have been derived of the rate of the homogeneous and electrochemical concerted and stepwise pathways give access to the parameters that governed the competition between them.

Illustrative Examples

Homogeneous Reactions. Two interesting systems that illustrate the application of the above theoretical analysis have been recently investigated in detail. One of these involves an intramolecular electron transfer triggered by the addition of an

ion-pairing agent as depicted in Scheme 2.^{21a,b} In acetonitrile at 298 K, no intramolecular electron transfer occurs in the absence of an ion-pairing agent. It is triggered by addition of either Sc³⁺, or Y³⁺, or Eu³⁺ ions. It is remarkable that the

Scheme 2



reaction is first order toward the ion-pairing agent, as shown in Figure 3.

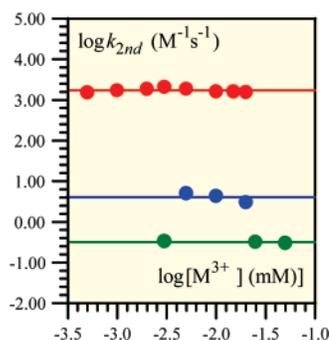


Figure 3. Second-order rate constants for the intramolecular electron transfer in Fc–NQ triggered by the addition of Sc³⁺ (red dots), Y³⁺ (blue dots), and Eu³⁺ (green dots).

The ensuing second-order rate constants at 298 K are thus

$$\log k_{2nd} (\text{M}^{-1} \text{s}^{-1}) = 3.23 (\text{Sc}^{3+}), 0.60 (\text{Y}^{3+}), -0.50 (\text{Eu}^{3+})$$

and, therefore, taking as approximate value of the collision frequency $Z_{bi}^{\text{hom}} = 3 \times 10^{11}$ in

$$\Delta G^\ddagger = RT \ln(Z_{bi}^{\text{hom}}/k_{2nd})$$

the values of the activation free energy, ΔG^\ddagger , are

$$\Delta G^\ddagger (\text{eV}) = 0.49 (\text{Sc}^{3+}), 0.64 (\text{Y}^{3+}), 0.71 (\text{Eu}^{3+})$$

The fact that the reaction becomes possible upon the addition of Sc³⁺, Y³⁺, or Eu³⁺ ions is the consequence of strong ion-pairing with the NQ⁻ moiety. The thermodynamics of the system is characterized by the driving force of the electron transfer between the Fc and the NQ moieties in the EIP pathway, $-\Delta G_{\text{Fc-NQ} \rightarrow \text{Fc-NQ}^-}^0$. The driving force of the ion-pairing assisted electron-transfer (CEIP pathway) between the Fc and the NQ moieties is $-\Delta G_{\text{Fc-NQ}^+ \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0$. These two standard reaction free energies are related to the characteristic standard potentials by the following equations,

$$\Delta G_{\text{Fc-NQ} \rightarrow \text{Fc-NQ}^-}^0 = F(E_{\text{Fc}^+/\text{Fc}}^0 - E_{\text{NQ}/\text{NQ}^-}^0)$$

$$\Delta G_{\text{Fc-NQ}^+ \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0 = F(E_{\text{Fc}^+/\text{Fc}}^0 - E_{\text{NQ}^+ \text{M}^{3+}/\text{NQM}^{2+}}^0)$$

noting that

$$E_{\text{NQ}^+ \text{M}^{3+}/\text{NQM}^{2+}}^0 = E_{\text{NQ}/\text{NQ}^-}^0 + \frac{RT}{F} \ln K_{IP}$$

$E_{\text{Fc}^+/\text{Fc}}^0$ and $E_{\text{NQ}/\text{NQ}^-}^0$ are obtained from the reversible cyclic voltammetric waves of Fc–NQ in the absence of an ion-pairing agent, which show fast electron-transfer kinetics. Upon the addition of Sc³⁺, Y³⁺, or Eu³⁺ ions, the apparent standard potential, E_{ap}^0 , shifts toward positive values by $(RT/F) \ln 10$ by decade of [M],

$$\begin{aligned} E_{\text{ap}}^0 &= E_{\text{NQ}/\text{NQ}^-}^0 + \frac{RT}{F} \ln K_{IP} + \frac{RT}{F} \ln [\text{M}^{3+}] \\ &= E_{\text{NQ}^+ \text{M}^{3+}/\text{NQM}^{2+}}^0 + \frac{RT}{F} \ln [\text{M}^{3+}] \end{aligned}$$

in line with the fact that ⁺Fc–NQ⁻ is strongly ion-paired, whereas Fc–NQ is not. These variations allow one to derive the ion-pairing equilibrium constant, K_{IP} and the standard potential $E_{\text{NQ}^+ \text{M}^{3+}/\text{NQM}^{2+}}^0$, which corresponds to the concerted reaction pathway and is equal to E_{ap}^0 for a molar concentration of M³⁺. As noted earlier, and unlike the interpretation in ref 21a, the driving force of the concerted pathway is indeed independent of the concentration of M³⁺. Rather, M³⁺ then plays the role of a reactant as pictured in Scheme 2.

From what precedes and the data in ref 21a, we obtain the following values of the various thermodynamic parameters (equilibrium constants in M⁻¹, standard potentials in V vs SCE, standard reaction free energies in eV).

$$E_{\text{Fc}^+/\text{Fc}}^0 = 0.38, E_{\text{NQ}/\text{NQ}^-}^0 = -0.81$$

$$\Delta G_{\text{Fc-NQ} \rightarrow \text{Fc-NQ}^-}^0 = 1.19$$

$$E_{\text{NQ}^+ \text{M}^{3+}/\text{NQM}^{2+}}^0 = 1.39 (\text{Sc}^{3+}), 1.02 (\text{Y}^{3+}), 0.93 (\text{Eu}^{3+})$$

$$\log K_{IP} = 37.2 (\text{Sc}^{3+}), 31.0 (\text{Y}^{3+}), 29.5 (\text{Eu}^{3+})^{21a}$$

$$\begin{aligned} \Delta G_{\text{Fc-NQ}^+ \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0 &= -1.01 (\text{Sc}^{3+}), -0.64 (\text{Y}^{3+}), \\ &\quad -0.55 (\text{Eu}^{3+}) \end{aligned}$$

On these bases, we may now discuss the mechanism of the homogeneous reaction, considering first the stepwise pathway. For the overall kinetics to be first order in M³⁺, the initial electron transfer should act as a pre-equilibrium to the successive ion-pairing step (in the other limiting situation where electron transfer is associated with a fast and reversible ion-pairing step, the reaction rate is independent of [M]). The equilibrium constant for the first step is 0.8×10^{-20} . Thus, if ion-pairing was so fast as being limited by diffusion, k_{2nd} would be smaller than $10^{-10} \text{ M}^{-1} \text{ s}^{-1}$, in obvious disagreement with experimental data. We are thus left with the concerted mechanism. As shown in the theoretical section, the activation free energy may be expressed by the quadratic expression,

$$\Delta G^\ddagger = \frac{\lambda^{\text{conc}}}{4} \left(1 + \frac{\Delta G_{\text{Fc-NQ}^+ \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0}{\lambda^{\text{conc}}} \right)^2 \quad (7)$$

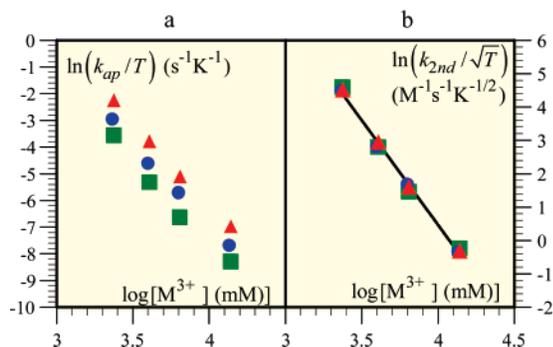


Figure 4. Intramolecular electron transfer in Fc-NQ triggered by the addition of Sc^{3+} . (a) Variation of the pseudo-first-order rate constant, k_{ap} , with temperature for $[\text{Sc}^{3+}] = 20$ (red triangles), 10 (blue dots), 5 (green squares) mM plotted as in ref 20. (b) Variation of second-order rate constant with temperature obtained from the same data and plotted according to eq 8 that characterizes the concerted pathway.

where λ^{conc} is the sum of the energies involved in solvent reorganization, intramolecular reorganization, and in the formation of the ion pair (eq 5). At variance with the interpretation given in ref 20, it is, from first principles, independent of the concentration of the ion-pairing agent as already emphasized. Fitting of the rate data, taking into account the above values of $\Delta G_{\text{Fc-NQ}^{\cdot-} + \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0$, leads to the following values of λ^{conc} , in eV.

$$\lambda = 3.55 (\text{Sc}^{3+}), 3.7 (\text{Y}^{3+}), 3.85 (\text{Eu}^{3+})$$

The variations of the rate constant with temperature in the case of Sc^{3+} , recast from ref 20 in Figure 4, are also consistent with the concerted mechanism. Indeed, the second-order rate constant may be expressed as

$$\ln k_{2\text{nd}} = \ln Z_{\text{bi}} - \frac{\Delta G^\ddagger}{RT}$$

$$\text{i.e.: } \ln \left(\frac{k_{2\text{nd}}}{\sqrt{T}} \right) = \left[\ln \left(N_a d^2 \sqrt{\frac{8\pi R}{M}} \right) + \frac{\Delta S^\ddagger}{R} \right] - \frac{\Delta H^\ddagger}{RT} \quad (8)$$

(ΔS^\ddagger and ΔH^\ddagger , activation entropy and enthalpy respectively; M , reduced molar mass of the reactants; d , collision distance; N_a , Avogadro number).

From the intercept, one obtains $\Delta S^\ddagger = 0.17 \text{ meV/K}$. Differentiation of eq 7, assuming that λ^{conc} is independent of temperature leads to the following relationship,

$$\Delta S^\ddagger = \alpha \Delta S_{\text{Fc-NQ}^{\cdot-} + \text{M}^{3+} \rightarrow \text{Fc-NQ}^{\cdot-}, \text{M}}^0$$

where the symmetry factor (transfer coefficient) α is expressed as,

$$\alpha^{\text{conc}} = \frac{1}{2} \left(1 + \frac{\Delta G_{\text{Fc-NQ}^{\cdot-} + \text{M}^{3+} \rightarrow \text{Fc-NQM}^{2+}}^0}{\lambda^{\text{conc}}} \right)$$

Because α^{conc} is close to 0.5, we obtain the following an estimate of the standard entropy of the reaction,

$$\Delta S_{\text{Fc-NQ}^{\cdot-} + \text{Sc}^{3+} \rightarrow \text{Fc-NQSc}^{2+}}^0 = 0.34 \text{ meV/K}^+$$

meaning that the entropic contribution to the standard free energy of reaction is 0.100 eV at 298 K. This appears as a reasonable value for the concerted reaction where the entropy

decrease resulting from the formation of the ion-pair is overcompensated by the increase of solvation entropy from Sc^{3+} to Fc-NQSc^{2+} . The decrease of the entropy contribution due to the formation of the ion pair may be estimated as ca. 0.08 eV at 298 K, if the two reactants are approximated by two equivalent hard spheres. The contribution of the solvation entropy increase may thus be estimated as ca. 0.18 eV at 298 K.

If we consider the ion-pairing reaction itself, $^+\text{Fc-NQ}^- + \text{M}^{3+} \rightarrow ^+\text{Fc-NQM}^{2+}$, rather than the concerted electron-transfer reaction, $\text{Fc-NQ} + \text{M}^{3+} \rightarrow ^+\text{Fc-NQM}^{2+}$, the entropic contribution to the standard free energy of reaction is expected to be even smaller. We thus infer that

$$\Delta H_{\text{IP}}^0 \approx \Delta G_{\text{IP}}^0 = -RT \ln K_{\text{IP}}$$

$$= 2.20 (\text{Sc}^{3+}), 1.83 (\text{Y}^{3+}), 1.74 (\text{Eu}^{3+}) \text{ eV}$$

Coming back to the values of the reorganization energy, if we assume a small solvent reorganization energy on the order of 0.5 eV as for other intramolecular electron-transfer reactions²⁷ and neglecting the intramolecular reorganization, the contribution of ion-pairing to the reorganization energy, λ_{IP} may be estimated as

$$\lambda_{\text{IP}} \approx 3.05 (\text{Sc}^{3+}), 3.2 (\text{Y}^{3+}), 3.35 (\text{Eu}^{3+})$$

These values are much larger than the values of ΔH_{IP}^0 . This is not surprising because the dissociation energy of the ion pair within the solvent cage involved in the Morse curve model is expected to be much larger than the heterolytic dissociation energy into individually solvated fragments ions. It is even likely that, within the solvent cage, the Morse curve ends with $\text{Q} + \text{M}^{2+}$ rather than with $\text{Q}^- + \text{M}^{3+}$ fragments (in the gas phase, the $\text{M}^{2+}/\text{M}^{3+}$ ionization potential is on the order of 9–12 eV, whereas quinone electron affinities are on the order of 2 eV²⁸). It is clear that such strong ion-pairing constants and reorganization energies are relevant to contact rather than solvent-separated ion pairs. We also note that the reorganization energy does not vary strongly from one metal ion to the other. An independent estimate of the homolytic bond dissociation energy in the solvent cage where an ion pair is formed by neutralization of one of the three positive charges of the cation by the quinone anion radical negative charge, whereas the two remaining positive charges continue to induce a strong solvation, is not possible from existing gas phase and crystallographic data.

Another system of interest is the reduction in dichloromethane in the presence of *n*-tetrabutylammonium cations, of *p*-benzoquinone, and naphthoquinone (NQ) by the triplet excited-state of tetraphenylporphyrin, $^3\text{H}_2\text{P}$, leading to the quinone anion radicals and to the porphyrin cation radical (Scheme 3).^{21b}

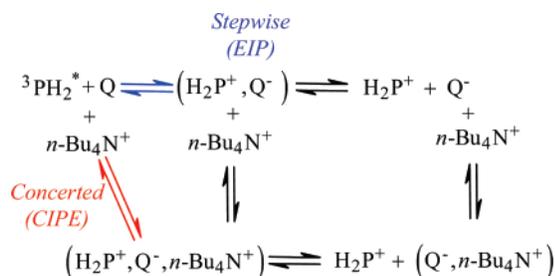
The rate of the reaction is proportional to the concentration of *n*-tetrabutylammonium cations, as seen in Figure 5, which shows that the third-order rate constant is indeed independent of the concentration of *n*-tetrabutylammonium cations.

The concerted pathway, if followed, would involve a termolecular reaction between the porphyrin triplet state, the quinone,

(27) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 105.

(28) *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, FL, 2001–2002; pp 10-153, 10-175.

Scheme 3



and the tetrabutylammonium cation, leading directly to a triple ion as sketched in Scheme 3. The rate constant thus writes

$$\ln k_{3\text{rd}} = \ln Z_{\text{ter}}^{\text{hom}} - \frac{\Delta G^\ddagger}{RT}$$

The termolecular pre-exponential factor, Z_{ter} , may be estimated as being approximately, $10^{10} \text{ M}^{-2} \text{ s}^{-1}$ at 298 K, as already mentioned. The activation free energies are therefore obtained from the data in Figure 5, $\log k_f = 9.44$ and 7.94 leading to $\Delta G^\ddagger = 0.033$ and 0.121 eV for *p*-benzoquinone and naphthoquinone, respectively.

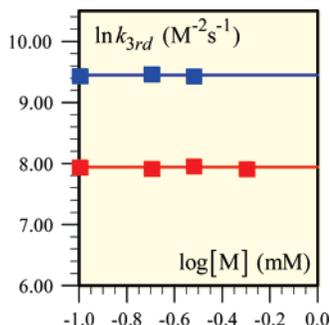


Figure 5. Electron transfer from the triplet excited-state of tetraphenylporphyrin to *p*-benzoquinone (blue squares) or naphthoquinone (red squares) in dichloromethane in the presence of *n*-tetrabutylammonium cations. Third-order rate constant as a function of the concentration of *n*-tetrabutylammonium cations.

As discussed in the theoretical section, the driving force of the reaction, measured by its standard free energy $\Delta G_{{}^3\text{PH}_2^* + \text{Q} + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0$, is not a function of the concentration of the *n*-tetrabutylammonium ion-pairing cation and so is the reorganization energy, λ^{conc} . Rather, *n*-Bu₄N⁺ is simply one of the reactants. The driving force may be expressed as

$$\begin{aligned}
 \Delta G_{{}^3\text{PH}_2^* + \text{Q} + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 &= \\
 F(E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^-/\text{Q}}^0) - E_{{}^3\text{PH}_2^*} &+ \\
 \Delta G_{\text{H}_2\text{P}^+ + \text{Q}^- + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 &= \\
 F(E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^- + n\text{-Bu}_4\text{N}^+ / (\text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0) - E_{{}^3\text{PH}_2^*} &+ \\
 \Delta G_{\text{H}_2\text{P}^+ + (\text{Q}^-, n\text{-Bu}_4\text{N}^+) \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 &
 \end{aligned}$$

where $E_{{}^3\text{PH}_2^*}$ is the energy of the triplet state of tetraphenylporphyrin (1.43 eV²⁹), and the E^0 's are the standard potentials of the subscript couples. The difference $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^-/\text{Q}}^0$ is not

exactly known because the cyclic voltammetric experiments that allow the determination of the E^0 's are carried out in the presence of a minimum amount (0.02 M) of *n*-Bu₄N⁺ serving as a supporting cation. We may infer from the latter experiments that $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^-/\text{Q}}^0 \geq 1.59$ and 1.79 V in the case of *p*-benzoquinone and naphthoquinone, respectively. In fact, the potential difference of interest in the estimation of the driving force for the concerted reaction is $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^- + n\text{-Bu}_4\text{N}^+ / (\text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0$, which can be derived from the plots of the standard potentials versus the *n*-Bu₄N⁺ concentration (Figure 12 in ref 21) taken for the standard conditions, that is, for $[n\text{-Bu}_4\text{N}^+] = 1$ M, leading to $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}^- + n\text{-Bu}_4\text{N}^+ / (\text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = 1.38$ and 1.61 V for *p*-benzoquinone and naphthoquinone, respectively. Another important ingredient of the driving force of the concerted reaction is $\Delta G_{\text{H}_2\text{P}^+ + (\text{Q}^-, n\text{-Bu}_4\text{N}^+) \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0$, the energy required for passing from the ion pair involving the quinone anion radical and *n*-Bu₄N⁺ to the triple ion cluster involving the same two ions and the porphyrin cation radical, which is the immediate product of the photochemical electron-transfer reaction. If this parameter is ignored, as it is in ref 21, $\Delta G_{{}^3\text{PH}_2^* + \text{Q} + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = -0.25$ and 0.18 eV for *p*-benzoquinone and naphthoquinone, respectively.

The reorganization energy, λ^{conc} , may accordingly be estimated from the application of

$$\Delta G^\ddagger = \frac{\lambda^{\text{conc}}}{4} \left(1 + \frac{\Delta G_{{}^3\text{PH}_2^* + \text{Q} + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0}{\lambda^{\text{conc}}} \right)^2$$

It follows that λ^{conc} would then be equal to 0.22 eV for *p*-benzoquinone. For naphthoquinone, there is no value of λ^{conc} that is compatible with the driving force and the experimental value of ΔG^\ddagger . The value for *p*-benzoquinone is obviously much too small to correspond to solvent reorganization and ion-pair formation.

In fact, the driving force is larger in both cases because the ion interaction energy is larger in the triple ion cluster than it is in the ion pair. A simplified picture of the structure of the triple ion cluster consists in placing the quinone anion radical in the center and one positive ion on each side at a distance d from the center. The interaction energy in the (H_2P^+ , Q^- , *n*-Bu₄N⁺) cluster may then be estimated as,

$$\begin{aligned}
 \Delta G_{\text{H}_2\text{P}^+ + \text{Q}^- + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 &= \\
 -\frac{14.4}{\epsilon} \left(\frac{2}{d} - \frac{1}{2d} \right) &= -\frac{3}{2} \frac{14.4}{\epsilon d}
 \end{aligned}$$

where ϵ is the solvent dielectric constant, ΔG is in eV, d is in Å, and, in the ion pair,

$$\Delta G_{\text{Q}^- + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = -\frac{14.4}{\epsilon d}$$

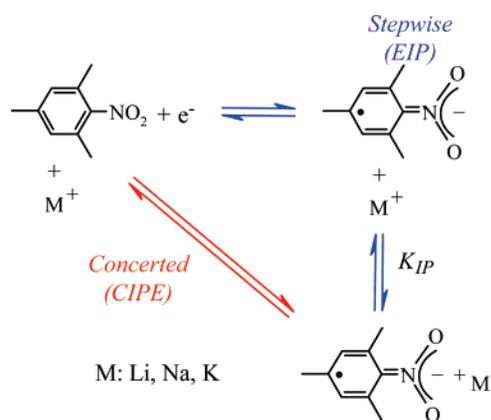
leading to

$$\Delta G_{\text{H}_2\text{P}^+ + (\text{Q}^-, n\text{-Bu}_4\text{N}^+) \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = -\frac{14.4}{2\epsilon d}$$

Taking $d = \sim 4$ Å, $\Delta G_{\text{H}_2\text{P}^+ + (\text{Q}^-, n\text{-Bu}_4\text{N}^+) \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = 0.2$ eV, and the driving forces may be re-estimated as $\Delta G_{{}^3\text{PH}_2^* + \text{Q} + n\text{-Bu}_4\text{N}^+ \rightarrow (\text{H}_2\text{P}^+, \text{Q}^-, n\text{-Bu}_4\text{N}^+)}^0 = -0.25$ and -0.018 eV for *p*-benzoquinone and naphthoquinone, respectively, thus leading

(29) Murow, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 2006; p 56.

Scheme 4



to $\lambda^{\text{conc}} = 0.31$ and 0.50 eV, respectively. Although larger, these values are still much too small to correspond to solvent reorganization *and* ion-pair formation, therefore ruling out the occurrence of the concerted pathway.

We are thus left with the stepwise EIP pathway. To follow the experimental kinetic order, the first electron-transfer step should act as a pre-equilibrium to the ion-pairing step. Maximizing the occurrence of this pathway implies considering that the ion-pairing rate constant is at the diffusion limit, say $k_{\text{dif}} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Then,

$$k_f = k_{\text{dif}} \exp\left[-\frac{\Delta G_{3\text{PH}_2^*+\text{Q}\rightarrow(\text{H}_2\text{P}^+, \text{Q}^-)}}{RT}\right]$$

Fitting of the experimental data requires that $\Delta G_{3\text{PH}_2^*+\text{Q}\rightarrow(\text{H}_2\text{P}^+, \text{Q}^-)}^0 = 0.03$ and 0.12 eV for *p*-benzoquinone and naphthoquinone, respectively. The standard free energy of the initial electron-transfer step may be expressed as

$$\Delta G_{3\text{PH}_2^*+\text{Q}\rightarrow(\text{H}_2\text{P}^+, \text{Q}^-)}^0 = F(E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}/\text{Q}^-}^0) - E_{3\text{PH}_2^*+\text{Q}}^0 + \Delta G_{\text{H}_2\text{P}^++\text{Q}\rightarrow(\text{H}_2\text{P}^+, \text{Q}^-)}^0$$

From the preceding estimations, $\Delta G_{\text{H}_2\text{P}^++\text{Q}\rightarrow(\text{H}_2\text{P}^+, \text{Q}^-)}^0 \approx 0.4$ eV. It follows that $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}/\text{Q}^-}^0$ should be equal to 1.86 and 1.95 V to match the experimental data for *p*-benzoquinone and naphthoquinone, respectively. This is quite possible because $E_{\text{H}_2\text{P}^+/\text{H}_2\text{P}}^0 - E_{\text{Q}/\text{Q}^-}^0 \geq 1.59$ or 1.79 V, as obtained from the values corresponding to the lowest concentration of *n*-Bu₄N⁺ for *p*-benzoquinone and naphthoquinone, respectively.

We may thus conclude that the stepwise EIP pathway is quite likely to be followed. As compared to the preceding experimental example, the change in mechanism falls in line with a much weaker ion-pairing, likely to involve solvent-separated rather than contact ion pairs. In such a low dielectric constant medium, it is also likely that some of the *n*-Bu₄N⁺ ions form ion-pairs with the PF₆⁻ counter-anions, thus influencing the ion-pairing equilibrium with the quinone anion-radicals.

Electrochemical Reactions. An early example is provided by the reduction (Scheme 4) of nitromesitylene in *N,N*-dimethylformamide in the presence of alkali metal cations (Li⁺, Na⁺, K⁺).¹¹ The forward rate constant, was determined by an impedance technique as a function of the alkali metal cation concentration. Mechanism assignment is unambiguous because the forward rate constant is independent of the cation concentra-

tion. This observation rules out the concerted mechanism and point to the occurrence of a stepwise EIP mechanism in which the rate determining step is electron transfer, whereas ion-pairing acts as a follow-up equilibrium. We note that this predominance of the stepwise mechanism parallels the fact that ion-pairing is not very strong ($K_{\text{IP}} = 660$ (K), 4800 (Na), 14 100 (Li)), much weaker than in the first homogeneous example discussed earlier.

Concluding Remarks

Ion-pairing-triggered electron-transfer reactions may occur in a concerted manner. When strong ion-pairing is involved, such concerted pathways have a definite thermodynamic advantage over stepwise pathways where the initial electron transfer is followed by the ion-pairing step in the sense that they avoid going through a high-energy intermediate. There is a kinetic price to pay for this thermodynamic advantage, namely the contribution of ion-pair formation to the activation barrier. An estimation of this contribution may be obtained through the modeling of the potential-energy profile of this associative electron-transfer reaction by means of repulsive and attractive Morse curves similarly to the theory of dissociative electron transfer. The familiar Marcus quadratic equation then relates the activation free energy to the driving force. Besides solvent and intermolecular reorganization, the contribution of ion-pair formation to the total reorganization energy is equal to the bond energy. From first principles, the driving force is independent of the ion-pairing agent concentration. It is indeed related to the *standard* chemical potential of the ion-pairing agent (usually defined for a 1 M concentration) through

$$FE_{\text{A}+\text{M}/\text{BM}}^0 = \mu_{\text{A}}^0 + \mu_{\text{M}}^0 - \mu_{\text{BM}}^0$$

Competition with the stepwise pathway should also take into account the fact that the concerted pathway involves a triple collision. This is the case for homogeneous intermolecular reactions and for electrochemical reactions involving free-moving reactants. A simple bimolecular collision is required in the case where ion-pairing triggers an intramolecular electron transfer.

In all of the cases, the reaction order in the ion-pairing agent allows the discrimination between the concerted and the stepwise pathway when the latter involves a fast and equilibrated ion-pairing step. The forward reaction is indeed first order in the ion-pairing agent in the first case and zero order in the second. Distinction is more ambiguous when the initial electron transfer acts as a pre-equilibrium toward a rate-determining ion-pairing step because the reaction is then first order in the ion-pairing agent. It is, however, still possible by introduction of the oxidized form of the electron donor and determination of the corresponding reaction order. This is also the case for the electrochemical reaction where the characteristics of the current–potential responses can equivalently be used in this purpose.

The first experimental system we have examined provides an example of a concerted mechanism, whereas the two others clearly follow a stepwise pathway. This is related to the fact that ion-pairing is very much stronger in the first case than in the two others, rendering the thermodynamic advantage decisive in spite of a large contribution of ion-pairing to the reorganization energy. An additional favorable factor is the fact that the

electron transfer is intramolecular, leading to a very large equivalent concentration of the electron donor because the termolecular collision is replaced by a simple bimolecular collision. This system provides the first example so far identified of an electron transfer/concertedly triggered by ion-pairing.

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