Coordination Chemistry Reviews, 132 (1994) 249–258

Electron Transfer Reactions of Geminate Pairs at High Exergonicities

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Abstract

Three systems have been designed to study the roles of driving force, distance, and static and dynamics solvent effects on the rates of electron transfer (ET) reactions of geminate pairs at high exergonicities. The bimolecular ET reaction of electrogenerated geminate pairs, and the unimolecular ET reactions of covalently tethered geminate pairs, and geminate pairs juxtaposed by a hydrogen-bonded interface are described.

A. Introduction

The electron transfer (ET) reactivity of geminate pairs can be dramatically modified at high exergonicities. The rates of ET reactions between ions or molecules in inert solvents are characterized by three distinct regimes as described by Marcus' classical theory of ET [1]. In simplest form, the ET rate constant is given by [2],

$$k = A\exp\left[\frac{-\Delta G^*}{RT}\right] \tag{1}$$

$$\Delta G^* = \frac{(\lambda + \Delta G^o)^2}{4\lambda} \tag{2}$$

where ΔG^o is the free energy driving force for ET, λ is the sum of energies required to reorganize the inner (λ_i) and outer (λ_o) coordination environments, and A is a frequency prefactor for the ET reaction. The relative magnitudes of energies ΔG^o and λ that contribute to the activation energy in eq (1) lead to the three regimes defined by Marcus of normal ($|\Delta G^o| < \lambda$), activationless ($|\Delta G^o| = \lambda$), and inverted ($|\Delta G^o| > \lambda$) [2]. We have been interested in providing quantitative relations between the rate constants for unimolecular and bimolecular ET reactions in the inverted region with the variables of free energy, distance, and solvent.

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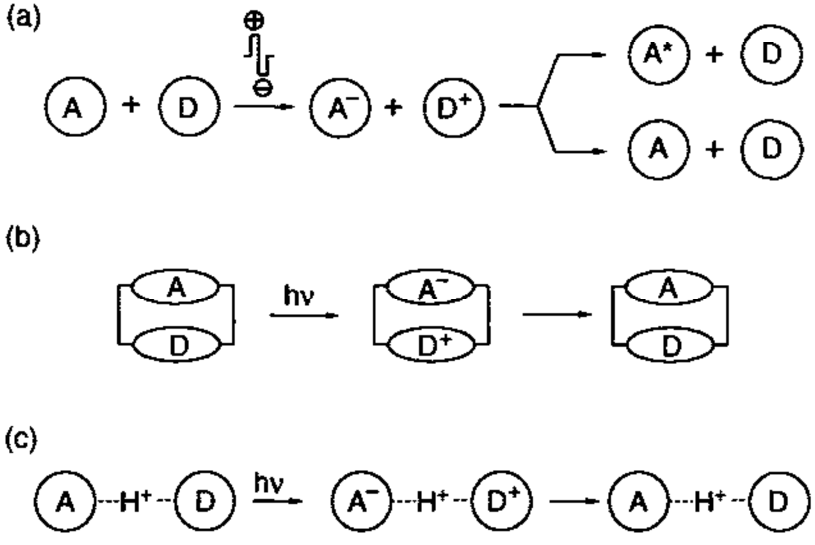


Figure 1. Three systems designed to study the mechanisms of electron transfer reactions in the inverted region.

Figure 1 summarizes the three types of systems that we have designed for our investigations. The systems comprise (a) the bimolecular reaction of electrochemically prepared geminate pairs, and the unimolecular reaction of photogenerated geminate pairs that are (b) covalently tethered by a rigid spacer and (c) juxtaposed by a hydrogen-bonded interface. This article reviews our recent progress in each of these areas.

B. Bimolecular Reactions of Geminate Pairs in the Inverted Region - Electrogenerated Chemiluminescence of Inorganic Cluster Ions

The generation of electronically excited products upon ET between electrochemically generated intermediates (electrogenerated chemiluminescence, ecl) is a useful probe of highly exothermic oxidation-reduction processes. In an electrochemiluminescent system, annihilation of oxidized and reduced reactants to generate the excited state proceeds in the Marcus normal region, whereas direct reaction to ground state occurs in the inverted region [3-5]. Specifically, the excited state yield, ϕ_{es}, is related to the rates of the competing excited (normal) and ground state (inverted) pathways by the expression, $\phi_{es} = k_{es}/(k_{gs} + k_{es})$, where k_{es} and k_{gs} are the rate constants for ET to produce excited state and ground state species, respectively.

We have found that ecl from $M_6X_8Y_6^{2-}$ ions in nonaqueous solutions is particularly useful in the study of highly exergonic ET reactions [6]. Ecl originating from the $Mo_6Cl_{14}^{2-}$ excited state ($\lambda_{em,max}$ =

760 nm, $\phi_{em} = 0.19$) is produced upon ET between the electrochemically generated $Mo_6Cl_{14}^-$ and $Mo_6Cl_{14}^{3-}$ ions [7]. Moreover, owing to the significant magnitudes of the $Mo_6Cl_{14}^{-/2-}$ and $Mo_6Cl_{14}^{2-/3-}$ reduction potentials ($E_{1/2} = 1.36$ and -1.70, respectively) and the relatively low energy of the $Mo_6Cl_{14}^{2-}$ excited state ($E_{0,0} = 1.79$ eV); ecl from the annihilation of the monoanion and trianion by a variety of electroactive donors and acceptors, respectively, can be observed [6] according to the following reactions,

$$Mo_6Cl_{14}^- + D^- \longrightarrow Mo_6Cl_{14}^{2-*} + D \tag{3}$$

$$Mo_6Cl_{14}^{3-} + A^+ \longrightarrow Mo_6Cl_{14}^{2-*} + A \tag{4}$$

where D^- represents a one-electron reduced aromatic nitro or pyridinium compound and A^+ is a one-electron oxidized aromatic amine compound. An important result to emerge from our ecl studies is that the unit excited state yields for reactions (3) and (4), predicted by simple ET treatments, are never attained.

We find that the partitioning between the excited and ground state reaction channels, and hence ecl efficiency, is extremely sensitive to the distance of the ET reaction [6,8]. Annihilation of the electrogenerated reactants is a bimolecular event and hence ET can occur over a range of distances rather than the single distance at contact between the reactant pair (which is assumed for most bimolecular reactions). The rate of the ground state ET pathway becomes comparable, and in some cases surpasses that of the excited state pathway at distances greater than contact.

The dependence of the ET rate constant on distance is found in the frequency prefactor A and the reorganization energy. Briefly the frequency prefactor for the conventional static ET rate in the nonadiabatic weak electronic coupling limit is [2],

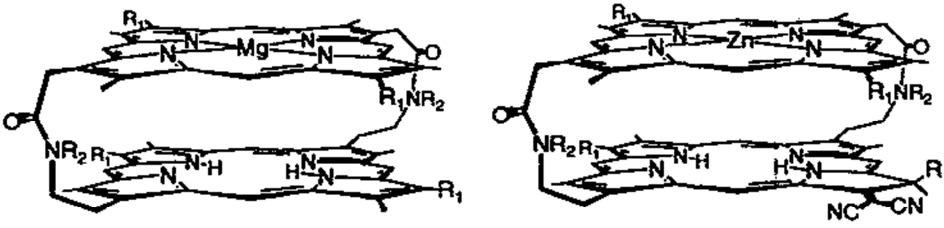
$$A = (2\pi/\hbar)\left\{H_{ij}^{\circ}\, e^{[-\beta(r-\sigma)/2]}\right\}^2 \frac{1}{(4\pi\lambda RT)^{1/2}} \tag{5}$$

where r is the ET distance, H_{ij}° is the coupling between the reactant and product electronic states at contact distance σ, and β is a characteristic constant. The distance dependence for ET in the inverted and normal regions is typically ascribed to the exponential decrease of this electronic coupling term with increasing separation between reactants. Yet there is also a distance dependence in the outer-sphere reorganization energy, which increases monotonically with increasing r [1,2]. In the normal region, the increase in the reorganization energy causes an increase in the activation energy and a decrease in the rate constant. Hence the decrease in the ET rate constant in the normal region (i.e. excited state production) imparted by the electronic term is augmented by the contribution from the nuclear term. Conversely, electronic and nuclear factors oppose each other in the inverted region. As discussed by Marcus [9] and Sutin [10], an increase in the outer sphere reorganization energy serves to attenuate the activation barrier in the inverted region. Over long distances the contribution of the nuclear factor to the overall rate may be dominant and a maximum in a plot of the inverted ET rate constant is observed at distances greater than contact [6,8]. This result is specific to ET at high exergonicities and we believe it is for this reason that ecl yields of less than unity are observed.

Why does the ecl reaction occur over long distances? We have addressed this issue by studying the ecl chemistry of $Mo_6Cl_{14}^{2-}$/4-cyanomethylpyridinium in a variety of solvents [11]. We have integrated the steady-state equilibrium pair distribution function for the excited state and ground state observed rate constants [9] to ascertain the ET distance in the different solvents. The difference between the calculated reaction and contact distances ($\Delta r = r_{et} - \sigma$) increases monotonically with increasing kinetic diameter of polar solvents. This result suggests that ET occurs to $Mo_6Cl_{14}^-$ encapsulated in a solvent shell when ecl is performed in polar solvents such as acetone, acetonitrile, propionitrile, and butyronitrile. Conversely, despite a significant difference in the kinetic diameters of the more weakly coordinating solvents such as dichloromethane and 1,2-dichloroethane, similar excited-state formation yields imply that the solvent shell about the $Mo_6Cl_{14}^-$ ion is not retained during electron transfer annihilation; in these cases ET appears to occur near contact ($r_{et} < 11$ Å). Our observations are consistent with simple ion-solvent models [12,13], which predict that the specific solvation of the cluster monoanion is sufficiently energetic that the polar nitrile and ketone solvent molecules in the primary coordination sphere are not shed prior to the ET reaction. However, the ion-dipole potential is dramatically attenuated for the weakly coordinating chlorocarbons. These ecl results clearly demonstrate the crucial role of distance and solvent in governing the rates of highly exergonic ET.

C. Unimolecular Reactions of Geminate Pairs in the Inverted Region – Cofacially Tethered Porphyrins

Solvent control of ET rates in the inverted region is not necessarily a perquisite of static contributions. Limitations imposed by solvent motion on the ET rate constant arise from the dielectric coupling between the solvent dipoles and the transfer of charge accompanying the ET reaction [14-17]. As we have discussed, strongly adiabatic ET for rigid donor-acceptor complexes occurring in the inverted region best emphasizes solvent dynamics effects [18]. We have investigated the role of solvent dynamics on highly exergonic ET reactions with cofacially juxtaposed porphyrin-porphyrin and porphyrin-chlorin complexes [19] such as those designated by Mg—H_2 and Zn—$H_2(=C(CN)_2)$ in Figure 2. For both systems, the geminate pair is generated from a localized $\pi\pi^*$ excited state, occurring within picoseconds of the excitation. Subsequent CR for Mg^+—H_2^- and Zn^+—$H_2(=C(CN)_2)^-$ geminate pairs is slower than CS, consistent



Mg—H$_2$ **Zn—H$_2$(=C(CN)$_2$)**

Figure 2. Cofacial porphyrins employed in the study of solvent dynamics control of highly exergonic electron transfer reactions.

with the former ET occurring in the Marcus inverted region, as opposed to the normal region kinetics of CS.

When solvent dynamics effects dominate the rate (as opposed to static effects), eq (5) is not adequate for A. In the case of dynamics control, a simple expression for A is given by

$$A = \frac{1}{\tau_s}\left[\frac{\Delta G^*}{\pi RT}\right]^{1/2} \tag{6}$$

where τ_s is the average microscopic relaxation time of the solvent [14,20], and is represented by the amplitude weighted average of the observed dielectric relaxation times obtained from time-resolved fluorescence Stokes shift measurements of excited state probe molecules. As has been discussed, τ_s better describes the dynamics of solvent motion relating to ET as compared to single exponential relaxation times [14,20]. We have shown that the observed rate constant for inverted region ET influenced by solvent dynamics is [18]

$$k_{obs} = k_d\, k_{ET} / (k_d + k_{ET}) \tag{7}$$

It has the form of a consecutive reaction mechanism consisting of diffusion along the solvent reaction coordinate, with rate constant k_d, followed by electron transfer with rate constant k_{ET}.

Within the consecutive reaction formalism of eq (7), solvent dynamics information is included in k_d. Solvent dynamics will influence the observed rate when k_{ET} is large with respect to k_d. In this case, $k_{ET} >> k_d$ and in eq (7), $k_{obs} = k_d$. Consequently, the observed ET rate constant will depend intimately on τ_s; and when static solvent contributions are isolated, k_{obs} should vary linearly with $1/\tau_s$, even when the observed rate is much slower than solvent motion. This regime is referred to as solvent-controlled adiabatic ET, as k_{obs} is independent of the

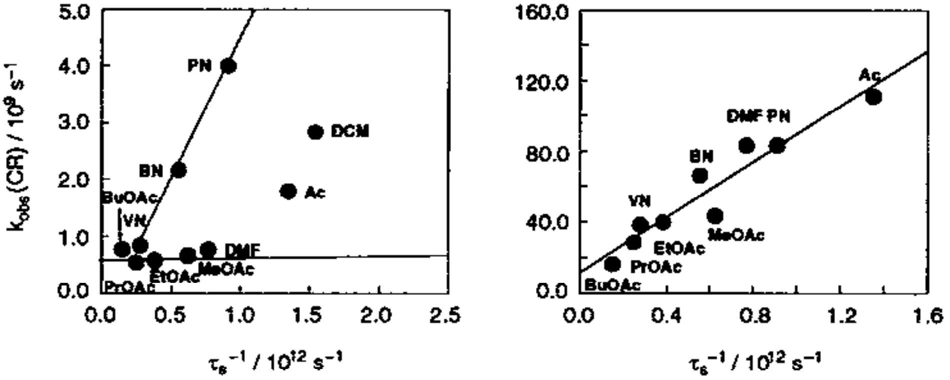


Figure 3. Plot of the observed CR rate constants of $Mg^+—H_2^-$ (at left) and (b) $Zn^+—H_2(=C(CN)_2)^-$ (at right) in acetone (Ac), dichloromethane (DCM), N,N-dimethylformamide (DMF), propionitrile (PN), *n*-butyronitrile (BN), *n*-valeronitrile (VN) and methyl, ethyl, *n*-propyl, and *n*-butyl acetates (MeOAc, EtOAc, PrOAc, BuOAc, respectively) vs. the reciprocal of the microscopic solvent relaxation times (which were taken from ref. 14).

electronic coupling. Conversely, rapid well dynamics relative to crossing (*i.e.*, $k_d >> k_{ET}$) will equilibrate the well population and the conventional static rate expression is obtained (*i.e.*, $k_{obs} = k_{ET}$). If the actual ET event is very nonadiabatic, due to poor electronic coupling, then k_{ET} will be rate limiting and solvent dynamics information will not be experimentally accessible.

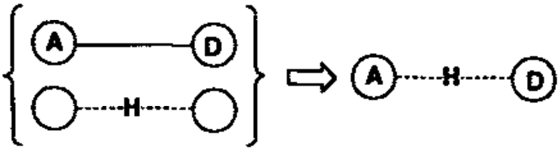
As shown in Figure 3, the rate constants of CR are markedly solvent dependent, but as we have discussed, they lack any consistent correlation with solvent polarity [19]. For the case of the $Mg^+—H_2^-$, the correlation of rate with $1/\tau_s$ is observed only within a homologous solvent series. The rate constant k_d is an activated process, and thus even though the well dynamics may be fast, the activation barrier for diffusion to the surface crossing point must be surmounted for charge-recombination to occur. We believe that it is this activation energy that accounts for the differences between the $k_{obs}(CR)$ vs $1/\tau_s$ plots for the acetate and nitrile solvent series and the incongruous behavior of the rate constants in DMF, Ac, and DCM (see Figure 3). The activation energy contains the contributions of solvent reorganization and free energy; changes in these parameters will affect ΔG^* in eq (6) and lead to nonlinearity in a plot of rate constant vs $1/\tau_s$. By measuring the CR kinetics within a homologous solvent series, variations in the solvent reorganization and free energy are minimized and the contribution of ΔG^* to the overall rate should be relatively constant. This is observed in Figure 3 for the nitrile or acetate series. But across the two solvent series, differences in ΔG^* are not normalized. The more polar nitrile solvents possess a greater reorganization energy for CR and they can better stabilize the charge separated state (by at least 0.13 V). Both of these effects will serve to decrease the activation barrier for ET in the inverted region. Hence the observed slope for the k_{obs}(CR) vs $1/\tau_S$ plot for the nitriles is greater than that observed for the less polar acetates.

Disparate dynamics behavior for different solvent series should disappear as the CR reaction approaches an activationless limit because the argument of the exponent will approach zero. It was with this motivation that we undertook studies on Zn—H_2(=C(CN)$_2$). Introduction of the dicyanomethide group on the porphyrin ring decreases the magnitude of the free energy of the CR reaction by ~0.4 V with respect to Mg—H_2, which lowers the barrier to ET in the inverted region. We see from Figure 3 that this decrease in the activation barrier is accompanied by the same linear dependence of the CR electron transfer rate constant on dynamics, regardless of the solvent series. By reducing the driving force of the CR reaction, we have made the reaction less inverted and attenuated the contributions of static solvent effects to the dynamically-controlled CR reaction of Zn—H_2(=C(CN)$_2$). Thus the simple relation k_{obs}(CR) approaching $1/\tau_S$ is obeyed.

Our observations further emphasize the important role that solvent can play in governing the rates of ET in biological and chemical charge separating networks. In a static sense, the importance of solvent in mediating CS and CR kinetics by affecting the activation energy of ET has been emphasized [21-24]. Yet as we have shown here, the dynamics of solvation may dominate the reactivity of charge-separated states, even when the overall rate for the electron transfer reaction is slow.

D. Unimolecular Reactions of Geminate Pairs in the Inverted Region – Acceptor/Donor Pairs Juxtaposed by a Hydrogen-Bonded Interface

We have investigated highly exergonic ET reactions of non-covalently assembled pairs by combining the strategy of photoinduced fixed-distance ET [25-28] with that of photoinduced proton transfer [29,30],



Here the photoactivated ET between an acceptor/donor pair is channeled through a proton-coupled interface. Our initial study has exploited the propensity of carboxylic acids to form cyclic dimers in low polarity, non-hydrogen bonding solvents [31-33] where D is a photoexcitable ET donor Zn(II)P porphyrin (3,17-diethyl-3,7,8,12,18-pentamethylporphine-2-acetic acid) and A is the ET acceptor 3,4-dinitrobenzoic acid (Figure 4).

Photoexcitation of the deuterated form of dimer leads to the prompt appearance of the Zn(II) porphyrin cation radical with a rate constant of $3.0(3) \times 10^{10}$ s^{-1}. The radical cation decays subsequently with a lifetime of

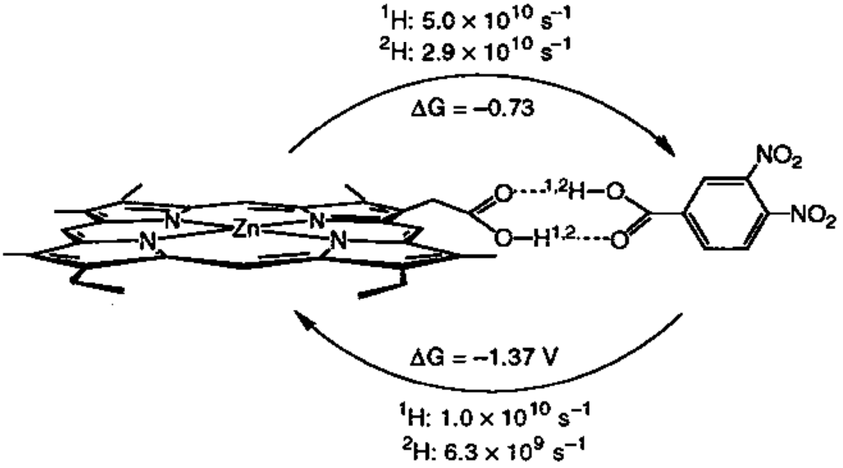


Figure 4. A summary of the electron transfer kinetics of a hydrogen-bonded geminate pair and its parent complex.

$6.2(3) \times 10^9$ s^{-1}. Transient absorption spectra of the protiated dimer show an acceleration in the quenching of the $^1\pi\pi^*$ singlet in 20 ps and we infer a forward ET rate constant of $5.0(5) \times 10^{10}$ s^{-1}; the rate constant for charge recombination is $1.0(2) \times 10^{10}$ s^{-1}. The data for the forward and reverse ET reactions of the protiated and deuterated forms are shown in Figure 4.

Our experimental observations show that ET through hydrogen bonded interfaces is fast as predicted early in Beratan's theoretical work on proton-mediated ET [34]. The importance of proton motion on the electronic coupling of the acceptor/donor pair is in evidence from a comparison of the rate data for the protiated and deuterated form. Interestingly, the pronounced deuterium isotope effect of $k_H / k_D = 1.6$ for the forward and back ET rate constants for the associated hydrogen-bonded pair is consistent with the 1.7 - 2.0 deuterium isotope effects measured for the oxidation of a soluble analog of Vitamin E by organochloro peroxides [35]. In this latter system, the rate determining step has been proposed to involve the transfer of an electron from substrate to the peroxy radical via a hydrogen bonding network formed from the incipient hydroperoxide and solvent.

E. Concluding Remarks

The study of highly inverted ET can lead to mechanistic insights not obtainable in the normal region. Highly exergonic ET reactions for bimolecular, covalently, and noncovalently juxtaposed geminate pairs show that inverted region ET rate constants are especially sensitive to the influence of medium. Solvent can affect rate constants of inverted ET dramatically in a static sense by modifying the activation energetics of reaction due to both changes in ΔG^0 and λ as the dielectric constant of the solvent varies. More subtly, static solvent effects on the rates of inverted region ET can be manifested in the distance dependence of the reorganization energy. This effect can be large enough to counteract the distance dependence of the electronic term to the point that the rate of ET in the inverted region may increase as the separation between reaction partners increases! But medium effects are not relegated to influencing highly exergonic ET reactions only in a static sense. The study of inverted region ET of geminate pairs is central to uncovering the role of medium dynamics even when the overall charge transfer is slow. When the surface crossing corresponding to the ET event is high on the potential surface, diffusion within the well is activated and therefore solvent dynamics effectively gate the overall reaction. Finally medium effects are not only important external to the geminate pair but internal to it as well. The rates of highly exergonic ET reactions are mediated by proton motion within a hydrogen-bonded interface. This result of proton coupled motion to ET relates directly to the mechanism of many charge-separating networks found in nature.

Acknowledgments. I thank my friends and colleagues for their best wishes upon my return from a harrowing venture into the inverted region during my lecture. The financial support of the National Institutes of Health (GM 47274) is gratefully acknowledged.

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