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Three-State Model for Two-Electron Transfer Reactions

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Much of electron transfer based catalysis relies upon multielectron rather than single-electron transfer processes. If the multielectron events proceed through stable one-electron intermediates, conventional theory describes the events. However, when an unstable one-electron intermediate plays a role, when a stable intermediate lives for a brief period of time, or when concerted multielectron events occur, the electronic coupling and free energy dependence of the rate is distinct from that arising in one-electron theories. We describe several new features that can arise in multielectron processes, predict their experimental signature, and show how these ideas can be applied to specific experimental systems.

I. Introduction

Recent progress in understanding single-electron transfer processes has been dramatic.[1] Predictive methods now exist to compute the electronic and nuclear contributions to single-electron transfer reaction rates, in systems ranging from small molecules to proteins.[2,3] Much significant chemistry and biochemistry occur by a two-electron transfer mechanism. These reactions often take place in the condensed phase, and two-electron processes are particularly important in bioenergetic processes that occur in proteins. The goal of this paper is to describe the general structure−function features of these reactions. Some of these features can be anticipated from our understanding of single-electron events, while others are rather different.

It is generally accepted that two-electron transfer can proceed by two different pathways—stepwise or concerted. The stepwise mechanism can be of two kinds:[4] (1) conventional in the sense that the reaction occurs through diffusionally separated reaction intermediates or (2) an unconventional stepwise mechanism when two one-electron steps occur within a collision complex and no diffusionally separated reaction intermediates appear during the course of reaction. Although the conventional stepwise mechanism is more common than the unconventional one, the conventional stepwise mechanism cannot be described in terms of an apparent rate constant for overall two-electron transfer. At the same time, the unconventional stepwise mechanism can imitate the concerted mechanism and, like the concerted mechanism, can be described in terms of the apparent rate constant for overall two-electron transfer. In real two-electron transfer reactions, it is frequently unclear by which mechanism (conventional stepwise, unconventional stepwise, or concerted) the reaction occurs. This situation is illustrated, for example, in the case of Tl(I)/Tl(III) exchange, where the conventional stepwise mechanism was proposed by Sutin,[5] while the merits of the unconventional stepwise mechanism have been considered in ref 6a. Concerted two-electron exchange in this system was considered in ref 6b.

Because the unconventional stepwise ET cannot be distinguished from the concerted one by kinetic experiments only, both mechanisms should be considered together in a common framework, and theoretical analysis strategies should be developed to help distinguish between these two possibilities. Such strategies might exploit the dependence of the rate on the driving force of the two-electron transfer or the dynamical solvent effect which is predicted to be unusual for two-electron transfer reactions. We attempt in this paper to present the results of this kind of analysis in such a way that the mathematics need not overwhelm the reader.

The paper is organized in the following way. Section II discusses a three-well model for two-electron transfer. The model encompasses the unconventional stepwise and concerted mechanisms in a general manner. Section III details the predictions of the model and illustrates these predictions for the Tl(I)/Tl(III) exchange reaction. The paper ends with a discussion of the predictions and results.

II. A Three-Well Model for Two-Electron Processes

Electron transfer (ET) between a donor and acceptor in polar solvent can be modeled successfully as a two-level system coupled to the polarization of the medium.[8−11] The thermal fluctuations of solvent dipoles cause the electronic energy levels of the two states to fluctuate and, occasionally, to coincide. At or near this degeneracy, the electron can tunnel from donor to acceptor. When the initial and final localized states differ from each other by *two* electrons, a conventional two-state description is insufficient and a third intermediate state (singly reduced donor/singly reduced acceptor) should be added to the description. This third state adds the possibility of a stepwise ET mechanism:

$$\mathrm{D}^{=} + \mathrm{A} \rightleftharpoons [\mathrm{D}^{=}\cdots\mathrm{A}] \rightleftharpoons [\mathrm{D}^{-}\cdots\mathrm{A}^{-}] \rightleftharpoons [\mathrm{D}\cdots\mathrm{A}^{=}] \rightleftharpoons \mathrm{D} + \mathrm{A}^{=} \quad (1a)$$

This mechanism is somewhat unconventional in the sense that no diffusionally separated intermediate appears during the course of reaction in contrast with the case shown in eq 1b.

$$\mathrm{D}^{=} + \mathrm{A} \rightleftharpoons [\mathrm{D}^{=}\cdots\mathrm{A}] \rightleftharpoons [\mathrm{D}^{-}\cdots\mathrm{A}^{-}] \rightleftharpoons \mathrm{D}^{-} + \mathrm{A}^{-} \rightleftharpoons [\mathrm{D}^{-}\cdots\mathrm{A}^{-}] \rightleftharpoons [\mathrm{D}\cdots\mathrm{A}^{=}] \rightleftharpoons \mathrm{D} + \mathrm{A}^{=} \quad (1b)$$

We will not consider the mechanism of eq 1b here. It can be dealt with using conventional single-electron ET theory. An alternative mechanism involves the concerted two-electron transfer:

$$\mathrm{D}^{=} + \mathrm{A} \rightleftharpoons [\mathrm{D}^{=}\cdots\mathrm{A}] \rightleftharpoons [\mathrm{D}\cdots\mathrm{A}^{=}] \rightleftharpoons \mathrm{D} + \mathrm{A}^{=} \quad (1c)$$

Here, $^{=}$ marks the doubly reduced species and $^{-}$ denotes the singly reduced.

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The reaction kinetics associated with the various schemes in eq 1 are:

$$\frac{d\bar{\rho}_1}{dt} = -k_{12}\bar{\rho}_1 + k_{21}\bar{\rho}_2 - k^{c}_{13}\bar{\rho}_1 + k^{c}_{31}\bar{\rho}_3 \tag{2a}$$

$$\frac{d\bar{\rho}_2}{dt} = -k_{21}\bar{\rho}_2 + k_{12}\bar{\rho}_1 - k_{23}\bar{\rho}_2 + k_{32}\bar{\rho}_3 \tag{2b}$$

$$\frac{d\bar{\rho}_3}{dt} = -k_{32}\bar{\rho}_3 + k_{23}\bar{\rho}_2 - k^{c}_{31}\bar{\rho}_3 + k^{c}_{13}\bar{\rho}_1 \tag{2c}$$

The populations of the three states, $D^{=}A$ (1), $D^{-}A^{-}$ (2), and $DA^{=}$ (3) averaged over solvent fluctuations, are $\bar{\rho}_1$, $\bar{\rho}_2$, and $\bar{\rho}_3$, respectively.

The rates of forward and reverse transitions between the first and second states are k_{12} and k_{21}. k_{23} and k_{32} are the rates of forward and reverse transitions between the second and third states. Concerted two-electron transfer occurs with rates k^{c}_{13} and k^{c}_{31}.

The rate constants of the overall two-electron processes, k_{31} and k_{13}, can be found using the steady state approximation, i.e. $d\bar{\rho}_2/dt = 0$. Substituting 2b into 2a and 2c, we obtain

$$\frac{d\bar{\rho}_1}{dt} = -k_{13}\bar{\rho}_1 + k_{31}\bar{\rho}_3 \tag{3a}$$

and

$$\frac{d\bar{\rho}_3}{dt} = -k_{31}\bar{\rho}_3 + k_{13}\bar{\rho}_1 \tag{3b}$$

where

$$k_{13} = \frac{k_{12}k_{23}}{k_{21} + k_{23}} + k^{c}_{13} \tag{4a}$$

$$k_{31} = \frac{k_{32}k_{21}}{k_{21} + k_{23}} + k^{c}_{31} \tag{4b}$$

The rate constants for one-electron transfer (k_{12}, k_{21}, k_{23}, k_{32}) and the rates of concerted two-electron transfer (k^{c}_{13} and k^{c}_{31}) can be computed from the analysis of transitions between three parabolic diabatic free energy curves[12]

$$F_1 = \frac{E_1^2}{4\lambda_{31}} + G_1 \tag{5a}$$

$$F_2 = \frac{(E_1 - \lambda_{31})^2}{4\lambda_{31}} + G_2 \tag{5b}$$

$$F_3 = \frac{(E_1 - 2\lambda_{31})^2}{4\lambda_{31}} + G_3 \tag{5c}$$

where E_1 is the reaction coordinate and G_1, G_2, and G_3 are the equilibrium free energies of the first, second, and third redox states respectively. λ_{31} is the solvent reorganization energy associated with concerted two-electron transfer.

Three-state models for sequential single electron-transfer reactions via an intermediate state were examined recently by several groups.[13] Although at first glance that problem appears formally similar to the present investigation, the results are different in several important respects. First, the coordinates of the minima for the three parabolas (eq 5) are not adjustable parameters but have precise definitions through the parameter λ_{31}. In the study of Hu and Mukamel,[13b] the dynamical solvent controlled regime was considered for sequential electron transfer, including coupling up to fourth order. In the present paper, coupling to all orders is included (see eqs 4 and 7). In other studies[13c,d] where the coupling was included to all orders, the sequential rate constant differs from that described here because of the different models employed and because the friction—which is qualitatively similar to the dynamical solvent effect (but not exactly equal to it)—was included in the model[13c,d] only for the intermediate electronic state. In the present study, the dynamical solvent effect is included[12] for all three participating electronic states. As such, the predictions of the present treatment are entirely new.

In a structureless dielectric, λ_{31} has the form

$$\lambda_{31} = \frac{c_0}{8\pi}\int [\vec{D}_3(\vec{r}) - \vec{D}_1(\vec{r})]^2 \, d\vec{r} \tag{6a}$$

where $\vec{D}_1$ and $\vec{D}_3$ are dielectric displacements in the first and third electronic states respectively. Here

$$c_0 = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_S} \tag{6b}$$

ϵ_∞ is the high-frequency and ϵ_s is the static dielectric constant.

Electronic transitions occur in the intersection points of the parabolas in eq 5. Motion on the parabolas can, in some limits,[9,11,12] be described as diffusion with diffusion coefficient $D = (2k_BT\lambda_{31})/\tau_L$ where k_B is Boltzmann's constant, T is the absolute temperature, and τ_L is the solvent longitudinal relaxation time. The rates, computed as describe in ref 12 are

$$k_{12} = \frac{4\pi V_{12}^2}{\hbar}\phi(2E_{02})\left\{1 + \frac{4\pi V_{12}^2\tau_L}{\hbar}[f(2E_{02},2E_{02}) + f(2E_{02}-\lambda_{31},2E_{02}-\lambda_{31}) - f(2E_{02}-\lambda_{31},2E_0)]\right\}^{-1} \tag{7a}$$

$$k_{21} = \frac{4\pi V_{12}^2}{\hbar}\phi(2E_{02}-\lambda_{31})\left\{1 + \frac{4\pi V_{12}^2\tau_L}{\hbar}[f(2E_{02},2E_{02}) + f(2E_{02}-\lambda_{31},2E_{02}-\lambda_{31}) - f(2E_{02}-\lambda_{31},2E_0)]\right\}^{-1} \tag{7b}$$

$$k_{23} = \frac{4\pi V_{23}^2}{\hbar}\phi(2E_0)\left\{1 + \frac{4\pi V_{23}^2\tau_L}{\hbar}[f(2E_0-\lambda_{31},2E_0-\lambda_{31}) + f(2E_0,2E_0) - f(2E_0,2E_{02}-\lambda_{31})]\right\}^{-1} \tag{7c}$$

$$k_{32} = \frac{4\pi V_{23}^2}{\hbar}\phi(2E_0-\lambda_{31})\left\{1 + \frac{4\pi V_{23}^2\tau_L}{\hbar}[f(2E_0-\lambda_{31},2E_0-\lambda_{31}) + f(2E_0,2E_0) - f(2E_0,2E_{02}-\lambda_{31})]\right\}^{-1} \tag{7d}$$

$$k^{c}_{13} = \frac{2\pi V_{13}^2}{\hbar}\phi(E_{03})\left\{1 + \frac{2\pi V_{13}^2\tau_L}{\hbar}\left[\frac{1}{|E_{03}|} + \frac{1}{|E_{03} - 2\lambda_{31}|}\right]\right\}^{-1} \tag{7e}$$

$$k^{c}_{31} = \frac{2\pi V_{13}^2}{\hbar}\phi(E_{03}-2\lambda_{31}) \times \left\{1 + \frac{2\pi V_{13}^2\tau_L}{\hbar}\left[\frac{1}{|E_{03}|} + \frac{1}{|E_{03} - 2\lambda_{31}|}\right]\right\}^{-1} \tag{7f}$$

In these rate expressions, $2E_{02}$ is the intersection point between surfaces F_1 and F_2, $2E_0 + \lambda_{31}$ is the intersection point between surfaces F_2 and F_3, and E_{03} is the intersection point between surfaces F_1 and F_3. These intersection points are simply related to the thermodynamic driving forces ($\Delta G_{21} = G_2 - G_1$, $\Delta G_{32} = G_3 - G_2$, and $\Delta G_{31} = G_3 - G_1$ as

$$2E_{02} = 2\Delta G_{21} + \frac{\lambda_{31}}{2} \tag{8a}$$

$$2E_0 = 2\Delta G_{32} + \frac{\lambda_{31}}{2} \tag{8b}$$

$$2E_{03} = \Delta G_{31} + \lambda_{31} \tag{8c}$$

The electronic coupling elements between the redox states (noted by the subscripts) are V_{12}, V_{23}, and V_{13}. V_{13} is a two-electron coupling matrix element. The factor $\phi(E_1)$ accounts for the equilibrium thermal distribution over reaction coordinate geometries and has the form

$$\phi(E_1) = \frac{1}{2\sqrt{\pi\lambda_{31}k_BT}} \exp\left[-\frac{E_1^2}{4\lambda_{31}k_BT}\right] \tag{9}$$

The function $f(E_1,E')$ accounts for nonequilibrium effects associated with diffusional motion along the reaction coordinate. It can be calculated from

$$f(E_1,E') = \frac{1}{\tau_L}\int_0^\infty [G(E_1,E_1',t) - \phi(E_1)]\,dt \tag{10}$$

where

$$G(E_1,E_1',t) = \frac{1}{2}[\pi\lambda_{31}k_BT[1 - \exp(-2t/\tau_L)]]^{-1/2} \times \exp\left[-\frac{[E_1 - E_1'\exp(-t/\tau_L)]^2}{4\lambda_{31}k_BT[1 - \exp(-2t/\tau_L)]}\right] \tag{11}$$

Equations 4 and 7 give us the full solution of the two-electron transfer problem including competition between the two possible mechanisms—stepwise and concerted. These rates of two-electron transfer encompass the golden rule regime and the solvent dynamics controlled regime, as well as all intermediate regimes for any arrangement of free energy wells.

III. Predictions of the Model

A. Activation Free Energies. Consider the parabolas (eq 5) shown in Figure 1. In this situation, the intersection point of curves 1 and 3 lies higher than the two other intersection points. This means that the activation energy of the concerted mechanism is larger than that for the stepwise mechanism. In this regime we expect the stepwise mechanism to dominate. The rate of the overall two-electron process will take the form

$$k_{13} \simeq \frac{k_{12}k_{23}}{k_{21} + k_{23}} \tag{12}$$

Here, the activation energy of reaction ($\Delta F^\ddagger$) will be determined by the first one-electron step:

$$\Delta F^\ddagger = \frac{(2E_{02})^2}{4\lambda_{31}} = \frac{[\Delta G_{21} + (\lambda_{31}/4)]^2}{\lambda_{31}} \tag{13}$$

Note that the activation free energy is independent of the overall reaction driving force, ΔG_{31}; the activation free energy depends only upon the free energy change associated with the first step of the process.

In the situation shown in Figure 2, it is possible that the intersection points of free energy curves (1 with 2 and 2 with 3) lie close to the intersection point of parabola 1 with 3. In this case the stepwise mechanism likely dominates because we expect V_{13} to be much smaller than V_{12} and V_{21}. In the case drawn, the 2−3 intersection lies higher than the 1−2 intersection, so the activation energy associated with the 2−3 intersection controls the overall reaction. As such, the activation free energy, $\Delta F^\ddagger$ is

$$\Delta F^\ddagger = \Delta G_{21} + \frac{(2E_0)^2}{4\lambda_{31}} = \Delta G_{21} + \frac{[\Delta G_{32} + (\lambda_{31}/4)]^2}{\lambda_{31}} \tag{14}$$

In this case, the activation free energy for two-electron transfer depends on the free energy changes of each one-electron step,

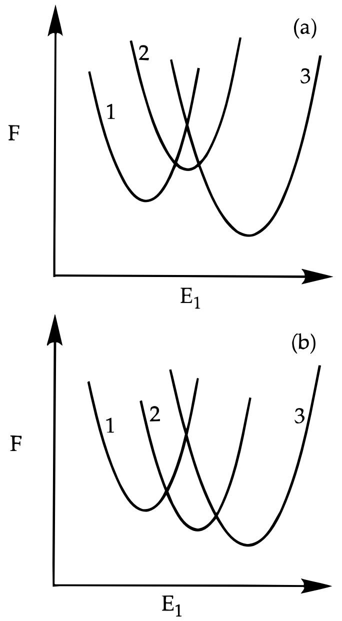

Figure 1. Arrangement of the solvation dependent free energy wells associated with the three redox states in cases that lead to dominance of the stepwise mechanism: (a) stepwise mechanism through an unstable intermediate; (b) stepwise mechanism through a stable intermediate.

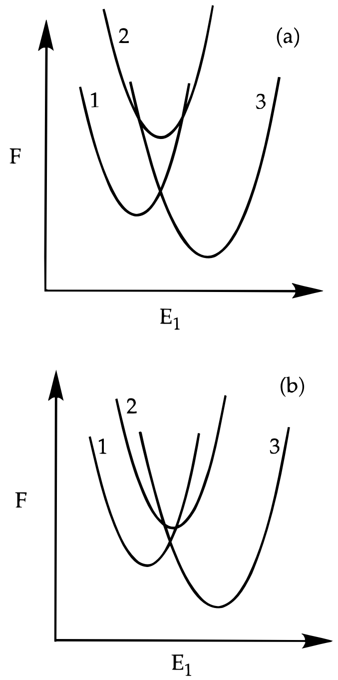

Figure 2. Arrangement of the solvation dependent free energy wells associated with the three redox states in cases that lead to interference of stepwise and concerted channels, or even dominance of the latter.

and, because $\Delta G_{32} = \Delta G_{31} - \Delta G_{21}$, the activation energy depends upon the overall driving force of the reaction (ΔG_{31}) if we *fix* ΔG_{21}.

In the case of Figure 2, the stepwise pathway free energy of activation is sufficiently large that the concerted process contributes substantially to the overall rate. If the concerted mechanism dominates

$$\Delta F^{\ddagger} = \frac{E_{03}^2}{4\lambda_{31}} = \frac{(\Delta G_{31} + \lambda_{31})^2}{4\lambda_{31}} \tag{15}$$

and the usual Marcus parabolic dependence on overall driving force is recovered. These simple activation free energy predictions should help distinguish between the reaction mechanisms in experimental studies. In intermediate regimes, when the concerted mechanism contribution is comparable to the stepwise contribution, we predict a non-Arrhenius dependence of the rate upon temperature.

B. Golden Rule Rate Regime. Consider the regime in which all of the rates fall in the golden rule regime. This is the case when the coupling matrix elements are sufficiently small that the adiabaticity parameter inequalities of eq 16 are valid:

$$\frac{4\pi V_{12}^2}{\hbar}\tau_{\rm L}[f(2E_{02}, 2E_{02}) + f(2E_{02}-\lambda_{31}, 2E_{02}-\lambda_{31}) - f(2E_{02}-\lambda_{31}, 2E_0)] \ll 1 \tag{16a}$$

$$\frac{4\pi V_{23}^2}{\hbar}\tau_{\rm L}[f(2E_0-\lambda_{31}, 2E_{02}-\lambda_{31}) + f(2E_0, 2E_0)] - f(2E_0, 2E_{02}-\lambda_{31}) \ll 1 \tag{16b}$$

$$\frac{2\pi V_{13}^2}{\hbar}\tau_{\rm L}\left[\frac{1}{|E_{03}|} + \frac{1}{|E_{03}-2\lambda_{31}|}\right] \ll 1 \tag{16c}$$

The rate constant in this regime, k_{13}, is

$$k_{13} = \frac{1}{\hbar}\,\frac{4\pi V_{12}^2 V_{23}^2 \phi(2E_{02})\phi(2E_0)}{V_{12}^2\phi(2E_{02}-\lambda_{31}) + V_{23}^2\phi(2E_0)} + \frac{2\pi V_{13}^2}{\hbar}\phi(E_{03}) \tag{17}$$

This two-electron rate constant has a nonlinear dependence on the coupling matrix elements associated with each single-electron transfer step, even though the rate constants for the individual sequential one-electron transfer steps each fall in the golden rule regime.

Assuming that the coupling matrix elements have an exponential dependence upon the distance between donor and acceptor, the rate constant of two-electron transfer—even in the golden rule regime—is predicted to have a nonexponential dependence on the donor acceptor distance. While electronic structure calculations are needed to quantify the one and two-electron matrix elements, the presence of two different kinds of coupling matrix elements could provide additional control in biological ET processes, some of which have been implicated as involving simultaneous two-electron transfer steps.

Equation 17 can be used to explore the driving force dependence of the rate constant k_{13}. For example, we plot ln k_{13} in Figure 3. Here we have fixed ΔG_{21} and varied $\Delta G_{13} = -\Delta G_{31}$ for $V_{12} = V_{23} = 10^{-3}$ eV, $V_{13} = 10^{-4}$ eV, $\lambda_{13} = 4$ eV, and $T = 300$ K.

The rate constant k_{13} over the range 0 eV $\leq \Delta G_{13} \leq$ 1.4 eV is independent of the overall reaction driving force. This means that the stepwise mechanism dominates in this range. Over the range 1.4 eV $\leq \Delta G_{13} \leq$ 1.8 eV, the rate constant drops by about an order of magnitude and the mechanism remains in the stepwise regime. The rate drops because in this range of ΔG_{13}, the free energy of reaction is described by eq 14, i.e. the free energy increases with an increase in ΔG_{13}. In the range of ΔG_{13} greater than 1.8 eV, the electron transfer mechanism is concerted and the logarithm of k_{13} has the parabolic Marcus dependence on driving force. It is obvious from Figure 3 that using the driving force dependence of the rate constant, we can clearly distinguish between concerted and stepwise mechanisms.

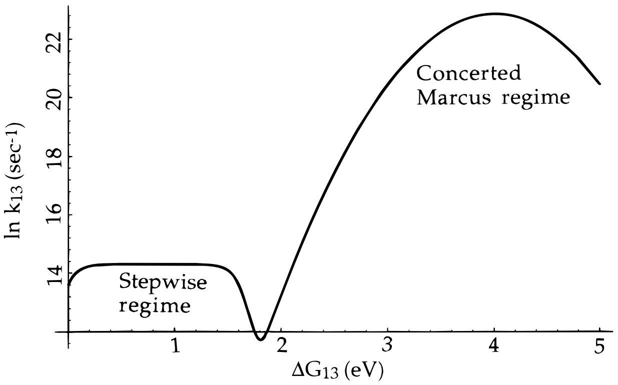

Figure 3. Driving force dependence of the two-electron transfer rate constant in the case where ΔG_{21} is held fixed. The curve is calculated $V_{12} = V_{23} = 10^{-1}$ eV, $V_{13} = 10^{-3}$ eV, $\Delta G_{21} = 0.2$ eV, and $\lambda_{31} = 4.0$ eV from eq 17.

C. Dynamical Solvent Control of Two-Electron Transfer. Let us now consider the overall rate of two-electron transfer when each of the one-electron steps falls in the dynamical solvent controlled regime. This regime arises when the parameters of adiabaticity (which are similar to the parameters of adiabaticity for one-electron transfer[9]) are

$$\frac{4\pi V_{12}^2}{\hbar}\tau_{\rm L}[f(2E_{02}, 2E_{02}) + f(2E_{02}-\lambda_{31}, 2E_{02}-\lambda_{31}) - f(2E_{02}-\lambda_{31}, 2E_0)] \gg 1 \tag{18a}$$

$$\frac{4\pi V_{23}^2}{\hbar}\tau_{\rm L}[f(2E_0-\lambda_{31}, 2E_{02}-\lambda_{31}) + f(2E_0, 2E_0) - f(2E_{02}-\lambda_{31}, 2E_0)] \gg 1 \tag{18b}$$

It seems plausible that the two electron matrix element, V_{13}, will be much smaller than the one-electron matrix elements V_{12} and V_{23}. As such, in a wide range of solvent relaxation times we might expect that the parameter of adiabaticity for concerted two-electron transfer

$$\frac{2\pi V_{13}^2}{\hbar}\tau_{\rm L}\left[\frac{1}{|E_{03}|} + \frac{1}{|E_{03}-2\lambda_{31}|}\right] \ll 1 \tag{19}$$

and the rate of concerted two-electron transfer, $k_{13}^{\rm c}$ would fall in the golden rule regime, giving the overall rate

$$\frac{A}{\tau_{\rm L}} + \frac{2\pi V_{13}^2}{\hbar}\phi(E_{03}) \tag{20a}$$

where

$$A = \phi(2E_{02})\phi(2E_0)\{\phi(2E_{02}-\lambda_{31}) \times [f(2E_0, 2E_0) + f(2E_0-\lambda_{31}, 2E_0-\lambda_{31}) - f(2E_0, 2E_{02}-\lambda_{31})] + \phi(2E_0)[f(2E_{02}, 2E_{02}) + f(2E_{02}-\lambda_{31}, 2E_{02}-\lambda_{31}) - f(2E_{02}-\lambda_{31}, 2E_0)]\}^{-1} \tag{20b}$$

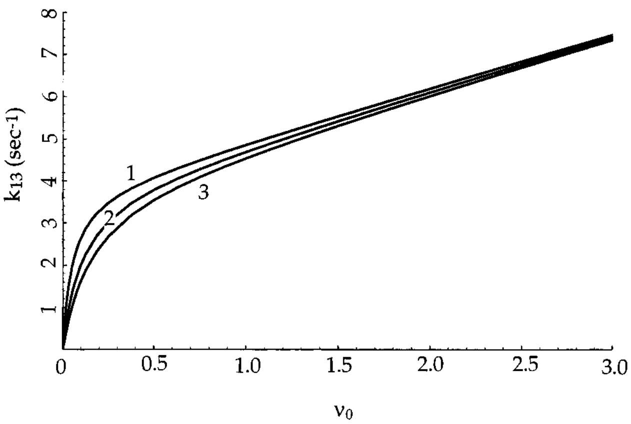

Figure 4. Dependence of the two-electron transfer rate on $\nu_0 = 10^{-11}$ s/τ_L in the dynamical solvent controlled regime. Curve 1 is calculated for $V_{12} = V_{23} = 10^{-2}$ eV, $V_{13} = 10^{-3}$ eV, $\Delta G_{21}/\lambda_{31} = 0.14$, and $\Delta G_{32}/\lambda_{31} = -0.39$. Curve 2 is calculated for $V_{13} = 2 \times 10^{-3}$ eV, and curve 3 is calculated for $V_{13} = 3 \times 10^{-3}$ eV.

Only in very slow solvents, when the inequality in eq 19 is violated and concerted two-electron transfer becomes solvent controlled, would the overall two-electron transfer rate be proportional to $1/\tau_L$. This dependence on $1/\tau_L$ is shown in Figure 4. Linear extrapolations of the $1/\tau_L$ in k_{13}—determined in the regime where k_{13}^c falls in the golden rule regime and the stepwise rates are solvent dynamics controlled—to $1/\tau_L = 0$ gives the rate of golden rule rate k_{13}^c. Equation 20, like the golden rule formula (eq 17), can be used to explore the driving force dependence of the overall rate. The relevant plot is qualitatively similar to that in Figure 3.

D. Analysis of Tl(I)/Tl(III) Exchange. We now illustrate how this theory can be used to analyze a two-electron exchange process. The activation free energy for Tl^{+1}/Tl^{+3} electron transfer is known to be 17.4 kcal/mol or 0.76 eV.[7] This value includes contributions from the work term (w) which arises from the electrostatic work required to bring together the two ions from infinite separation. This work term has the form

$$\frac{Z_1 Z_2 e^2}{\epsilon_S(r_1 + r_2)} \tag{21}$$

where Z_1 and Z_2 are the charges of the ions, e is the electron charge, and r_1 and r_2 are the ionic radii. From ref 14, $r_1 = 0.95$ Å and $r_2 = 1.44$ Å. Assuming $\epsilon_S = 75$ for perchloric acid we obtain from eq 21 $w = 0.24$ eV. Assuming that the reaction proceeds through a stepwise pathway, we have from eq 13 and the work term

$$\frac{[\Delta G_{21} + (\lambda_{31}/4)]^2}{\lambda_{31}} + 0.24 \text{ eV} = 0.76 \text{ eV} \tag{22}$$

The equilibrium free energy of the first redox state G_1 can be expressed through the free energies $G_{Tl(III)}$ and $G_{Tl(I)}$ of the two ions in solution and the work term as

$$G_1 = G_{Tl(III)} + G_{Tl(I)} + w \tag{23}$$

Similarly, the equilibrium free energy of the second redox state G_2 can be written in terms of the free energies of the two Tl(II) ions in solution and the work term ($\tilde{w}$) associated with bringing together two Tl(II) ions from infinity

$$G_2 = G_{Tl(II)} + G_{Tl(II)} + \tilde{w} \tag{24}$$

In this case, the work term $\tilde{w}$ is 0.32 eV. From eqs 23 and 24

$$\Delta G_{21} = G_{Tl(II)} - G_{Tl(III)} + G_{Tl(II)} - G_{Tl(I)} + \tilde{w} - w \tag{25}$$

Using the redox potentials φ_1 and φ_2 for Tl(II)/Tl(I) exchange and Tl(III)/Tl(II) exchange respectively

$$\varphi_1 = -(1/e)[G_{Tl(I)} - G_{Tl(II)}] \tag{26a}$$

$$\varphi_2 = -(1/e)[G_{Tl(II)} - G_{Tl(III)}] \tag{26b}$$

we can express ΔG_{21} through these expressions as

$$\Delta G_{21} = -e(\varphi_2 - \varphi_1) + 0.08 \text{ eV} \tag{27}$$

Hush[14] has computed the redox potentials of $\varphi_1 = 1.5$ V and $\varphi_2 = 1.$ V. Hence $\Delta G_{21} = 0.58$ eV. Substituting this value into eq 22, we find that this equation has no real solutions for λ_{31}. Hence, the stepwise pathway seems unrealistic.

Assuming that Tl(I)/Tl(III) exchange occurs through a concerted pathway, we use eq 15 and the work term to find $\Delta G^{\ddagger} = \lambda_{31}/4 + w = 0.76$ (recall that ΔG_{31} is zero for self-exchange) so $\lambda_{31} = 2.068$ eV. This is a realistic reorganization energy for a two-electron process (recall that reorganization energy scales with the square of the charge transfered). Using this reorganization energy in eq 7e for concerted two-electron transfer in the golden rule limit when the inequality of eq 19 is satisfied, we find $k_{13}^c \sim (2 \times 10^3 V_{13}^2)$ s^{-1}. The bimolecular rate constant is

$$k_{13}^{\text{bimolec.}} = k_{13}^c \Delta V N e^{-w/k_B T} \tag{28}$$

where the reaction volume ΔV is $\sim 12.56 \times 10^{-27}$ L and N is Avogadro's number. The experimental rate $k_{13}^{\text{bimolec.}} = 7 \times 10^{-5}$ M^{-1} s^{-1} provides an estimate of $V_{13} \sim 2 \times 10^{-3}$ eV, a realistic value for electron transfer between two coordinated ions in contact. As such, the only pathway that seems reasonable for the two-electron self-exchange reaction in Tl is the concerted one. This conclusion is in agreement with the conclusions reached purely through the analysis of experiments.[6b]

IV. Discussion

We have described the theory of two-electron transfer reactions in polar solvents. Solvent reorganization controls the activation energy, and intramolecular degrees of freedom were neglected. The coupled master equations were solved in a steady state approximation. From the rate expressions, it is clear that two competing pathways exist: stepwise and concerted.

The analytical expressions obtained for the rate constants allow ready prediction of the activation free energy dependence of the rates. The activation free energy dependence on ΔG_{21}—for small values of this free energy—is quadratic in ΔG_{21} when the overall reaction driving force (ΔG_{31}) is held fixed. For very large ΔG_{21} values, the activation energy is independent of ΔG_{21}. This peculiar free energy dependence reflects the fact that at small ΔG_{21}, the stepwise pathway dominates over the concerted one. At larger ΔG_{21}, reaction occurs through a concerted pathway so that the activation energy depends only on the overall driving force, ΔG_{31}, but not upon ΔG_{21}. Analysis of Tl(I)/Tl(III) exchange with these rate expressions suggest a concerted two-electron mechanism.

When ΔG_{21} is fixed and is small enough (as in Figure 3) we find that the rate of two-electron transfer has a weak driving force dependence at small ΔG_{13} because two-electron transfer falls in the stepwise regime. At intermediate ΔG_{13}, the rate drops by about an order of magnitude (as shown in Figure 3) and two-electron transfer is still stepwise. At large driving forces, two-electron transfer is concerted and the dependence of rate on driving force can be described well with Marcus theory. If ΔG_{21} is fixed large enough (even when ΔG_{13} is zero), two-electron transfer is concerted, and the Marcus parabolic dependence of rate on driving force is predicted. Thus, we expect that studies of two-electron rate dependence on driving force will provide a means of distinguishing between stepwise and concerted mechanisms.

The dynamical solvent effect can also be used to probe the relative rates of stepwise and concerted ET reactions. For example, in the regime of dynamical solvent control and a dominant stepwise mechanism, the rate is expected to be a linear function of $1/\tau_L$ for a wide range of τ_L. If the rate of concerted two-electron transfer is nonzero, linear extrapolation of the τ_L dependence to $1/\tau_L = 0$ will give the golden rule rate of concerted two-electron transfer. Additional tests of the rate and dynamical solvent effects predicted here appear to be accessible with unimolecular two-electron transfer organic model compounds.[15]

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