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THE DISTANCE AND TEMPERATURE DEPENDENCE OF ELECTRON-TRANSFER RATES

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ABSTRACT. Electron transfer occurs over relatively long distances in a variety of systems. In interpreting the measured electron-transfer rates it is usually assumed that the rate constants depend exponentially on the distance separating the two redox sites and that this distance dependence arises from the decrease in the electronic coupling of the redox sites with increasing separation. Although the electronic coupling is an important factor determining the distance dependence of the rate, theoretical considerations suggest that the nuclear factors are also important. The various factors determining long-range electron-transfer rates are discussed and it is shown that very different distance dependences are predicted for reactions in the normal and inverted free-energy regions. The effect of the enthalpy change on the electron-transfer rate is also considered; three enthalpy regions are identified depending on the overall free energy and entropy changes for the reaction.

1. INTRODUCTION

Long-range electron transfer is an important process in photosynthesis and in many biological, chemical and electrochemical systems [1]. The factors determining long-range electron-transfer rates are therefore of considerable interest and a variety of experimental approaches are being used to obtain rates as a function of separation distance. One approach involves the measurement of intramolecular electron-transfer rates in synthetic systems in which the two redox sites are separated by a rigid bridging group of varying length [2,3]. Another approach involves the modification of naturally occurring systems; typically one of the metal centers in a multi-site metalloprotein is replaced by a different metal center (e.g., one of the iron atoms in hemoglobin is replaced by a zinc atom) which is then photo-excited to initiate electron transfer [4]. Alternatively, a redox center may be covalently or electrostatically attached to a specific region of a single-site metalloprotein; the latter may be the native protein (e.g., cytochrome c) or a derivative (e.g., zinc-substituted

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cytochrome c) [5-9]. Other approaches include the study of electron transfer to or from electrodes through monolayers or polymers deposited on the electrode surface [10] and the measurement of electron-transfer rates in frozen media [11].

The various experimental approaches have yielded a substantial amount of rate-constant data. In interpreting these data it is generally assumed that the distance dependence arises solely from the decrease in the electronic coupling of the two redox sites with increasing separation. Although this is an important consideration, the distance dependence of the nuclear factor also needs to be considered. One purpose of the present paper is to draw attention to the importance of the nuclear factors in determining the distance dependence.

Another aspect that is considered is the effect of the overall free-energy and entropy changes for the reaction on the activation enthalpy for the electron transfer. It will be shown that three enthalpy regions can be distinguished depending on the free-energy and entropy changes for the reaction.

2. THEORETICAL CONSIDERATIONS

For the present purpose we adopt a model in which the electron transfer occurs at the intersection of two (free-energy) curves, one for the reactants and the other for the products [1,12]. We further restrict the discussion to intramolecular electron-transfer processes. For such systems the electron-transfer rate constants can be expressed as

$$k = \kappa_{el} \nu_n \kappa_n \quad (1)$$

where κ_{el} is the electronic transmission coefficient, ν_n is a nuclear-vibration frequency, and κ_n is the nuclear factor [13]. If nuclear tunneling effects are neglected then the nuclear factor is related to the classical free-energy barrier ΔG^* for the electron transfer by

$$\kappa_n = \exp(-\Delta G^*/RT) \quad (2a)$$

$$\Delta G^* = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \quad (2b)$$

where λ is the reorganization parameter and ΔG° is the standard free-energy change for the electron transfer in the prevailing medium [1,12,13].

2.1. The Electronic Transmission Coefficient

When the redox sites are close together the electronic coupling between them will be relatively strong. If the coupling is

sufficiently strong the reaction will be adiabatic ($\kappa_{el} = 1$). On the other hand, if the redox sites are far apart, the electronic coupling between them will be weak, and the reaction will be nonadiabatic ($\kappa_{el} \ll 1$). In this case the product $\kappa_{el}v_n$ is independent of v_n and is given by [1,13,14]

$$\kappa_{el}v_n = \frac{2H_{AB}^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2} \quad (3)$$

where H_{AB} is the electronic coupling matrix element. For many systems H_{AB}^2 decreases exponentially with increasing separation distance and $\kappa_{el}v_n$ is expressed as

$$\kappa_{el}v_n = 10^{13} \exp[-\beta(r-r_0)] \quad (4)$$

where r_0 is defined so that $\kappa_{el}v_n$ is equal to a typical nuclear vibration frequency (10^{13} s^{-1}) when $r = r_0$, i.e. the reaction is adiabatic at $r = r_0$ [1].

The electronic coupling of the redox sites in bridged systems can be considered within a superexchange formalism [14,15]. The superexchange contribution to the electronic coupling is a function of the number of sequential bridging units (n) and is given by

$$H_{AB} = \frac{\prod_{i=0}^n (H_{i,i+1})}{\prod_{i=1}^n (\Delta E_i)} \quad (5)$$

where the bridging units are either coupled to one another ($H_{i,i+1}$) or, in the case of the terminal units, to the redox sites ($H_{0,1}$ and $H_{n,n+1}$), and ΔE_i is the vertical difference between the energies of the electron donor and bridging unit i . The superexchange mixing occurs at the nuclear configuration appropriate to the intersection region. If all the interactions are similar then H_{AB} is given by

$$H_{AB} = \bar{H} \left(\frac{\bar{H}}{\Delta E} \right)^n \quad (6)$$

where n is the number of bridging units. In this case the decrease of H_{AB}^2 with increasing separation distance is exponential with β given by

$$\beta = \left(\frac{2}{l} \right) \ln \left(\frac{\Delta E}{\bar{H}} \right) \quad (7)$$

where l is the length of the bridging unit; in the present context $l = (r-r_0)/n$ [14,15].

Experimental studies place β at $\sim 1.2 \text{ \AA}^{-1}$ [1]. However, it is apparent from the above discussion that β is likely to vary from system to system and to depend both on the nature of the intervening medium and on the nature of the redox sites. The exponential dependence of H_{AB}^2 on the separation distance has not been established for large distance changes. In certain cases, for example in some σ -bond systems, an inverse power dependence on separation distance may be more appropriate [2].

2.2. The Nuclear Factor

The reorganization parameter λ appearing in the expression for the nuclear factor (eq 2) is equal to the sum of inner-shell (λ_{in}) and medium or solvent (λ_{out}) contributions [1,12].

$$\lambda = \lambda_{out} + \lambda_{in} \quad (8)$$

λ_{in} is usually assumed to be independent of the separation distance (although this may be a poor assumption when hydrogen-bonding or other specific medium interactions are present) while λ_{out} increases with increasing separation distance. Based on eq 2 and the distance dependence of λ_{out} , two limiting cases can be distinguished depending on the relative magnitudes of λ and ΔG° . When $-\Delta G^\circ < \lambda$ (normal free-energy region) κ_n will decrease with increasing separation distance while, when $-\Delta G^\circ > \lambda$ (inverted free-energy region), κ_n will increase with increasing separation distance.

The distance dependence of λ_{out} is clearly an important consideration and we next examine various models for λ_{out} . In the familiar two-sphere model, in which each redox site is represented by a sphere in a dielectric continuum, $d\lambda_{out}/dr$ is proportional to $1/r^2$, where r is the distance separating the two redox sites [1,12,16]. In this case λ_{out} becomes independent of separation distance at large r ; in the case of two identical spheres λ_{out} changes only a factor of 2 from when the two spheres are in contact to when they are an infinite distance apart. On the other hand, λ_{out} is much more distance dependent when the two redox sites are considered to be embedded in an ellipsoidal or spherical cavity immersed in a dielectric continuum [16,17]. In this case $d\lambda_{out}/dr$ is proportional to r^n where $n = 1$ at separations small compared with the cavity dimensions and $n > 1$ when the separations are large and one or both of the redox sites are close to the surface of the cavity. This is illustrated in Figure 1 for two redox sites symmetrically located either on the long axis of an ellipsoidal cavity (solid curve) or on the diameter of a spherical cavity (dashed curve). Note the very rapid increase in λ_{out} as $r \rightarrow 2a$, where $2a$ is the length of the major axis of the ellipsoid or the diameter of the sphere (30 Å); the values of λ_{out} and its overall increase are larger for the ellipsoidal cavity where, for a given $r/2a$, the external medium is closer to the redox sites than in the case of the spherical cavity.

Figure 1. Plot of λ_{out} vs. the distance separating two redox sites embedded in an ellipsoidal (major axis = 30 Å, minor axis = 15 Å, solid curve) or spherical (diameter = 30 Å, dashed curve) cavity (internal dielectric constant = 2.0) immersed in a polar medium (static dielectric constant of the medium = 78.5, optical dielectric constant of the medium = 1.78).

Although the discussion of the nuclear factor has focussed on the distance dependence of λ_{out} , it should be noted that ΔG° is also distance dependent since the free-energy change for the electron transfer depends upon the interaction of the sites with each other and with the medium.

3. DISTANCE DEPENDENCE OF THE RATE CONSTANT

The above considerations show that both $\kappa_e \lambda v_n$ and κ_n depend upon the distance between the two redox sites and, since the rate constant is the product of $\kappa_e \lambda v_n$ and κ_n , the rates will exhibit a complex dependence on separation distance. Moreover, this distance dependence is different for the normal and inverted free-energy regions [18,19].

Values of $\log(k/k_0)$, where k_0 is the value of k at $r = r_0$, calculated for the normal and inverted regions are plotted as a function of separation distance in Figures 2 (ellipsoidal cavity) and 3 (spherical cavity). The properties of the cavities are given in the caption to Figure 1; in addition, $\lambda_{in} = 4 \text{ kcal mol}^{-1}$, $r_0 = 7 \text{ \AA}$ and $\beta = 1.2 \text{ \AA}^{-1}$. The trends for both types of cavity are similar: the rate constants decrease monotonically with separation distance in the normal region (solid curve), but exhibit a maximum as a function of separation distance in the inverted region (dashed curve). The dotted curve shows the distance dependence of the electronic factor (slope = $-\beta/2.303$). The slope of the $\log(k/k_0)$ vs r plot for the normal region is larger than β and increases with increasing separation. Note that, because of the larger values of λ_{out} for the ellipsoidal cavity, a more negative ΔG° is required to access the inverted region in this case. The maximum in the $\log(k/k_0)$ plot in the inverted region arises from the opposing distance dependences of $\kappa_{el}v_n$ and κ_n : this rate maximum occurs at shorter separations for the ellipsoidal cavity.

It is evident from Figures 2 and 3 that considerable care needs to be exercised in interpreting the slopes of $\log k$ vs distance plots. Clearly the slopes of such plots are not solely determined by β and identifying β with the slopes can lead to erroneous conclusions, particularly for rate measurements in the inverted region. Moreover, this conclusion, although reached on the basis of a specific model for λ_{out} , is expected to be quite general. The effects discussed above will be particularly marked for systems in which one or both of the redox sites are near the surface of the molecule, λ_{in} is small, and the medium has a high static dielectric constant. As a corollary, when the distance variation is obtained by changing the positions of one of the redox sites on or near the surface of a macromolecule (metalloprotein), changes in the measured rate constants may reflect variations in the nuclear factors as much as in the electronic coupling of the two redox sites.

In principle, the temperature dependence of the rate constants affords a means of separating the electronic and nuclear contributions. The dependence of $\kappa_{el}v_n$ on temperature is expected to be small while that of κ_n (eq 2) can be quite large. Consequently the electronic and nuclear contributions can be obtained from the temperature independent (entropy) and temperature dependent (enthalpy) parts of the rate, respectively. However, there are several difficulties with this approach: κ_{el} is not, strictly speaking, temperature independent since some dependence on temperature arises from the $(\lambda RT)^{1/2}$ and ΔE factors in the denominators of eqs 3 and 5, respectively. In addition, the magnitudes of H_{AB} and β can be affected by temperature-dependent conformation changes. Further, the interpretation of the temperature-dependent part of the rate can also be quite complicated, as shown in the following section.

Figure 2. Plot of $\log(k/k_0)$ vs. separation distance for an ellipsoidal cavity: solid line, normal region, $\Delta G^\circ = 0$; dashed line, inverted region, $\Delta G^\circ = -1.33$ eV; dotted line, electronic factor.

Figure 3. Plot of $\log(k/k_0)$ vs. separation distance for a spherical cavity: solid line, normal region, $\Delta G^\circ = 0$; dashed line, inverted region, $\Delta G^\circ = -1.0$ eV; dotted line, electronic factor.

4. ACTIVATION PARAMETERS

The free energy of activation for the electron transfer (deriving from the need to adjust the nuclear configurations prior to the electron transfer) is given by eq 2b. The activation enthalpy and entropy associated with the nuclear reorganization can be obtained from the free energy by use of the Gibbs-Helmholtz equation. If λ is assumed to be temperature independent, the following expressions are obtained [1,20,21]

$$\Delta H^* = \frac{(\lambda + \Delta H^\circ)^2}{4\lambda} - \frac{(T\Delta S^\circ)^2}{4\lambda} \quad (9)$$

$$\Delta S^* = \frac{\Delta S^\circ(\lambda + \Delta G^\circ)}{2\lambda} \quad (10)$$

It is evident that ΔH^* will be negative when the second term on the RHS of eq 9 is larger than the first. The plot of ΔH^* vs ΔH° (or ΔG°) at constant ΔS° is a parabola with characteristics summarized in Table I. Note that, in common with λ and ΔG° , ΔH^* and ΔS^* are also distance dependent.

TABLE I. Reorganization Enthalpy as a Function of Thermodynamic Parameters

$-\Delta H^\circ$ (kcal mol ⁻¹)	$-\Delta G^\circ$ (kcal mol ⁻¹)	ΔH^* (kcal mol ⁻¹)
$(\lambda - T\Delta S^\circ)^a$	λ^a	0
λ	$\lambda + T\Delta S^\circ$	$-\frac{(T\Delta S^\circ)^2}{4\lambda}^{2b}$
$\lambda + T\Delta S^\circ$	$\lambda + 2T\Delta S^\circ$	0

^a Note that ΔG^* (and ΔS^*) are also equal to zero under these conditions.

^b Minimum value of ΔH^* .

The origin of the trends in ΔH^* is illustrated in Figures 4 and 5. Figure 4 shows the free-energy, entropy, and enthalpy curves for the reactants and products as a function of the reaction coordinate X for the case that $\Delta G^\circ = 0$ [21]. When $\Delta G^\circ = 0$ then $\Delta H^\circ = T\Delta S^\circ$ and ΔH° is not equal to zero unless ΔS° also equals zero. When $\Delta S^\circ \neq 0$ the enthalpy curves (which have the same force constants as the free-energy curves) are displaced relative to the free-energy curves. This is illustrated in the bottom of Figure 4 for the case that $T\Delta S^\circ$ is negative. Along the reaction coordinate the reactants' and products' enthalpy curves are displaced by the same amount (so that the distance along the reaction coordinate between the minima in the

Figure 4. Upper curves: free energy of the reactants (left-hand curve) and products (right-hand curve) as a function of the reaction coordinate (X) for the case that $\Delta G^\circ = 0$ and the two curves have identical force constants. The minima in the reactants' and products' free-energy curves are at $X = 0$ and $X = 1.0$, respectively. Middle line: entropy of the reactants and products as a function of the reaction coordinate for the case that $T\Delta S^\circ$ is negative. Lower curves: enthalpy of the reactants and products as a function of the reaction coordinate for the above case ($\Delta G^\circ = 0$ and $T\Delta S^\circ < 0$). The minima in the reactants' and products' enthalpy curves are at $X = -T\Delta S^\circ/2\lambda$ and $X = 1 - T\Delta S^\circ/2\lambda$, respectively.

Figure 5. Plot of ΔG^* and ΔH^* vs ΔG° and ΔH° ($= \Delta G^\circ + T\Delta S^\circ$) for $-T\Delta S^\circ = 2\lambda/3$ (left-hand ΔH^* curve) and $+T\Delta S^\circ = 2\lambda/3$ (right-hand ΔH^* curve).

enthalpy curves is the same as the distance between the minima in the free-energy curves). On the other hand, vertically they are displaced by different amounts (so that $\Delta H^\circ \neq 0$). The important point is that the free energy, but not necessarily the enthalpy, is a minimum at the equilibrium configuration of the reactants (or products), i.e., in Figure 4 the minimum in the free energy, but not in the enthalpy, of the reactants' and products' curves occurs at $X = 0$ and $X = 1$, respectively. The middle line in Figure 4 shows the entropy of the reactants and products as a function of the reaction coordinate; since there is no entropy change in the vertical transition the reactants and products have the same entropy ($S^R = S^P$) at any given value of the reaction coordinate (see ref. [21] for a more detailed discussion).

In Figure 5 ΔG^* and ΔH^* are plotted as a function of ΔG° and ΔH° for $-T\Delta S^\circ = 2\lambda/3$ (left-hand ΔH^* curve) and $+T\Delta S^\circ = 2\lambda/3$ (right-hand ΔH^* curve). The minimum in ΔG^* occurs at $-\Delta G^\circ = \lambda$ and the minimum in ΔH^* at $-\Delta H^\circ = \lambda$. Note that, if $\Delta S \neq 0$, three enthalpy regions can be distinguished depending on the magnitude of ΔG° . If $T\Delta S^\circ$ is negative,

then ΔH^* is positive when $-\Delta G^\circ < (\lambda + 2T\Delta S^\circ)$, negative when $(\lambda + 2T\Delta S^\circ) < -\Delta G^\circ < \lambda$, and positive when $-\Delta G^\circ > \lambda$. Similarly, if $T\Delta S^\circ$ is positive, then ΔH^* is positive when $-\Delta G^\circ < \lambda$, negative when $\lambda < -\Delta G^\circ < (\lambda + 2T\Delta S^\circ)$, and positive when $-\Delta G^\circ > (\lambda + 2T\Delta S^\circ)$. Regardless of the sign of $T\Delta S^\circ$ (and provided that $\Delta S^\circ \neq 0$), ΔH^* will undergo a change in sign as the system passes from the normal to the inverted free-energy region. This change in the sign of ΔH^* (and of ΔS^* , see eq 10) is an important characteristic of the transition from the normal to the inverted free-energy region, and can provide experimental verification of the cross-over.

4.1. Relationship to the Experimental Activation Parameters

The relationship between the Arrhenius activation parameters defined by the expression

$$k = A \exp(-E_a/RT) \quad (11)$$

and the parameters discussed above is

$$E_a \sim \Delta H^* \quad (12a)$$

$$A \sim \kappa_{el} v_n \exp(\Delta S^*/R) \quad (12b)$$

Alternatively, if the experimental activation parameters are defined by the transition-state expression

$$k = (kT/h) \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (13)$$

then, since kT/h is approximately 10^{13} s^{-1} at room temperature,

$$\Delta H^\ddagger \sim \Delta H^* \quad (14a)$$

$$\Delta S^\ddagger \sim R \ln \kappa_{el} + \Delta S^* \quad (14b)$$

When $v_n = 10^{13} \text{ s}^{-1}$ and the electron transfer is nonadiabatic with κ_{el} given by eq 4, the expressions for A and $\Delta S^\ddagger$ become

$$A = 10^{13} \exp(\Delta S^\ddagger/R) \quad (15a)$$

$$\Delta S^\ddagger \sim -\beta R(r - r_o) + \Delta S^* \quad (15b)$$

Note that since ΔS^* is a function of ΔS° and ΔG° (eq 10), A and $\Delta S^\ddagger$ will also depend upon these parameters. This dependence may be partly

responsible for the complex trends seen in certain systems, for example, in electron transfers across polypeptides [3a].

5. CONCLUSIONS

Theoretical considerations show that electron-transfer rate constants possess a complex dependence on the distance separating the two redox sites, and that there is an optimum distance for electron transfer. In the normal free-energy region the optimum distance corresponds to close contact of the two redox sites but in the inverted free-energy region the optimum distance can occur at quite large site separations. The rate maximum at large site separations arises from the opposing distance dependence of the nuclear and electronic factors. Since the condition for inverted behavior is $-\Delta G^\circ > \lambda$, this region can be attained by increasing the driving force and/or decreasing λ . Such changes can be effected through modifications of the redox sites and/or the surrounding medium. The inverted region thus affords a means of obtaining relatively rapid electron-transfer rates at large site separations and this can be an important consideration in the design of supramolecular systems.

Information about the relative contributions of the nuclear and electronic factors can be obtained from the temperature dependence of the electron-transfer rate. In interpreting such data it is important to take into consideration the overall entropy change for the reaction. The overall entropy change will be very different from zero when one of the redox sites is highly solvated (e.g., an aquo ion or an ammine complex) while the other site is weakly solvated (e.g. a polypyridine complex or a buried heme group). For such systems small, or even negative, enthalpies of activation have been reported [5,6,22,23], arising primarily from the very negative values of ΔS° . As discussed above, negative values of ΔS° give rise to negative ΔS^* values in the normal free-energy region and it is important that negative ΔS^* values arising in this manner not be ascribed to a weak electronic interaction of the two redox sites.

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