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Long-Range Electron Transfer in Biomolecules. Tunneling or Hopping?

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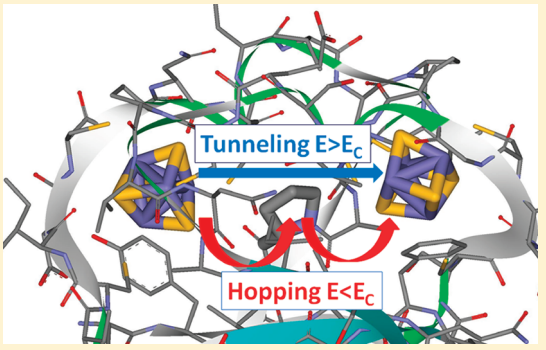
ABSTRACT: Two competing mechanisms are relevant for long-range electron transfer (ET) in biomolecules: direct electron tunneling between donor (D) and acceptor (A), D → A, and multistep hopping D → X → A, where an electron or an electron hole is transiently localized on intermediate sites X. Which of these mechanisms dominates the ET reaction is determined by the arrangement and electronic properties of the redox centers. For thermal ET, it is shown that single-step tunneling is overcome by hopping when the energy gap E between D and X is smaller than the crossover barrier E_C, $E_C = (\Delta G/2) + (3/4)k_BT\beta R_{DA}$, where ΔG is the driving force, β the decay parameter, and R_{DA} the donor−acceptor distance. In proteins at $T = 300$ K, hopping will dominate when $E < E_C = (\Delta G/2) + (R_{DA}/50)$ (E and ΔG are in eV, R_{DA} in Å); single-step tunneling will be operative when $E > E_C$. Thus, one can explore the ET mechanism using three quantities E, ΔG, and R_{DA}. When $\Delta G = 0$ and $E = 0.5$ eV (the difference in redox potentials of D and X is 0.5 V), two-step hopping D → X → A will be favored at $R_{DA} > 25$ Å. In protein ET chains, the distance between redox cofactors is often smaller than 20 Å, but the gap E between the cofactors and surrounding amino acid residues is larger than 0.5 eV. Therefore, ET in the systems should occur by single-step tunneling D → A. In the activationless regime ($\Delta G \approx -\lambda$, λ is the reorganization energy) often observed for *photoinduced* ET, the crossing point energy is determined by $E_C = (2\lambda kT\beta R_{DA})^{1/2} - \lambda$. The suggested expressions for the threshold barrier may be useful to predict the ET mechanism in natural and artificial redox systems.



INTRODUCTION

In biological molecules, electron transfer (ET) can occur between donor (D) and acceptor (A) separated by a long distance.[1−5] To describe this process quantitatively, sophisticated atomistic models are required.[6−9] The intrinsic dynamics of the redox centers and their surroundings can significantly modulate the efficiency of the ET reactions.[10−13] Nevertheless, simple coarse-grained models remain of considerable interest for exploring ET in natural and artificial systems.[1−5,14−16] Two different mechanisms for long-range ET are considered:[1−17] (1) direct electron tunneling from donor to acceptor, D → A, facilitated by the intervening medium and (2) multistep hopping D → X→ A with one or more intermediate states X, where an electron or an electron hole can transiently be localized. In the latter case, the long-range ET reaction is broken into several tunneling steps, "hops". Which of these complementary mechanisms will dominate depends on the arrangement and electronic properties of the redox centers.[1−5] As the tunneling rate decreases exponentially with the donor−acceptor distance R_{DA}, the single-step mechanism becomes unlikely at large distances. On the other hand, a significant difference in redox potentials of D and X makes the population of the intermediate state negligibly small and suppresses two-step hopping. Thus, varying the parameters of D, A, or X one can change the dominant ET mechanism as demonstrated for DNA,[4,5,17] oligopetides,[18,19] and proteins.[1−3,12,20] The conditions for transition between the tunneling and hopping transport have been of particular theoretical and experimental interest.[20−27]

Although the tunneling and hopping channels are always accessible, $k_{ET} = k_{tun} + k_{hop}$, their contributions may differ by several orders of magnitude.[1−5] For low injection energies E, $k_{hop} \gg k_{tun}$, and the hopping mechanism dominates the ET process, $k_{ET} \approx k_{hop}$. When the barrier is high, thermal activation D → X becomes unlikely, and the ET reaction occurs by unistep tunneling D → A, $k_{ET} \approx k_{tun}$. At some value of the energy gap, $E = E_C$, there is a crossover of the tunneling and hopping regimes, $k_{tun} = k_{hop}$. Knowing the crossover barrier E_C and the energy gap E between D and X, one can predict whether tunneling ($E > E_C$) or hopping ($E < E_C$) will dominate the ET reaction. In the paper, we obtain simple equations to estimate the threshold barrier E_C for thermal and photoinduced ET processes.

MODEL

We use a well-established kinetics model, which has been successfully applied to analyze charge transport in biomolecules.[1−3,28,29] Let us consider two ET processes: direct electron tunneling D → A and two-step hopping

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \xrightarrow{k_2} A$$

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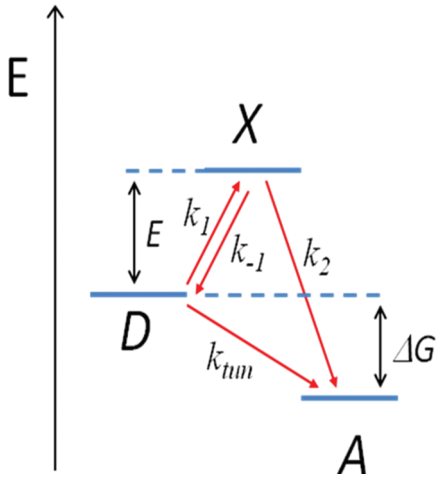
Scheme 1



where thermal activation D → X (the rate-limiting step) is followed by the exergonic reaction X → A (see Scheme 1).

Assuming the stationary condition, the rate k_{hop} for the two-step reaction

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \xrightarrow{k_2} A$$

reads

$$k_{hop} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (1)$$

where k_1, k_{-1}, and k_2 are the ET rate for D → X, X → D, and X → A, respectively (see Scheme 1). The energy gap E, $E = E(X) - E(D)$, determines the transient population of X, $p(X) \sim \exp(-E/kT)$. A general expression of the multistep ET rate in terms of rates characterizing each individual step is given by Berlin and Ratner.[30]

Gray and Winkler developed a numerical model to compare the tunneling and hopping mechanisms in proteins.[2] They considered two-step hopping

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A$$

taking into account the probability of the back reaction A → X defined by k_{-2}. That model (unlike eq 1) obeys the detailed balance condition. The hopping rate is described by biexponential expression, which can be well approximated by a single exponential function with an effective rate constant k_x (see Appendix for details). Numerical treatment of the system for different sets of ET parameters allows one to find conditions that determine the transition from tunneling to hopping.[2]

In this paper, we obtain explicit expressions of the crossing barrier in terms of the ET properties of a system by using several simplifying approximations. In particular, eq 1 for the hopping rate assumes that the rate of the back ET A → X is negligibly small (k_{-2} is set to be zero). Because of that, the model does not obey the condition of detailed balance, which in some cases may introduce errors in estimated values of the crossing barrier. As shown in the Appendix, the data derived using eq 1 are very similar to those obtained for the model

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A$$

considered by Gray and Winkler.[2]

The absolute rate of individual ET steps is described by semiclassical theory for nonadiabatic electron transfer[31]

$$k = \frac{2\pi}{\hbar} V^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta G + \lambda)^2}{4\lambda k_B T}\right) \quad (2)$$

Three key parameters, electronic coupling V, driving force ΔG, and reorganization energy λ, determine the ET rate. ΔG is defined through the difference of the D and A redox potentials. In a protein matrix, these quantities may significantly deviate from their values measured in aqueous solutions or in organic solvents. In particular, ΔG depends on the protonation state of amino acid residues and the orientation of polar groups and water molecules in the vicinity of the redox sites.[32−34] The electronic coupling V decays exponentially with the distance R between D and A[1−7]

$$V \sim V^0 \exp\left[-\frac{\beta}{2}(R - R_0)\right] \quad (3)$$

The parameter β is determined by the superexchange interaction of D and A with their surroundings.[1−7,14,15] In proteins, β is found in the range of 1.0−1.4 Å^{-1}. The distance dependence of ET rates has been discussed in many experimental and theoretical studies.[1−35] Structural dynamics of biomolecules can strongly affect the computed electronic coupling.[12,36−40] However, averaging over thermally accessible configurations of the system decreases considerably the impact of the arrangement of D and A on the effective coupling.[41] Although different computational schemes can be applied to estimate the reorganization energy λ in proteins,[1,31−34,42] often this quantity is treated as an adjustable parameter in the range of 0.5−1.5 eV.[1−3,34,43,44] Note that proteins may assist in ET by reducing the reorganization energy as compared with the reactions in polar solvent.[31−34]

RESULTS AND DISCUSSION

By definition, the crossover or threshold barrier E_C is a value of the energy gap E when the tunneling and hopping rates become equal

$$k_{hop} = k_{tun} \quad (4)$$

As already mentioned, the rate of all elementary ET steps (D → A, D → X, X → D, and X → A) is described by eq 2, with the coupling matrix element V defined by eq 3. The quantities V^0, β, ΔG, λ, and R_{DA} are considered as parameters of the model. When these parameters are known for all reactions shown in Scheme 1, eq 4 can be solved numerically. Our aim is to derive a simple expression of the tunneling−hopping crossover barrier in terms of experimentally observed parameters. Two cases are to be considered.

Case 1. In most systems with exergonic ET ($\Delta G < 0$), $k_2 \gg k_{-1}$, and therefore

$$k_{hop} = \frac{k_1 k_2}{k_{-1} + k_2} \simeq k_1 \quad (5)$$

Substitution of eqs 2 and 3 into $\ln k_{hop} = \ln k_1$ leads to the equation

$$\ln V_{DX}^0 - \beta R_{DX} - \frac{(E_C + \lambda_{DX})^2}{4kT\lambda_{DX}} - \frac{1}{2}\ln \lambda_{DX} = \ln V_{DA}^0 - \beta R_{DA} - \frac{(\Delta G + \lambda_{DA})^2}{4kT\lambda_{DA}} - \frac{1}{2}\ln \lambda_{DA} \quad (6)$$

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After simple rearrangements one obtains

$$AE_C^2 + BE_C + C = 0 \quad (7)$$

where

$$A = \frac{1}{2\lambda_{DX}}$$
$$B = 1$$
$$C = \frac{1}{2}\left(\lambda_{DX} - \lambda_{DA} - \frac{\Delta G^2}{\lambda_{DA}} - 2\Delta G\right) - 2kT\left[\beta(R_{DA} - R_{DX}) + \ln\frac{V_{DA}^0}{V_{DX}^0} - \ln\frac{\lambda_{DA}}{\lambda_{DX}}\right] \quad (8)$$

Formally, E_C can be directly found by solving eq 7. In many cases, however, several ET parameters determining coefficients A and C in eq 8 are unknown. To make the next step, some approximations should be applied. First, we will assume that elementary steps D → A, D → X, and X → A have very similar values of the reorganization energy, $\lambda_{DA} = \lambda_{DX} = \lambda_{XA} = \lambda$. This condition is commonly applied. In eq 8, V_{DA}^0 and V_{DX}^0 are electronic couplings of D−A and D−X at the reference distance R_0 (see eq 3). As already noted, the matrix elements are very sensitive to structural changes even when the distance between redox sites remains unchanged. They become, however, rather insensitive to geometrical changes by averaging over thermally accessible configurations.[41] Moreover, the averaged quantities for different combinations of the redox sites should be quite similar, as demonstrated for nucleic base pairs.[39] Because of that, it seems to be unlikely that the values of V^0 for D−A, D−X, and X−A differ by a factor larger than 10, thus $|\ln V_{DA}^0/V_{DX}^0| < 2.3$. In many cases, this quantity is much smaller than $\beta(R_{DA} - R_{DX})$. Also, the fact that experimental ET rates for different proteins are satisfactorily described by the Moser−Dutton equation,[16] see eq 18, suggests that V^0 values should be similar for different redox sites. Using these simplifications, we can rewrite eq 7

$$\frac{1}{2\lambda}E_C^2 + E_C - \left\{\Delta G + \frac{\Delta G^2}{2\lambda} + \gamma\right\} = 0,$$
$$\gamma = 2kT\beta(R_{DA} - R_{DX}) \approx kT\beta R_{DA} \quad (9)$$

Solving the quadratic equation, we get

$$E_C = \lambda\left\{\left(1 + \frac{\Delta G^2}{\lambda^2} + 2\frac{\Delta G}{\lambda} + 2\frac{\gamma}{\lambda}\right)^{1/2} - 1\right\} \quad (10)$$

The driving force for thermal ET in biomolecules is usually relatively small, $-0.4 \le \Delta G \le 0.2$ (the difference of oxidation potentials of the donor and acceptor sites does not exceed 0.4 V); therefore, the term $\Delta G^2/2\lambda$ is significantly smaller than $|\Delta G|$ and can be neglected (these quantities differ by an order of magnitude when $\Delta G = -0.2$ eV and $\lambda = 1$ eV). Using the extension $(1 + x)^{1/2} \approx 1 + 1/2x - 1/8x^2$ and neglecting all terms containing ΔG^n with $n \ge 2$, we can reduce eq 10 to

$$E_C \approx \Delta G\left(1 - \frac{\gamma}{\lambda}\right) + \gamma\left(1 - \frac{\gamma}{2\lambda}\right) \quad (11)$$

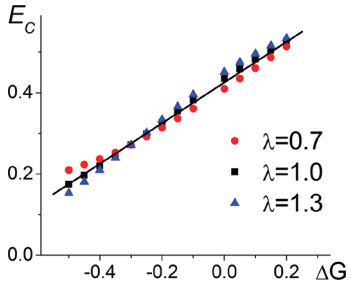

Figure 1. Dependence of the crossover barrier on the ET driving force ΔG in a system with $R_{DA} = 20$ Å, $\beta = 1.1$ Å^{-1}, and $\lambda = 0.7$, 1.0, and 1.3 eV. Accurate values of E_C are indicated by symbols. The black line refers to eq 16.

In typical ET protein systems ($\lambda \approx 1$ eV, $\beta \sim 1$ Å^{-1}, $R_{DA} \sim 20$ Å, $R_{DX} \approx 1/2R_{DA}$, $T = 300$ K), $\gamma/\lambda \approx 0.5$ and thus

$$E_C \approx \frac{1}{2}\Delta G + \frac{3}{4}\gamma = \frac{\Delta G}{2} + \frac{3}{2}kT\beta(R_{DA} - R_{DX}) \approx \frac{\Delta G}{2} + \frac{3}{4}kT\beta R_{DA} \quad (12)$$

Case 2. When $k_{-1} > k_2$ (e.g., at $\Delta G \approx 0$ and $R_{DX} < R_{XA}$)

$$k_{hop} = \frac{k_1 k_2}{k_{-1} + k_2} \approx \frac{k_1}{k_{-1}}k_2 = k_2 \exp^{-E/kT} \quad (13)$$

In the same manner as just done, we derive an approximate expression for E_C

$$E_C \approx \Delta G\frac{\gamma}{\lambda} + \gamma\left(1 - \frac{\gamma}{2\lambda}\right),$$
$$\gamma = 2kT\beta(R_{DA} - R_{XA}) \approx kT\beta R_{DA} \quad (14)$$

Again, taking into account that $(\gamma/\lambda) \approx 0.5$ we obtain

$$E_C \approx \frac{1}{2}\Delta G + \frac{3}{4}\gamma = \frac{\Delta G}{2} + \frac{3}{2}kT\beta(R_{DA} - R_{XA}) \approx \frac{\Delta G}{2} + \frac{3}{4}kT\beta R_{DA} \quad (15)$$

Thus, in both cases, the crossing barrier can be approximately expressed as

$$E_C \approx \frac{\Delta G}{2} + \frac{3}{4}kT\beta R_{DA} \quad (16)$$

In typical protein systems ($\beta \sim 1$ Å^{-1}) at $T = 300$ K

$$E_C \approx \frac{\Delta G}{2} + \frac{R_{DA}}{50} \quad (17)$$

where E_C and ΔG are in eV and R_{DA} is in Å.

Solving numerically eq 4 with k_{hop} defined by eq 1 for different sets of ET parameters (ΔG, β, λ, T, and R_{DA} were considered as variables), we found exact values of the crossing barrier for these systems. Linear fitting of the data using an empirical function $a\Delta G + bk_BT\beta R_{DA}$ gives $a \approx 0.5$ and $b \approx 0.75$ in line with eq 16.

Below we consider several examples, which demonstrate the performance of eq 16. Figure 1 shows the dependence of E_C on ΔG derived for three systems with λ values of 0.7, 1.0, and 1.3 eV. From these data, one infers that the crossover barrier does not strongly depend on the reorganization energy, and this effect may be neglected. As seen, eq 16 provides good estimates of E_C. The threshold barrier is lower for exergonic and higher for endergonic

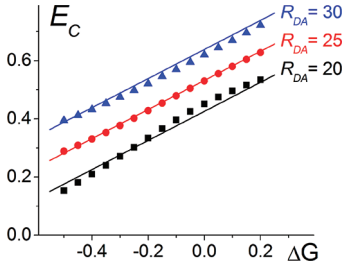

Figure 2. Dependence of the crossover barrier E_C on the driving force ΔG in systems with R_{DA} = 20, 25, and 30 Å. In all systems, β = 1.1 Å^{-1} and λ = 1.0 eV. Accurate values of E_C are shown by solid symbols; the straight lines refer to eq 16.

ET. Therefore, hopping should be more feasible in systems with $\Delta G \geq 0$. For instance, $E_C \approx 0.2$ eV when $\Delta G = -0.4$ eV, and $E_C \approx 0.4$ eV when $\Delta G = 0.0$ eV. Thus, if $E = 0.3$ eV, ET will occur by tunneling ($E > E_C$) when $\Delta G = -0.4$ eV and by hopping ($E < E_C$) when $\Delta G = 0.0$ eV.

Figure 2 shows how E_C depends on the donor−acceptor distance for systems with β = 1.1 Å^{-1}, λ = 1.0 eV, T = 300 K and different values of ΔG. Exact values of the barrier are well reproduced by eq 16. E_C increases with the donor−acceptor distance. At $\Delta G = -0.4$ eV, the barrier is found to be 0.2, 0.3, and 0.4 eV at R_{DA} = 20, 25, and 30 Å, respectively. In a system with E = 0.30 eV, the ET reaction will be controlled by tunneling when R_{DA} =20 Å but by two-step hopping at R_{DA} =30 Å; at R_{DA} = 25 Å, $E = E_C$, and both channels are expected to be significant, $k_{hop} \approx k_{tun}$.

The absolute rate of ET in proteins is often estimated using the Moser−Datton equation,[16] which takes implicitly into account the effect of the vibrational frequency coupled to ET. At T = 300 K, it reads

$$\log k \approx 13 - 0.6(R_{DA} - 3.6) - 3.1\frac{(\Delta G + \lambda)^2}{\lambda} \qquad (18)$$

where ΔG and λ are in eV and R_{DA} is in Å. If instead of eq 2 and 3 one takes eq 19 and repeats the whole procedure described above (including linear regression analysis), one gets

$$E_C \approx \frac{\Delta G}{2} + \frac{R_{DA}}{30} \qquad (19)$$

Equation 19 is similar to eq 17 and gives comparable values of the threshold barrier. In eq 18, the decay parameter β is assumed to be ca. 1.4 Å^{-1} (0.6 ln 10 = 1.382). It is significantly larger than β = 1.0 Å^{-1} employed in eq 17. Also, the constant 3.1 eV^{-1} at the activation energy in eq 18 is smaller than $1/(2.303 \cdot 4kT)$ = 4.175 eV^{-1} derived from eq 2. Because of these differences, the threshold barrier estimated using eq 19 is higher than that derived from eq 17.

Study of photoinduced ET in chemically modified proteins allows one to better understand how electronic and structural properties of the reaction centers affect the efficiency of ET. In this context, the reactions in the activationless regime, $\Delta G \approx -\lambda$, are of special interest.[3,20] When $\Delta G \approx -\lambda$, eq 9 gives

$$E_C = \sqrt{4\lambda kT\beta(R_{DA} - R_{DX})} - \lambda \approx \sqrt{2\lambda kT\beta R_{DA}} - \lambda \qquad (20)$$

Gray and Winkler analyzed the distance dependences of the rates of single-step and two-step electron tunneling reactions.[3]

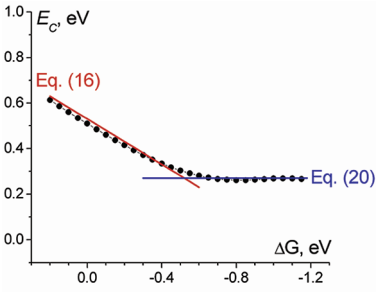

Figure 3. Dependence of the crossing barrier E_C on the driving force ΔG in a system with R_{DA} = 25 Å, β = 1.1 Å^{-1}, and λ = 0.8 eV. Accurate values of E_C are shown by solid circles; the straight lines present eq 16 and eq 20.

They concluded that "hopping can facilitate electron flow over distances 20 Å in cases where the free-energy changes for endergonic intermediate steps are no more than 0.2 eV".[3] Using eq 20, we can estimate the threshold barrier for a typical model protein (λ = 0.8 eV, β = 1.1 Å^{-1}, T = 300 K). For R_{DA} = 20 and 25 Å, E_C = 0.16 and 18 eV, in good agreement with the conclusion made of Gray and Winkler.

As seen from Figure 3, eqs 16 and 20 reproduce well the crossing barrier computed for thermal ($-0.4 \leq \Delta G \leq 0.2$) and photoinduced ($\Delta G \sim -\lambda$) ET.

The expressions for the crossover barrier can be applied to estimate the acceleration of ET caused by the intervening site X. The ratio of the ET rates at $E = E_X$ and $E = E_C$ is determined by a factor F

$$F = 10^{(E_C - E_X)/2.303kT} \qquad (21)$$

If the energies are in eV and T = 300 K, $F \approx 0^{16.7(E_C - E_X)}$.

Finally, we consider three systems studied experimentally.

Thermal ET in Membrane Proteins. In ET chains of the membrane proteins, the distance between the closest cofactors is smaller than 14 Å.[44] For an ET reaction with ΔG = 0 and R_{DA} = 15 Å, the threshold barrier estimated using eq 17 is 0.3 eV. Equation 19 gives a higher value, E_C = 0.5 eV. For exergonic ET, the barrier will be lower by $|\Delta G/2|$. In proteins, the energy gap E between redox cofactors and surrounding amino acid residues is usually higher than 0.5 eV (the difference in oxidation potentials of D and X is larger than 0.5 V[15]), resulting in $E > E_C$. It means that direct electron tunneling should dominate the ET, and the intervening residues cannot be intermediate states in the ET chains.

Photoinduced ET in Modified Azurines. Recently, Gray and co-workers studied photoinduced ET in modified azurine containing a Re complex.[45] They found that hopping [Re]* → Trp^{122} → [Cu] through the intermediate Trp radical cation is 300 times faster than direct electron tunneling between the metal sites. According to X-ray data, the distance between Re and Cu, R_{DA}, is 19.4 Å, and the distance between Re and Trp, R_{DX}, is 8.9 Å. The reorganization energy is assumed to be 0.8 eV.[45] Substituting these quantities into eq 20, we obtain $E_C \approx 0.15$ eV. The energy gap E_X between [Re]* and Trp, reported by Shih et al., is −0.03 eV.[45] Using eq 21, we get $F \approx 10^3$. Thus, we predict the hopping rate to be 1000 times as high as the tunneling rate. This finding agrees well with the observed data.[45] The energy gap between [Re]* and Tyr or Phe is ca. 0.20 eV higher than in the Trp system. Therefore, E_X becomes higher than E_C when Trp^{122} is replaced by Tyr or Phe. This should lead to

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switching the ET mechanism from two-step hopping to single-step tunneling and decreasing the ET rate by 3 orders of magnitude. This estimate is in line with the experimental result that substitution of Tyr or Phe for Trp[122] in the modified azurines leads to very slow ET.[45]

Thermal ET through π-Conjugated Bridges. Very recently, intramolecular ET was studied in systems consisting of up to five *p*-phenylenevinylene bridges connecting two polychlorinated triphenylmethyl moieties.[46] The decay parameter $\beta = 0.14$ A^{-1} and the energy gap $E = 0.08$ eV (1.9 ± 0.2 kcal/mol) were determined experimentally. The observed energy gap is equal to the activation barrier measured in 1,2-dichlorobenzene at 300 K for the complex with $n = 4$. Because the donor and acceptor sites are identical, $\Delta G = 0$. R_{DA} in the D−B$_n$−A systems was estimated as 18.8, 25.4, 31.9, 38.2, and 44.7 Å for n ranging from 1 to 5.[46] Substituting $\Delta G = 0$, $\beta = 0.14$ A^{-1}, $E = 0.08$ eV, and $T = 300$ K into eq 16, we get the donor−acceptor distance for the crossover point, $R^* \approx 29$ Å. Thus, the single-step tunneling should occur in compounds with $n = 1$ and 2 ($R_{DA} < R^*$), whereas hopping is expected to dominate in systems with $n \geq 3$, $R_{DA} > R^*$. This conclusion is in perfect agreement with experimental results.[46]

CONCLUSIONS

Several years ago, Gray and Winkler developed a numerical scheme to compare the tunneling and hopping mechanisms in proteins.[2] That approach was successfully used to explore ET reactions in different proteins and to establish how structural and ET parameters affect the tunneling and hopping rates.[2,3]

On the basis of a simplified model, we have suggested explicit expressions for the threshold barrier that controls the transition between the superexchange and hopping ET channels. For thermal ET, the barrier can be estimated as $E_C = \Delta G/2 + (3/4)k_BT\beta R_{DA}$, which leads to $E_C = (\Delta G/2) + (R_{DA}/50)$ for biomolecules ($\beta \sim 1$ Å^{-1}) at $T = 300$ K. For the activationless regime observed in photoinduced ET, the crossover point energy can be estimated as $E_C = (2\lambda kT\beta R_{DA})^{1/2} - \lambda$. These expressions may be very helpful by analyzing long-range ET and exploring the effects of electronic and structural parameters on the electron flow in natural and artificial systems as demonstrated above by several examples. The formulas provide good estimates of E_C values, which can be obtained numerically using more accurate models.[2]

The derived expressions for the crossing barrier appear to be also applicable to triplet excitation energy transfer, the absolute rate of which can be described by the Marcus equation.[47−50]

APPENDIX

The general reaction scheme for two-step hopping may be represented by

$$\mathrm{D} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{X} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{A} \qquad \text{(A1)}$$

The appearance of A for the boundary conditions [D] = 1, [X] = 0, and [A] = 0 at $t = 0$ can be found as[51]

$$[\mathrm{A}] = k_1k_2\left[\frac{1}{\alpha\beta} + \frac{1}{\alpha(\alpha-\beta)}e^{-\alpha t} - \frac{1}{\beta(\alpha-\beta)}e^{-\beta t}\right] \qquad \text{(A2)}$$

where α and β are determined by

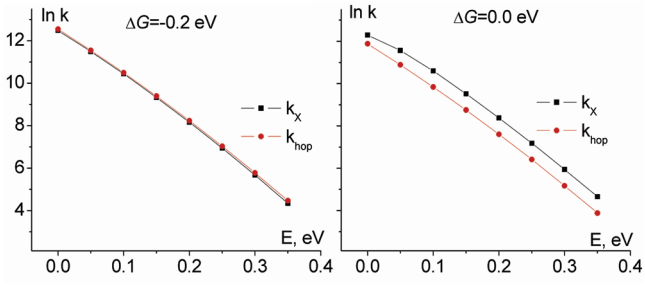

Figure A1. Effective rate constants k_X (eq A5) and k_{hop} (eq A8) calculated for a system ($R_{DA} = 25$ Å, $R_{DX} = 12.5$ Å, $\beta = 1.1$ Å^{-1}, and $\lambda = 1.0$ eV) with different energy gaps E and the driving force $\Delta G = -0.2$ and $\Delta G = 0.0$ eV.

$$\begin{aligned} \alpha + \beta &= k_1 + k_{-1} + k_2 + k_{-2} \\ \alpha\beta &= k_1k_2 + k_1k_{-2} + k_{-1}k_{-2} \end{aligned} \qquad \text{(A3)}$$

The biexponetial funcion, eq A2, may be approximated by a single exponetial expression

$$[\mathrm{A}] = [\mathrm{A}]_{t=\infty}[1 - e^{-k_X t}] = \frac{k_1k_2}{\alpha\beta}[1 - e^{-k_X t}] \qquad \text{(A4)}$$

with an effective rate constant k_X determined as

$$k_X = 1/\tau,\ \tau = \int_0^\infty \left(1 - \frac{[\mathrm{A}]}{[\mathrm{A}]_{t=\infty}}\right)dt \qquad \text{(A5)}$$

A very similar definition of k_X was used in the Gray and Winkler model.[2] The effective constant can also be defined as

$$k_X' = 1/t_x,\ [\mathrm{A}]_{t=tx} = [\mathrm{A}]_{t=\infty}(1 - e^{-1}) \qquad \text{(A6)}$$

k_X and k_X' values are found to be very close to each other (they differ by less than 5%). On the other hand, eq 1 suggests that the two-step hopping rate may be approximately described by

$$[\mathrm{A}]_t = [\mathrm{A}]_{t=\infty}(1 - e^{k_{hop}t}) \qquad \text{(A7)}$$

$$k_{hop} = \frac{k_1k_2}{k_{-1} + k_2} \qquad \text{(A8)}$$

Comparison of k_{hop} with the effective constants k_X or k_X' calculated for different sets of the ET parameters shows that k_X is satisfactorily reproduced by k_{hop} (see Figure A1). Largest deviations are found for systems with $\Delta G = 0$ (k_{hop} by a factor of ~2 smaller than k_X). Even in this case, rather small errors (less than 0.02 eV) in the crossing barrier are found. These estimates suggest that our model should provide reasonable values of the crossing barriers for different ET systems.

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