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Understanding Short-Range Electron-Transfer Dynamics in Proteins

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Abstract

Short-range electron-transfer (ET) reactions in biological systems are usually ultrafast, having transfer rates comparable to or even faster than corresponding environmental fluctuations, and often display nonexponential behaviors. To understand these nonequilibrium ET dynamics, we carried out detailed theoretical analyses based on the Sumi–Marcus model. It is shown that the ET dynamics is largely determined by the relative time scales of the ET reaction and its surrounding motions. Significantly, different environmental fluctuations can produce a variety of apparent ET dynamics even with the same driving force, G^0 , and reorganization energy, λ . We applied our analyses to an ultrafast ET process in DNA repair by (6–4) photolyase and directly obtained the inner and outer reorganization energies (λ_i and λ_o) as well as the free energy G^0 of various mutants, providing mechanical insight into ultrafast short-range ET reactions in proteins.

Graphical Abstract

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Supporting Information

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Supporting Figure S1(PDF)

The authors declare no competing financial interest.

Electron-transfer (ET) reactions in biological systems have shown a variety of dynamics with time scales ranging from femtoseconds to milliseconds.^{1–4} Among these reactions, a significant portion does not follow the exponential dynamics described by the classic Marcus theory.^{5–7} This nonexponential behavior of ET dynamics can be clearly seen in the ultrafast ET reactions inside proteins,^{8–15} such as photolyases^{16–23} and photosyntheses,²⁴ where the reaction rates are typically on the time scales from femtoseconds to picoseconds. On the other hand, it has been shown experimentally that environmental fluctuations around the donor–acceptor pair have a rate similar to that of the reaction or even slower.^{25,26} This is in contrast to the general picture of Marcus theory, in which the ET reaction happens at the equilibrium of the surroundings. In 1986, Sumi and Marcus²⁷ proposed a different model aiming to address nonequilibrium ET reactions. Although it has been successfully applied to different systems,^{28,29} the full implications of this model are not appreciated. In this work, by carrying out careful analyses of the Sumi–Marcus theory, the influence of environmental fluctuations on ET dynamics is further elucidated.

In the Sumi–Marcus model, the ET reaction is assumed to couple with two reaction coordinates.²⁷ One “fast” coordinate, q , represents vibrational relaxations of the donor–acceptor pair, which typically have frequencies much higher than the reaction rate. The other “slow” coordinate, x , represents diffusive fluctuations of the environment, which in a protein system can include hydration-water motions and conformational changes of proteins. The distribution of the reactants along the q coordinate is always at equilibrium, while along the x coordinate, the distribution follows a behavior of Debye relaxation.³⁰ As a result, given the

assumption that free energy curves of both reactants and products are quadratic (see Figure 1), the time evolution of the reactants' distribution $P(x, t)$ can be modeled as

$$\frac{\partial}{\partial t} P(x, t) = \left(\frac{1}{\tau_D} \widehat{\mathcal{L}} - k(x) \right) P(x, t) \quad (1)$$

$$\widehat{\mathcal{L}} = \frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial x} x \quad (2)$$

in which τ_D is the relaxation time of environmental fluctuations. $\widehat{\mathcal{L}}$ is the Liouville operator that governs the diffusive motion of $P(x, t)$. $k(x)$ is the ET reaction rate as a function of x (see Figure 1C), whose expression is given as

$$k(x) = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda_i k_B T}} \exp \left[-\lambda_o/2 \lambda_i \left(x - \frac{\lambda + \Delta G^0}{\sqrt{2\lambda_o k_B T}} \right)^2 \right] \quad (3)$$

To simplify the expressions, x is normalized to be unit-less by dividing the constant $\sqrt{k_B T}$. For a Gaussian function of $k(x)$, we define the following parameters:

$$\nu = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda_i k_B T}}, \quad x_c = \frac{\lambda + \Delta G^0}{\sqrt{2\lambda_o k_B T}}, \quad \alpha = \frac{\lambda_o}{2\lambda_i} \quad (4)$$

ν and x_c are the peak and mean of $k(x)$, while α is inversely related to the variance of $k(x)$. In the above expressions, the assumption of weak coupling between the donor-acceptor pair is used. In the adiabatic limit, the prefactor of $k(x)$ should be modified accordingly.³¹ The parameters involved in the equations are the electronic coupling constant, J , between the donor and acceptor; the reaction free energy, ΔG^0 ; the "inner" reorganization, λ_i , and the "outer" reorganization energy, λ_o , which are energies required to take the system from the reactant's global minimum to the product's global minimum along both coordinates, respectively. The sum of λ_i and λ_o is the total reorganization energy λ , that is, $\lambda = \lambda_i + \lambda_o$. In this work, only ET dynamics in the normal region, where $|\Delta G^0| < \lambda$, is discussed. The ET dynamics in the inverted region can be taken into account in a similar manner.³² Finally, the quantity of interest is the survival probability of reactants, $Q(t)$, defined as

$$Q(t) = \int_{-\infty}^{+\infty} P(x, t) dx \quad (5)$$

which can be directly compared to experimental data. Typically, $Q(t)$ can be described by a stretched exponential decay

$$Q(t) = e^{-(t/\tau_{ET})^\beta} \quad (6)$$

where β is the stretched parameter, quantifying the degree of deviation from exponential behaviors. With $Q(t)$ being a stretched exponential function, the average ET rate $\langle \tau_{ET} \rangle$ is given by

$$\langle \tau_{\text{ET}} \rangle = \int_0^\infty Q(t) dt = \frac{\tau_{\text{ET}}}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (7)$$

where $\Gamma(z)$ is the gamma function.

Inside the equilibrium region of ET reactions, the reaction time τ_{ET} is determined by the coupling constant, J ; the driving force, G^0 ; and reorganization energy, λ :

$$\tau_{\text{ET}}^{-1} = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_{\text{B}} T}} \exp\left[-(\lambda + \Delta G^0)^2 / 4\lambda k_{\text{B}} T\right] \quad (8)$$

However, in the nonequilibrium scenario, by fixing J , G^0 , G^0 , and λ_0 , different types of ET dynamics are produced with varying time scales of fluctuations, τ_{D} , as shown in Figure 2. The influence of different initial distributions on ET dynamics is presented as well (Figure 2A,B). Generally, the ET dynamics is slowed down with slower local fluctuations. These different behaviors of ET can be further understood by looking at the time evolution of the reactants' distribution, $P(x, t)$ (Figure 3). When local motions are much faster than the average ET rate $\langle \tau_{\text{ET}} \rangle^{-1}$ that is, $\tau_{\text{D}} \rightarrow 0$, the classic Marcus picture is recovered (Figure 2C). This is expected, because when $\tau_{\text{D}} \rightarrow 0$, local motions “immediately” bring $P(x, t)$ back to the equilibrium, regardless of the initial distribution (see the upper panel in Figure 3A,B). In addition, the instant distribution of the reaction rate $k(x)P(x, t)$ is always peaked at $x = x_{\text{m}}$ (see the lower panel in Figure 3A,B), where x_{m} is the x coordinate of the barrier's saddle point (Figure 1B,C). In this case ($\tau_{\text{D}} \rightarrow 0$), at any instant, the average rate of reaction is close to the rate predicted by eq 8, resulting in an exponential decay of the population (Figure 2A,B). As the fluctuation rate becomes comparable with ET, the asymmetric distribution of $k(x)$ leads to $P(x, t)$ deviating from its equilibrium distribution in intermediate times. In fact, $P(x, t)$, along with the reaction rate distribution $k(x)P(x, t)$, shifts left toward smaller $k(x)$. This results in stretched exponential dynamics (Figure 3C—F). As the fluctuations get slower, the influence of the reactants' initial distribution on the overall dynamics $Q(t)$ becomes more significant. In the limit of $\tau_{\text{D}} \rightarrow \infty$, $P(x, t)$ is effectively frozen along x and the ET reactions occur at different rates determined by $k(x)$ (Figure 3E,F). In this case, the delta function distribution of $P(x, t=0)$ leads to a single-exponential decay with the ET rate determined by $k(x=0)$ (Figure 2A,E).

Thus, if $P(x, t)$ is understood as the distribution of conformations of the environment, the rate of local fluctuations determines the amount of conformations that the system is able to access within the time window of the ET reaction. When local motions are fast compared to the ET rate, the conformational space can be sufficiently sampled such that the overall ET dynamics is close to the Marcus picture (Figure 2C). However, when the fluctuations are extremely slow, the overall ET dynamics is almost fully determined by the initial distribution of conformations (Figure 2E). For a thermal distribution, the stretched ET dynamics results from the initial distribution, or, in a sense, static heterogeneity.

To avoid the influence of initial distributions, in the rest of this work, all the ET dynamics is calculated with the initial distribution of $P(x, t)$ being a delta function, $\delta(x)$. In this way, the results obtained can be generalized to any initial distribution as follows: Assuming that the

solution of the differential equation (eq 1) is $P(x, t|x_0, t=0)$ with the initial distribution being $\delta(x - x_0)$, the solution of the differential equation with its initial distribution being $P(x_0, t=0)$ is given by

$$P(x, t) = \int_{-\infty}^{+\infty} dx_0 P(x, t|x_0, t=0) P(x_0, t=0) \quad (9)$$

It is straightforward to understand the effect of different parameters on ET reaction rates (Figure S1). Through the expression of $k(x)$ and definitions of different parameters (eqs 3 and 4), it can be inferred that the overall average ET rate $\langle \tau_{ET} \rangle^{-1}$ is decreased with larger x_c with everything else being equal. On the other hand, $\langle \tau_{ET} \rangle^{-1}$ is decreased with increasing α (therefore decreasing variance). Clearly, with a larger magnitude of v , the reaction rate increases (Figure S1).

The effects of parameters on the stretched factor, β (see eq 6), are more complicated. In Figure 2A, β decreases with increasing τ_D while τ_D is relatively small compared to τ_{ET} but increases when τ_D is significantly larger than τ_{ET} . As discussed before, the stretched dynamics comes from the deviation of $P(x, t)$ from its equilibrium distribution, which is the result of two motions. The diffusive motion along x always drives $P(x, t)$ toward the Boltzmann distribution, while the asymmetric distribution of $k(x)$, which controls the reaction motion along q , propels the system toward nonequilibrium (see the upper two panels of Figure 3). To better understand these competing forces, parameters that can modify these motions are analyzed individually. With everything else being equal, the plot of β versus $|\mathcal{G}^0|$ shows a parabolic shape (Figure 4A). Interestingly, the parabolas resulting from different values of λ are similar to each other, except that they get narrower with decreasing λ . With a fixed λ (along each parabola in Figure 4A), when $|\mathcal{G}^0|$ is large and close to λ , $\langle \tau_{ET} \rangle$ is small compared to τ_D . That is, the environment barely relaxes within the time scale of ET. Similar to the case of $\tau_D \rightarrow \infty$, the ET dynamics has $\beta \rightarrow 1$ (Figure 2E). When $|\mathcal{G}^0|$ decreases, which leads to an increase of x_c (eq 4), $\langle \tau_{ET} \rangle$ is increased and gets closer to τ_D . The diffusive motion and the ET reaction happen on a similar time scale, which lowers β (Figure 2D). While $|\mathcal{G}^0|$ becomes very small, $\langle \tau_{ET} \rangle$ is large compared to τ_D , which has the characteristic of an ET reaction happening at equilibrium, meaning $\beta \rightarrow 1$ (Figure 2C). Obviously, this physical picture stays valid with varying λ (Figure 4A), while the narrowing of the parabola with decreasing λ results from the decrease of λ_0 in x_c (eq 4), leading to a sensitive change of $\langle \tau_{ET} \rangle$ from the variation of $|\mathcal{G}^0|$. In consequence, this picture suggests that there exists a universal relation between β and $\langle \tau_{ET} \rangle / \tau_D$.

In Figure 4B, with a fixed value of α (see for example the purple curves, where $\alpha = 1.0$), the trend of β has a parabolic shape and β reaches minimum in the region where $\langle \tau_{ET} \rangle \sim \tau_D$, in consistent with Figure 4A. This figure also shows that the ratio between λ_i and λ_0 , α (eq 4), is the key factor in determining the “stretchedness” of overall ET dynamics. In Figure 4B, increasing α leads to the downshift of the parabolic curves. Because α determines the width of $k(x)$, higher α results in higher variation of $k(x)$ inside the region of $x \approx 0$, where $P(x, t)$ remains. When comparing the ET dynamics of different values of α at a similar value of

$\langle \tau_{\text{ET}} \rangle \approx \tau_{\text{D}}$, higher variation of $k(x)$ can certainly cause a higher deviation of $P(x, t)$ from the Boltzmann distribution over time, which gives rise to a smaller β .

With the above analyses, it is possible to analyze experimental data using the Sumi–Marcus model. The model system used in this work is a photoexcited ET reaction inside a protein of (6–4) photolyase. The ET to be analyzed is the first step of the protein's DNA repair in the enzyme mechanism, which happens between a photoexcited flavin adenine dinucleotide (FADH^{*-}) as the donor and the (6–4) photoproduct (6–4PP) as the acceptor. The ET dynamics of multiple mutants were resolved through transient absorptions of FADH^{*-} . The solvation dynamics of the system, which is assumed to be similar under mutation, was also resolved through the fluorescence dynamics of FADH^{*-} .²⁵ The resolved solvation dynamics has three components with time scales at 1.4, 17, and 730 ps. Because the observed ET dynamics occurs in more than 100 ps, only the slowest component, $\tau_{\text{D}} = 730$ ps, will be used in this analysis. Although it has been suggested that a time-dependent diffusion coefficient, $D(t) = -d \ln C(t)/dt$, can be used to generalize eq 1 in account of multiple solvation components,²⁸ the faster components make little difference. This is partly because $D(t)$ decays very fast to $1/\tau_{\text{D}}$ and the ET time scales in this system are in the range of hundreds of picoseconds. Furthermore, the coupling constant of the wild type (WT) was reported to be $J = 3$ meV.¹⁹ Because the average ET time scale and the stretched factor for each mutant, $\langle \tau_{\text{ET}} \rangle$ and β , were measured experimentally, the value of α for each mutant can be determined (Figure 4B). Here, it is further assumed that the inner reorganization energy, λ_{i} is invariant with respect to different mutants, because the mutation does not significantly change the configuration of the donor–acceptor pair. As a result, given G° of the wild type, λ_{i} is obtained by fitting the wild-type's ET dynamics with $Q(t)$ (eq 6), calculated by the current model. For any other mutant, the unknown parameter left to be determined is its free energy (G°). By knowing λ_{i} and α of each mutant, its G° is obtained by fitting each mutant's experimental ET dynamics (see Figure 4C). The values of parameters simulated are summarized in Table 1 (in bold). Surprisingly, compared to the result of WT, the mutants—H368M, H364Y, and H364M—have slower ET dynamics with larger driving forces G° by calculation, which is in contrast to the common belief that higher driving forces usually lead to faster ET rates (eq 8). According to this analysis, these mutants have more stretched dynamics, hence smaller β , which leads to larger α (Figure 4B) and larger λ_{o} under the constant λ_{i} . Thus, the differences of λ_{o} values, with respect to that of the wild type, overcompensate the variations of their driving forces. However, for H364N, the situation is the opposite, leading to a faster ET relative to the WT.

To conclude, we performed comprehensive analyses of the Sumi–Marcus model and influences on the overall ET dynamics of all related parameters. To understand the nontrivial dynamics of nonequilibrium ET reactions, the solvation dynamics of their environments need to be taken into account, which becomes especially prominent when the two time scales are comparable. Furthermore, the initial distribution of the population can have a lasting impact on the overall dynamics as well. Finally, we introduced an important and practical method: knowing τ_{D} , τ_{ET} , or β by experiment, we can determine $\alpha = \frac{\lambda_{\text{o}}}{2\lambda_{\text{i}}}$ and derive λ_{o} , λ_{i} , and the reaction free energy G° by simulation of experimental results, given the

electronic coupling constant J . This new method should be widely applied to other ultrafast ET systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Cartoon illustration of a solvation-coupled electron-transfer reaction between a photoexcited donor (D^*) and an acceptor (A). (B) Schematic presentation of the 2-D potential surface relevant to an ET reaction with R and P being the global minima of the reactant and product states, respectively. The bold line represents the reaction barrier intercepting with the x axis at x_c and having a saddle point at x_m , defined by

$$x_m = \sqrt{\frac{\lambda_0}{2k_B T}} \frac{\lambda + \Delta G^0}{\lambda}.$$
 (C) The ET reaction rate $k(x)$, which is a Gaussian distribution centered at x_c .

Figure 2.

(A) Simulations of ET dynamics as a stretched-exponential decay with different solvation time scales and delta distribution as the initial distribution. Other values of parameters used are $J = 3$ meV, $G^p = -0.45$ eV, $\lambda_o = 0.71$ eV, and $\lambda_o = 0.29$ eV. (B) Simulations of ET dynamics with initial distribution being the Boltzmann distribution. The values of the parameters are the same as those used in panel A. Note the significant differences between ET dynamics with different τ_D , even with the same ET parameters. (C) Illustration of ET dynamics when $\tau_D \rightarrow 0$. (D) Illustration of ET dynamics when τ_D is comparable to τ_{ET} . (E) Illustration of ET dynamics when $\tau_D \rightarrow \infty$.

Figure 3.

Time evolutions of the reactants' distributions, $P(x, t)$, under different conditions. Values of parameters used are the same as in Figure 2. The upper two panels and lower panels are simulated with the delta function (A, C, and E) and a Boltzmann distribution (B, D, and F) as $P(x, t = 0)$ with different τ_D values, respectively. The dashed lines are located at $x = x_m$.

Figure 4.

How is β affected by related parameters? (A) β versus ΔG^0 with different values of λ . Other values of parameters used are $J = 3$ meV, $\alpha = \lambda_o/(2\lambda_i) = 0.2$, and $\tau_D = 300$ ps. (B) β versus $\log[(\tau_{\text{ET}})/\tau_D]$. The graph is made under different values of α at $\tau_D = 30$ ps and $J = 3$ meV. Every three curves of each color are made with three different values of λ : 0.4, 1.0, and 1.6 eV. The points in each curve are simulated with varying ΔG^0 while fixing other parameters. The corresponding mutants of (6–4) photolyase are labeled on the graph. (C) Simulated

results of mutants of (6–4) photolyase. Absorption transients of selected mutants fitted by the Sumi—Marcus model. The obtained results of all mutants are shown in Table 1.

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Table 1.Energetics of Forward Electron Transfer Reactions in (6–4) Photolyase^{a,b}

mutant	$\langle\tau_{\text{ET}}\rangle^c$	β	α	λ_i	λ_o	λ	G°
WT	273	0.86	0.1	0.78	0.16	0.94	-0.39^d
H364D	346	0.83	0.1	0.78	0.16	0.94	-0.37
H368M	372	0.83	0.15	0.78	0.24	1.02	-0.45
H364 K	363	0.85	0.1	0.78	0.16	0.94	-0.37
H364A	389	0.84	0.1	0.78	0.16	0.94	-0.37
H364N	188	0.79	0.2	0.78	0.31	1.09	-0.58
H364M	304	0.79	0.2	0.78	0.31	1.09	-0.54
H364Y	355	0.72	0.35	0.78	0.55	1.33	-0.77

^aThe electronic coupling constant J is fixed to be 3 meV.^bAll energies, G° and λ , are in the unit of eV.^cThe time in ps^dThe value was taken from ref 22.