

DONOR-ACCEPTOR TWO-ELECTRON TRANSFER REACTIONS: CONCERTED AND SEQUENTIAL PATHWAYS IN PROTEIN STRUCTURES

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Nonadiabatic donor-acceptor (DA) two-electron transfer (TET) is described by a model where the intersite electronic transitions are assumed to proceed against the background of fast relaxations (a) within the electronic substates as well as (b) between those substates related to the same electronic state. It is shown that the DA TET appears as a single-exponential reaction between the initial and final electronic states, and the corresponding overall transfer rate can be represented as an additive contribution of the concerted and sequential electronic pathways. Two specific two-electron superexchange mechanisms of DA TET are proposed (the repeated and direct mechanisms), and the conditions of their realization are discussed in detail.

If the electronic substates are associated with protonated and deprotonated states, the used model allows one to derive the dependence of the overall transfer rate on the actual pH-value, and thus the pH-dependence of the proton-assisted TET can be explained.

Introduction

One of the important problems of enzyme-catalyzed oxidation-reduction reactions is related to the understanding of the stepwise (sequential) and concerted electron transfer (ET) pathways which couple distant redox-centers of proteins. Typically, such reactions are of the multielectron type and, as a rule, are accompanied by a proton delivery or a proton uptake (see, for example, reviews [1, 2]). The reactions take place via a number of intermediate steps which reflect conformational transitions and ET processes. Although the theory of single-electron transfer reactions in protein structures is well-established [3–7], a complete description of multielectron transfer processes has to be elaborated.

The goal of the present paper is to derive the kinetics of two-electron transfer (TET) when the total TET process is characterized by strongly different transition rates so that each kinetic stage is described by a two-exponential or single-exponential overall transfer rate. Note that such a reduction of a multiexponential kinetics to a series of more simple kinetic steps is typical of a

number of enzyme-mediated TET reactions in substrate enzyme (SE) complexes [8–11]. In the case of a single-exponential kinetics, the overall transfer rate is shown to be represented by the sum of sequential and concerted contributions.

1. Coarse-grained Description of the Transfer Process

Despite the fact that a number of intermediate electronic states characterize each enzyme-catalyzed oxidation-reduction reaction, there exist definitely fixed ET steps, where each step is described by one or two exponents and thus can be described in the framework of a two- or three-state model, respectively. Generally, in biological systems, every electronic state contains more than one electronic substate. The specific form of substates can be a manifold of states including the associated and dissociated states of an SE complex. For example, different conformational states of the SE complex as well as the states with a different number of accepted protons can form the substates. Thus, the problem appears to derive an appropriate method which takes into consideration the substates and leads to a reduced set of kinetic equations describing the ET process between the precisely fixed *electronic* states. One of such reduction methods is based on the coarse-grained approach for the description of nonadiabatic ET [12].

Nonadiabatic ET as well as TET is characterized by intersite electron transitions (with the characteristic time τ_{TET}) which are slow compared to the fast intrasite vibrational relaxation (characteristic time τ_{rel}). Just such an inequality is typical of TET reactions in most SE complexes, where the overall transfer time τ_{TET} and the characteristic time for the transitions between the substates, τ_{subst} , largely exceed τ_{rel} . Therefore, employing the reduction method that was proposed in [12], we arrive at the following set of coarse-grained

kinetic equations describing a nonadiabatic electron transfer process:

$$\dot{P}_j(t) = - \sum_{s \neq j} [k_{js} P_j(t) - k_{sj} P_s(t)]. \quad (1)$$

Here, the quantity $P_j(t)$ denotes the integral population of the j th electronic state. This state indicates the site of electron localization and specifies also the number of the transferred electrons located at this site. The transfer rate

$$k_{js} \equiv k_{j \rightarrow s} = \sum_{l_j=1}^{N_j} \sum_{l_s=1}^{N_s} Q_{l_j}^{(j)} k_{l_j \rightarrow l_s} \quad (2)$$

characterizes the transfer as a single-electron or two-electron transfer which may take place between the j 'th and s 'th sites. Furthermore, the rate accounts for different ET channels between the l_j 'th and l_s 'th substates which belong to the j 'th and s 'th electronic states, respectively. In the case of nonadiabatic transfer processes, the corresponding rate constants can be represented in the standard way as the product of a pure electronic contribution and the Franck–Condon factor (FC) i.e.,

$$k_{j l_j \rightarrow s l_s} = \frac{2\pi}{\hbar} |V_{s l_s j l_j}|^2 (\text{FC})_{j l_j \rightarrow s l_s}. \quad (3)$$

Here, $V_{s l_s j l_j}$ is the electron coupling between the l_j 'th and l_s 'th substates. Moreover, each ET channel related to the transfer from the l_j 'th substate is weighted with the factor

$$Q_{l_j}^{(j)} = Z_{j l_j} / Z_j, \quad (Z_j = \sum_{l_j} Z_{j l_j}), \quad (4)$$

where $Z_{j l_j}$ is the partition function of this substate. Its specific form depends on the character of the substates. For instance, in the case of two substates which correspond to the protonated ($l_j = \text{p}$) or deprotonated ($l_j = \text{dp}$) form of certain groups, one gets $Q_{\text{p}}^{(j)} = f_{\text{p}}^{(\text{B})}$ and $Q_{\text{dp}}^{(j)} = f_{\text{dp}}^{(\text{B})}$, where

$$f_{\text{p}}^{(\text{B})} = \frac{[\text{H}^+]}{[\text{H}^+] + K_b}, \quad f_{\text{dp}}^{(\text{B})} = \frac{K_b}{[\text{H}^+] + K_b} \quad (5)$$

are those functions which characterize the probability of proton binding to the B-group ($[\text{H}^+]$ is the proton concentration in the solution, and K_b is the dissociation constant of the B-group).

Finally we would like to underline that the set of coarse-grained kinetic equations is of basic importance

for the description of various nonadiabatic ET processes whenever the inequality

$$\tau_{\text{rel}} \ll \tau_{\text{subst}} \ll \tau_{\text{TET}} \quad (6)$$

is fulfilled for the ET reaction. It only remains the problem to specify the couplings $V_{s l_s j l_j}$, the weights $Q_{l_j}^{(j)}$, and the Franck–Condon factors $(\text{FC})_{j l_j \rightarrow s l_s}$. This represents a well-established procedure for single-electron ET [3–7] but such a procedure is less investigated for multielectron transfer reactions. In the following, therefore, we will restrict ourself to the exclusive consideration of donor-acceptor (DA) TET processes.

2. Formation of Sequential and Concerted DA TET

It has been already mentioned in Introduction that ET reactions in SE complexes may proceed as single- or two-exponential ET processes. This means that each elementary step of the ET reaction can be represented as an ET process which generally occurs with the participation of an intermediate state. If the intermediate state is well populated, one observes a two-exponential transfer kinetics; otherwise the transfer appears as a single-exponential kinetic process with a certain overall transfer rate. Just the single-exponential kinetics corresponds to a DA ET. For a single-electron transfer, the transformation of two-exponential kinetics to single-exponential kinetics has been described in detail in [12].

In the case of TET, we can define the states D^{--} and A^{--} as two-electron states where both transferred electrons are located at the donor and acceptor of the ET system, respectively. And the TET process $\text{D}^{--} \rightarrow \text{A}^{--}$ itself can be understood as an oxidation-reduction reaction which has two alternative electronic pathways, the sequential pathway $\text{D}^{--} + \text{A} \rightarrow \text{D}^- + \text{A}^- \rightarrow \text{D} + \text{A}^{--}$ and the concerted pathway $\text{D}^{--} + \text{A} \rightarrow \text{D} + \text{A}^{--}$. Therefore, three different electronic states participate in the TET, the state 1 $\equiv (\text{D}^{--}\text{A})$, the state 2 $\equiv (\text{D}^-\text{A}^-)$, and the state 3 $\equiv (\text{DA}^{--})$. Since biological macromolecules are characterized by electronic states which split off into manifolds of substates, TET reactions have to be described by taking into consideration these substates. Here, we assume that the relaxation between the substates is related to each specific electronic state, and thus the TET process can be evaluated using the set of kinetic equations (1). The specific expressions for the

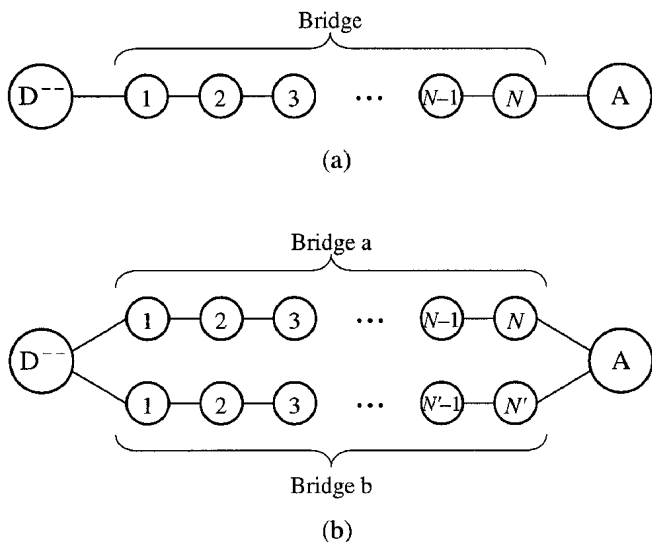


Fig. 1. Distant TET reactions through a single bridge (a) and two bridges (b)

corresponding intersite rate constants (2) in Eqs. (1) are defined by the character of the transfer system. Nevertheless, one can establish some general properties of TET reactions without specifying the rate constants. To this end, we consider DA TET in a three-state transfer system with the initial state (1), the transient state (2), and the final state (3). The corresponding coupled set of kinetic equations follows from set (1) and reads

$$\begin{aligned} \dot{P}_1(t) &= -(k_{12} + k_{13})P_1(t) + k_{21}P_2(t) + k_{31}P_3(t), \\ \dot{P}_2(t) &= -(k_{21} + k_{23})P_2(t) + k_{12}P_1(t) + k_{32}P_3(t), \\ \dot{P}_3(t) &= -(k_{31} + k_{32})P_3(t) + k_{13}P_1(t) + k_{23}P_2(t). \end{aligned} \quad (7)$$

The exact solution $P_j(t) = P_j(\infty) + A_{1j} \exp(-K_1 t) + A_{2j} \exp(-K_2 t)$, ($j = 1, 2, 3$) of this set of rate equations can be found in [12]. Here, we only note that if the rate constant K_1 largely exceeds K_2 , then, at times $t \gg K_1^{-1}$, one observes a single-exponential TET with the transfer rate

$$K_{\text{TET}} = K_2 \approx k_{13} + k_{31} + \frac{k_{12}k_{23} + k_{32}k_{21}}{k_{21} + k_{23}}. \quad (8)$$

This expression for the TET rate is correct if

$$k_{21}, k_{23} \gg k_{12}, k_{32}, k_{13}, k_{31}. \quad (9)$$

Bearing in mind that index 2 refers to the intermediate state, we may conclude that, according to inequality (9), the population of the intermediate state $2 \equiv (D^- A^-)$ becomes very small in the course of the TET, and thus

the TET appears as a DA TET with an overall transfer rate given by Eq. (8). In line with the definition of the electronic states 1, 2, and 3, rate constants k_{13} and k_{31} characterize the concerted forward ($D^- + A \rightarrow D + A^-$) and concerted backward ($D^- + A \leftarrow D + A^-$) TET, respectively, while the remaining rates $k_{jj'}$ characterize single-electron hops between the initial (the final) and intermediate electronic states. These remaining rate constants form a sequential pathway for the TET process. Therefore, we can represent Eq. (8) as the sum of concerted and sequential (stepwise) contributions

$$K_{\text{TET}} = \tau_{\text{TET}}^{-1} = K_{\text{TET}}^{(\text{con})} + K_{\text{TET}}^{(\text{seq})}, \quad (10)$$

where

$$K_{\text{TET}}^{(\text{con})} = K_{\text{con}}^{(\text{f})} + K_{\text{con}}^{(\text{b})}, \quad K_{\text{con}}^{(\text{f})} = k_{13}, \quad K_{\text{con}}^{(\text{b})} = k_{31},$$

$$K_{\text{TET}}^{(\text{seq})} = K_{\text{seq}}^{(\text{f})} + K_{\text{seq}}^{(\text{b})},$$

$$K_{\text{seq}}^{(\text{f})} = \frac{k_{12}k_{23}}{k_{21} + k_{23}}, \quad K_{\text{seq}}^{(\text{b})} = \frac{k_{32}k_{21}}{k_{21} + k_{23}}. \quad (11)$$

(In Eq. (11), the forward and backward transfer rates are indicated by the symbols f and b, respectively). Eqs. (10) and (11) form the basis to characterize the concerted and sequential pathways of the DA TET reaction. It only remains the problem to specify the specific form of the rate constants for the specific type of a TET reaction. Below we will consider the details of the formation of bridge-mediated superexchange pathways for sequential and concerted TET.

3. Length Dependence of Transfer Rate for Distant Sequential and Concerted TET

Let the D and the A center be separated by a single-bridge chain as shown in part a of Fig. 1. At the small bridge population under consideration, the rate constant of the elementary single-electron transfer consists of the sum of the sequential and superexchange contributions. Here, we will consider the role of superexchange mechanism only since, at short bridges, the superexchange mechanism dominates the ET (for details see [12]).

The sequential pathway of TET. The single-electron rate constants k_{12} , k_{21} , k_{23} , and k_{32} are given by expression (2), where the partial ET rate constant (which relates specific substates of different electronic states) is given by Eq. (3) with

$$|V_{sl_s j l_j}|^2 = \frac{|V_{sl_s} V_{j l_j}|^2}{(2V_B)^2} S_D S_A. \quad (12)$$

Here, V_{jl_j} is the matrix element of the single-electron transition between the D(A) center and the adjacent terminal bridge unit while V_B is the similar matrix element connecting neighboring bridge units (we consider a regular bridge with identical sites). The factor

$$S_{D(A)} = \frac{2}{N+1} \sum_{\mu=1}^N \frac{\sin \frac{\pi\mu}{N+1} \sin \frac{\pi\mu N}{N+1}}{a_{D(A)} - \cos \frac{\pi\mu}{N+1}} \quad (13)$$

characterizes the dependence of the single-electron rate constant on the distance when the ET proceeds between precise electronic substates. The quantities $S_{D(A)}$ strongly depend on the parameters

$$a_{D(A)} = \Delta E_{D(A)} / 2V_B, \quad (14)$$

where $\Delta E_{D(A)}$ denotes the energy gap between the D(A) electronic substates and the bridge electronic substates. For instance, in the case of the $D^{--} + A \rightarrow D^- + A^-$ reaction, we have $\Delta E_D = \Delta E_D(1l_1 \rightarrow 2l_2)$, while, for the $D^- + A^- \rightarrow D + A^{--}$ reaction, the similar energy difference follows as $\Delta E_A = \Delta E_A(2l_2 \rightarrow 3l_3)$. Note that, for the superexchange DA ET, the parameter $a_{D(A)}$ exceeds unity. As far as the sequential TET rate $K_{\text{TET}}^{(\text{seq})}$ is completely defined by the single-electron rate constants k_{12} , k_{21} , k_{23} , and k_{32} , there does not appear any principal problem to evaluate the dependence of the $K_{\text{TET}}^{(\text{seq})}$ on the number of bridge units since it is contained in expression (13). Note that, despite the fact that TET proceeds along a sequential pathway, each single-electron step of this pathway is originated by the superexchange mechanism.

The superexchange pathway of TET. To clarify the formation of such a pathway, we consider certain substates $l_1 \equiv \alpha$, $l_2 \equiv \beta$, $l_3 \equiv \gamma$ which belong to the electronic state 1, 2, and 3, respectively. Let $E(D^{--}) + E(A)$, $E(D^-) + E(A^-)$, and $E(D) + E(A^{--})$ be the energies of these substates. In the framework of the proposed model, the single-electron coupling $V_{\beta\alpha}$ between the substates α and β is caused by the superexchange mechanism. Therefore, the concrete form of $V_{\beta\alpha}$ follows from Eqs. (12) and (13), where $a_D = a_D^{(1)} = \Delta E_D^{(1)} / 2V_B$ and $a_A = a_A^{(1)} = \Delta E_A^{(1)} / 2V_B$. [The energy gaps $\Delta E_D^{(1)}$ and $\Delta E_A^{(1)}$ are shown in Fig. 2, a.] The single-electron coupling $V_{\gamma\beta}$ with $a_D = a_D^{(2)} = \Delta E_D^{(2)} / 2V_B$ and $a_A = a_A^{(2)} = \Delta E_A^{(2)} / 2V_B$ has an analogous form. (The energy gaps $\Delta E_D^{(2)}$ and $\Delta E_A^{(2)}$ are shown in Fig. 2, b.) When the energy $E(D^-) + E(A^-)$ of the substate β largely exceeds the energies $E(D^{--}) + E(A)$ and $E(D) + E(A^{--})$ of the D and A substates, one can consider the substate β as a virtual

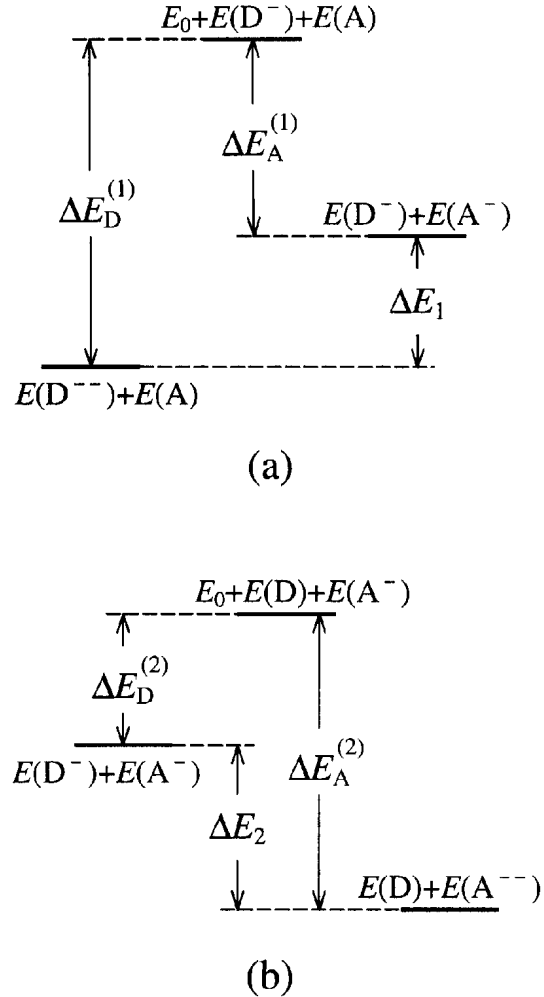


Fig. 2. Scheme of energy levels valid for the first (a) and the second (b) single-electron pathways forming the repeated superexchange pathway

one. It means that a specific superexchange coupling, $V_{\gamma\alpha}$, is formed between the initial (α) and final (γ) substates. Just the square of this coupling,

$$|V_{\gamma\alpha}|^2 = \frac{|V_{\beta\gamma} V_{\beta\alpha}|^2}{\Delta E_1 \Delta E_2}, \quad (15)$$

defines the rate constants k_{13} and k_{31} . (Here we give the simplest form of the coupling by noting that only a

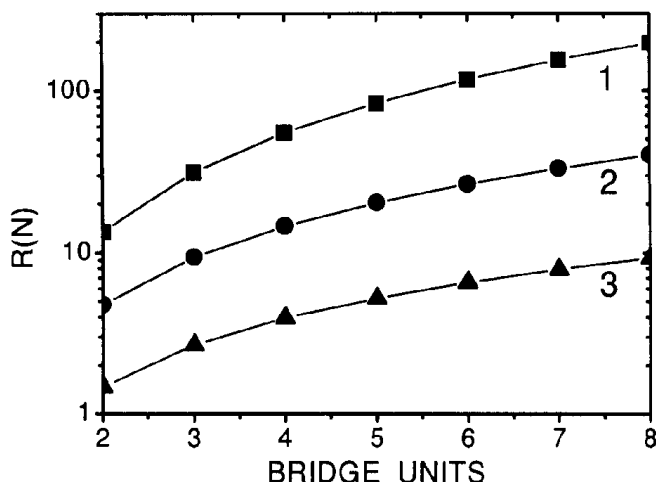


Fig. 3. Behavior of the factor, Eq. (21) (determining the length-dependence of the rate), for different energy gaps. Curves 1, 2, and 3 correspond to the set $(a_1 = 1.2, a_2 = 1.4)$, $(a_1 = 1.8, a_2 = 2.2)$, and $(a_1 = 3.2, a_2 = 3.6)$, respectively

single virtual substate $l_2 = \beta$ participates in the formation of the coupling $V_{\gamma\alpha}$. Of course, in a more general case, the sum over all possible virtual substates l_2 has to be taken.) The energy gaps ΔE_1 and ΔE_2 are shown in Fig. 2. The two-electron coupling $V_{\gamma\alpha}$ is expressed via the product of two independent single-electron superexchange couplings, $V_{2l_2 1l_1} \equiv V_{\beta\alpha}$ and $V_{3l_3 2l_2} \equiv V_{\gamma\beta}$, and thus the quantity $V_{3l_3 1l_1} \equiv V_{\gamma\alpha}$ characterizes a repeated single-electron superexchange through a single bridging molecular chain. Correspondingly, the two-electron DA coupling $V_{\gamma\alpha}$ defines a concerted mechanism of TET through a single bridge.

Changing to the case of two bridges (see Fig. 1,b) we have to note that an additional two-electron pathway is formed. For the sake of simplicity, we consider two identical bridges with $N = N'$. Bearing in mind the presence of these two bridges and taking into account Eqs. (12), (13), and (15), we may realize that the earlier described single-electron mechanism of the formation of a concerted DA TET leads to the following expression for the square of the two-electron coupling between the D and A centers

$$|V_{\gamma\beta}^{(\text{rep})}|^2 = 4 \frac{|V_A^{(1)} V_D^{(1)}|^2 |V_A^{(2)} V_D^{(2)}|^2}{(2V_B)^4 \Delta E_1 \Delta E_2} \times S_D^{(1)} S_A^{(1)} S_D^{(2)} S_A^{(2)}. \quad (16)$$

Here, $V_D^{(1(2))}$ denotes the coupling $V_{\beta\alpha}$ (the electron is transferred from the $D^{--}(D^-)$ to the adjacent bridge

unit). A similar notation, $V_A^{(1(2))}$, is used for the coupling $V_{\beta\gamma}$. We have also introduced the symbol “rep” to indicate the repeated mechanism of the distant two-electron coupling.

The presence of two bridges promotes the simultaneous transfer of each electron along one of the separated bridges (if the Coulomb interaction between the transferred electrons is negligible). However, if the Coulomb electron–electron interaction V_{e-e} cannot be neglected, it becomes responsible for the formation of the specific two-electron matrix elements, $V_D = \langle 1a, 1b | V_{e-e} | D^{--} \rangle$ and $V_A = \langle Na, Nb | V_{e-e} | A^{--} \rangle$. Both matrix elements indicate that a pair of coupled electrons initially located at the D(A) center can be transferred to separate bridges a and b . As far as each bridge forms a separated single-electron superexchange pathway, an additional type of two-electron coupling between the D and A centers, $V_{\gamma\alpha}^{(\text{dir})}$, appears. The square of this coupling has a form

$$|V_{\gamma\alpha}^{(\text{dir})}|^2 = \frac{|V_D V_A|^2}{(2V_B)^2} S_{DD} S_{AA}, \quad (17)$$

where the

$$S_{DD(AA)} = \left(\frac{2}{N+1} \right)^2 \times \sum_{\mu=1}^N \sum_{\mu'=1}^N \frac{\sin \frac{\pi\mu}{N+1} \sin \frac{\pi\mu N}{N+1} \sin \frac{\pi\mu'}{N+1} \sin \frac{\pi\mu' N}{N+1}}{a_{D(A)}^{(1)} + a_{D(A)}^{(2)} - \cos \frac{\pi\mu}{N+1} - \cos \frac{\pi\mu'}{N+1}} \quad (18)$$

are the factors defining the length dependence of this direct concerted two-electron pathway.

To clarify the contribution of the repeated and direct mechanisms to the concerted TET, one has to compare the quantities $|V_{\gamma\alpha}^{(\text{rep})}|^2$ and $|V_{\gamma\alpha}^{(\text{dir})}|^2$. We consider a self-exchange TET reaction, where D and A are identical centers and thus $V_A^{(1)} = V_D^{(1)} \equiv V_s^{(1)}$, $V_A^{(2)} = V_D^{(2)} \equiv V_s^{(2)}$, $V_D = V_A \equiv V_d$, $a_D^{(1)} = a_A^{(1)} \equiv a_1$, $a_D^{(2)} = a_A^{(2)} \equiv a_2$, $S_D^{(1)} = S_A^{(1)} \equiv S_1$, $S_D^{(2)} = S_A^{(2)} \equiv S_2$, $S_{DD} = S_{AA} \equiv S$, and $\Delta E_1 = \Delta E_2 \equiv \Delta E$. In this case, the ratio of the corresponding overall transfer rates coincides with

$$\eta = \frac{|V_{\gamma\alpha}^{(\text{rep})}|^2}{|V_{\gamma\alpha}^{(\text{dir})}|^2} = QR(N) \quad (19)$$

where the quantity

$$Q = \frac{|V_s|^8}{|V_d|^4 (2V_B)^2 \Delta E^2} \quad (20)$$

does not depend on the number of bridging units. Instead, this dependence is given by the factor

$$R(N) = \frac{S_1^2 S_2^2}{S^2}. \quad (21)$$

Fig. 3 indicates that, at a given choice of parameters a_1 and a_2 , the factor $R(N)$ exceeds unity. Thus, if $Q > 1$, then the repeated superexchange mechanism is responsible for a concerted TET while, at $Q < 1$, either repeated single-electron or direct two-electron superexchange defines the DA TET.

4. The pH-dependence of the Overall Transfer Rate for the Sequential and Concerted Mechanisms of TET

The pH-dependence of the oxidation-reduction reaction is specified by the weight $Q_{l_j}^{(j)}$ of the substate l_j in the j 'th electronic state. In line with Eq. (2), this weight also determines the efficiency of the precise ET channel. We can derive a concrete expression for $Q_{l_j}^{(j)}$ if the substates l_j are associated with protonated and deprotonated forms of those concrete sites which participate in the ET. The character of these sites is determined by the structure of a concrete SE complex under consideration. However, without specifying these site, it is possible to formulate a basic physical principle. It determines the pH-dependence of the overall transfer rate if the protonation-deprotonation process occurs independently for each active group participating in the ET. Namely, the $Q_{l_j}^{(j)}$ become a product of distribution functions (5) related to these active groups. As an example, we consider the appearance of an pH-dependence for the repeated superexchange TET through a bridge of 3 units (B_1 , B_2 , and B_3). Let unit B_1 be in the protonated form, while the two remaining units stay in the deprotonated form. If the A center occurs in the deprotonated form, then the possible TET channels are associated with the type of protonation of the D center. For instance, if the D center is in the protonated form, we derive the following pH-dependence of the TET transfer rate:

$$K_{1\text{con}}^{(f)} = K_f^{(1\text{rep})} Q_{l_1=1}^{(1)},$$

$$Q_{l_1=1}^{(1)} = f_p^{(D^{+-})} f_p^{(B_1)} f_{dp}^{(B_2)} f_{dp}^{(B_3)} f_{dp}^{(A)}. \quad (22)$$

If the D center is in the deprotonated form while the A center is in the protonated form, then

$$K_{2\text{con}}^{(f)} = K_f^{(2\text{rep})} Q_{l_1=2}^{(1)},$$

$$Q_{l_1=2}^{(1)} = f_{dp}^{(D^{--})} f_p^{(B_1)} f_{dp}^{(B_2)} f_p^{(B_3)} f_p^{(A)}. \quad (23)$$

Analogously, one can derive the pH-dependence of the TET rates for all possible protonated-deprotonated forms of a common D — bridge — A system. Note that pH-independent factors $K_f^{(1\text{rep})}$ and $K_f^{(2\text{rep})}$ are different from each other, thus the efficiency of each transfer channel is defined not only by the weights $Q_{l_1}^{(1)}$.

Conclusion

In the present paper, we have considered bridge-mediated nonadiabatic DA TET which occurs against the background of fast relaxational transitions not only within the global electronic states but also between different substates belonging each to a particular electronic state. These electronic states are defined by the sites of electron localization at the donor and the acceptor as well as at the bridge sites. The main results have been derived in the model of three electronic states which corresponds to the initial, $1 \equiv (D^{--}A)$, the intermediate, $2 \equiv (D^-A^-)$, and the final, $3 \equiv (DA^{--})$ state. Special attention has been put on the way how to clarify the mechanisms of the formation of the concerted mechanism of the $D^{--}A \rightarrow DA^{--}$ TET process. Two new DA TET superexchange mechanisms, the repeated single-electron mechanism and the direct two-electron one, have been proposed and the conditions are derived under which each mechanism is more preferable with respect to the other. Besides, the pH-dependence of the TET rate is discussed in detail.

The results of the study can be employed to a description of TET oxidation-reduction reactions in concrete SE complexes. This will be the subject of separate studies.

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ДВОХЕЛЕКТРОННІ ДОНОРНО-АКЦЕПТОРНІ
РЕАКЦІЇ ПЕРЕНЕСЕННЯ: СИНХРОНІЗОВАНИЙ
ТА СТРИБКОВИЙ ШЛЯХИ В БІЛКОВИХ СТРУКТУРАХ

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Резюме

Було проведено опис неадиабатичного донорно-акцепторного (ДА) двохелектронного перенесення (ДЕП) в умовах, коли міжцентрові електронні переходи відбуваються на фоні швидкої релаксації як в окремих підстанах, що належать до різних електронних станів, так і між самими підстанами, які відносяться до одного і того ж самого електронного стану. Показано,

що ДА ДЕП виявляє себе як одноекспонентне перенесення між початковим та кінцевим електронними станами, а відповідна швидкість перенесення може бути представлена як сума синхронізованого та стрибкового електронних шляхів. Запропоновано модель двох специфічних (повторного та прямого) двохелектронних суперобмінних механізмів ДА ДЕП та з'ясовано умови, за яких вони реалізуються. Коли підстави зіставляються з протонною та депротонною формами транспортної системи, запропонована модель дозволяє пояснити залежність швидкості ДЕП від концентрації протонів у середовищі.

ДВУХЭЛЕКТРОННЫЕ ДОНОРНО-АКЦЕПТОРНЫЕ
РЕАКЦИИ ПЕРЕНОСА: СИНХРОНИЗИРОВАННЫЙ
И ПРЫЖКОВЫЙ ПУТИ В БЕЛКОВЫХ СТРУКТУРАХ

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Резюме

Проведено описание неадиабатического донорно-акцепторного (ДА) двухэлектронного переноса (ДЭП) в условиях, когда межцентровые электронные переходы происходят на фоне быстрой релаксации как в отдельных подсостояниях, принадлежащих различным электронным состояниям, так и между самими подсостояниями, относящимися к одному и тому же электронному состоянию. Показано, что ДА ДЭП проявляется как одноэкспоненциальный перенос между начальным и конечным электронными состояниями, а соответствующая скорость переноса может быть представлена как сумма синхронизированного и прыжкового электронных путей. Предложена модель двух специфических (повторного и прямого) двухэлектронных суперобменных механизмов ДА ДЭП и выяснены условия, при которых они реализуются. Когда подсостояния сопоставляются с протонированной и депротонированной формами транспортной системы, предложенная модель позволяет объяснить зависимость скорости ДЭП от концентрации протонов в среде.