Electron transfer in reaction centers within two-dimensional model. New role of local charges.

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Electron transfer (ET) reactions in reaction centers (RC) are considered within a two-dimensional model. The key points of the model are the separate contributions of temperature independent vibrational (v) and temperature dependent diffusive (d) coordinates to the preexponential factor, to the reorganization energy $\lambda=\lambda_v+\lambda_d(T)$ and to the free energy of reaction $\Delta G = \Delta G_v + \Delta G_d(T)$. The distribution in the position along the diffusive coordinate and distribution of protein dielectric relaxation times along the diffusive coordinate are take into account. The broad set of non-exponential ET kinetics between heme c-559 of cytochrome and dimer of bacteriochlorophyll P^+ in RC for different state of cytochrome reduction in temperature range 297-40 K are fitted within this model. The tunneling matrix element V_{ab}, the relaxation time τ and the distribution parameters, as well as ΔG_v, ΔG_d, λ_v, and λ_d are determined.

The model allows one to propose new mechanisms of the ET rates regulation under the influence of local charges, connected with variation of the position and direction of electron transfer path way along two-dimensional surface of electron transfer reaction.

The dark ET reactions following a flash in the cytochrome-RC complex are as follows:

$$c-559 \xrightarrow{k_{et}} P^+ \xleftarrow{k_r} Q_A^-$$

All experimental kinetics can be considered as a sum of two curves A_1 and A_2,

$$F(t) = A_1 \int_0^\infty g(\tau)\exp\left[-k_{et}(\tau)t\right]d\tau + A_2\exp\left(-k_r t\right)$$

which differ significantly in their behaviour. The initial part A_1 of the kinetic curves in the time interval 0.1- 40 μs is fast ($k_{et}=10^7$-10^4 s^{-1}), temperature-dependent and non-exponential. The next part A_2 from 0.1 μs to 4500 μs is described by a one-exponential function with a slow nearly temperature-independent characteristic rate around (1-4) 10^2 s^{-1}. Since the rate of the initial part of kinetic curves is much higher than the rate of the $P^+ \leftarrow Q_A^-$ reaction, it seems reasonable to relate A_1 kinetics to the $c-559 \rightarrow P^+$ reaction and the slow exponential part A_2 to the recombination process $P^+ \leftarrow Q_A^-$. The ratio of parameters A_1/A_2, describing the equilibrium between two states of the protein complex, depends on temperature and on the state of cytochrome reduction.

In order to explain the existence of a significant fraction of A_2 with low rate of electron transfer we have to assume that two populations A_1 and A_2 of proteins exist in the samples studied. In the first one the fast electron transfer from c-559 to P^+ takes place with $k_{et}=10^7$-10^4 s^{-1}. In the second population the direct reaction has $k_{et}<<10^2$ s^{-1}, and P^+ reduction is due to the back reaction $P^+ \leftarrow Q_A^-$.

The following two important questions increased:

1. What is the reason for a large difference in ET kinetics between the “fast” and “slow” protein populations?

2. What is the reason for variations of parameters A_1 and A_2 (describing the equilibrium between the two populations of the cytochrome-RC complex) with temperature and with the state of cytochrome reduction?

The key to the resolution of these puzzles resides in the existence of two different states of the protein, B_1 and B_2, with a small difference in free energy [1]. B_2 can go to B_1 only by slow motion along the diffusive coordinate with a characteristic time $\tau >> 10^{-2}$ s even at room temperature. The population densities of these two states B_1 and B_2 correspond to the coefficients A_1 and A_2 in Eq. 1.

The dependence of the free energy difference between B_1 and B_2 states of the protein on the level of cytochrome reduction means that these proteins have different charges distribution in the vicinity of the proximal heme. The hydrogen bonding or the protonation of some group(s) in the vicinity of the proximal heme with an activation energy around 0.1-0.2 eV may be a real “physical” interpretation for these two states.

For example, a carboxyl group near the proximal heme could be negatively charged at room temperature and become protonated at a lower temperature. In the first state of cytochrome reduction, a negative carboxyl group would create favourable energetic and dynamic conditions for fast ET reaction from state B_1 to the final state C. At lower temperatures the protonation of the carboxyl group takes place by a diffusive proton motion with characteristic times $\tau >> 10^{-2}$ s into the interior of the protein globule, leading to a decrease of the electron free energy for the protein in state B_2. The rate of ET reactions from B_2 to C along both paths is smaller than 10^2 s^{-1}. Following reduction of heme c-556, the equilibrium between H^+ and negative carboxyl group shifts to the unprotonated state due to electrostatic interaction of the reduced heme with H^+. As a result, the ET rate increases at a given temperature, and the ET kinetics are observed at lower temperatures. Placing the third electron on heme c-552 increases attraction of H^+ from the site of the proximal heme. Hence, deprotonation increases further, and electron transfer remains fast at lower temperatures.

Large variations of ET rate can be explained in the frame of the Ovchinnikova-Sumi-Marcus approach by changing relative contributions of vibrational and diffusive degrees of freedom to parameters λ and ΔG. This means that the protonation of carboxyl group(s) leads to a change of vibrational interaction of the proximal heme with the protein matrix and to a change in remote electrostatic interactions, which leads to dipole orientational reorganisation (diffusive motion). Combination of different contributions of vibrational and diffusive modes to the protein reorganization opens a possibility to explain the large difference in activation energy and in ET reaction rates at low temperature from two different protein states B_1 and B_2, and consequently the existence of a large fraction of RC with “slow” ET kinetics.

This opens a possibility for large variations of ET rates under the conditions where the protein internal mobility is restricted: in large protein complexes and at lowered temperatures.

1. Kotelnikov A.I., Ortega J.M., Medvedev E.S., Psikha B.L., Garsia D., Mathis P. Russian J. of Electrochemistry, 2002, 38, No 1, 90-101.

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