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Molecular Processes in the Primary Reaction of Photosynthetic Reaction Centers

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Abstract: The primary electron transfer is investigated for wildtype reaction centers from Rhodobacter sphaeroides, mutant reaction centers and reaction centers with modified bacteriochlorophyll. Experimental results are presented which strongly support the idea that the electron transfer is stepwise involving the accessory bacteriochlorophyll as a real intermediate electron carrier.

1. Introduction

The energy converting processes of bacterial photosynthesis start in a large chromoprotein called reaction center (RC). At first light energy leads to electronic excitation of a chromophore. Subsequently the electronic excitation initiates an electron transfer (ET) via several acceptor molecules. Finally the electron reaches the quinone \(Q_B\). Further secondary transfer processes involve diffusive motion of protons and large organic molecules. Schematically the structural arrangement of the electron carrying pigments in the RC's is shown in Fig. 1 /1, 2/. The pigments are incorporated in two branches (A and B) related by an approximate \(C_2\) symmetry. The two branches cross at two strongly interacting bacteriochlorophyll molecules forming the special pair P which acts as a primary electron donor. Subsequently each branch contains a monomeric bacteriochlorophyll molecule \(B_A\) and \(B_B\), a bacteriopheophytin (\(H_A, H_B\)) and a quinone (\(Q_A, Q_B\)). Various experiments have revealed that the two pigment branches are not equivalent and that the reactive electron transfer uses the A branch.

The very first reaction processes include the initial charge separation and the ET until the bacteriopheophytin \(H_A\). These events take several picoseconds /3-9/. In the next step the electron reaches within approximately 200 ps the quinone \(Q_A\). The secondary quinone \(Q_B\) is reduced only much slower on the \(10^{-6}\) s time scale. Transient absorption spectroscopy of the

![Fig. 1: Schematic of the molecular arrangement of the four bacteriochlorophylls (P, B\(_A\), B\(_B\)), the two bacteriopheophytins (H\(_A\), H\(_B\)) and the two quinones (Q\(_A\), Q\(_B\)) in reaction centers](image-url)
primary reaction dynamics at room temperature exhibit one time constant around 3.5 ps (in the literature values are reported between 2.8 ps and 4 ps /3-9/ related to the decay of the excited electronic state \(P^*\) and a weak subpicosecond kinetic (0.9 ps in \(\text{Rb. sphaeroides}\)) best seen in the absorption range of the \(\text{BChl}\) and the \(\text{BChl anion} /7-9/\). Until now no generally accepted molecular interpretation of the fast kinetic component exists /10-12/. Two reaction models are currently discussed (see Fig. 2a and b):

The structural arrangement of the reaction centers strongly suggests the stepwise electron transfer model of Fig. 2a: According to this model the electronically excited state \(P^*\) of the special pair decays with the time constant of 3.5 ps. Simultaneously an electron is transferred from the special pair to the monomeric bacteriochlorophyll \(\text{B}_{\text{A}}\). The second electron transfer is faster and carries the electron with a time constant of 0.9 ps to the bacteriopheophytin \(\text{H}_{\text{A}}\). Finally the 200 ps process generates the radical pair \(P^+Q_{\text{A}}^-\) where the electron has reached the first quinone.

In model 2b the fast time constant of 0.9 ps is assigned to an excited state relaxation process of the special pair. This process should be vibrational relaxation from the initially populated Franck-Condon-state. In this reaction model the first electron transfer drives the electron with a time constant of 3.5 ps directly to the bacteriopheophytin \(\text{H}_{\text{A}}\). This fast long-distance electron transfer is only possible if the monomeric \(\text{BChl B}_{\text{A}}\) is involved as a virtual intermediate in a superexchange interaction. In this case the energy level of the corresponding radical pair \(P^+B_{\text{A}}^-\) is higher than the energy of \(P^*\). From extensive experimental studies the absorption spectra of the different intermediates could be calculated for both models /7-9/. These data were fully consistent with the molecular interpretation of the respective model.

In this paper we will present transient absorption data on RC of \(\text{Rb. sphaeroides}\) where additional information on the reaction model is obtained by: (i) biochemical modifications of the RC and (ii) changing the temperature of the sample.

2. Results and Discussion

Measurements on low temperature RC are performed on quinone depleted RC from the carotenoid free strain R26.1. The preparation of RC where \(\text{BChl a}\) at the accessory position \(\text{B}_{\text{A}}\) is exchanged to approximately 70 % by [3-vinyl]-132-OH-BChl a is described in Ref. 13. The time resolved absorption experiments are performed using the excite and probe technique with weak subpicosecond pulses (pulse duration \(\approx 150\) fs) generated by a laser-amplifier-system.
Delay Time [ps]

Fig 3: Transient absorption data on [3-vinyl]-132-OH-RC-preparations. Probing in the gain region at \( \lambda = 920 \text{ nm} \) (a) and in special pair absorption band \( \lambda = 850 \text{ nm} \) (b) with a repetition rate of 10 Hz. The temporal width of the instrumental response function is below 300 fs. Details of the experimental system are described in reference /14/.

Upon lowering the temperature of the RC preparation the picosecond kinetics become faster /14, 15/. The decay of the gain having a time constant of around 3.5 ps at room temperature speeds up to 1.4 ps at 25 K. The 0.9 ps kinetic component also accelerates at lower temperatures. At 25 K a value of 0.3 ps is reached. Throughout the whole temperature range from 300 K to 25 K the spectral signature of the fast component does not change.

Experiments on [3-vinyl]-132-OH-BChl a containing RC's are shown in Fig. 3. The modification due to the 3 vinyl group is expected to change the redox potential of the BChl and the energy of the radical pair state P*+B: This change should have pronounced consequences on the ET when the accessory BChl B_A is involved. Indeed, one finds a strong slowing down of the decay of P* (see Fig. 3a for a measurement in the gain region). The experimental data indicate that the RC's containing [3-vinyl]-132-OH-BChl a have a decay time of P* of 32 ps. Fig. 3b, measured at a wavelength where the P absorption is strong, shows a long-lasting bleaching of P. These observations prove that the exchange leads to RC's which are still photochemically active but where the ET-step out of P* is slowed down by a factor of ten. In the [3-vinyl]-132-OH-BChl a containing RC's the 0.9 ps component is not visible. Experimental indications exist that a related process appears with a longer time constant in the 5 ps domain. The disappearance of the 0.9 ps component can be taken as a strong indication that the 0.9 picosecond process in wildtype RC is not related to vibrational relaxation of P* since P* is unchanged upon modifying B. This finding argues against the superexchange electron transfer of model 2b.

Additional support of the stepwise model of Fig. 2a comes from the low temperature hole-burning experiments where narrow holes related to \( \tau > 1 \text{ ps} \) process are observed. According to these experiments the 0.3 ps process observed in transient absorption spectroscopy can not
be the first reaction. As a consequence the 0.3 ps time constant (and due to the smooth temperature dependence the 0.9 ps time at room temperature) must be related to the second reaction step.

Other important experimental information is obtained from transient absorption spectroscopy of an antenna deficient mutant (strain U43, pTXA6-10) of Rb. capsulatus. Here whole chromatophores are investigated instead of isolated RC's. The experiments exhibit the same subpicosecond component as observed in the RC preparation. This finding clearly indicates that the subpicosecond component is not an artefact due to the preparation procedure. Recently emission experiments on RC have shown that the 3.5 ps kinetic component of wildtype RC has to be split into a 2.3 ps and a 7 ps process/17/. Within the scope of the stepwise ET model this biexponentiality can be explained by a transient ET to the accessory bacteriochlorophyll on the B branch as indicated in scheme C of Fig. 2. According to this interpretation the ET on the B branch would be blocked efficiently only between $B_B$ and $B_H$.

In conclusion, we have shown that the primary processes in photosynthetic RC can be explained by a stepwise electron transfer from the special pair over the different electron carrying pigments. The distance between the pigments is small enough to allow fast and efficient electron transfer in the stepwise model.

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References