Electric Field Modulation of Electron Transfer in Bacterial Photosynthetic Reaction Centers

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Abstract

Multilayer Langmuir-Blodgett (LB) films of reaction centers from the photosynthetic bacterium *Rhodopseudomonas sphaeroides* have been fabricated with partial net orientation. From measurements of the light induced electron transfer reactions in reaction center films, we have succeeded in quantitating the electric field dependence of (1) the quantum yield of charge separation and (2) the kinetics of charge recombination.

1. Introduction

A feature common to photosynthetic reaction centers is light- induced electron transfer [1]. In the reaction center of the photosynthetic bacterium *Rhodopseudomonas sphaeroides*, this process involves several redox components contained within the protein. Following light absorption a bacteriochlorophyll dimer, (BChl)$_2$,
assumes an excited singlet state, \((\text{BChl})_2^*\), and transfers an electron, possibly via a monomeric (BChl), to a bacteriopheophytin (BPh) to form \((\text{BChl})_2^+\cdot\text{BPh}^-\). Before useless recombination can occur, the BPh\(^-\) reduces a ubiquinone-10 molecule, designated \(Q_A\), to form \((\text{BChl})_2^+\cdot\text{BPh}Q_A^-\). A simplified representation of the rate constants, energy levels and distances between the different components in the reaction center are summarized in Figure 1. (The values for the forward rates are reported in [2-6]. The recombination rates are reported in [7-10]. The value for \(\Delta G\) between \((\text{BChl})_2^*\cdot\text{BPh}Q_A\) and \((\text{BChl})_2^+\cdot\text{BPh}^-\cdot Q_A\) is reported in [11,12]; the value for \(\Delta G\) between \((\text{BChl})_2^+\cdot\text{BPh}^-\cdot Q_A\) and \((\text{BChl})_2^+\cdot\text{BPh}Q_A^-\) is given in [13-15]. The scaling distance of 4.4 nm between the non-heme iron and the cytochrome c iron was obtained by resonance x-ray diffraction [16].)

In the native membrane the \(Q_A\) reduces a second ubiquinone (\(Q_B\)) in 100\(\mu s\) half-time and a cytochrome c reduces the \((\text{BChl})_2^+\) in microseconds to stabilize the process further [1,17]. The reaction center is considered to span the cytoplasmic membrane [18-20] with cytochrome c and \(Q_B\) associated with the reaction center, but located on opposite sides of the membrane. Thus, the system is organized so that following light excitation electron transfer is coupled to the separation of charges within the protein directed across the membrane.

Expressions of the charge separation in photosynthetic bacteria have been seen in vivo as electrochromic responses of the carotenoid complement of the membrane [21,22], by enhanced fluorescence yield indicative of a reversal of the light reaction [23] and by shifts in redox equilibria between cytochrome c and \((\text{BChl})_2^+\) [24]. Direct measurements of the charge separation have since been made in vivo with reaction centers incorporated into planar phospholipid bilayer membranes [25-30], as monolayers on solid supports [31] and on the interfacial region of immiscible liquids [32]. See also [33] for a review.

There is a consensus of agreement from the different approaches that the separation of charge across the membrane is effected by several distinct contributing electron transfer steps. Electron transfer from ferrocytochrome c to \((\text{BChl})_2^+\) contributes in the region of 40-50% of the separation of charge across the membrane [22,24,27,29], while electron transfer from \(Q_A^-\) to \(Q_B\) contributes little or nothing to the transmembrane charge separation [22,26,27,29]. Thus the charge