

Primary processes in photosynthetic reaction centers

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Abstract— Photosynthetic reaction centers realize the primary steps of the bioconversion of light energy. They are complex membrane proteins which contain several molecules of pigments and electron carriers, organized so as to transfer electrons efficiently along a well-defined path. Reaction centers can be classified in four categories found in purple bacteria (the best known), in green sulfur bacteria, and in plants (which have two categories : PS-I and PS-II). Reaction centers share common properties, which are discussed mainly on the basis of what is known in purple bacteria. The following aspects are considered : coupling between reaction centers and antenna ; the role of the membrane ; the means to minimize wasteful charge recombination ; the primary step and the dimeric structure of the primary electron donor ; the properties of quinones ; the role of a Fe^{2+} atom; the roles of the protein ; the symmetric structure of the reaction center ; the primary radical pair and triplet state formation.

INTRODUCTION

Photosynthesis is well known as a large-scale biological process which makes use of the energy of light for sustaining the growth of plants, and ultimately for allowing the development of all living organisms on earth. The universal importance of photosynthesis is thus easily recognized. It is less known, however, that this immense activity, storing annually 3×10^{21} J of free energy, is powered by microscopic proteins, named REACTION CENTERS, which are the biological analogs of solar cells. The photosynthetic machinery is in fact more complex ; it includes the following elements, arranged in chronological order after absorption of light :

Antenna This is a set of pigments, carried by proteins, which are tightly packed so as to transfer the absorbed energy toward the reaction centers, by a resonance (Förster) mechanism. In the average there are 100–1000 pigment molecules per reaction center. The pigments belong to several chemical classes: chlorophylls, carotenoids, phycobilins; they give photosynthetic organisms their color and their capacity to absorb light of various wavelengths. Photosynthetically useful light may extend from the near UV to the near IR (around 1000 nm).

Electron and proton carriers. ATPase The primary steps of photosynthesis lead to the reduction of a reducing substance (NADPH) and to the synthesis of ATP, a cellular energy vector. The coupling between the activity of reaction centers and the formation of NADPH and ATP requires several proteins which are involved in electron transfer, proton transfer, and the use of the proton chemical potential for ATP synthesis. This coupling requires that

all the components, including reaction centers, are inserted in (or associated with) a membrane, the photosynthetic membrane. This one also carries most of the antenna pigment-protein complexes, insuring an efficient energy transfer to the reaction centers. A cytochrome b/c complex and a proton ATP-synthase are the major proteins involved in the coupling.

Soluble enzymes All the later steps of photosynthesis are realized by a large number of enzymes which are soluble in the cellular medium. In plants, their main function is to reduce carbon dioxide into sugars, a process which takes place in the chloroplast. This production of metabolites is the end of the process named photosynthesis, which finally is intermixed with the general cellular metabolism.

In plants, there are two types of reaction centers, named Photosystem I and Photosystem-II (PS-I and PS-II). The same situation is found in other organisms (such as algae or cyanobacteria) which use water as a source of electrons to reduce CO_2 . Transferring an electron from water ($E_{m,7} = +0.81 \text{ V}$) to ferredoxin ($E_m = -0.42 \text{ V}$; this is the protein which reduces NADP^+) is endergonic by 1.23 V. For this to be powered by a photon absorbed by chlorophyll would require an energetic yield well above that encountered in the reaction centers. That is the rationale for the occurrence of two types of reaction centers, PS-I and PS-II: they are functioning in series (following the analogy with photoelectric devices) with a negative pole in PS-I, connected to ferredoxin, and a positive pole in PS-II, which oxidizes water with evolution of dioxygen. Photosynthetic processes also take place in purple or green bacteria, which do not oxidize water. These bacteria contain only one type of reaction center which is analogous to PS-I (in green sulfur bacteria) or to PS-II (in purple and in green non-sulfur bacteria). The reaction center of purple bacteria is rather simple and it has revealed to be a good model for all kinds of reaction centers. Its properties are now rather well known, and I shall start with their description in some detail, focussing on what might be of more interest to photochemists.

THE REACTION CENTER OF PURPLE BACTERIA

The concept of reaction center was discovered before these objects were effectively isolated, to account for the behaviour of photosynthesis under short flashes of light. Reaction centers are hydrophobic objects, embedded in the photosynthetic membrane. Their isolation, which was first succeeded in purple bacteria, requires to replace the lipids by detergent molecules. After suitable purification, a complex protein is obtained, which has the following composition (for the bacterium *Rhodobacter sphaeroides*, wild type): 3 polypeptides, named L,M,H of molecular weight about 30 kDa; 4 bacteriochlorophylls \underline{a} , 2 bacteriopheophytins \underline{a} , 2 ubiquinones, 1 carotenoid (sphaeroidene), and one Fe^{2+} atom. Altogether, for a total MW around 100 kDa, the polypeptide chains contribute for 90% only, and the cofactors (10%) are thus more abundant than in many proteins.

As shown for all other proteins, the reaction center has a well-defined 3-D structure. That structure is now well known since the protein has been crystallized for two bacterial species (*Rhodospseudomonas viridis* and *Rhodobacter sphaeroides*), permitting detailed studies by X-ray crystallography. Elucidation of this structure is the first (and still unique) case among membrane proteins. As such it has had a profound impact on

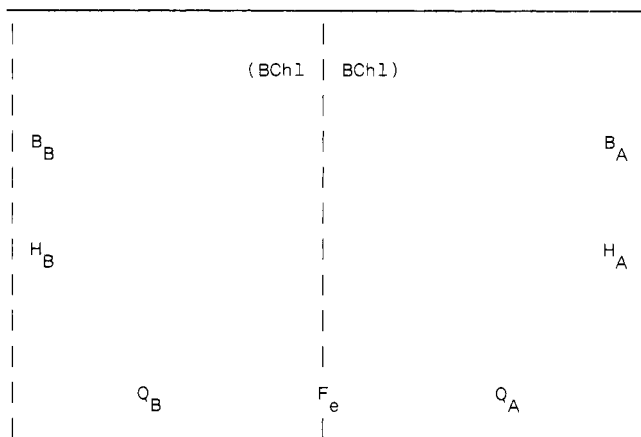
biochemical thinking, in proportion to the biological importance of that class of proteins. I shall not detail the structure (several aspects of which will be discussed below), but simply mention a few aspects (for recent reviews, see refs. 1,2) :

- the structure is very similar for the reaction center from the two species from which it has been crystallized ;

- many aspects of the structure had been predicted previously on the basis of spectroscopic measurements : dimeric nature of the primary electron donor, symmetric arrangement of the quinones, orientations of the plane of tetrapyrrolic pigments, etc. This is not to diminish the interest of the radiocrystallographic work, but to stress that structural information can be obtained about reaction centers which have not yet been crystallized.

- pigments and electron carriers are arranged in a regular manner within the protein, as shown in the scheme below. The most surprising feature is their symmetric arrangement around an axis going from the Fe^{2+} atom to inbetween the bacteriochlorophyll dimer. It happens that electrons are going from the bacteriochlorophyll dimer to Q_B via the right side ("A" branch) and that the "B" branch is essentially inactive.

- the structure is imposed by the protein. The presence of the cofactors probably contributes to the stability of the ensemble, but there is no bonding between cofactors. This absence is specially striking in the case of the bacteriochlorophyll dimer, which is held together by the polypeptides, without any chemical interaction between the two bacteriochlorophylls (contrary to what can be expected from the known tendency for these molecules to dimerize in solution).

Cyt c

The functioning of reaction centers in purple bacteria is rather well understood, qualitatively. Electronic excitation is trapped by the bacteriochlorophyll dimer (named P, or primary donor) which rapidly transfers an electron to the bacteriopeophytin. This takes around 2 ps, and it is still debated whether the bacteriochlorophyll B_A is a discrete intermediate in electron transfer from P to H_A . The next step is electron transfer from H_A to the quinone Q_A , which takes about 200 ps. The next step of electron transfer, from Q_A to Q_B , is much slower : 10-100 μ s, according to the species. After its photooxidation, P is

re-reduced by a cytochrome of the c type. In most cases, this electron donation will occur in times of the order of 1 μ s, from a bound cytochrome. The mode and strength of cytochrome binding are rather variable among bacterial species.

It thus appears that reaction center functioning is basically simple, although many features remain poorly understood and although their quantitative analysis remains a formidable task.

THE REACTION CENTERS OF PLANTS AND NON-PURPLE BACTERIA

In the plant-type (oxygen-evolving) photosynthetic apparatus, the PS-II reaction center shares many properties with its counterpart from purple bacteria (refs 3-5). Adopting a very simplifying presentation, one can say that the PS-II reaction center has an inner part (a core) made of two polypeptides, named D_1 and D_2 , which are in many respects analogous to L and M, in purple bacteria : they have highly significant homology in their sequences of amino-acids and presumably an analogous tertiary structure with five alpha-helices in each polypeptide ; they carry electron carriers which have analogous chemical structures and display very similar thermodynamic and kinetic properties. The PS-II reaction center, however, is more complex than its bacterial counterpart in at least two important respects (refs 6-8) :

- it realizes the oxidation of water. The primary donor P-680, which is a monomer or a dimer of chlorophyll a, has a very positive reduction potential (for the P-680/P-680⁺ couple) : at least + 1.0 V, which renders it able to irreversibly oxidize water ($E_m = + 0.81$ V). Water oxidation is an enzymatic reaction which is catalyzed by a specific part of the PS-II reaction center. This site, which is still poorly known and is the subject of intense research, includes a cluster of four manganese atoms bound to the protein. Water oxidation takes place as a concerted four-electron reaction : $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$. For that purpose, the manganese cluster serves as storage device for the progressive accumulation of four oxidizing equivalents. The cluster is not oxidized directly by P-680⁺, but a tyrosine residue (Tyr161 of D_1) serves as an intermediate : it is oxidized by P-680⁺ and then oxidizes the cluster. These properties are really specific of PS-II and of course not found in purple bacteria.

- the PS-II reaction center is rather complex in terms of polypeptide composition. In addition to D_1 and D_2 , it includes one or two copies of a cytochrome b, two chlorophyll a binding polypeptides named CP-47 and CP-43, three extrinsic polypeptides involved in the stable binding of the manganese cluster, and several small polypeptides, the function of which is unknown. Part of this complexity is obviously directly related to the water oxidation process. It may also be associated to the "screening" of potentially harmful positive charges, to repair or biosynthesis processes, or to a control of the coupling between reaction center and antenna.

The plant-type photosynthetic apparatus also includes the PS-I reaction center, which is largely different from the above-mentioned ones. In a teleological perspective this difference is due to the function of PS-I, which is to reduce ferredoxine which subsequently reduces NADP⁺. Ferredoxine has a reduction potential (-420 mV) much lower than the quinones which are reduced by PS-II or purple bacteria. Also, it is a one-electron carrier whereas the quinones operate as two-electron carriers. The PS-I reaction center is still poorly known, but a few features are established (refs. 3,9,10) :

- the core is made of two large polypeptides (MW around 83 kDa) which carry a large number of pigment molecules (at least 50 chlorophyll a) in addition to the electron carriers.

- the best established electron carriers are the primary donor (named P-700, probably a dimer of chlorophyll a) and three low-potential iron-sulfur centers. The very primary electron acceptor is presumably a chlorophyll a molecule, and the secondary acceptor is presumably a naphthoquinone (phylloquinone), but this point is still controversial.

A counterpart to PS-I is found in two classes of photosynthetic bacteria : the green sulfur bacteria and some Gram-positive bacteria (*Heliobacterium* sp. and *Heliobacillus* sp.). These bacteria are adapted to very reducing environments, where they develop in the total absence of oxygen, using sulfide as a source of electrons. They have been discovered rather recently and are not yet well known. Their known properties, however, make them close neighbours to PS-I : core of reaction center with a large number of pigment molecules, low potential for all the electron carriers, presence of three bound iron-sulfur centers with EPR properties similar to those found in PS-I, etc. These analogies, together with parallel analogies between PS-II and purple bacteria, may be useful for tracking the past evolution of photosynthetic organisms.

DISCUSSION OF REACTION CENTERS PROPERTIES

1. Coupling between antenna and reaction centers

Economy of means is a general principle for basic processes in biology. The cross section for the absorption of light by chlorophyll is rather small. Thus, if each reaction center had only a few molecules of pigments, it would turn-over very slowly, even under full sunlight (about once every second). The antenna appears as a plastic apparatus which permits a full use of reaction center capabilities and the adaptation of organisms to actual light conditions in their growth environment.

In a given organism, the antenna is usually heterogeneous : it includes pigment sub-sets which are more or less close to the reaction centers both in spatial and energetic terms (ref. 12). Among the most interesting questions in that respect, is the relation between the antenna structure and the rapid energy transfer which takes place in a few picoseconds and brings excitation energy to the reaction center with a nearly 100% yield in most cases. These antenna properties are of great interest for the construction of artificial photochemical devices.

2. Why reaction centers are in a membrane

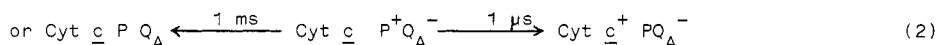
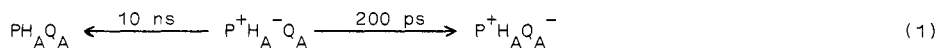
This is essentially because energy is stored under two forms : redox energy (which in principle does not require a membrane) and ATP, which is necessarily synthesized by a membrane protein, the ATP-synthase. This enzyme is driven by a membrane potential which has two components : an electrical potential, and more importantly the chemical potential of H^+ . At a rather primary level, reaction centers in most photosynthetic bacteria can be simply considered as light-driven H^+ pumps, whereas in plant photosystems the redox form of energy is largely predominant.

3. How are wasteful charge recombinations avoided

This, of course, is a fundamental question for photochemists. In many molecular systems, a primary step of photoinduced electron transfer can take place very efficiently,

but it will be followed by a rapid charge recombination. The chlorophyll-quinone system is a good example in that respect. Is there anything mysterious in biological reaction centers, which gives them a nearly 100% quantum yield ?

In that respect, the most obvious property of reaction centers is the multiplicity of electron carriers, which insures that a primary step is followed by further ones that separate progressively the electron and the hole. This device works because each forward transfer is much faster than the corresponding back-reaction. For example :



This kind of behaviour is found in all reaction centers, and the number of steps is included between 3 and 5. Charge recombination occurs altogether with a low probability, below 10%, except under pathological conditions which are created by the experimentalist or which take place naturally in damaged reaction centers or when the light intensity is too strong. This situation is frequently encountered for PS-II, under field conditions, in a process named photoinhibition.

It remains to be understood why forward electron transfer is for each step so much faster than recombination (ref. 2). Considering reactions (1) above, the driving force is about 0.65 eV for the forward process and 1.2 eV for the back-reaction (assuming a direct return to the ground state) which thus will be thermodynamically favored. Quantitative theories of electron transfer have been applied to the reaction center of purple bacteria, using the atomic coordinates and a few known thermodynamic and electronic properties (refs. 13-16). One usually relies on Marcus theory of electron transfer, where the rate is determined by three factors : the free energy of the reaction, the reorganisation energy and the electronic matrix element. The consecutive electron transfer steps have very different properties (for example, the free energy change is 0.65 eV in the transfer from H_A to Q_A , and nearly less than 0.1 eV in transfer from Q_A to Q_B , in Rh. sphaeroides). Detailed studies have not yet been done. In particular, it is presently difficult to assess the structural changes which accompany electron transfer and the vibrational modes which are coupled to it (see the interesting attempt in ref. 17). Structural relaxations may be important in decreasing the rate of back-reactions.

4. The primary donor P is a (bacterio-)chlorophyll dimer. The primary step

The dimeric nature of P is established in purple bacteria. In other types of reaction centers, various spectroscopic arguments permit to conclude that P is also probably a dimer: CD spectrum, EPR spectra of P^+ and of the triplet state 3P , ENDOR spectrum of P^+ , etc. Is there any advantage in that structure ? It could be thought that a dimer, having a low-energy excitonic excited state, could be a good energy trap. This is probably not a decisive argument since in PS-II the low-energy Q_Y transition of P is at the same level as many chlorophyll molecules in the antenna ; the trap is thus very shallow, but it works well nonetheless. A clue to the problem perhaps resides in recent hole-burning experiments on purple bacteria, which show that holes burnt in the Q_Y P absorption band are very broad. An interpretation is that the excited state P^* is in resonance with a very close internal charge transfer state which can be considered as the first step of electron transfer (ref. 18). The charge-transfer character of the excited state of P has also been concluded from

the electric field effect on pigment absorption (Stark effect) and on the yield and polarization of fluorescence (19).

The precise nature of the primary step is the object of much debate. Experimentally, it is clear that an electron arrives on H_A in about 2 ps (ref. 20). How does it arrive? Examination of the reaction center structure leads one to think that B_A will be an intermediate, but flash picosecond spectroscopists disagree in that respect: most of them find no evidence for a transient bleaching of B_A , whereas a recent report does find such an evidence (ref. 21). In that case it is proposed that electron transfer from excited P to B_A (time constant 3.5 ps) is slower than from B_A to H_A (0.9 ps), so that B_A^- does not accumulate. These experimental findings are of course essential for an adequate theoretical treatment of the primary reactions (ref. 22).

5. Quinones as electron acceptors

It has been established for a long time that Q_A and Q_B are quinones with a long isoprenoid side chain: plastoquinone in PS-II, ubiquinone in purple bacteria (in some of them Q_A is a menaquinone, i.e. a substituted naphthoquinone instead of a substituted benzoquinone). The functional properties of these quinones are quite interesting: Q_A is a one-electron carrier that remains permanently bound at its site, whereas Q_B accepts successively two electrons and (with two H^+) becomes a quinol which does not bind any more to the protein and moves in the membrane for further electron transfer. There are very active competitive inhibitors for Q_B , which most often act both in PS-II and in bacteria. The very similar behaviour of Q_A and Q_B in PS-II and purple bacteria was the first very strong argument for the similarity between both reaction centers. The sites of quinone binding are now well known from crystallographic data, but the reason for the dissymmetric behaviour of Q_A and Q_B remains a problem. Reaction centers of *Rps. viridis* have also been crystallized with an inhibitor instead of Q_B , and also for strains that a mutation renders resistant to inhibitors (ref. 23). These works, together with molecular modelling and with systematic studies of the effects of inhibitor structure and of point mutation, give some hope to obtain an accurate view of the Q_B binding pocket in PS-II, which is important for the chemical synthesis of new herbicides.

Recently it has been shown that PS-I contains two molecules of phylloquinone (a naphthoquinone derivative) and that one of them acts as a secondary electron acceptor, named A_1 (ref. 10). Similar observations were made in green sulfur bacteria. Although the functional studies on A_1 are still preliminary, they imply that this quinone operates at a very low oxidation potential (about -0.8 V, versus NHE). It may be so because it stays in a very apolar environment.

6. Role of Fe^{2+} in PS-II and purple bacteria

The crystal structure of purple bacteria reaction centers clearly show the Fe^{2+} atom, on the symmetry axis, inbetween Q_A and Q_B . An Fe^{2+} atom is also found in PS-II, presumably with a similar location. The role of this atom is not understood. It is located on the potential electron path between Q_A and Q_B , but it does not normally change of redox state and can be replaced by other ions without any substantial alteration of the electron transfer rate.

7. Roles of the protein

The polypeptides of the reaction center can be viewed as a scaffolding which maintains the "active" molecules (pigment, redox centers) in a well-defined position. This view is of course essentially correct. The modes of binding are now partly understood, thank to the crystal structure and to spectroscopic techniques which are more sensitive to atomic interactions : resonance Raman spectroscopy, infra-red absorption, isotopic substitution in ENDOR. It is clear, however, that the reaction center apoprotein certainly play other roles :

i) In PS-II, it is now well established that two tyrosine residues can get oxidized, and that one of them is a definite electron carrier between P^+ and the manganese cluster (ref. 8). Recent experiments tend to indicate that a histidine residue may also become oxidized at the active center for water oxidation (A. Boussac, J.L. Zimmermann, A.W. Rutherford and J. Lavergne, personal communication).

ii) Aromatic amino-acids may play a role in electron transfer, by a super-exchange mechanism. This possible role has been invoked in several cases, and dealt in some detail for a tryptophan residue which would bring superexchange coupling between H_A and Q_A (ref. 24). A different but related effect is that due to polar or charged groups which exert an electrostatic influence on electronic properties of the cofactors.

iii) Reorganisation energy is an important factor of electron transfer (ref. 25). This parameter is small for the cofactors and may thus get all its value from changes in the protein structure. These changes probably contribute to slowing back- compared to forward-reactions.

iiii) Proton conduction. This role is still highly hypothetical, but it has been proposed for the quinol formation in bacteria, and for transmembrane proton movements in PS-II, by a mechanism analogous to that postulated in proton pumps.

8. Reaction center symmetry

It is established that the reaction center of purple bacteria has an approximate two-fold symmetry axis. The knowledge that we have of other types of reaction centers leads to hypothesize that they also have a symmetric organization (ref. 26). We still have few indications on the biological interest of that kind of organization, and on its relation to gene duplication which has occurred in ancestors of each reaction center type. A very interesting puzzle resides in the fact that, despite the nearly symmetric structure, photo-induced electron transfer follows only one branch, the other being at least 50 x less efficient (ref. 27). The functional dissymmetry has been examined quantitatively (ref. 13), an approach which, complemented by site-directed mutagenesis, is very promising to understand the parameters which determine electron transfer rates.

9. Primary radical pair. Triplet state formation

Under normal conditions, the state ($P^+H_A^-$) is short-lived, about 200 ps. When forward electron transfer is blocked, for example by prior reduction of Q_A , that state lasts for about 10 ns, and decays by charge recombination. The radical-pair ($P^+H_A^-$) is born as a singlet state ; in the nanosecond time, it can evolve to a triplet state. In that case the recombination populates the triplet state 3P . This mechanism is interesting for two reasons :

i) Firstly, a detailed study of the radical-pair dynamics and of the effect of magnetic fields has led to important parameters involved in electron transfer, such as the energy level of ($P^+H_A^-$) (see e.g. ref. 19).

ii) Secondly, these properties have now been observed, with relatively minor differences, in all studied reaction centers. This reinforces other arguments which lead to propose common structures and mechanisms to the partners of primary photochemistry.

CONCLUDING REMARKS

It is remarkable to note that the development of our knowledge on photosynthetic reaction centers makes these objects more and more interesting to physical chemist. Most sophisticated spectroscopic tools become applicable, and necessary to bring enough information for quantitative theoretical treatments. This short descriptive review mainly deals with reaction centers from various organisms, belonging to several classes, but with many common features. The most specific aspects are not the less interesting. In PS-II particularly, the structure of a tetranuclear manganese cluster and the mechanism of water oxidation are intensively studied and remain one of most poorly processes in bioenergetics.

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