

Photosynthesis

Electron-transfer theory in question

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THE reactions by which light is captured and stored as chemical energy in photosynthesis are distinguished by the extremely high quantum yield of the primary conversion process. On page 190 of this issue¹, Fleming *et al.* present data which provide new insights into this process. Using ultrafast spectroscopy, these authors have been able to detect the rate of formation of the initial charged transfer state in the isolated reaction centres of purple photosynthetic bacteria. This occurs in just a few picoseconds and, surprisingly, increases as the temperature is lowered to that of liquid helium.

Their results emphasize that a complete theoretical description of this remarkable primary reaction will require a better understanding of how the protein environment around the reactants influences the very fast electron-transfer rate. One particular challenge which emerges from their observations is to explain, in terms of quantum mechanics, how an intermediate bacteriochlorophyll molecule aids the primary charge separation.

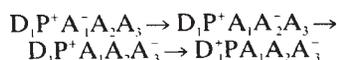
Reaction centre

All photosynthetic organisms have similar molecular machinery for catalysing the primary storage processes of photosynthesis. The machinery is contained within a protein complex embedded in a membrane and called a reaction centre. The reaction centre is excited by the energy of a photon which is initially absorbed by an antenna system of many hundreds of pigment molecules. The energy of the absorbed photon is rapidly transferred by exciton migration to the reaction centre which acts as a trap. All types of reaction centres contain either chlorophyll (oxygenic organisms, such as higher plants and algae) or bacteriochlorophyll (anoxygenic organisms, such as photosynthetic bacteria) which acts as a primary electron donor, P. When excited, P rapidly gives an electron to a primary electron acceptor, A₁, and a charged transfer state or radical pair, P⁺A₁⁻, is created.

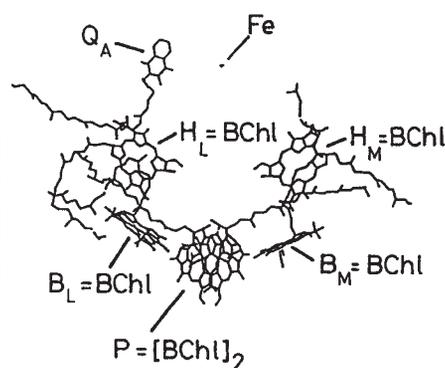


The transfer of an electron from P^{*} to A₁ must be very fast to avoid de-excitation by other routes such as by fluorescence. Also, for the photosynthetic reaction centre to have a very high quantum yield of energy conversion, there must be a negligible back-reaction between P⁺ and A₁⁻. The latter is achieved by rapidly transferring

the electron away from A₁⁻, to secondary electron acceptors A₂, A₃ and so on, and by passing an electron to P⁺ from the secondary donors D₁ and so on.



For some years now, the best experimental system to study these primary electron-transfer processes has been reaction centres isolated from purple photosynthetic bacteria. The importance



of this experimental system has been particularly elevated by the recent determination of the three-dimensional structure, to a resolution of atomic distance, of the reaction centres of *Rhodospseudomonas viridis*² and *Rhodobacter sphaeroides*³. These outstanding studies indicate that there are two different symmetrically related possible pathways for the primary electron transfer to occur, the L and M branches (see figure).

For reasons which are not fully understood, the pathway of choice is L. The primary donor P is a dimeric form of bacteriochlorophyll (BChl)₂, and is shared by both pathways. In addition to this, there are two monomeric bacteriochlorophylls (B_L and B_M) and two bacteriopheophytins (H_L and H_M). The secondary electron acceptors are bound quinone molecules called Q_A and Q_B. The donor (D₁) to P⁺ is the haem of a cytochrome which may be bound to the reaction centre,

as in the case of *Rps. viridis*, or may be a soluble protein, as in the case of *Rb. sphaeroides*.

According to the crystal structure (see figure), it would be logical if A₁ was B_L, but the data of Fleming *et al.* in this issue¹ do not support this idea. Using stimulated emission in the infrared to monitor the PA₁ to P⁺A₁⁻ transition in both *Rps. viridis* and *Rb. sphaeroides*, they conclude that A₁ is the bacteriopheophytin H_L. According to their data, if there is an involvement of B_L in the electron exchange between P and H_L, then it must include an adiabatic step or be incorporated into a superexchange mechanism with very strong quantum mechanical coupling.

Relevant to these possibilities is the finding that rate of primary charge separation increases with decreasing temperatures. At room temperature, the rate for P⁺A₁⁻ formation is identical for both bacterial systems, but at 8 K not only does the rate increase dramatically but it is almost twice as fast in *Rps. viridis* as it is in *Rb. sphaeroides*.

Discrepancy

Although Fleming *et al.*¹ try hard to explain these data in terms of conventional theory for non-adiabatic electron transfer, they are forced to conclude that the validity of the arguments is not convincing, particularly in the case of *Rps. viridis*. The problem is that the components involved in primary charge separation are embedded in a protein environment^{3,4}, and it is this complication which probably underlies the discrepancy between theory and the differences obtained with the two bacterial systems. Indeed, the crystallographic data indicate small differences in organization of the chromophore within the *Rps. viridis* and *Rb. sphaeroides* reaction centres^{3,4}, the implications of which are not fully understood in terms of the kinetics of primary charge separation. Also, the static structure obtained by X-ray diffraction does not reveal the conformational changes that may occur when the reaction centre is activated by light.

Clearly, Fleming *et al.* provide the necessary experimental data which, together with the crystallographic structures, will allow theoreticians to modify existing ideas and to develop new ones about how photosynthetic organisms so efficiently bring about the fastest bimolecular reactions known in photochemistry. □

1. Fleming, G. R., Martin, J. L. & Breton, J. *Nature* **333**, 190-192 (1988).
2. Deisenhofer, J., Epp, O., Miki, K., Huber, R. & Michel, H. *J. molec. Biol.* **180**, 385-398 (1984).
3. Allen, J. P., Feher, G., Yeates, T. O., Komiya, H. & Rees, D. C. *Proc. natn. Acad. Sci. U.S.A.* **84**, 5730-5734 (1987).
4. Deisenhofer, J., Epp, O., Miki, K., Huber, R. & Michel, H. *Nature* **318**, 618-624 (1985).

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