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Photosynthesis—the first nanosecond

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Abstract - The two principal kinetic processes of importance in photosynthesis are electronic energy transfer and electron transfer and there are separate pigment-protein complexes for each of these. Reported briefly in this communication are the following systems studied, along with observations made: (i) the light harvesting complexes (L.H.C.); (ii) reaction centre of photosynthetic bacteria; (iii) reaction centres in green plants; (iv) model systems.

Most of the true photochemical processes of photosynthesis, that is to say those involving electronically excited states, occur in the first nanosecond following the absorption of light. Time-resolved fluorescence and flash photolysis with transient absorption spectroscopy are now able to resolve the shortest times of interest but the spectra are complex, involving many components, and further progress depends on the separation and isolation of the various pigment-protein complexes from the membrane. Rapid progress is being made in this area as well; a few of the components have been crystallised and, in three cases of great interest, structure determinations at the molecular level have been possible. We are therefore near to the situation where it will be possible to study the kinetics of very complex molecular aggregates in which the exact positions of the various components relative to each other are known.

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THE LIGHT HARVESTING COMPLEXES (L.H.C.)

These consist of proteins containing chlorophyll or other pigments from a few to about 300 (in the case of large numbers the whole L.H.C. is made up of smaller sub-units). Two types of L.H.C. have been studied by time-resolved spectroscopy.

(1) Units on the surface of the membrane of red and blue algae contain several phycobilin (linear tetrapyrrole) pigments with a morphology such that the energy is transferred from one pigment shell to another of lower excitation energy. Time-resolved fluorescence studies have shown that the transfers do indeed occur in succession (no "overbumps") with a transfer efficiency greater than 0.99.

(2) Earlier work had shown that the average transfer time in the L.H.C. of the green plant (L.H.C.2) to the reaction centre of photosystem 2 was about 450 picoseconds when the trap was open and that there was little or no transfer between the separate units. This L.H.C. 2 has recently been crystallised and its structure determined to a resolution of 17Å by Kühlbrandt using electron microscopy. The units were shown to be triads of smaller units, each of 26 k.D and containing about 6 chlorophylls, with equal amounts of Chl a and Chl b overall. Kinetic studies of these two dimensional crystals both in emission and absorption have shown that the energy transfer properties, and consequently the lifetime of the excited chlorophyll, are critically dependent on the state of aggregation which itself is determined by the protein/surfactant ratio.

"Bleaching" at wavelengths where there is no absorption, and time dependent shifts in transient absorption spectra, have recently been interpreted by David Klug in terms of stimulated emission whose relative magnitude is independent of intensity and comparable to the reduced absorption of the ground state.

Although the energy transfer between molecules in the L.H.C. is well interpreted in terms of Förster resonance energy transfer, there are still unresolved problems concerning the absence of concentration quenching.

REACTION CENTRE OF PHOTOSYNTHETIC BACTERIA

The paradigm of kinetic-structural studies of photosynthetic structures is undoubtedly that provided by Deisenhofer, Hüber and Michel and by Parson, Windsor *et al*, on structure and kinetics respectively, of this protein complex. The structural results, at 2Å resolution, confirmed, in a spectacular manner, the predictions of the time-resolved flash-photolysis investigations.

The reason for the multiple electron-transport chain is now clear; its purpose is to prevent the tunneling back-reaction by increasing the spacial separation between the separated charges.

REACTION CENTRES IN GREEN PLANTS

These reaction centres, which are at the heart of the most important of all photosynthetic processes, are less well characterised than those of bacteria. The pigment-protein complexes of the reaction centres of the two photosynthetic units are, however, now being obtained in ever purer form, although they have not been crystallised and their molecular structures are still unknown.

Picosecond time-resolved studies of the reaction centre of P.S.1 (Linda Giorgi, Bryson Gore and David Klug) have shown the instantaneous bleaching of P 700 due to oxidation (in reduced particles) and its recovery, with a half-time of 75 p.s., with concomitant decay of ground-state antenna bleaching.

Similar studies of isolated reaction centres of P.S.2 indicate a slower recovery time but, owing to overlapping spectra, the kinetics of the 680 nm transient have not yet been resolved.

MODEL SYSTEMS

The construction of *in vitro* models of molecular aggregates provides the most convincing way of confirming the theories of energy and electron transfer pertaining to the photosynthetic unit. Energy transfer in synthetic, covalently bound porphyrin-porphyrin dimers and electron transfer in chemically bound redox pairs, studied on the picosecond time scale, have, on the whole, reproduced the main aspects of *in vivo* photosynthesis. Attempts to construct the whole system *in vitro* have been less successful because of the stringent requirements of spacial organisation of the molecular components. The low efficiency of natural photosynthesis compared with the thermodynamic and kinetic optimum presents a challenge both to plant biologists and to photochemists.