

Photoacoustic calorimetry of purple membrane

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Photoacoustic measurements on suspensions of purple membrane fragments extracted from the halophilic bacterium *Halobacterium halobium* were used to determine the thermal energy changes associated with the photochemically induced intermediates and conformational states of bacteriorhodopsin. The photoacoustic technique monitors thermal oscillations in the sample which are induced by a modulated light input. These thermal changes are sensed as modulated pressure changes with a microphone in contact with the air layer above the sample. Several of the decay times associated with the enthalpy changes, as calculated from the frequency response of the photoacoustic signal, can be correlated with known lifetimes of the photocycle intermediates. The frequency response curve at 280 nm exhibits the same pattern of peaks as that seen with a visible excitation wavelength (565 nm), indicating photoactivity induced by absorption at that wavelength. Energy changes which are not directly correlated with the known photocycle can be associated with conformational changes in the protein retinal complex. These energy changes are a function of pH and ionic strength.

Some aspects of the photochemistry of indole and tryptophan

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The photochemistry of indole and tryptophan (Trp) was studied with respect to two phenomena: (a) the influence of the excitation wavelength on the photoionization of the indole ring; (b) the effect of the environment on the photodegradation of Trp residues in proteins.

(1) We showed that in oxygen-free neutral aqueous solution the photoionization efficiencies of indole and Trp are constant within the first absorption band, which excludes a threshold process. In the second band the efficiency increases, indicating that this process competes with the internal conversion to the S_1 state.

(2) The environment effect on the photochemistry of Trp residues was studied on three proteins containing only one Trp: (a) glucagon (exposed residue); (b) endonuclease; (c) Rnase T₁ (buried residues). It was shown that in degassed solutions the photolysis process (photodegradation rate and photo-products) depends on the residue environment. In particular the degradation yield is larger (about 3 - 4 times) for exposed residues than for buried residues.

Photochemical behaviour of 8-methoxypsoralen in micelles and liposomes

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The purpose of the present study was to simulate the photochemical behaviour of 8-methoxypsoralen (8-MOP) in a biomembrane such as human skin by use of sodium dodecyl sulphate (SDS) micelle solution or dimyristoyl lecithin (DMPC) liposome as a model membrane. On the basis of the absorption and emission spectra of 8-MOP in various kinds of solvents, SDS micelle solution and DMPC liposome, the following results were obtained.

(1) The micelle exerts a polar atmosphere on 8-MOP. The effective dielectric constant is about 60.

(2) The polarity of DMPC liposome experienced by 8-MOP is nearly equal to that of methanol. The effective dielectric constant is about 32.

(3) It is suggested that 8-MOP exists in the close vicinity of the polar group of a DMPC liposome rather than close to the non-polar hydrocarbon chain of DMPC.

It is considered that DMPC liposome may be a useful model for 8-MOP photochemotherapy. The reaction scheme of 8-MOP in SDS micelle solution or DMPC liposome is also discussed.