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The Role of the Protein in the Photochemistry of the Retinal Chromophore of Visual Pigments and the Purple Membrane Protein*

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Abstract. First various models that have been proposed for the primary photoevent in vision are critically discussed. It is concluded that the classical picture of a single cis-trans isomerization step is the only one which satisfactorily accounts for all the available experimental data. Experiments are performed showing that this process is temperature independent over a range of 200° C. In contrast to the efficient and wavelength independent photobleaching of rhodopsin, the yields of the 11-cis → all-trans isomerization of the free protonated Schiff base chromophore are small, exhibiting a marked dependence on the excitation wavelength. Potential energy curves for both ground and excited states of rhodopsin are derived from the analysis of the accumulated experimental data (Rosenfeld, Honig, Ottolenghi, and Ebrey, Pure Appl. Chem., in press). In variance with the behavior of model compounds, photoisomerization in the pigment proceeds via the quantitative population of a common, barrierless, thermally relaxed excited state along the 11—12 torsional coordinate separating the 11-cis (rhodopsin) and all-trans (bathorhodopsin) configurations. In the ground state, interactions with the protein destabilize the all-trans isomerization product, leading to storage of a significant fraction of the photon's energy in the primary step.

Next, the photochemistry of the purple membrane protein of *Halobacterium halobium* is discussed. It is suggested that, as in the case of visual pigments, the primary photoevent is a geometrical change in the chromophore. Also, as with visual pigments, the resulting primary photoproduct must have the highest free energy of any form of the pigment. The quantum yield for the formation of the 412 nm intermediate ("M") is c. 0.26, while that for the back reaction is c. 0.68 (Becher and Ebrey, Biophys. J., in press). The sum of these two quantum yields is c. 1.0, suggesting, again like rhodopsin, that the primary photochemistry proceeds through a common excited state shared by the pigment and its bathoproduct.

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