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Kinetic vs. Thermodynamic Control of Bacteriorhodopsin Pumping[1]

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Bacteriorhodopsin is a transmembrane proton pump that converts light energy to a transmembrane electrochemical gradient. Retinal, bound in the center of the protein, absorbs light and isomerizes from the all-trans to 13-cis configuration. A series of conformational changes and proton transfers then restores the structure to the all-trans ground state while pumping one proton from the high pH cell interior to the low pH exterior, saving energy in an electrochemical gradient. Poorly understood gating elements control key steps where incorrect proton transfer would return the protein to the ground state without pumping. The gate's barrier height determines how much the pump leaks. Analysis of high-resolution structures trapped in different intermediates has produced ideas for how bacteriorhodopsin ensures pumping. There are two contrasting strategies, one primarily thermodynamic and the other relying on kinetic control to ensure that protons are moved uphill. With thermodynamic control, residue protonation states always remain in quasi-equilibrium. Relatively slow conformational changes shift the energy landscape modifying site pKas. Residues then change ionization remaining in equilibrium in each metastable intermediate. The sequence of intermediates imparts the directionality to the transfers. Alternatively, the direction of transfer is determined by the accessibility of low energy pathways so is thus is under kinetic control. We will discuss which steps in the bacteriorhodopsin photocycle are under thermodynamic or under kinetic control. The role of three specific conformational changes (retinal isomerization, Arg82 reorientation and Glu194 and 204 separations) on the degree of proton transfer will be described. Supported by NFS MCB 1022208.

[1]Carried out with Yifan Song now at the University of Washington Department of Biochemistry