Thermodynamics of Photosystem I

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Summary
Methods of obtaining the free energy and enthalpy of the steps of electron transfer through the Photosystem I reaction center are presented. The values are tabulated and discussed from the viewpoint of efficiency of the process. The bacterial system resembles Photosystem I but Photosystem II is quite different. It appears that more energy is lost

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than strictly required by thermodynamics. A greater understanding is obtained by decomposing the free energy into its components of enthalpy and entropy. These identify changes in bonding energy in contrast to changes in structure/ordering of the system. It is found that the contribution of entropy to these processes is substantial. In fact, the A$_1$ to F$_{A/B}$ step is entropy driven. The volume changes associated with these electron transfer steps give information on the effective dielectric coefficient of the reaction center protein and show fairly large effects of substituting plastoquinone for phylloquinone at the A$_1$ site. They provide confirmation that the electron is delocalized over the complete Fe$_2$S$_4$(Cys)$_4$ complex. Thus, these thermodynamic measurements can contribute significantly to our understanding of the remarkable process of photosynthesis.

I. Introduction

Knowledge of both the thermodynamics and the kinetics of a process are required for its full understanding. Extensive spectroscopic investigations have led to good knowledge of the intermediates in the process of Photosystem I (PS I) and the kinetics of the intermediate steps (see Chapters 16–29 of this volume). The successful determination of the structure of reaction centers and antenna proteins (see Chapters 6–8 of this volume) has added much to our understanding of the process. However, knowledge of the thermodynamics of the process is far less well advanced. Since the early photosynthetic reactions are electron transfer processes, the focus has been on the redox potentials of the intermediates. As discussed below, these values are not known at all well. There are two reasons to wish to know these values more accurately. One is the question of efficiency of the process. This word is used in different contexts with quite different meanings. It often refers to the efficiency of utilization of solar energy. This is a small and variable number. It is small because about half the solar energy is in the near and far infra-red regions which are not used in photosynthesis and because all the photon energy greater than the trap energy is rapidly degraded to heat. The trap energy is the energy of the excited state of the pigment(s) in the reaction center that do the first charge separation step. The theoretical efficiency is that fraction of the trap energy that is stored in the particular intermediates under consideration. It is thus a function of time, reaching a minimum when the final products of photosynthesis are reached. It is the prime subject of this chapter. The second reason to know the thermodynamics of a process is the far greater understanding obtained by breaking up the free energy into its components: enthalpy and entropy. From the viewpoint of statistical mechanics, a further breakdown into the change in heat capacity at each step is the most useful. Unfortunately, we are still quite a ways from the precise measurements required for this much knowledge of the intermediates. Knowledge of the components of the free energy allows us to separate this energy into its bonding or enthalpy and structural or entropy components. The latter is often a small component in many chemical reactions at normal temperature, ~300 K. However, in structured environments such as proteins and the particular solvent, water, the contribution of entropy can be the determining factor. This is exemplified in the denaturation of proteins where the massive configuration entropy determines the thermal reaction.

II. Components of Photosystem I

It was not long after the discovery of P$_{700}$, the primary photoreactant of Photosystem I (PS I) by absorption spectroscopy (Kok, 1957; Ke, this volume, Chapter 3) that its redox potential was determined (Kok, 1961). The redox potential with a change of units is the free energy of the reaction: $\Delta G^\prime = -nFE^\prime$, where $n$ is the number of electrons exchanged and $F$ is the Faraday constant. Since it is the Gibbs free energy that determines the equilibrium of a reaction, interest in thermodynamics of electron transfer reactions has often stopped there and the focus has been on the kinetics of the processes. This attitude has been reinforced by the success of the Marcus theory (Marcus and Sutin, 1985; Moser and Dutton, this volume, Chapter 34) in correlating the kinetics of electron transfer with the free energy of the reaction. However, a much greater understanding of the process can be obtained by decomposing the free energy into its components of enthalpy and entropy. The former is a measure of the change in bonding

Abbreviations: A$_0$ – primary acceptor of PS I, chlorophyll; A$_1$ – secondary acceptor in PS I, phylloquinone; A$_P$ – secondary acceptor in PS I, menA,B mutants, plastoquinone; B$_{560}$ – trap of bacterial photosystem; DMF – dimethylformamide; EPR – electron paramagnetic resonance; F$_{A/B}$ – second and third Fe/S cluster acceptors in PS I; Fd – ferredoxin; FNR-Fd – ferredoxin nucleotide reductase–ferredoxin complex; F$_X$ – first Fe/S cluster acceptor in PS I; P$_{700}$ – trap of PS I; PS I – photosystem I; PS II – photosystem II; QA – primary quinone acceptor in bacterial photosystem; RC – reaction center.