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# THE PRIMARY CHARGE SEPARATION AND A BIOMIMETIC MODEL OF PHOTOSYNTHETIC OXYGEN EVOLUTION

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The transformation of light into the chemical energy that drives the fixation of CO$_2$ and the evolution of O$_2$ in green plant photosynthesis is mediated by two photosystems (PS I and PS II). The initial photoreactions in both photosystems consist of the absorption of light by chlorophyll a (Chl a) and the subsequent formation of chlorophyll $\pi$-cation radicals by photoejection of electrons to nearby acceptors (2).

We consider here the identity and chemical nature of the primary donor and acceptor of PS II. These species are of prime concern to biomimetic solar energy conversion because the primary photosynthetic reaction produces a strong oxidant capable of driving O$_2$ evolution, and because the electronic configurations of the donor and acceptor must influence the efficient forward electron transfer from the donor while inhibiting wasteful back reactions of the photoproduced cation and anion radicals.

## Primary Donor of PS II

The primary Chl a donors of PS I and PS II (P700 and P680 respectively) exhibit unique and puzzling differences. P700, which has been demonstrated (3) to consist of two Chl molecules, absorbs at $\sim$ 700 nm; 20 nm to the red of P680. Photooxidation of P700 results in the formation of a weak oxidant ($E_m \approx 0.5$ v vs NHE), while oxidation of P680 occurs at $\geq 0.8$ v and produces an oxidant capable of driving the oxidation of H$_2$O (2). By analogy with P700, P680 was thought to be an aggregated form of Chl a (4). However, our in vitro studies of monomeric Chl a indicate that changes in the solvation sphere of the monomer can sufficiently alter its physical properties so that the latter approach those observed for P680. The oxidation potential for Chl a in tetrahydrofuran (THF) is + 0.9 v (vs NHE) and, although Chl a$^+$ in THF exhibits a narrowed electron spin resonance (esr) linewidth (normally assigned to a dimer), the electron nuclear double resonance (ENDOR) spectrum is that of a monomeric Chl a$^+$. In addition, the optical difference spectrum reported for the oxidation of P680 resembles that of monomeric Chl a (5). These data suggest therefore that P680 may simply be a ligated Chl a monomer whose function in the phototrap is determined by interactions with its immediate environment, probably protein residues.

## Primary Acceptor of PS II

Short lived transients have recently been implicated as mediators in the light-induced charge separation of photosystems I and II (2). In PS II, the 1.82 ev of incident light (680 nm) is thus converted to a strong monomeric oxidant, P680$^+$, ($E_m \geq + 0.8$ v) and a reductant, I$^-$, with a midpoint potential of $-0.6$ v (6). By analogy with bacterial photosynthesis (7), this initial acceptor was postulated to be pheophytin (Pheo) (8). The magnetic characteristics (esr linewidths, g value and saturation properties, as well as ENDOR transitions) of I$^-$

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are in fact analogous to those of monomeric $Pheo^-$ in vitro (8). Furthermore, the optical changes observed on reduction of I as well as the midpoint potential for the reduction, mirror those of Pheo and further support the conclusion that Pheo is the most likely candidate for the primary electron acceptor in PS II.

It is enticing to speculate that the interposition of a chlorophyll-like molecule between the chlorophyll donor and subsequent acceptors in the electron transport chain, favors the forward reaction because of the very similar electronic configurations of donor and acceptor, while it inhibits the back reaction because of the very different electronic profiles of the resulting cation and anion.

## Biomimetic Model for $O_2$ Evolution

We have proposed above that the initial electron transfer reaction in PS II is: P680 (ligated Chl monomer) + Pheo $\xrightarrow{h\nu}$ $P680^+$ + $Pheo^-$. Additional support for this model derives from picosecond results for a synthetic diporphyrin in which a magnesium and a free base porphyrin are covalently linked by two five membered bridges (Mg-$H_2$5) and separated by $\sim 4$ Å. In $CH_2Cl_2$, containing 0.1 M $Cl^-$ to ligate the magnesium, a charge transfer state is formed from the excited singlet state in less than 6 psec, and it decays to the ground state in 620 ps (9). These results establish that a dimeric donor is not obligatory for rapid and efficient charge separation, and demonstrate that photo-induced charge separation can occur in a synthetic system with kinetic and thermodynamic energy efficiencies that approach those of photosynthetic organisms.

## References

1. a) Dept. of Energy and Environment; b) Medical Research Center; c) Chemistry Dept.

2. K. Sauer, Ann. Rev. Phys. Chem. 30, 155 (1979).

3. J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer and M. R. Wasielewski, Ann. Rev. Biophys. Bioenerg. 7, 393 (1978).

4. M. P. J. Pulles, H. J. Van Gorkum and G. M. Verschoor, Biochim. Biophys. Acta. 440, 98 (1976).

5. M. S. Davis, A. Forman and J. Fajer, Proc. Nat'l. Acad. Sci. U.S. 76, 4170 (1979).

6. V. V. Klimov, E. Dolan and B. Ke, FEBS Lett. 112, 97 (1980).

7. J. Fajer, D. C. Brune, M. S. Davis, A. Forman and L. D. Spaulding, Proc. Nat'l. Acad. Sci. U.S. 72, 4956 (1975).

8. I. Fujita, M. S. Davis and J. Fajer, J. Am. Chem. Soc. 100, 6280 (1978); J. Fajer, M. S. Davis, A. Forman, V. V. Klimov, E. Dolan and B. Ke, ibid, submitted for publication.

9. T. L. Netzel, P. Kroger, C. K. Chang, I. Fujita and J. Fajer, Chem. Phys. Lett. 67, 223 (1979); T. L. Netzel, I. Fujita, C.-B. Wang and J. Fajer, this conference.

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