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### Primary radical pair in the Photosystem II reaction centre

Yuichiro Takahashi <sup>a, b</sup> ... Kimiyuki Satoh <sup>b</sup>

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#### Abstract

Primary Photosystem II (PS II) reactions have been studied by flash absorption spectroscopy with nanosecond resolution. In isolated reaction centers which are devoid of the 47- and 43-kDa chlorophyll-binding polypeptides, an absorption change ( $\Delta A$ ) is induced immediately by a flash. The difference spectrum (450–560 nm, 820 nm) indicates the formation of a radical pair ( $P-680^+$ ,  $Pheo^{\dot{\alpha}}$ ) decaying with  $t_{1/2} = 40$  ns at 120 K. At 140 ns after the flash the  $\Delta A$  can be attributed to the triplet state of P-680 ( $^3P-680$ ) and of a carotenoid ( $^3Car$ ,  $\lambda_{max} = 545$  nm).  $^3Car$  is formed with a yield of  $\sim 3\%$  and it rises with  $t_{1/2} \sim 12$  ns. At 276 K, the radical pair decays, with  $t_{1/2} \sim 32$  ns. One radical pair is formed per 20 chlorophylls. The data are best interpreted if  $^3P-680$  is formed as a product of radical pair recombination with a yield of

complexes. The T<sub>1</sub>A at 820 nm disappear under conditions (addition of dithionite and methyl viologen, plus continuous illumination) designed to reduce pheophytin. The signals reappear after turning off the continuous light. More intact PS II particles (core complex) were also studied. At 820 nm, the data show that P-680<sup>+</sup> is formed under oxidizing conditions and is re-reduced in the microsecond time range. Under reducing conditions the primary biradical decays with  $t_{12} = 25$  ns. <sup>3</sup>P-680 is formed, with properties analogous to those in isolated reaction centers. <sup>3</sup>Car is also formed ( $\hat{I}_{\text{max}} = 535$  nm). The results show that the PS II reaction center has strong functional analogies with the reaction center of purple bacteria. The behavior of the carotenoid is a remarkable exception. The primary biradical decays much more slowly than expected on the basis of fluorescence measurements.



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## Keywords

Photosynthesis; Electron transfer; Triplet state; Pheophytin; Carotenoid

## Abbreviations

<sup>3</sup>, Carcarotenoid triplet state; P-680, primary donor of Photosystem II; <sup>3</sup>P-680, triplet state of P-680; Pheo, pheophytin; P, primary electron donor; I, primary electron acceptor; PS II, Photosystem II

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