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LIGHT-INDUCED ELECTRON-TRANSFER FROM PHEOPHYTIN *a* TO QUINONE STUDIED BY CIDNP TECHNIQUE —— A SIMULATION OF THE PRIMARY PROCESS IN PHOTOSYNTHESIS

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Strong CIDNP indicating the electron-transfer from pheophytin *a* to quinone was observed upon illumination of a methanol solution of pheophytin *a* and quinone. The intensities of the CIDNP signals are dependent upon the concentration of added acid.

Electron-transfer process from photo-excited chlorophyll to quinone has been widely investigated bacause of its believed major contribution to the primary process in photosynthesis.[1] Recently a new technique, CIDNP, was applied in a hope to elucidate the details of the electron-transfer process, though it was succeeded partly in a selected system in a preliminary manner.[2]

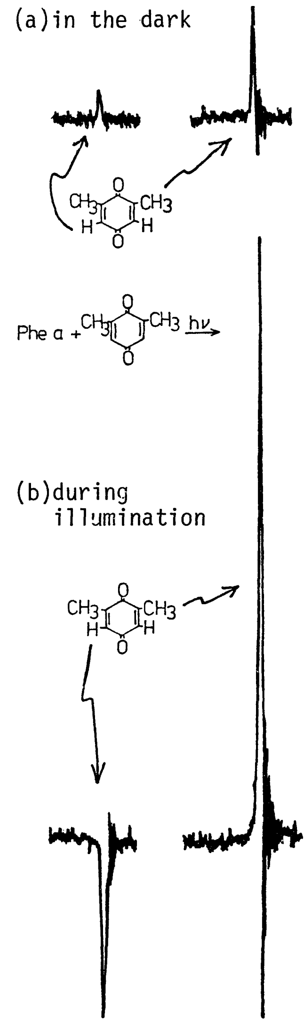
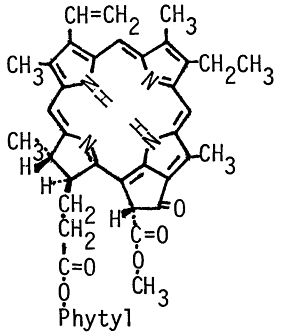


Fig.1



Pheophytin *a* (Phe *a*)

Fig.1.NMR spectra of a solution of Phe *a* and 2,6-dimethyl-*p*-BQ in methanol-d_4 containing DCl at ambient temperature. ([Phe *a*]:$7\mathrm{x}10^{-5}$ M/l, [2,6-dimethyl-*p*-BQ]:$1\mathrm{x}10^{-2}$M/l, [DCl]: $2.5\mathrm{x}10^{-3}$M/l).
(a) in the dark.
(b) during illumination.

Here light-induced electron-transfer from pheophytin *a* (Phe *a*)[3] to a variety of quinones was detected without any exception by means of CIDNP technique.[4] When a methanol-d_4 solution of Phe *a* and 2,6-dimethyl-*p*-benzoquinone, as a typical example, was illuminated with red-light[5] in the presence of DCl under argon atmosphere, the strong ^{1}H-CIDNP was observed in both the methyl-H and the ring-H of the quinone at ambient temperature (Fig.1).[6] The signal intensities are dependent upon the concentration of added acid.[7] In the absence of acid no polarization was detected, but the signals showed broadening. On the contrary, the distinct CIDNP signals were observed at low temperature, *e.g.*, -80°C, even in the absence of acid. Lowering the temperature of the reacting system, thus, causes an effect similar to that brought about by addition of acid. This strongly suggests that an aggregate between Phe *a* and quinone could be formed by adding acid at ambient temperature. Since chlorophyll *a* was reported to form the charge-transfer complex with 2-methyl-1,4-naphthoquinone even in the absence of acid,[8] such a remarkable effect of the added acid may reflect the essential role of metal ion such as Mg^{2+} in the intact reaction center of photosynthesis.

The similar CIDNP signals were observed when Phe *a* was subjected to the light-induced reaction with a variety of quinone:[9] *p*-benzoquinone(*p*-BQ), 2-methyl-*p*-BQ, 2-isopropyl-*p*-BQ, 2-*t*-butyl-*p*-BQ, 2-methoxy-*p*-BQ, 2-dimethylamino-*p*-BQ, 2-chloro-*p*-BQ, 2,5-dimethyl-*p*-BQ, 2-isopropyl-5-methyl-*p*-BQ, 2,5-dichloro-*p*-BQ, 2,6-dichloro-*p*-BQ, 2,3,5-trimethyl-*p*-BQ, 2,3-dimethoxy-5-methyl-*p*-BQ, 2,3,5,6-tetramethyl-*p*-BQ, coenzyme Q_1, coenzyme Q_{10}(ubiquinone-10), and 2-methyl-1,4-naphthoquinone. In every case the α-H of the side chain of quinone showed an enhanced absorption, whereas the ring-H an enhanced emission. These CIDNP signals clearly indicate the light-induced electron-transfer from Phe *a* to quinone generating the radical pair **A**, which, in turn, regenerates Phe *a* and quinone *via* the back process (Eq.1). By analyzing the polarization on the basis of Kaptein's rule,[10] the radical pair **A** is suggested to have the triplet multiplicity.[11]

$$\begin{tikzcd} \text{Phe } a + \text{Quinone} \arrow[r, "h\nu"] & \text{Phe } a^{*} + \text{Quinone} \arrow[r] & \underset{\mathbf{A}}{\overline{\text{Phe } a^{+\cdot}\ \ \text{Quinone}^{-\cdot}}} \arrow[ll, bend left] \end{tikzcd} \qquad \text{(Eq.1)}$$

References and Notes.

1) a) J.Amesz, *Biochim.Biophys.Acta*, 301, 35 (1973). b) G.Tollin, *J.Phys.Chem.*, 80, 2274 (1976). c) R.E.Blankenship and W.W.Parson, *Ann.Rev.Biochem.*, 47, 635 (1972).

2) A.A.Lamola, M.L.Manion, H.D.Roth, and G.Tollin, *Proc.Natl.Acad.Sci.USA*, 72, 3265 (1975). The first approach by CIDNP was misleading, presumably bacause they excited 2,6-dimethyl-*p*-BQ instead of chlorophyll *a* by applying a 1000W-high-pressure mercury-xenon lamp as light-source. *Cf.* M.Tomkiewicz and M.P.Klein, *Proc.Natl.Acad.Sci.USA*, 70, 143 (1973).

3) Phe *a* was obtained by demetalation of chlorophyll *a*, which was isolated from fresh spinach. *Cf.* K.M.Smith Ed., "Porphyrins and Metalloporphyrins", Elsevier Scientific Publishing Co., Amsterdam, 1975.

4) The device used for measurement of CIDNP during illumination was described elsewhere. K.Maruyama, T.Otsuki, A.Takuwa, and S.Arakawa, *Bull.Chem.Soc.Jpn.*, 46, 2470 (1973).

5) Tungsten halide lamp (650W) was used as a source of red-light in combination with the Toshiba R-63 filter.

6) No net chemical change was observed.

7) At present we are inclined to consider that the ease of the formation of an aggregate is dependent upon the concentration of acid, estimating from the change of the ^{1}H-relaxation time of quinone (in this point we will publish elsewhere).

8) H.A.O.Hill, A.J.Macfarlane, B.E.Mann, and R.J.P.Williams, *J.Chem.Soc.,Chem. Commun.*, (1968) 123.

9) The CIDNP was measured at ambient temperature in the presence of acid.

10) R.Kaptein, *J.Chem.Soc.,Chem.Commun.*, (1971) 732.

11) Concerning the electron-transfer process there have been many controversies (see ref.(1)). To elucidate it, the quenching experiments of the photo-excited Phe *a* are under way in our laboratory.

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