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CIDNP STUDY OF LIGHT-INDUCED ELECTRON-TRANSFER FROM HYDROQUINONE TO PHEOPHYTIN *a*

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Light-induced electron-transfer from hydroquinone to pheophytin *a* was investigated by means of CIDNP technique. Spin multiplicity of the excited pheophytin *a* concerned was solvent-dependent.

Recent investigations have demonstrated an important contribution of pheophytin anion radical to the primary charge separation process in the reaction center of photosynthesis.[1] However, the model studies on light-induced anion radical formation process of pheophytin have been rather limited, whereas light-induced formation of pheophytin cation radical has been studied by a variety of techniques.[2] By means of ESR technique Tollin and his colleagues detected electron-transfer from hydroquinone to pheophytin *a* upon illumination.[3] On the other hand, CIDNP technique has never been applied to the similar system in spite of the possible formation of radical pair as a result of electron-transfer from hydroquinone to pheophytin *a*.

Here the light-induced electron-transfer from hydroquinone to pheophytin *a* (Phe *a*) was investigated by means of CIDNP technique. In Fig.1 were illustrated typical CIDNP signals, which were observed upon illuminating a methanol solution of Phe *a* (2×10^{-4}M) in the presence of 2,5-dimethylhydroquinone (2,5-Me-H_2Q)(5×10^{-3}M). The CIDNP signals would result from back electron-transfer in radical pair such as $\overline{\text{2,5-Me-H}_2\text{Q}^{+\cdot}\ \text{Phe}\ a^{-\cdot}}$, once produced via electron-transfer from 2,5-Me-H_2Q to photoexcited Phe *a*. The methyl-H and the ring-H signals of 2,5-Me-H_2Q showed enhanced emission and enhanced absorption, respectively. On the contrary, the completely different polarizations were observed when benzene was used as solvent instead of methanol. That is, the methyl-H and the ring-H signals showed enhanced absorption and enhanced emission, respectively (Fig.2). These results strongly indicate that spin multiplicity of the excited Phe *a* concerning the electron-transfer process is solvent-dependent. By analyzing the CIDNP signals[4] the singlet radical pair is suggested to intervene in methanol, while the triplet radical pair in benzene. Contribution of the different spin multiplicity of the excited Phe *a* was further confirmed by quenching the fluorescence of Phe *a* by hydroquinone. In methanol the fluorescence of Phe *a* was quenched linearly by addition of hydroquinone; on the other hand, in benzene, it was not the case.

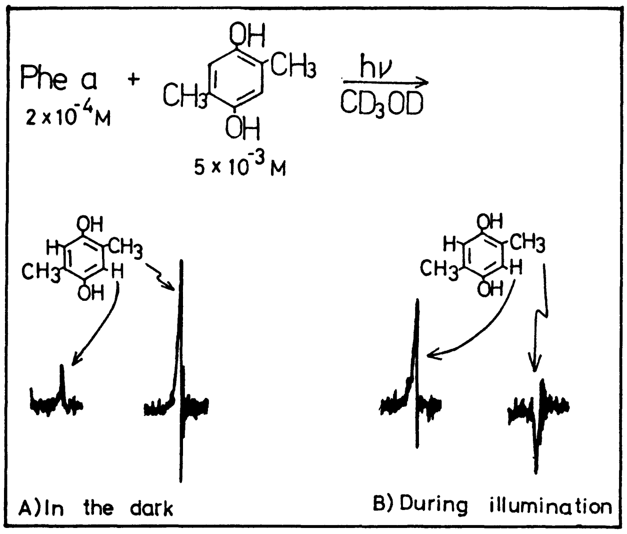

Fig.1 CIDNP signals observed upon illumination of a methanol solution of Phe *a* (2x10^{-4}M) in the presence of 2,5-Me-H_2Q (5x10^{-3}M) at ambient temperature.
(A) In the dark.
(B) During illumination.

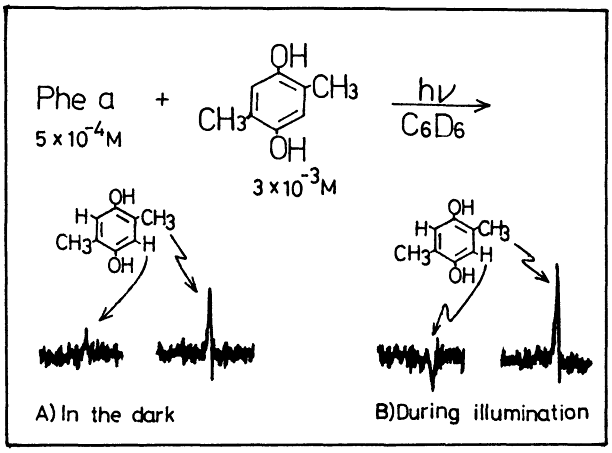

Fig.2 CIDNP signals observed upon illumination of a benzene solution of Phe *a* (5x10^{-4}M) in the presence of 2,5-Me-H_2Q (3x10^{-3}M) at ambient temperature.
(A) In the dark.
(B) During illumination.

Similar light-induced electron-transfer from hydroquinone to Phe *a* was also detected by means of CIDNP technique when other methylated hydroquinones such as 2-methyl-, 2,3-dimethyl-, 2,6-dimethyl-, 2,3,5-trimethyl-, and 2,3,5,6-tetramethylhydroquinone were used as electron donors. Although the CIDNP signals due to Phe *a* could not be detected in these experiments presumably because of its low concentration (∿ 10^{-4}M), the signals due to tetraphenylporphyrin (TPP) as well as hydroquinone were observed when Phe *a* was substituted for TPP in rather high concentration (>10^{-3}M) as an electron acceptor from hydroquinone.

1)J.Jortner, J.Am.Chem.Soc., 102,6676(1980) and the references cited therein.

2)CIDNP technique has also been applied to study the light-induced electron transfer from chlorophyll to quinone. See (a)A.A.Lamola, M.L.Manion, H.D.Roth, and G.Tollin, Proc.Natl.Acad.Sci. USA, 72,3265(1975). (b)K.Maruyama, H.Furuta, and T.Otsuki,Chem.Lett., 1980,857, 1981, 709.

3)a)A.K.Baberjee and G.Tollin,Photochem.Photobiol.,6,315(1966). (b)D.H.Cho and G.Tollin, ibid.,8, 317(1968). (c)R.A.White and G.Tollin,ibid.,14,15(1971).

4)The CIDNP signals were analyzed qualitatively on the basis of Kaptein's rule(R.Kaptein, J.Chem. Soc.Chem.Commun.,(1971)732). 2,5-Me-$H_2Q^{\dot{+}}$:g=2.0038, a_{CH_3} = + 3.81G, a_H= - 0.95G(P.D.Sullivan and J.A.Bolton, J.Am.Chem.Soc.,90,5366(1968)). Phe $a^{\dot{-}}$:g=2.0030(I.Fujita, M.S.Davis, and J.Fajer, J.Am.Chem.Soc.,100,6280(1978)).

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