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FIRST OBSERVATION OF CIDNP SIGNALS DUE TO PORPHYRIN DURING THE COURSE OF LIGHT-INDUCED ELECTRON-TRANSFER FROM PORPHYRIN TO QUINONE

Kazuhiro MARUYAMA, Hiroyuki FURUTA, and Tetsuo OTSUKI
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

The CIDNP signals due to porphyrin as well as quinone were observed upon illumination of porphyrin in the presence of quinone, indicating unambiguously the light-induced electron-transfer from porphyrin to quinone.

As an approach to disclose the details of the charge separation process in the reaction center of photosynthesis, light-induced electron-transfer from chlorophyll(Chl) and/or porphyrin to quinone(Q) has been investigated by a variety of techniques. Of these techniques photo-CIDNP is unique and fruitful because it could give a lot of informations on radical pairs produced upon illumination. Two research groups have reported observation of the CIDNP signals due to quinone upon illumination of chlorophyll in the presence of quinone.[1,2] However, none of them have ever succeeded in detecting the CIDNP signals due to chlorophyll, which should be expected as a result of formation of the radical pair: $\overline{\text{Chl}^{+\bullet}\ \text{Q}^{\bullet-}}$.[3]

In this report detection of the CIDNP signals due to porphyrin as well as quinone is described. This is the first evidence by photo-CIDNP technique, which confirms formation of porphyrin cation radical unambiguously. Thus, the present investigation would complete the story of formation of the radical pair such as $\overline{\text{Chl}^{+\bullet}\ \text{Q}^{\bullet-}}$ upon illumination of chlorophyll in the presence of quinone.

Similar to the chlorophyll-quinone system,[1] addition of acid is necessary for detection of the CIDNP signals in tetraphenylporphyrin(TPP)-quinone system upon illumination of TPP in rather low concentration(*e.g.*, $\sim 10^{-5}$M).[5] Added acid would contribute to the complex formation between TPP and quinone, facilitating the light-induced electron-transfer reaction.[6] Whereas in the presence of acid quinone gave rise to the strong CIDNP signals, none of the CIDNP signals due to TPP was detected presumably because of its low concentration. On the contrary,

starting with rather high concentration of TPP(*e.g.*, ~10^{-3}M), the distinct CIDNP signals due to TPP as well as quinone were observed even without addition of acid. With the concentration of TPP increased, the complex formation between TPP and quinone would be favoured, giving rise to CIDNP signals upon illumination. In Fig.1 is illustrated typical CIDNP signals observed upon illumination of TPP(3×10^{-3}M) in the presence of 2,5-dimethyl-*p*-benzoquinone(1.1×10^{-2}M). Polarization of the methyl-H and the ring-H of quinone shows the similar pattern to the chlorophyll-quinone system(methyl-H:enhanced absorption; ring-H:enhanced emission).[1] Moreover, the ring-H of TPP shows the enhanced emission polarization.[7] These polarized signals indicate unambiguously formation of the radical pair: $\overline{TPP^{+\cdot}\ Q^{-\cdot}}$. TPP is not a unique example observed by us; other porphyrins such as tetraphenylchlorin and tetraphenylbacteriochlorin were found to exhibit the analogous behaviors. In every case the light-induced electron-transfer from porphyrin to quinone was confirmed by detecting the CIDNP signals due to porphyrin as well as quinone.

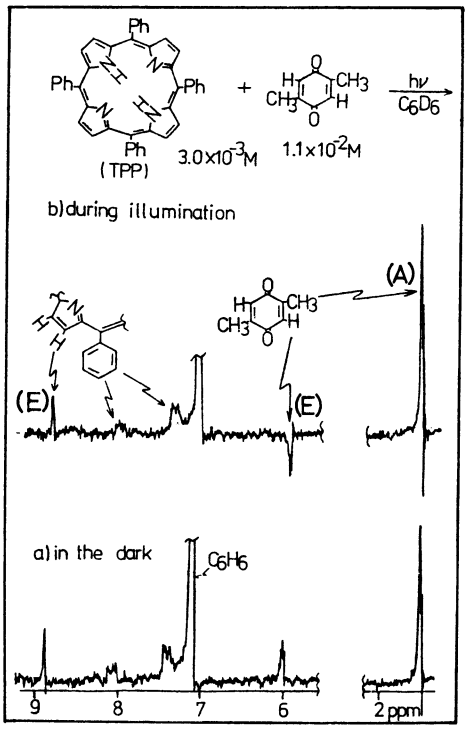

Fig.1. CIDNP signals observed upon illumination of TPP in the presence of 2,5-dimethyl-*p*-benzoquinone at ambient temperature([TPP]:3×10^{-3}M, [2,5-dimethyl-*p*-benzoquinone]:1.1×10^{-2}M, Solvent: C_6D_6).

1)K.Maruyama, H.Furuta, and T.Otsuki, Chem.Lett., 1980, 857.
2)A.A.Lamola, M.L.Manion, H.D.Roth, and G.Tollin, Proc.Natl.Acad.Sci.USA, 72, 3265 (1975).
3)The formation of Phe *a*$^{+\cdot}$ was suggested by the fact that the absorption of Phe *a* is bleached upon illumination of Phe *a* in the presence of quinone. *Cf.*,Ref.(4).
4)K.Maruyama, H.Furuta, and T.Otsuki, The Third International Conference on Photochemical Conversion and Storage of Solar Energy. Presentation I-6(Abstract p 17) (Boulder, Colorado, USA, 1980.8).
5)The strongest CIDNP signals were observed when the molar ratio of TPP to added acid such as CF_3COOD is around two.
6)The complex formation between Phe *a* and quinone upon addition of acid was further suggested by ESR measurements. *Cf.*, Ref.(4).
7)The sign of the *hfc* of the ring-H of TPP$^{+\cdot}$ has not been given unequivocally yet by experiments. Though the enhanced emission polarization shown in the text may not be clear-cut, the reproducibility of the enhanced emission polarization is confirmed without doubt in every experiment.

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