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PORPHYRIN ANION RADICALS DETECTED BY CIDNP TECHNIQUE. FIRST OBSERVATION OF CIDNP SIGNALS DUE TO PORPHYRIN IN THE PHOTOREACTION BETWEEN PORPHYRIN AND PHENOLS

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Photo-CIDNP signals due to porphyrin were observed for the first time in the photoreaction of porphyrin and phenols in benzene. The intensities of CIDNP signals increased in proportion to the oxidation potential of phenol compounds. Relative magnitude of hyperfine coupling constants of porphyrin anion radicals is discussed.

One potent use of Chemically Induced Dynamic Nuclear Polarization (CIDNP) is the determination of the relative magnitude of hyperfine coupling constants (rel. hfcc) of short lived radicals because the signal intensities of CIDNP are much dependent on the magnetic properties (g-factor, hfcc) of their precursor radicals.[1] With this technique, Closs and Sitzmann have succeeded in determining the rel. hfcc's of cation radicals of chlorophyll derivatives in the photoreaction between chlorophylls and benzoquinone, although they have needed some special time resolving instrument.[2] On the other hand, anion radicals of these and related compounds have not been successfully investigated by CIDNP technique due to the lack of the appropriate photoreaction in spite of their important roles in the primary charge separation in photosynthesis.[3] ESR and ENDOR as well as TRIPLE resonance techniques have been applied to disclose the ESR characteristics of their anion radicals. However, few compounds display hfcc's and assignments are occassionally incomplete.[4] Here we report the first observation of CIDNP signals due to porphyrin during the course of photo-induced electron transfer from phenol to porphyrin in non-polar solvent.

When a benzene-d_6 solution of 5,10,15,20-tetraphenylporphyrin (TPP) (1 x 10^{-3} M) and 4-methoxyphenol (1)(5 x 10^{-2} M) was irradiated under argon atmosphere (> 490 nm, halogen lamp 500 W) in the probe of 100 MHz ^{1}H-NMR, the strong CIDNP signal was observed in β-pyrrolic hydrogens of TPP at ambient temperature (Fig. 1). The intensity of the CIDNP signal increased in proportion to the phenol concentration in the range 1 x 10^{-2} M — 3 x 10^{-1} M. Aside from the porphyrin polarization, CIDNP signals due to the ring-hydrogens of 1 were also observed at low concentration of 1 (1 x 10^{-2} M) as weak but distinct emission signals. Judging from the Kaptein's rule, these CIDNP signals were reasonably explained by formation of the triplet ion radical pair; $^3\overline{TPP^{\cdot-}\ 1^{\cdot+}}$.[5] Photo-induced electron transfer from 1 to triplet TPP might occur and in-cage electron return between ion radical pair gives rise to these polarization.[6,7]

Similar CIDNP signals were observed when TPP was subjected to the photo-induced reaction with a variety of phenols, such as 4-methylphenol, 4-t-butylphenol, 2,6- and 3,5-dimethylphenol and 2,4,6-trimethylphenol. The magnitude of the CIDNP signal intensities due to TPP decreased with the oxidation potential of the phenols used and no CIDNP signals were observed in the case of phenol, 4-bromophenol, 4-chlorophenol, and 4-nitrophenol whose oxidation potential are higher than 0.6 V (vs. SCE.).[8] Among phenols examined, 4-methoxyphenol gave the strongest CIDNP signal, presumably because methoxy group could stabilize the phenol cation radical by its electron donating property resulting in the stable ion radical pair formation.

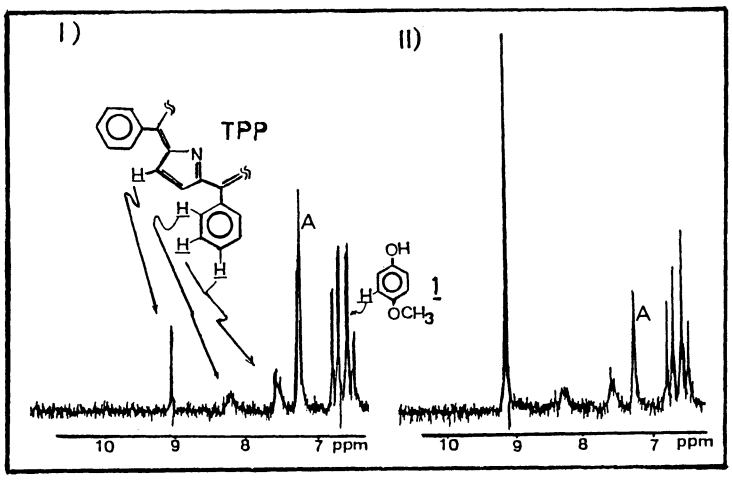

Fig. 1. 100 MHz ^{1}H-NMR CIDNP spectra observed in the photoreaction between TPP and 1 in benzene-d_6.
I) dark.
II) light.
A: solvent.

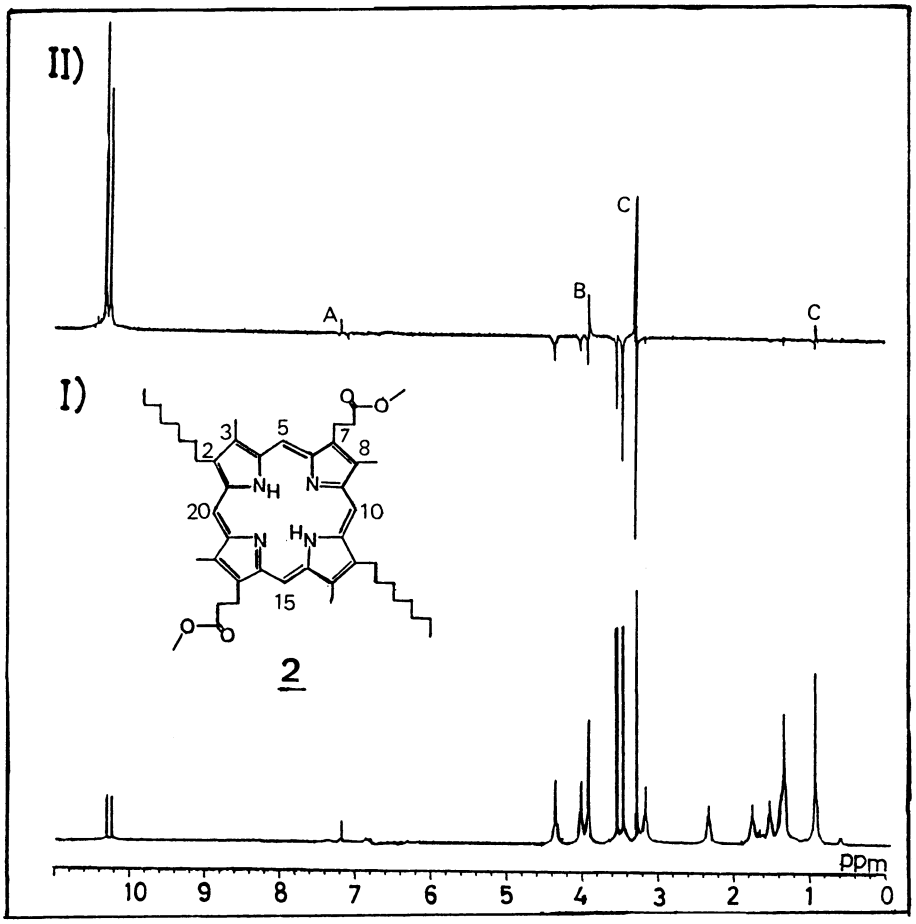

Fig. 2. 400 MHz ^{1}H-NMR CIDNP spectra observed in the photoreaction between 2 and deuterated 1 in benzene-d_6. Accumulation 100 times.
I) dark.
II) light-dark.[9]
A: solvent.
B: OH of 1.
C: incomplete cancellation.

Assignments (ppm)	Rel. hfcc's[a]
10,20-meso-H (10.30)	- 11.40
5,15-meso-H (10.24)	- 9.43
7,17-CH_2 (4.37)	+ 0.70
2,12-CH_2 (4.07)	+ 0.44
3,13-CH_3 (3.54)	+ 0.58
8,18-CH_3 (3.47)	+ 1.00

Table 1.
Assignments of CIDNP signals and relative hyperfine coupling constants (Rel. hfcc's).
a) 8,18-CH_3 signal served as a normalization point.

We have investigated 400 MHz ^{1}H-NMR CIDNP in these photoreactions in order to obtain the information on more complicated porphyrin anion radicals.[9,10] Fig. 2 shows CIDNP spectra observed in the photoreaction between "octyl porphyrin" (2) and deuterated compound 1.[11] The polarized signals for meso-H's and methyl-H's appear in the opposite direction, which indicates the different signs of their hfcc's in the anion radical of 2. Assignments of CIDNP signals and the rel. hfcc's are summarized in Table 1.[12] Thus, this method will be complementary to ENDOR studies of radicals because of the ease of NMR assignments, but it gives only the ratios of hfcc's and requires at least determination of the one of the ENDOR frequencies to convert the ratios to absolute values, as Closs has pointed out.[2]

References

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5) R.Kaptein, J. Chem. Soc., Chem. Commun., 1971, 732.

6) Formation of phenol cation radical was further confirmed by the detection of hydrolysis products in the course of CIDNP measurements; when 2,3,6-trimethyl-4-methoxyphenol was subjected to the photoreaction in the presence of a small amount of water in this porphyrin-phenol-benzene system, formation of trimethylhydroquinone and methanol was observed.

7) We have reported the cation radical formation in the photoreaction between porphyrin and hydroquinone in benzene solution. K.Maruyama, H.Furuta, and T.Otsuki, Chem. Lett., 1981, 1509.

8) M.L.Mihailović and Z.Cekovič, "The Chemistry of the Hydroxyl Group," ed by S.Patai, Wiley, London (1971), p.505.

9) For FT 400 MHz CIDNP experiments, the following pulse sequence was applied; presaturation random pulse (0.1 s)- light pulse (0.3 s)- rf pulse (flip angle, $\theta = 30^{\circ}$). Difference spectra were taken by subtracting dark signals from light signals in order to complete cancellation of unpolarized signals. S.Schäublin, A.Wokaun, and R.R.Ernst, J. Magn. Reson., 27, 273 (1977).

10) In contrast to the 100 MHz CIDNP experiments in the photo-steady-state, 400 MHz CIDNP spectra were taken immediately after irradiation by using computer-controlled mechanical shutter interposed in front of the Ar laser (514.5 nm, 1 W) apparatus.

11) Deuterations were undertaken in order to obtain well resolved CIDNP signals.

12) The rel. hfcc's were calculating with an assumption that polarization factor was proportional to the magnitude of hfcc, (Ref. 2).

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