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PROTON-ASSISTED CHARGE SEPARATION BETWEEN PORPHYRIN AND QUINONE

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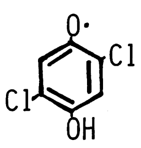
Photo-induced electron transfer reaction between porphyrin and quinone was investigated by means of CIDNP technique in benzene. In the presence of acid, formation of neutral semiquinone radical instead of quinone anion radical was confirmed by using 2,5- and 2,6-dichlorobenzoquinone as electron acceptors.

As simple models of initial event in photosynthesis, photo-induced electron transfer reaction between porphyrin and quinone (Q) has attracted considerable interest and thus has been intensively studied with a variety of techniques. Among these, photo-CIDNP technique has been applied by the groups of Roth$^{1)}$ and Closs$^{2)}$ to the detection of ion radical pair formed in the reversible photoreaction between chlorophylls and quinones in protic solvents (CD_3OD, $CD_3OD/CDCl_3$). However, discrete evidence has not been put forth whether quinone anion radical ($Q^{\overline{\cdot}}$) or neutral semiquinone radical ($QH\cdot$) is responsible for the CIDNP effects due to benzoquinone in their conditions. On the other hand, no CIDNP signals were observed in non-polar solvent because of rapid reverse electron transfer in the geminate radical ion pair and/or exciplex formation.$^{3)}$ In the present communication we will report the CIDNP study of photo-induced electron transfer reaction between porphyrin and quinone in benzene solution.

When a benzene-d_6 solution of 5,10,15,20-tetraphenylporphyrin (TPP) (5×10^{-4} M) and p-benzoquinone $\underline{1}$ (1×10^{-2} M) was illuminated in the presence of trifluoroacetic acid (1×10^{-2} M) with light of wavelength longer than 490 nm under argon atmosphere, strong emission signal due to $\underline{1}$ was observed.$^{4)}$ Without the acid, no signal change was observed. However, it is also impossible to determine which of two, $Q^{\overline{\cdot}}$ and $QH\cdot$, is involved as the intermediate in this reaction. The remaining problem was solved by the use of 2,5- and 2,6-dichlorobenzoquinone ($\underline{2}$,$\underline{3}$) as electron acceptors. In Fig.1 is illustrated CIDNP signals observed in the presence of $\underline{2}$ and $\underline{3}$ (1×10^{-2} M) instead of $\underline{1}$. Opposite direction of polarization due to quinone ring-H was only consistent with the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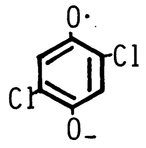
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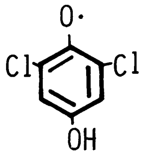
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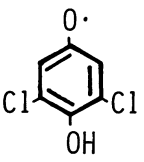
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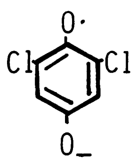
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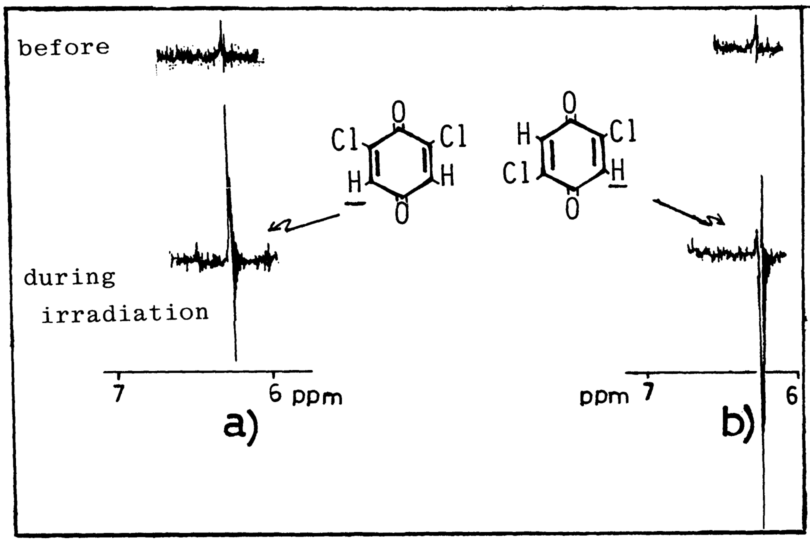

Fig.1.
CIDNP signals observed during photoreaction between TPP and quinone,
a) 2,6-dichloroquinone
b) 2,5-dichloroquinone
in the presence of acid in benzene-d_6.

formation of neutral semiquinone radical 2a and 3a (3b could be excluded because of its thermodynamical instability), since the hyperfine coupling constants (hfcc's) of the ring-H's (a_H) in 2a and 3a have different signs $a_{H(o)} < 0$, $a_{H(m)} > 0$,5) but those in the corresponding anion radicals 2b, 3c should have the same ($a_{H(o)}$, $a_{H(m)} < 0$)6). In the phenoxy type radical 2a , two ring-H would contribute to the polarization in different manners because of their different signs of the hfcc. Of these the larger magnitude of the hfcc of ortho-H gives rise to the net emission polarization against CIDNP effect due to meta-H.7)

Since exciplex formation is generally accepted in photochemistry between porphyrin and quinone in non-polar media, these results strongly indicate that the charge separated state involving $TPP^{+\cdot}$ is stabilized by the formation of neutral semiquinone radical (QH·) counter part, which has sufficient life time to afford CIDNP signals.8)

References

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4) Illumination was performed with an Ushio-halogen lamp (500W) equipped with a Toshiba VY-49 color filter. Sample solutions were bubbled with argon gas (99.99%) immediately before illumination.
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7) For 2,5-dichloroquinone $\Gamma_{ne} = a\cdot\mu\cdot\varepsilon\cdot\Delta g < 0$ ($a < 0$, $\mu > 0$, $\varepsilon > 0$, $\Delta g > 0$). R.Kaptein, J. Chem. Soc., Chem. Commun. 1971, 732.
8) 10^{-9}-10^{-8} s are required for S-T mixing based on radical pair theory, R. Kaptein, "Chemically Induced Magnetic Polarization ," ed by T.L.Muss et. al., Reidel, Holland (1977), p.1.

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