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DISCRETE RADICAL SPECIES DEPENDENT UPON SOLVENT AS DETECTED BY CIDNP IN THE LIGHT-INDUCED ELECTRON TRANSFER FROM HYDROQUINONES TO PHEOPHYTIN *a*

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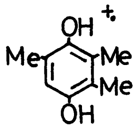
Light-induced electron transfer from hydroquinones to Phe *a* was studied by means of CIDNP technique. Depending upon the solvent, electron transfer proceeds in different manners. In benzene, ion radical pair; hydroquinone cation radical and Phe $a^{\bar{\cdot}}$, of the triplet spin multiplicity was formed, whereas neutral radical pair;phenoxyl radical and Phe a-H•, of the singlet spin multiplicity in methanol.

In the previous report,[1] the CIDNP signals observed upon illumination of pheophytin *a*(Phe *a*) in the presence of hydroquinones were described to be solvent-dependent, suggesting the different spin multiplicity of the ion radical pair involved:the singlet radical pair in methanol and the triplet radical pair in benzene. However, the CIDNP patterns observed in a system of 2,3,5-trimethylhydroquinone(2,3,5-Me-HQ)-Phe *a* dissolved in methanol could not be explained simply by assuming the formation of the ion radical pair;$\overline{\text{hydroquinone cation radical } \mathbf{1} \text{ Phe}\, a^{\bar{\cdot}}}$, of the singlet spin multiplicity as suggested previously.[1] As the result of the back electron transfer in the ion radical pair, three methyl-H's should be expected to give rise to the same polarization, since the hyperfine coupling constants(hfcc's) of all the methyl-H's in **1** have the positive sign.[2] Actually the methyl-H indicated as ① appeared in enhanced absorption, whereas the methyl-H's ② and ③ in enhanced emission (Fig.1(B)).[3] These results strongly indicate that an unsymmetrical neutral radical species such as phenoxyl-type radical **2a** is involved in the process, paired with Phe a-H•. When the contribution of the neutral radical pair;$\overline{\mathbf{2a} \text{ Phe } a\text{-H}\bullet}$,of the singlet spin multiplicity was assumed, the results obtained in methanol were explained clearly, since the hfcc's of the methyl-H's in phenoxyl-type radical were reported to have the different signs:$a_{CH_3(o)}>0$, $a_{CH_3(m)}<0$.[4] Although the possible formation of two isomeric radicals as illustrated in **2a** and **2b** is expected, starting with hydroquinone without having C_2 symmetry, one isomer **2a** would be formed much more favourably because of its thermodynamic



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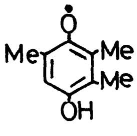
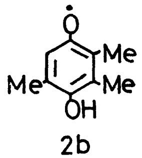
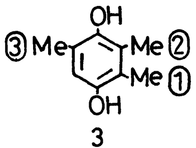


2a



2b



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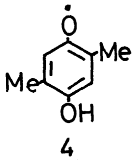

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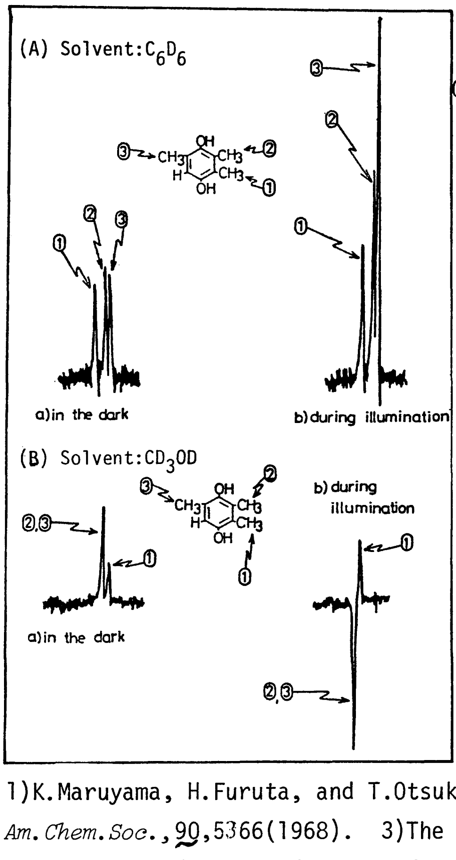
stability[5] The CIDNP signals due to the methyl-H of 2,5-dimethylhydroquinone(2,5-Me-HQ) in the light-induced reaction with Phe *a* in methanol appeared in enhanced emission[1] In the phenoxyl-type radical **4** derived from hydroquinone of C_2 symmetry such as 2,5-Me-HQ, two methyl-H's,whose chemical shifts are the same,would contribute to the polarization in different manners because of the different signs of the hfcc's of the two methyl-H's[4] Of these the larger absolute value of the hfcc of the *o*-methyl-H could give rise to the stronger polarization, resulting in the overwhelming effect to the net polarization. Although the detailed mechanism of the formation of the neutral radical pair such as $\overline{\mathbf{2a}\ \text{Phe}\ a\text{-H}\cdot}$, remains to be clarified, the radical pair would be formed by the initial electron transfer and the subsequent proton transfer, which is facilitated by the higher polarity of methanol as solvent.

In benzene the CIDNP signals(Fig.1(A)) were explained by assuming the intervention of the ion radical pair;$\overline{\mathbf{1}\ \text{Phe}\ a^{\cdot}}$, of the triplet spin multiplicity as described before[1] Thus, the solvent dependency of the formation of the radical pair is summarized as in Eq.(1). These results would reflect an important contribution of the medium to the light-induced electron transfer in the reaction center of photosynthesis.



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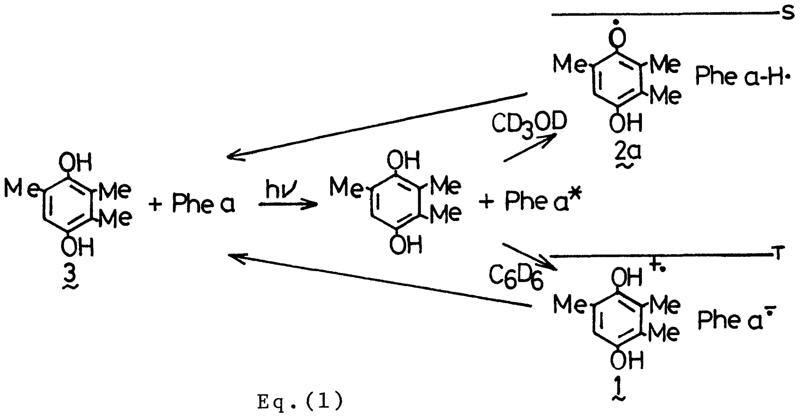

Eq.(1)

Fig.1. NMR spectra of Phe *a*(∿10^{-4}M) and 2,3,5-Me-HQ(∿10^{-3}M) at ambient temperature. (A)Solvent:benzene-d_6; (a)in the dark, (b) during illumination. (B)Solvent:methanol-d_4; (a)in the dark, (b) during illumination.

1)K.Maruyama, H.Furuta, and T.Otsuki, *Chem.Lett.*,(1981)1025. 2)*Cf.*P.D.Sullivan and J.R.Bolton, *J. Am.Chem.Soc.*, **90**,5366(1968). 3)The chemical shifts of three methyl-H's were determined unequivocally by using the deuterated compounds. 4)*Cf.*T.A.Claxton, T.E.Gough, and M.C.R.Symons, *Trans.Faraday Soc.*, **62**,279(1966). T.E.Gough, *ibid.*, **62**,2321(1966). For example, the hfcc's of 4-hydroxy-2,3,5,6-tetramethylphenoxyl radical were as follows:$a_{CH_3(o)}$=+4.80*G*,$a_{CH_3(m)}$=-0.68*G*. 5)B.B.Adeleke and J.K.F.Wan, *J.Chem.Soc.Perkin II*,(1980)225.

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