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# CIDNP STUDY OF PHOTO-INDUCED RADICAL REACTION. EFFECT OF APPLIED MAGNETIC FIELD

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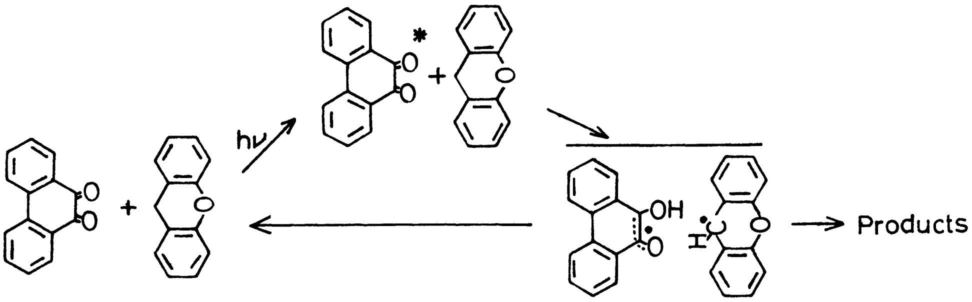
The strength of the applied magnetic field was found to be an important factor in detecting the CIDNP signals in the photo-induced radical reaction. The effect of the magnetic field can be understood on the basis of the radical pair theory.

Since its discovery, CIDNP technique has been applied successfully to elucidate the detailed mechanism of radical reactions, still adding an increasing number of the experimental and/or theoretical findings.

Here we wish to report that the strength of the applied magnetic field could be an important factor in detecting the CIDNP signals. Although the photochemical reaction of 9,10-phenanthrenequinone with hydrogen donors such as xanthene has well been investigated by means of $^1$H-CIDNP technique (by using 60 MHz- and 100 MHz-CW-NMR machine, whose magnetic field is ∿14 kG and ∿24 kG, respectively),[1,2] $^{13}$C-CIDNP signals of the similar system have never been reported presumably because of their poor sensitivity. However, the recent improvement of $^{13}$C-NMR technique allowed us to detect the $^{13}$C-CIDNP signals during the course of the photochemical reaction of 9,10-phenanthrenequinone with hydrogen donors. In Fig.1(B), the $^{13}$C-CIDNP signals observed by the 90 MHz-FT-NMR machine (whose magnetic field is ∿21 kG) are illustrated, indicating the unequivocal evidence of the radical pair mechanism, compatible with the previously proposed one(see Scheme 1). However, by using the 400 MHz-FT-NMR machine (whose magnetic field is ∿94 kG), the similar CIDNP signals could hardly be detected in the reacting system. Thus, the detection of the CIDNP signals are quite dependent upon the strength of the applied magnetic field in the photo-induced reaction of 9,10-phenanthrenequinone with hydrogen donors.



Scheme 1.

On the other hand, the $^1$H-CIDNP signals of the photo-induced reaction of flavin with phenols were reported to be easily detected by using the 360 MHz-FT-NMR machine (whose magnetic field is ∿85 kG) as well as the 100 MHz-CW-NMR machine.[3)] Here the dependency of the applied magnetic field could not be observed or would be very small if any. Thus, the two reacting systems described above could be concluded to show the different behaviors upon the strength of the applied magnetic field.

Based upon the accepted radical pair theory, the $T_0$-S mixing in the radical pair is effected by the difference, $\Delta\omega$, of the Larmor precession frequency of the component radicals as shown in Eq. 1 , which is divided into two parts: g-value dependent term and hyperfine-coupling dependent term.4) Of these the CIDNP effects

$$\Delta\omega = \Delta g\beta H + \Sigma a_i m_i \quad (1)$$

could be transferred from the radical pair to the resulting diamagnetic products through the hyperfine-coupling dependent mixing of $T_0$-S states ($\Sigma a_i m_i$) in the radical pair. The relative contribution of these two terms should be dependent upon the strength of the applied magnetic field, since the g-value dependent term ($\Delta g\beta H$) is a function of the applied magnetic field. In the present system the difference in the g-values ($\Delta g$) is estimated as ∿0.0026 which is rather large compared with that of flavin-phenols system as mentioned above($\Delta g$:∿0.0002).5) The different behaviors of the above two systems under the strength of the applied magnetic field would be understood by the important contribution of the g-value dependent term ($\Delta g\beta H$) to the mixing of $T_0$-S states of the radical pair in the 9,10-phenanthrenequinone-hydrogen donor system, resulting in the weak polarization at the higher magnetic field such as ∿94 kG.6)

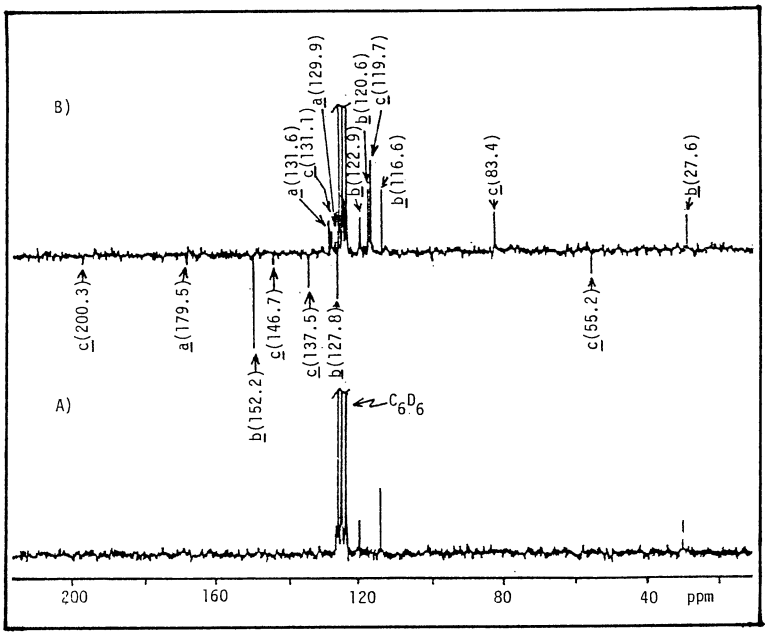


Fig.1. $^{13}$C-CIDNP signals observed during the photochemical reaction of 9,10-phenanthrenequinone with xanthene(The magnetic field:∿21 kG. Accumulation:50 times. Solvent:$C_6D_6$). A)Before irradiation B)During irradiation. The numbers in parentheses are the corresponding chemical shifts in ppm. The signals indicated as a are assigned to those of 9,10-phenanthrenequinone, the signals b to those of xanthene and the signals c to those of the products.

Summarizing the results, the CIDNP signals originated from the radical pair whose $\Delta g$-value is rather large, could hardly be detected at higher magnetic field such as ∿94 kG as used in the 400 MHz-NMR machine, although the quantitative analysis remains to be developed.

## References

1)The product analysis was also performed and supported the reaction mechanism shown in Scheme 1. Cf. K.Maruyama,T.Otsuki,and Y.Naruta, Bull.Chem.Soc.Jpn.,49,790(1976) and the references cited therein.

2)The magnetic field dependence of the intensity of CIDNP signal was suggested in the thermal decomposition of benzoylperoxide. Cf. H.Fischer and J.Bargon, Acc.Chem.Res.,2,110(1969).

3)R.Kaptein,K.Dijkstra,F.Muller,C.G.vanSchagen,and A.J.W.Visser,J.Mag.Res.,31,171(1978) and the references cited therein. The similar results were obtained independently by us and will be published elsewhere.

4)L.T.Muus,P.Atkins,K.A.McLauchlan,and J.B.Pedersen ed.,Chemically Induced Magnetic Polarization, D.Reidel Pub.Com., Dordrecht, 1977. In Eq.1 , $\Delta g$ represents the difference in the g-values of the component radicals, $\beta$ Bohr's magneton, H the applied magnetic field (in G), $a_i$ the hyperfine-coupling constant of the nucleus i in the radical state and $m_i$ the magnetic quantum number of the nucleus i, respectively.

5)$\Delta g$-Value is estimated on the basis of the following g-values reported: 9,10-phenanthrene semiquinone radical, g=2.0052; benzyl radical, g=2.0026, flavin anion radical, g=2.0032, hydroquinone cation radical, g=2.0034.

6)The photochemical reaction of 9,10-phenanthrenequinone with acetaldehyde was found to show the similar magnetic field dependence to the present system. In the presumed radical pair: 9,10-phenanthrene semiquinone radical and acetyl radical, $\Delta g$-value is estimated to be ∿0.0045.

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