SNP Studies on the Structure of the Short-Lived Radical Pair Generated in the Hydrogen Abstraction Reaction of Anthraquinone from Xanthene

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Nuclear-polarization-detected ESR (NP-detected ESR) spectra were measured in the hydrogen abstraction reaction of anthraquinone from xanthene for the purpose of assigning of the radical pair and the geminate product generated from the radical pair. By properly choosing of the nuclear spin of the product, we can obtain the SNP spectra of the two component radicals individually. The sign of the hyperfine coupling constant is discussed and the SNP spectra are assigned as 9-xanthenyl radical and 10-hydroxy-9-anthryloxyl radical from the spectrum simulated by the radical pair theory. Additionally, the features of the cross relaxation process in the intermediate free radical are discussed by examining the DNP components of spectra.

Analysis of the structure of the radical pair created in the first step of photo-induced hydrogen abstraction reaction of carbonyl compounds is very important for understanding the spin polarization and magnetic effects.[1] The SNP[2] (stimulated nuclear polarization) technique, which is a component of the nuclear-polarization-detected ESR (NP-detected ESR) spectrum, is one powerful method for elucidation of the spin structure of radical pair. One of the characteristics of the SNP method is that one can detect the unclei of products by high-resolution NMR spectroscopy. Utilizing this characteristic we can assign the individual radicals forming the radical pair and also can assign the products generated from that radical pair. Specifically, if a radical pair consists of radical A having a proton H_A and radical B having a proton H_B, we can separately observe the SNP spectra of radical A and radical B by monitoring the NMR peaks of proton H_A and proton H_B, respectively. This is in contrast to the fact that RYDMR (Reaction yield detected magnetic resonance) or time-resolved ESR only gives the overlap of the spectra for the radical components, and in some cases the identification of the spectrum of one radical component is rather difficult. In this way the SNP method is advantageous to assign the radicals that form the radical pair.

In a previous paper,[3] we investigated the hydrogen abstraction reaction of anthraquinone from xanthene by high-field CIDNP and CIDEP methods. We suggested the existence of two kinds of geminate recombination products; however, we failed to assign the radical pairs that generate these products unambiguously because of the following reasons: Both CIDNP and CIDEP spectra should basically reflect the properties of radical pair provided the polarization is mainly governed by radical pair mechanism. In our CIDNP study, however, the assignment of radical pair was difficult because of the following reasons. First of all, the magnetic parameters such as Δg value are unknown, and further, the contribution of cross-relaxation was hard to estimate. In our CIDEP study, the assignment of radical pair was also difficult because the electron spin polarization was mostly governed by the triplet mechanism, and consequently the spectrum showed the hyperfine structure of only 9-xanthenyl radical. We could only estimated the structure of the radical pair in view of the products and the free radicals assigned by CIDEP spectrum.

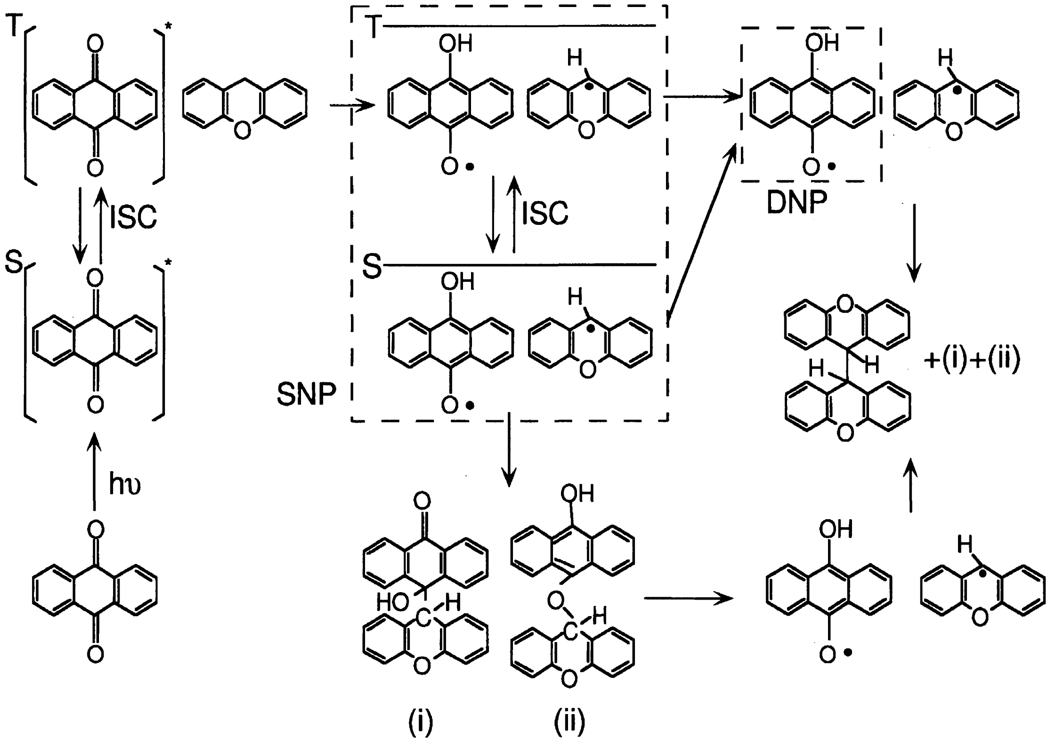
This paper aims to remove the ambiguity discussed above. In order to establish unambiguous correlations between radical pairs and products, we measured SNP spectra by monitoring four NMR peaks that correspond to different nuclei of the products. By this method, the structures of individual radical pairs that generate each specific recombination product can be unambiguously assigned.

Experimental

Experimental setup is identical to that reported in a previous paper.[4] The sample was irradiated by an Ushio 500 W Hg–Xe lamp in a JEOL RE-1X ESR magnet and was transferred to a sample tube in a JEOL JNM-100 NMR spectrometer, where unclear polarization was measured. Sample transfer was carried out by applying the pressure of nitrogen gas.

Results and Discussion

The reaction scheme obtained in the high field CIDNP study of the hydrogen abstraction reaction of anthraquinone from xanthene is shown in Scheme 1. In the previous study,[3] we have suggested the existence of two kinds of recombination products (i) and (ii). The CIDNP intensity of the product (i) is much larger than that of (ii), and we concluded that the main geminate recombination product is the product (i). But the estimation by the consideration of the spin densities calculated by INDO method: $\rho(11)=0.55>\rho(10)=0.39$ gives a different result. The slow diffusional rotation of 10-hydroxy-



Scheme 1. Reaction scheme of the photoinduced hydrogen-abstraction reaction of anthraquinone from xanthene.

9-anthryloxyl radical restricts the possibility of bond formation with 9-xanthenyl radical at the oxyl oxygen. In contrast, the relative orientation of the radicals that forms the radical pair generated from the free radical encounter is random. Therefore the possibility of the generation of recombination product (ii) is much higher at free radical encounter than that in the geminate process. The nuclear polarization was observed only in the geminate recombination product and no CIDNP of escaped products (dimer of the 9-xanthenyl radical) was observed; this is probably due to a fast relaxation process in the free radicals.

Although we have determined the reaction scheme from the high-field CIDNP spectrum, the reaction schemes discussed above are not completely clear because the nuclear polarization may change due to the cross-relaxation in the intermediate free radicals. Nuclear polarization generated from the radical pair without the disturbance of the cross-relaxation may be studied by extracting the SNP component from the NP-detected ESR spectrum.[5]

Figure 1 shows the NMR spectrum observed without light irradiation. The spectrum is assigned as solely due to the reactant molecules (anthraquinone and xanthene) and the nondeuterated solvent molecule (impurity of deuterated chloroform). During the light irradiation, we found four small CIDNP signals at the positions indicated as A, B, C, and D. We assign all the four CIDNP signals as being from the geminate recombination product, by analogy of the results of our high-field CIDNP.[3] The CIDNP signal designated as A is assigned as the aliphatic proton of the product (i), and this assignment is also shown in Fig. 1. Peaks B, C, and D are due to aromatic protons. However, it is hard to make an exact assignment. It is certain that peak B corresponds to product (i) or (ii) coming from 9-xanthenyl radical. Similarly, peaks C and D correspond to the product coming from 10-hydroxy-9-anthryloxyl radical. We obtained NP-detected ESR spectra by plotting the change of the nuclear polarization during the microwave irradiation as a function of the external magnetic field for peaks A, B, C, and D. These spectra are shown in Figs. 2 and 3.

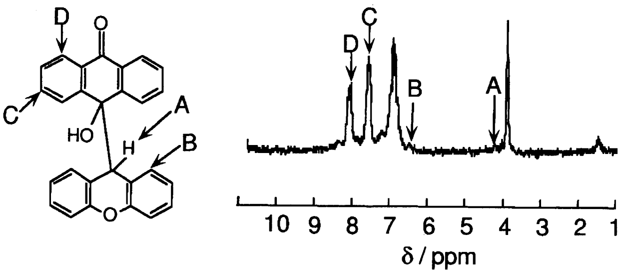


Fig. 1. NMR spectra in photolysis of anthraquinone and xanthene in $CDCl_3$.

Spectra Obtained for Peaks A and B. The observed NP-detected ESR spectra for peaks A and B are shown by dots in Fig. 2. These spectra are very similar. This fact is unexpected because the hyperfine coupling constants of 9-xanthenyl radical for the protons that correspond to peaks A and B are much different; reported hyperfine coupling constants[6] of 9-xanthenyl radical are shown in Fig. 2. In order to understand this unexpected behavior, we theoretically calculated the SNP spectra for these two protons. In the calculation, we applied the perturbation method proposed by Mikhailov et al.[7] The sign of the hyperfine coupling con-

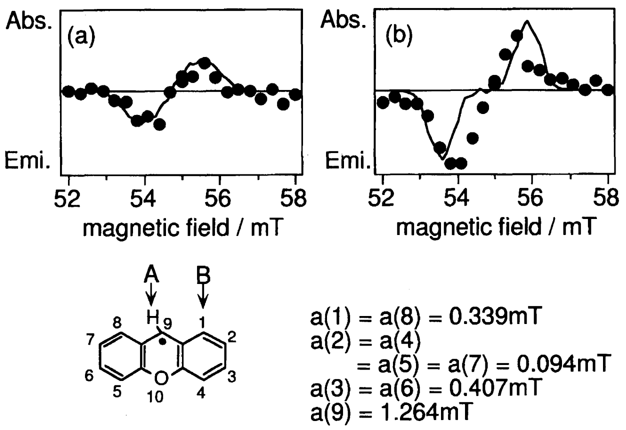


Fig. 2. NP-detected ESR spectra. a) for peak A, and b) for peak B, and the values of hyperfine coupling constants of proton in 9-xanthenyl radical. The solid line shows the calculated SNP spectrum.

stants for peak A and peak B can easily be determined from the phase (E/A) of the observed SNP spectra; negative for both of the protons for peak A and peak B. The spectra calculated by using appropriate parameters[8] are drawn by solid lines in Figs. 2a and 2b. The calculated spectrum for pear A agrees quite satisfactorily with the observed one (see Fig. 2a). In contrast, for peak B, the shape of the observed spectrum is similar to the spectrum calculated for peak A rather than that for peak B. This fact shows the existence of some nuclear polarization transfer from peak A to peak B during the sample transfer. In conclusion, one component of the radical pair is 9-xanthenyl radical and the main geminate product is product (i). This correspondence between the component of the radical pair and the product agrees with the suggestion from the high-field CIDNP and CIDEP in the previous work.

Spectra Obtained for Peaks C and D. The NP-detected ESR spectra for peaks C and D are shown in Fig. 3. These spectra show that the nuclear polarization is the sum of SNP (A/E) and DNP (net E). We can determine from the emissive DNP that the mechanism of the cross relaxation for the aromatic protons in the 10-hydroxy-9-anthryloxyl free radical is $\Delta m = 2$ (Δm is change of the total quantum number for Z component of the electron spin and the nuclear spin). Since the SNP components in Figs. 3a and 3b have an A/E pattern, the sign of hyperfine coupling constants is positive. The hyperfine coupling constants[9] corresponding to peak C and peak D are the same (see Fig. 3). Therefore the SNP intensity and the spectral shape in Figs. 3a and 3b should be same. The theoretical spectra calculated by the method discussed above are drawn by a solid line in Fig. 3. From the similarity between the calculated and observed spectra, we can assign the SNP spectra as the 10-hydroxy-9-anthryloxyl radical.

Discussion about the Reaction Scheme. All the observed SNP spectra support reaction Scheme 1. The main radical pair is composed of 10-hydroxy-9-anthryloxyl radical and 9-xanthenyl radical, and the main product generated from this radical pair is product (i). There is no nuclear polarization of aliphatic proton in either product (ii) or dimer of XH. This fact shows that both of the products are escaped product. Furthermore the nuclear relaxation time of the aliphatic proton of 9-xanthenyl radical is short as compared with its lifetime. The existence of the DNP for the peak C and peak D shows that the lifetime of the 10-hydroxy-9-anthryloxyl radical is longer than the time scale of the polarization transfer from electron spin to nuclear spin by the cross relaxation.

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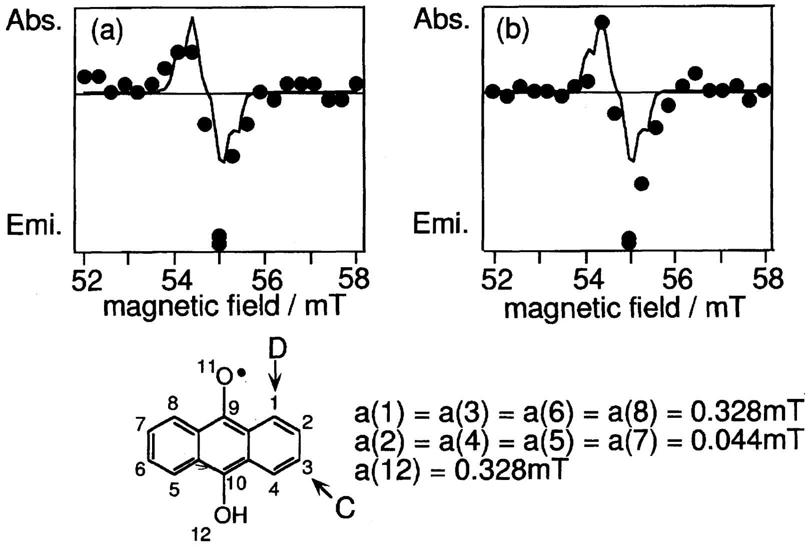

Fig. 3. CIDNP detected ESR spectra a) for peak C, and b) for peak D, and the values of hyperfine coupling constants of hydrogen in 10-hydroxy-9-anthryloxyl radical. The solid line shows the calculated SNP spectrum.

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5) SNP spectrum is formed from SNP components and DNP components. The SNP is generagted from the radical pair, and the DNP is generated by the cross relaxation in the free radical. The shape of SNP component is E/A (emission at lower external magnetic field and absorption at higher external magnetic field) or A/E, and that of DNP component is emission or absorption for all external magnetic field. Therefore, we can easily distinguish between the SNP component and the DNP component from the spectral shape of the NP-detected ESR spectrum.

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