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Control of a Photochemical Reaction by Manipulating the Electron Spins of a Transient Radical Pair as Evidenced by HPLC Analysis

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Product analysis was made for the photoreduction of anthraquinone in SDS micellar solution under the various magnetic fields with a simultaneous microwave irradiation. It has been confirmed that control of a chemical reaction is possible by inducing the ESR transitions of the intermediate radical pair.

Many magnetic-field-dependent phenomena have been observed so far and those are explained with the radical pair model of CIDNP.[1,2] The spin coherence of the radical pair, which is changed by an external magnetic field, affects the following reactions.[3] Irradiation of a microwave field also causes some modifications on these magnetic field-dependent phenomena because it flips the electron spins of the radical pair under the resonance magnetic field.[4-6] A most interesting demonstration of this resonant-microwave effect may be the control of a chemical reaction which was first demonstrated with the aid of the spin trapping technique.[7-9] In these experiments ESR spectrum of the radical pair is obtained by plotting the spin adduct yield with respect to the external magnetic field under which the reaction proceeded. We call this method product-yield-detected ESR (PYESR),[8] which is similar to RYDMR (reaction-yield-detected magnetic resonance) where ESR spectrum of the radical pair is obtained through detecting mostly the recombination fluorescence.[5,6] Although these techniques are convenient to detect the ESR spectrum of a radical pair, some ambiguities remain about the total feature of the reaction system. So, one might consider that what we

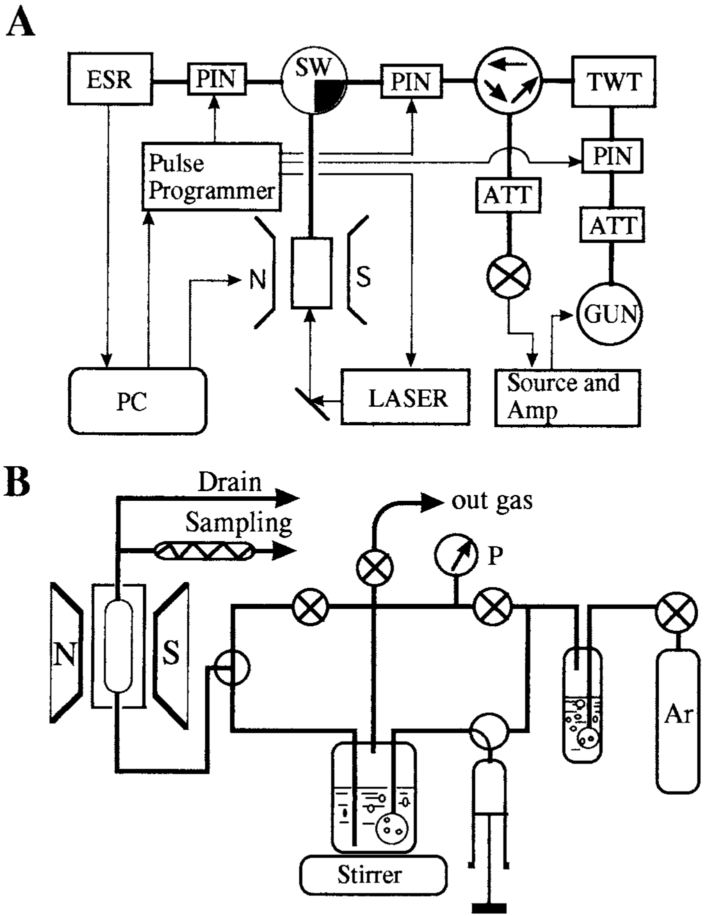

Fig. 1. Apparatus to control a photochemical reaction using spin manipulation technique. A: Laser and microwave unit, B: Flow system for sample charging. Sample solution degassed with humidified argon flows into the irradiation cell in the ESR cavity.

observed is not in the main process but in a rather minor process, which happened to be dependent on the magnetic and microwave fields. However this possibility can be denied, at least for PYESR, by indicating that the molar concentration of the spin adduct is large enough as the main product of the reaction. In the present study we analyzed the products of the same reaction system as in a previous study[9] by using the high performance liquid chromatography (HPLC). This is the first report describing the total analysis of the products of a reaction which is controlled by spin manipulation of the transient radical pair.

Figure 1 shows the apparatus used in the present study. The microwave circuit (**A**) is divided into two parts, one is for irradiation and the other is for observation of the spin adduct, either of which is connected to the cavity through a mechanical waveguide switch. The PIN diodes and the laser (GCR 160-10; Spectra Physics; λ=355 nm) are controlled by a pulse generator (SY8220, Iwatsu). A personal computer is used to control the pulse generator as well as an ESR spectrometer (RE-1X, JEOL). Tubes and valves of the flow system (**B**) are made of stainless steel. The inner thickness, the width, and the length of the flat cell made of high purity qualtz are about 0.25, 10, and 40 mm, respectively. A capillary tube is put at the end of the flow system as a resistance to control the flow rate by a gas pressure. Anthraquinone (AQ) and Xanthene (XH_2) were obtained from Wako Pure Chemicals (Tokyo, Japan) and purified by recrystallization from ethanol, SDS was from Nakarai Chemicals (Kyoto, Japan) and used without further purifications. Dibromonitrosobenzenesulfonate (DBNBS) was synthesized following a literature.[10] Concentrations of AQ and DBNBS in a 0.2 M SDS micellar solution were 0.03 and 0.5 mM, respectively. The repetition rate and the power of the YAG laser were 10 Hz and 160 mJ, respectively. Duration and power of the microwave pulse were 16W (ca. 0.4 mT in amplitude) and 10 μs, respectively. The sample solution was flowed at a constant rate of 0.3 ml/min, and was collected from the outlet of the capillary tube. The solution was frozen immediately after collection using liquid nitrogen and was thawed before HPLC analysis, which was made with a Waters 302 apparatus with a photodiode array detector which can monitor the UV-spectrum simultaneously. The column used was a reversed phase type (Pursil C-18, Millipore) with a diameter of 4.6 mm and a length of 150 mm. The eluent was a mixture of water and methanol at the ratio of 2:8, and the flow rate was 1.0 ml/min.

The present reaction system has been well studied as a representative one whose reaction is dependent on the magnetic field.[11] The reaction mechanism was assumed in previous works as follows;[8,9]

$$\begin{array}{lcll}
\mathrm{AQ} & \rightarrow & {}^3\mathrm{AQ}^* & (1)\\
{}^3\mathrm{AQ}^* + \mathrm{SDS} & \rightarrow & {}^3(\mathrm{AQH}\cdot\ \cdot\mathrm{SDS}) & (2)\\
{}^3(\mathrm{AQH}\cdot\ \cdot\mathrm{SDS}) & \rightarrow & {}^1(\mathrm{AQH}\cdot\ \cdot\mathrm{SDS}) & (3)\\
{}^1(\mathrm{AQH}\cdot\ \cdot\mathrm{SDS}) & \rightarrow & \mathrm{AQH\text{-}SDS} & (4)\\
{}^3(\mathrm{AQH}\cdot\ \cdot\mathrm{SDS}) & \rightarrow & \cdot\mathrm{AQH} + \cdot\mathrm{SDS} & (5)\\
\cdot\mathrm{SDS} + \mathrm{ST} & \rightarrow & (\mathrm{SDS})\mathrm{ST}\cdot & (6)
\end{array}$$

Where AQH · represents anthrasemiquinone. The rate of intersystem crossing in (3) is modified by the magnetic and microwave fields. The escaped

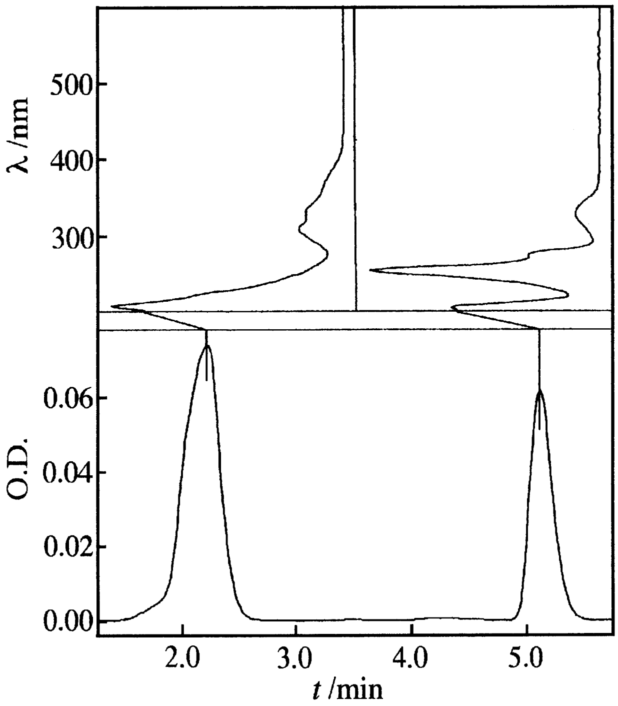

Fig.2. HPLC and UV spectra at the peak tops observed before reaction for SDS micellar solution of AQ and DBNBS.

SDS radical is trapped by a spin trap (ST) to form the corresponding spin adduct, which is stable and can be observed with conventional ESR . Since reaction (4) proceeds very rapidly, the escaped radicals may be produced exclusively from the triplet radical pair.

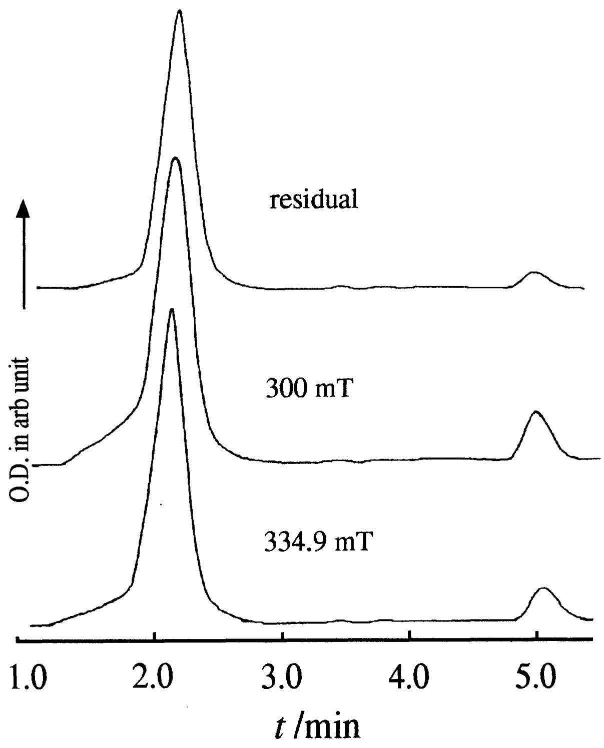

Fig.3. HPLC's of the reaction products for (DBNBS, AQ)/SDS at the magnetic field of: upper, residual field; middle, 300 mT; lower, 334.9 mT. Microwave was irradiated in all cases. At 334.9 mT anthrasemiquinone becomes on resonance.

In the present study, we analyzed the reaction product using the HPLC method. Figure 2 shows the HPLC of the solution before reaction together with the UV spectra at the two main peaks. The spectrum observed for the eluent at 2.1 min is identified as that of the spin trap DBNBS and that at 5.1 min is of anthraquinone. In this study, spin trap is added to separate the escaped SDS radical as a stable product, since without such reagents a large part of the escaped radicals are converted into the same compounds as the cage products. Figure 3 shows the HPLC's for the same system after reaction at various magnetic fields. Microwave at X-band was irradiated in all runs. There are three main signals including the two observed before reaction. The two peaks were optically pure and identical to those observed before photo-irradiation. The newly observed is a very broad shoulder at the retention time of less than 2.1 min, which has an absorption peak at about 260 nm but no peak with a large ε in $\lambda > 300$ nm. We assigned this shoulder to the spin adduct of SDS radical because: **1.** the retention time indicates that the molecule is highly soluble in water in accord with the molecular structure of the spin adduct, which has two SO_3^- groups, **2.** this shoulder is not observed for the system without a spin trap, **3.** the shoulder is broad as supposed for the spin adduct, since many kinds of SDS radicals exist depending on the position of hydrogen abstraction, and **4.** the hyperfine coupling constant for nitrogen nucleus is nearly equal to that for alkyl-substituted nitroxide which has an absorption peak at ca. 240 nm with a ε more than 1000.

Under a high magnetic field of 300 mT the height of the shoulder measured at 1.7 min becomes 2.9 (±0.4) times as high as that at the residual filed. However, this ratio decreased to 1.8 (±0.2) when the magnetic field is adjusted to be resonant to anthrasemiquinone radical. These ratios were obtained from the independent three observations under the same condition. Since these are very similar to those (2.6[12] and 1.6[13], respectively) obtained from the ESR observation of the spin adduct, our chromatographic analysis should be correct. The corresponding ratios for the peak height of anthraquinone is 2.0 (±0.2) and 1.4(±2), respectively. The fact that these values are also similar to those for the spin adduct indicates that anthraquinone, once reacted almost quantitatively, is recovered mostly from the escape radical, its semiquinone, by disproportionation.

$$\mathrm{AQH}\cdot + \mathrm{AQH}\cdot \longrightarrow \mathrm{AQ} + \mathrm{AQH_2} \qquad (7)$$

Recovery of the quinone from the photoreduction product in SDS micelle is frequently referred in the literatures,[11,14] where it was simply postulated that quinone was recovered from both the escaped and the cage products. Since the assumption was made without any definite evidences, the details of the mechanism have not been clarified. It is well known that semiquinone disproportionate at a high rate, which approaches to the diffusion limit value in some cases.[15)]

Figure 4 shows a same kind of observation for the system where xanthene, a hydrogen donor, was added at 1.0 mM to the above system. In this case spin adduct of xanthenyl radical appears at about 3.3 min in addition to the spin adduct of SDS radical. The former shows a UV-spectrum very similar to that of xanthene. It was confirmed from many independent observations that ESR transition of anthrasemiquinone reduces the concentration of these spin adduct by ca. 20% as can be seen in Fig.4. This tendency is also the case for the 5.1 min peak. In this case, a small peak at around 5.3 min is overlapped and appears to increase at a lower magnetic field.

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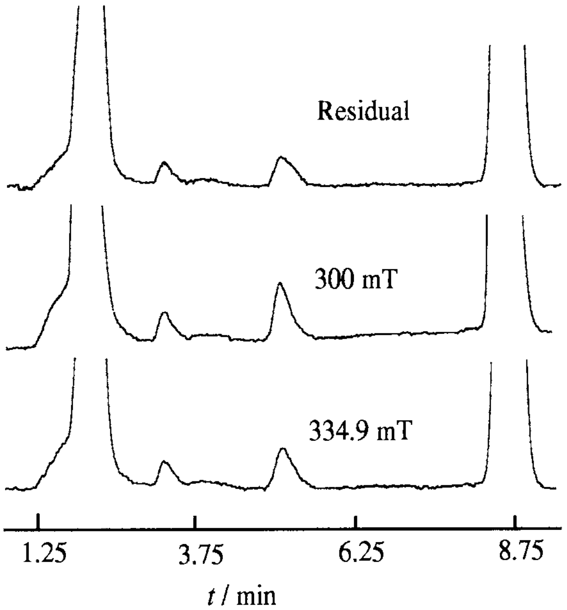

Fig.4. HPLC of the reaction product for (DBNBS, AQ, XH2)/SDS system at various magnetic fields. Microwave was irradiated in all cases. At 334.9 mT anthrasemiquinone becomes on resonance.

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