

Control of a Chemical Reaction by Spin Manipulation of the Transient Radical Pair As Demonstrated for Isotope Enrichment

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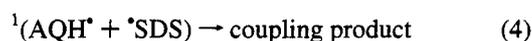
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Reaction control with the "spin manipulation technique" is demonstrated for the D/H isotopic enrichment of the spin adduct of SDS radical detected in the photoreduction of anthraquinone in a D/H-mixed micellar solution of sodium dodecylsulfate. This spin manipulation technique for the intermediate radical pair comprises two elementary spin operations: "spin inversion" to convert the spin state between $T_{\pm 1}$ and T_0 and "spin locking" to lock the spin state.

In the transient state of a chemical reaction that accompanies dissociation of a chemical bond, a pair of electron spins (a radical pair) is frequently produced with an exchange interaction that is weaker than the hyperfine interaction with the magnetic nuclei.¹ The total spin states are time-dependent and are described with the spin functions for the triplet (T_1 , T_0 , T_{-1}) and the singlet (S) states. Under these situations, manipulation of the spins is possible by irradiating with a microwave that is resonant to one or both of the spins in the magnetic field to control the succeeding reaction steps. The spin manipulation technique comprises two elementary spin operations: "spin inversion" to convert the spin state between $T_{\pm 1}$ and T_0 and "spin locking" to lock the spin state.^{1,2} Here, we demonstrate this technique for the first time for the D/H isotopic enrichment of the spin adduct of sodium dodecylsulfate (SDS) radical detected in the photoreduction of anthraquinone in a D/H-mixed micellar solution of deuteriated and unlabeled SDS. Deuterium enrichment of more than 60% was achieved with this technique by setting the microwave pulse amplitude so that the radical pair with the deuteriated radical is mainly spin-locked and the other is spin-inverted.

The reaction employed here is the photoreduction of anthraquinone (AQ) in a micellar solution of SDS in the presence of a spin trap. This reaction proceeds with the following scheme:³⁻⁵



Here, the triplet state of anthraquinone (${}^3\text{AQ}^*$), produced by UV irradiation *via* the singlet excited state (1), abstracts a hydrogen atom from one of the SDS molecules to produce a triplet radical pair (2). The triplet radical pair is converted into the singlet one and *vice versa* (3) by the hyperfine interactions. From the singlet state, bond formation occurs rapidly between the radical centers to produce a coupling product (4). This

product is called the cage product since it is produced in the original cage (micelle) where the radical pair was born. For the triplet pair, recombination is prohibited. The component radicals of the singlet pair (without recombination) and those of the triplet pair may escape to the bulk phase or to the other micelles as escaped radicals (5). Regardless of the state, forming a radical pair or being an escaped radical, SDS radical is reactive to produce an addition compound with dibromonitrosobenzene sulfonate (DBNBS) (6). Here, DBNBS is a "spin trap"⁶ and the produced nitroxide radical is the "spin adduct", which is easily detected by the usual ESR method. At zero magnetic field, intersystem crossing between the triplet and the singlet states occurs very rapidly, say 10^8 s^{-1} . At a high field, however, this process occurs only between the T_0 and S levels, since the other two levels, T_{+1} and T_{-1} , are separated by the Zeeman interaction energy. Thus, the radical pair in T_{+1} or T_{-1} is long lived and the yield of spin adduct increases *via* reactions 5 and 6.

Experimental Section

Anthraquinone obtained as a guaranteed grade reagent from Wako Pure Chemicals (Tokyo, Japan) was recrystallized from ethanol. Unlabeled SDS at the purest grade from Nakarai Chemicals (Kyoto, Japan) and the perdeuteriated SDS (98.6 atom % D) from Isotec Inc. (Ohio) were used without further purifications. DBNBS was synthesized according to literature procedures.⁷ The apparatus includes the microwave irradiation unit, laser unit, pulse programmer for adjusting the timing, ESR spectrometer for spin adduct observation, and a computer to control these units. The reactant solution was supplied with a flow system into a quartz flat cell set in the ESR cavity where photoirradiation and microwave irradiation were performed. After irradiation, the spin adduct was detected by using a conventional ESR technique. Experiments were conducted at a temperature within $300 \pm 2 \text{ K}$. The details of the apparatus and the method were described elsewhere.^{8,9}

Results and Discussion

Figure 1 shows the ESR spectra of the spin adducts detected in the photochemical reaction of anthraquinone in a D/H-mixed micellar solution made with deuteriated-SDS (SDS(D)) and unlabeled SDS (SDS(H)) at a 3:1 molar ratio. An X-band microwave (9375 MHz) at 0, 16, and 1000 W power for a, b, and c, respectively, was irradiated in a magnetic field of ca. 334 mT for 10 s immediately after the laser excitation. As indicated with a stick diagram, the sextet lines are due to the

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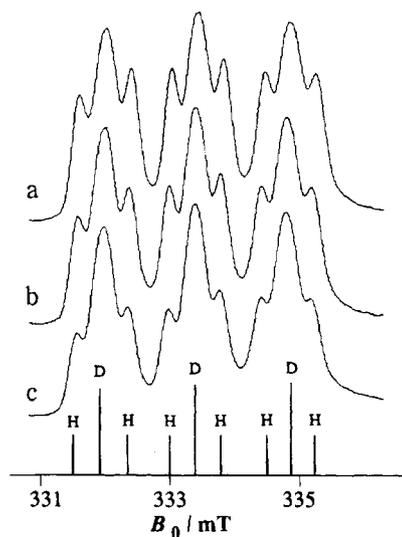


Figure 1. ESR spectra (integrated form) of the spin adducts detected in the photochemical reaction of anthraquinone in a mixed micellar solution with deuterated and unlabeled SDS at a ratio of 3:1. The total concentration of SDS was 0.1 M. The output heights are set equal to show the qualitative changes clearly. A stick diagram below the spectra shows the assignment of each peak to the two isotopic components: the spin adducts of SDS(H) and SDS(D) radicals. The reaction was performed under a magnetic field of 334 mT with simultaneous irradiation of an X-band (9375 MHz) microwave which is resonant to the center line of anthrasemiquinone. The irradiation microwave power was 0, 16, and 1000 W for spectra a, b, and c, respectively.

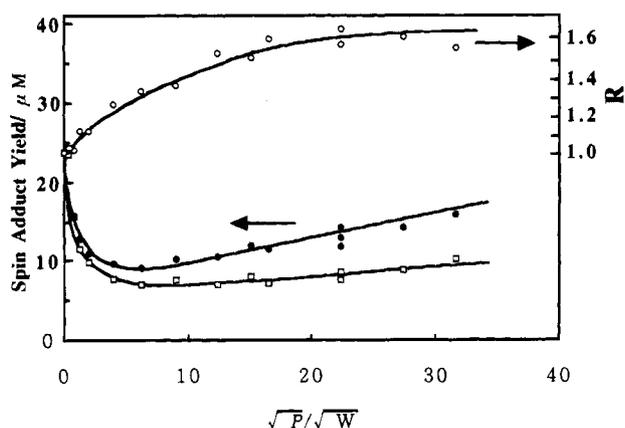


Figure 2. Spin adduct yields for SDS(D) (●) and SDS(H) (□) radicals and the ratio between the two (○) as functions of the square root value of the microwave power, which was employed to control the photochemical reaction of anthraquinone in the mixed micellar solution with deuterated and unlabeled SDS at a ratio of 3:1. (For details see caption for Figure 1.)

adduct of SDS(H) radical and the triplet lines are that of SDS(D) radical.¹⁰ It is noticed that the D/H ratio increases considerably with increasing the microwave power. Figure 2 shows the spin adduct yields of these two radicals as well as the ratio between them determined from simulation of the ESR spectra. The D/H enrichment factor R , at microwave power of p W, is defined as

$$R = \frac{[Y(\text{SDS(D)})/Y(\text{SDS(H)})]_p \text{ W}}{[Y(\text{SDS(D)})/Y(\text{SDS(H)})]_0 \text{ W}} \quad (7)$$

where $Y(X)$ represents yield of the spin adduct of radical X. As shown in Figure 2, upon increasing the microwave power, the spin adduct yield decreases first and reaches its minimum at around 20 W, which is common to both systems and corresponds to the microwave field of about 0.7 mT. This result can be

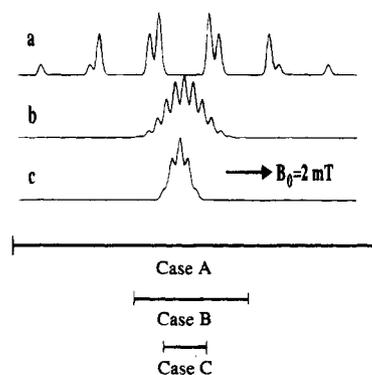


Figure 3. Simulated ESR spectra (a, b, and c) for SDS(H), SDS(D), and anthrasemiquinone radicals,¹³ which are expected as components of the intermediate radical pair. The three bars indicate the microwave amplitudes which are employed in the three typical "spin manipulation" experiments. When the microwave radiation applied during the reaction has an amplitude much larger than the spectral widths of both the SDS(H) and SDS(D) radicals, spin locking occurs for both the radical pair of SDS(H) radical and that of SDS(D) radical (case A). Here anthrasemiquinone is a common component in both the radical pairs. If the microwave amplitude is considerably larger than the spectral width of SDS(D) radical but is smaller than that of SDS(H) radical, spin locking occurs for the SDS(D) pair and spin inversion occurs for the SDS(H) pair (case B). In case C, the microwave field covers almost the entire spectral range of anthrasemiquinone but is considerably smaller than the width of SDS(D) radical; therefore, spin inversion occurs for both systems.

explained with the fact that the other component of the radical pair is common, i.e. anthrasemiquinone, whose ESR spectral width is close to 0.7 mT. Spin inversion of the radical pair occurs most efficiently when the two components of the radical pair have different spectral widths (i.e. distribution of the hyperfine lines) and only the narrower component is fully covered by the microwave field. With a further increase in the microwave power, the effect reverses direction. This is due to the spin locking effect,² which occurs when the two electron spins rotate simultaneously with preserving the relative phase along the microwave field (in the rotating frame). Under these circumstances both the transitions within sublevels of the triplet state and the intersystem crossing from T_0 to S are inhibited.

Figure 3 shows the simulated ESR spectra a, b, and c for SDS(H), SDS(D), and anthrasemiquinone radicals, respectively, and three representative cases for the microwave effect on the relative spin adduct yield between the two isotopic systems. Since the hyperfine coupling constant (hfc) for the deuteron is about 1/6.5 of that for the proton,¹¹ the total ESR width of deuterated SDS radical is considerably smaller ($<1/3$) than that of unlabeled material. When the microwave amplitude is much larger than the spectral widths of the three radicals, spin locking occurs for both radical pairs (case A). If the microwave amplitude is larger than the spectral width of SDS(D) radical but smaller than that of SDS(H) radical, spin locking occurs preferentially for the radical pair with SDS(D) radical (case B; Figure 1c). When the microwave field is considerably smaller than the width for SDS(D) radical, spin inversion occurs for both systems (case C; Figure 1b). This classification is made for the averaged responses of the two systems. Even in case B spin locking occurs to some extent for the radical pair with SDS(H) radical whose ESR spectrum occurs at the nearest position to that of the semiquinone radical.

A much larger increase in the spin adduct yield for SDS(D) radical at high microwave powers can be explained when microwave irradiation is close to case B of Figure 3. The total ESR width of the radical pair with SDS(D) radical is about 4 mT (Figure 3b,c), which is fully covered by the maximum

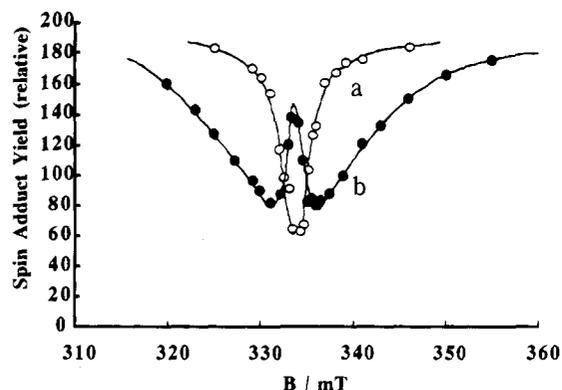


Figure 4. PYESR spectra of the radical pair produced in the photoreduction of anthraquinone in deuteriated SDS micellar solution at microwave powers of 16 W (a) and 1000 W (b).

microwave field (ca. 5 mT) obtained with our TWT amplifier. For the pair with SDS(H) radical, spin inversion occurs mostly due to a very wide distribution of the hyperfine lines of SDS-(H) radical. Therefore, SDS(D) radical is condensed to the spin adduct at high microwave powers. This fact was confirmed, by observing the product-yield-detected ESR (PYESR) spectra as shown in Figure 4, which were observed for the system with pure deuteriated micellar solution. At a low microwave power, the PYESR spectrum is sharp, since the line width is mainly determined by the hyperfine couplings of the two component radicals. However, at the maximum power of 1.0 kW, the line width is greatly broadened and at the same time the phase of the peak is reversed in the central portion of the PYESR spectrum. This dip at the center is due to the spin-locking effect. The spectrum should be inverted if we apply a strong microwave field that is several-fold larger than that used in the present experiment.

Figure 5 shows how spin manipulation is applied to control this chemical reaction. In the transient radical pair, further reaction depends on the spin state, as mentioned above (reaction steps 3–5). Inversion of the spins in the T_{+1} or T_{-1} states causes transition to the T_0 state, which is then easily converted into the coupling product (R_2COH-X) via the S state (spin inversion). On the other hand, locking of the spin state is possible if we apply a resonance microwave with a large amplitude. In this case, escape products ($X-X$, $(R_2COH)_2$, etc.) and the spin adduct of the SDS radical increase due to spin locking. In an ideal case, we can select one of the reaction paths by applying a microwave pulse whose amplitude is adjusted for either spin inversion or spin locking. In previous work using spin-trapping ESR^{12,13} as well as high-performance liquid chromatography,⁸ we showed that ESR transition of one of the two radicals that composes the radical pair actually changes the final product yield for photochemical reactions of quinones and ketones in micellar solutions. A small isotopic effect has been demonstrated for a similar system by irradiation with a weak microwave at the appropriate magnetic field.¹⁴ Buchachenko et al. also showed an isotopic enrichment for the $^{13}C/^{12}C$ pair with a similar technique.¹⁵

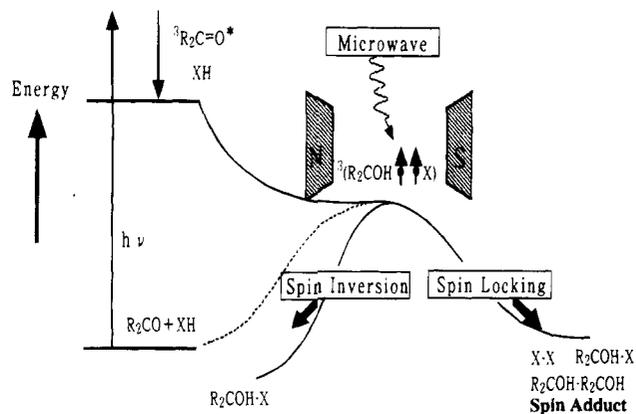


Figure 5. Schematic diagram which explains the spin manipulation technique for controlling a chemical reaction which has a radical pair as the intermediate. The photochemical hydrogen abstraction reaction of a carbonyl compound is employed as the model system. The photoexcited triplet state of a carbonyl compound ($^3R_2C=O^*$) abstracts a hydrogen atom from a hydrogen donor (XH) to produce a triplet radical pair ($^3(R_2COH\cdot X\cdot)$). Locking of the spin state is achieved by irradiating the radical pair with a very strong microwave in an appropriate magnetic field, resulting in an acceleration of the escape product formation. When irradiation with a microwave of a reduced amplitude is carried out, the spin inversion condition is satisfied and the reaction path will lead to cage product formation.

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