1892 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1892—1896(1993)* [Vol. 66, No. 7

Pulse Mode Product-Yield-Detected ESR on the Photoreduction of Anthraquinone in SDS Micellar Solution: Reaction Control by a Microwave Pulse

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(Received December 14, 1992)

A pulse mode PYESR (Product-Yield-Detected ESR) spectrometer was developed by using an excimer laser and a TWT microwave amplifier as the components. The effect of ESR transition of the transient radical pair on the yield of the spin adduct of one of the component radicals was observed at a high microwave power of up to 16 W without microwave heating of the solvent. The spin adduct yield of the SDS radical in the photoreduction of anthraquinone in SDS micellar solution initiated by a laser pulse of 308 nm was modulated by up to 45% by a microwave pulse of 10 μs with a peak power of 16 W, which is resonant on the ESR transition of the transient anthrasemiquinone radical. The ESR spectrum of the radical pair was obtained by tracing this modulation as a function of the magnetic field, under which the photoreaction occurred. From the dependence of the product yield on the microwave pulse duration, we could obtain a time profile of the appearance of the transient radical pair.

Correlation between the two electron spins of the intermediate radical pair formed in a photochemical or thermal reaction affects the path of the following reaction steps.[1—3] Therefore, it is possible in principle to control these reactions by "manipulating" the spins of the radical pair. In previous studies,[4,5] we actually showed that ESR transitions of the radical pair modify the yield of the spin adduct,[6] which is produced mainly from the escaped radical in the photoreduction of quinones in SDS micellar solution, and also that this change as a function of the magnetic field (under which the microwave irradiation is made) traces the ESR spectrum of the radical pair. In addition, isotope enrichment by ESR transition was first demonstrated for the same reaction system with a mixture of deuteriated SDS and protiated one as the detergent.[7] The principle of the above experiment is similar to that of optically detected ESR (ODESR) or fluorescence-detected ESR (FDMR),[12] which is sometimes called "reaction-yield-detected ESR" or "RYDMR".[13—16] However, in the "RYDMR" experiments the intensity of the luminescence, which is caused by the electronic transition from the excited state to the ground state of the original molecule, is measured. Therefore, we named our method product-yield-detected ESR or "PYESR"[5,7] to discriminate it from the "RYDMR" experiments, although the linguistic meanings of the two terms, PYESR and RYDMR, are quite similar to each other. It should be stressed that the vertical axis of a PYESR spectrum is usually graduated in units of mol dm^{-3} indicating the yield of the final product of the reaction.

In the present study, we have constructed a pulse mode spectrometer to observe the PYESR spectrum with a better S/N as an extension of the previous one[17] which works in the CW mode, and also to control a chemical reaction by "manipulating" the transient spins by a high-power microwave pulse. The results of this improvement are: (1) the dielectric heating of the sample, which was a serious problem in the CW experiment, has been diminished to almost zero. Therefore, we can apply a high microwave power to the system to observe a large effect of the ESR transition on the product yield (i.e. the amplitude of the PYESR spectrum). (2) Time domain information can be obtained.

We demonstrate here this "pulse mode PYESR" on the photoreduction of anthraquinone in SDS micellar solution.

Apparatus and Materials

Figure 1 shows a schematic diagram of our new PYESR spectrometer. The sample solution deoxygenated by N_2 or Ar bubbling is charged into a quartz flat cell with a flow system and is photo-irradiated with a XeCl excimer laser (Lambda Physik, LPX-105i) under various magnetic fields. A pulsed microwave of a certain length from a TWT amplifier (Keltec Florida, XR 625-20) is also irradiated during and after the laser pulse. The trigger signals for the laser and the gating pulse to PIN diodes, which are used to pulse the microwave field, are generated by a pulse programmer (Iwatsu, DS8631). The laser pulse was monitored with a pyroelectrics (Molectron, P501) and an oscilloscope (Iwatsu, SY8220). The AFC circuit as well as the microwave power meter (Hewlett Packard, HP-437B) are used only in the CW mode. The spin adduct yield is measured using the conventional ESR method after switching the connection of the cavity from the TWT amplifier to the original ESR system (JEOL, RE-1X). All these instruments are controlled with a personal computer (NEC, PC9801 DS).

Anthraquinone was obtained from Tokyo Kasei Kogyo (Tokyo) and was recrystallized from ethanol. Sodium dodecyl sulfate (SDS) and sodium 3,5-dibromo-4-nitrosobenzenesulfonate (DBNBS, a spin trap) were used as supplied from Nakarai Chemicals (Kyoto) and Sigma Chemical Company (St. Louis, Lot No. D0898), respectively. The sample solution was made by dissolving anthraquinone (0.1 mM) and DBNBS (1.0 mM) in 0.2 M SDS micellar solution buffered with 50 mM sodium phosphates at pH 6.0. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPOL) purchased from

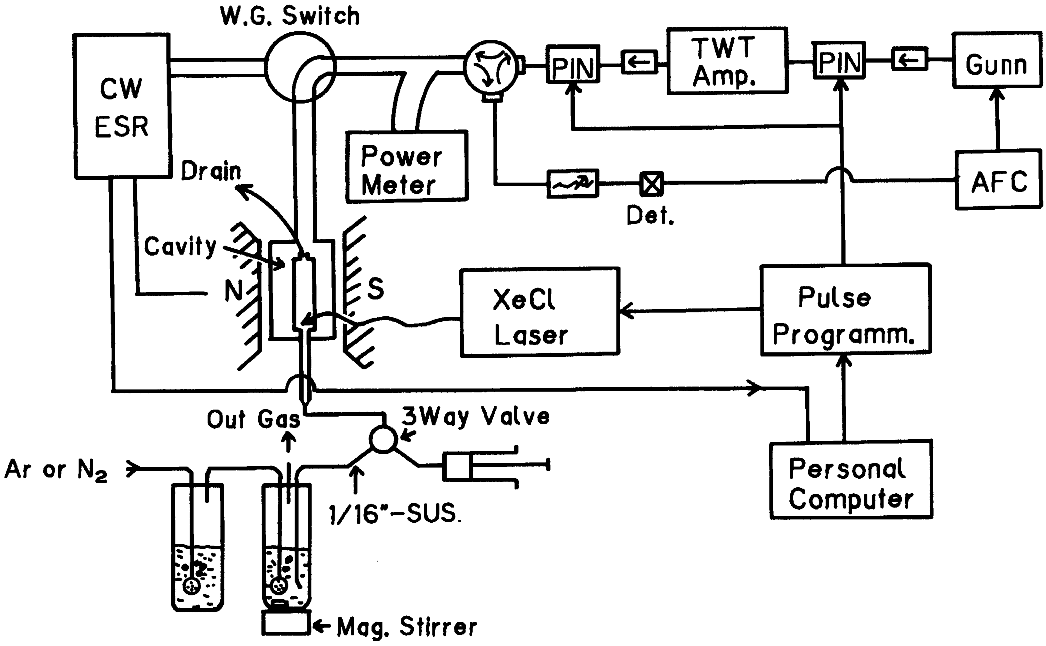

Fig. 1. Schematic diagram of the apparatus to control a spin trapping reaction by a microwave pulse: a pulse-mode PYESR spectrometer.

Wako Pure Chemicals (Tokyo) was used as the standard to determine the spin adduct concentrations. Experiments were performed at an ambient temperature (ca. 300 K).

Results and Discussion

Figure 2A shows the ESR spectra of the spin adduct formed in a UV-irradiated SDS (0.2 M, M=mol dm^{-3}) micellar solution of anthraquinone (0.1 mM) with simultaneous irradiation of a microwave pulse of 10 µs at 9.39 GHz at the magnetic fields resonant for the semiquinone radical (334.7 mT; upper) and off resonant for both the intermediate radicals (330 mT). The microwave power was about 16 W. The triplet hyperfine structure due to the nitrogen nucleus of the spin trap (DBNBS) splits further into doublets due to one hydrogen nucleus. The splitting of this doublet is about 0.76 mT and is easily assigned to the α-proton of the SDS radical as in the previous study.[18] Because alkyl radicals are much more reactive to nitrosobenzenes[19] than semiquinones, SDS radical is selectively trapped by DBNBS. The observed reduction in the spin-adduct yield due to the ESR transition of anthrasemiquinone is about 45% which is the maximum resonant microwave effect in the "RYDMR"-type experiments ever observed.

Figure 2B shows the PYESR spectrum of this system at a high microwave power of 4.0 W. Although the spectrum is considerably broadened compared with the previous spectrum observed at a low irradiating microwave power of 0.16 W,[4,5] broad peaks from the SDS radical at around 310 and 339 mT are observed on both sides of the central anthrasemiquinone peak. Since the spin trap used here is soluble only in the aqueous phase and may trap the SDS radical escaped from the micelle selectively, the decrease in the spin adduct yield by the ESR transition of either the SDS radical or the semiquinone radical implies that the two radicals form a transient radical pair in the triplet state and the magnetic interactions within the radical pair affect the following steps of the reaction. As was discussed in our previous studies,[4,5] this observation is direct evidence of the radical pair theory for this type of magnetic field-dependent chemical reaction. The solid curve is a simulated spectrum using Eqs. 1, 2, and 3 given below (described in a previous paper[5]) with a microwave amplitude of 0.3 mT. Since the calculated spectrum reproduces well the observed values, we know that the postulated kinetic parameters are reasonable. These parameters are nearly the same as those obtained by other researchers from time domain experiments[20] and were used to reproduce the previous PYESR spectrum[5] at an irradiation microwave power of 0.16 W.

Figure 3A shows the dependence of spin adduct yield on the duration of the microwave pulse at 1.0 and 4.0 W for the upper and the lower traces, respectively. The differentials of these curves are shown in Fig. 3B. The microwave effect increases with increasing pulse length but it almost saturates around 2.5 µs. The shift of the peak position toward time zero at a higher microwave power, shown in Fig. 3B, implies that at a high microwave field it takes less time to invert the spin. The pulse length needed to saturate the effect is related to the distribution of the appearance time of the radical pair. Thus, we performed a simple analysis of the curves as shown in Fig. 3.

The Hamiltonian of the system was assumed to be as follows:

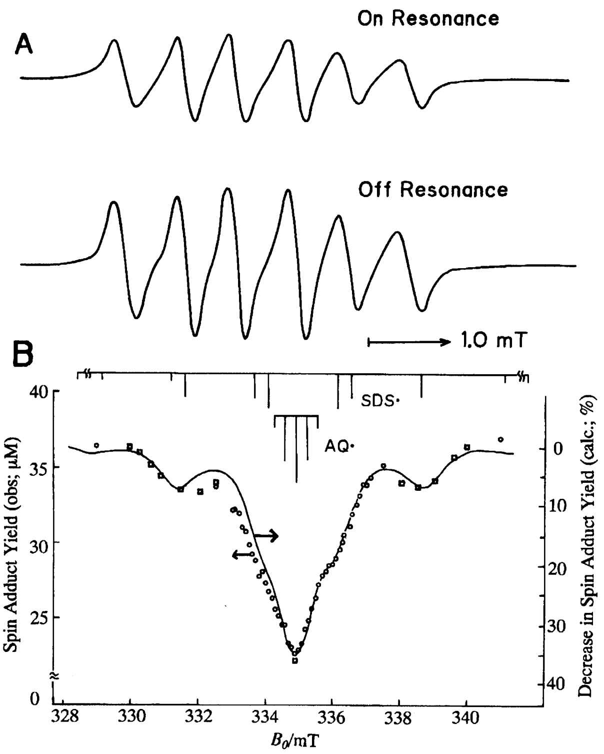

Fig. 2. A: Effect of the ESR transition of anthrasemiquinone on the ESR spectrum of the spin adduct of SDS radical; B: ESR spectrum detected by the spin adduct yield for the same system. Data points indicated with rectangles were collected in a different run of the experiment from those indicated with circles. The microwave power was 4.0 W and the duration of the laser pulse was 5.0 μs. The solid curve is a calculated PYESR spectrum using equations in the text with the parameters: $k_T=4\times10^6$, $k_S=3\times10^7 s^{-1}$, $B_1=0.3$ mT, $a_H(\alpha)=2.1$ mT, $a_H(\beta)=2.5$ mT for SDS radical, $a_H(1,3,7,9)=0.31$ mT for anthrasemiquinone, $\Delta g=1.2\times10^{-3}$.

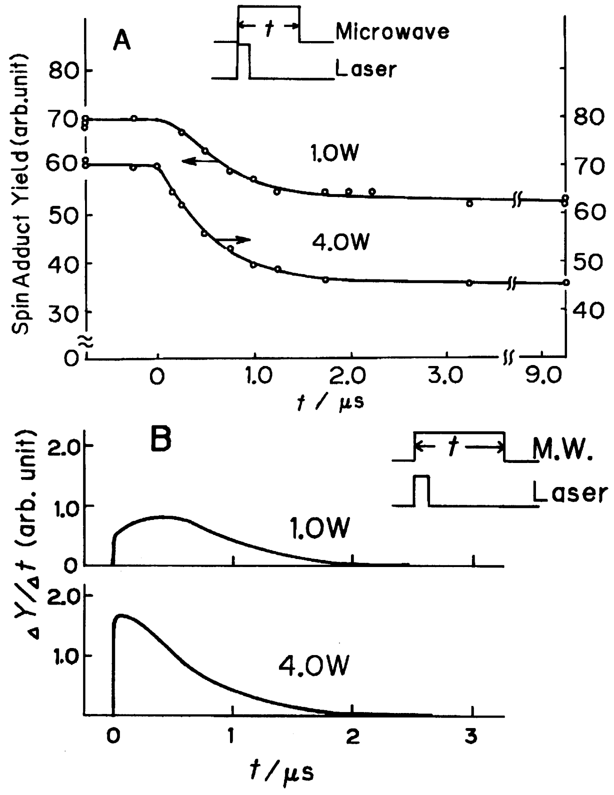

Fig. 3. A: Dependence of the spin adduct yield on the duration of the microwave pulse after the laser pulse. Microwave power was 1.0 and 4.0 W for the upper and lower traces, respectively. B: Derivative curves for the two solid lines in A.

$$\mathscr{H} = \sum_{m=1}^{2} \left\{ g_m \beta B_0 S_z{}^m + d_e \hbar \left[S_+{}^m \exp(-i\omega t) + S_-{}^m \exp(i\omega t) \right]/2 + \sum a_j{}^m I_{j,z}{}^m S_z{}^m \right\}, \qquad (1)$$

where m refers to the two component radicals forming the pair. The first term is the electron Zeeman interaction and the second one represents the interaction of the electron spin with the microwave field of amplitude B_1 $(=2d_e/\gamma)$ and angular frequency ω. The response of the reaction system can be calculated by integrating the kinetic equation of the density matrix of the system,[2,5] i.e.

$$d\rho^*/dt = -i/\hbar [H^*, \rho^*]_- - k_T [P_T, \rho^*]_+ /2 - k_S [P_S, \rho^*]_+ /2, \qquad (2)$$

where k_T and k_S represent the reaction rate constants from the triplet and the singlet states, respectively. Asterisks on the top of the operators indicate that they are expressed in the frame rotating at the microwave frequency. P_T and P_S are the operators which project out the triplet and the singlet states, respectively. $[\ ]_-$ and $[\ ]_+$ represent commutator and anticommutator, respectively. Since it is expected that most of the escaped radicals, which are preferentially trapped by the spin trapping reagent, are formed from the triplet radical pair, the spin adduct yield is parallel to the following integral.

$$Y_{SP} = \text{const} \times \int_0^\infty \left[P_T, \rho^* \left(t' \right) \right]_+ dt'. \qquad (3)$$

In the present case, the microwave exists in the time range from zero to t, thus the eigenfunctions of the spin state change at time "t". Since the integration of the matrix elements $\rho_{i,j}{}^*$ in Eq. 2 (subscripts refer to the energy levels of the radical pair) was performed after representing the matrices using the basis set composed of the eigenfunctions of the system, all the matrices were converted into the new space at time "t". Calculations are made for a number of four-level systems and those results are summed after multiplying the statistical degeneracy.[5] This method is valid only when the nuclear spin flip can be neglected. When radical m $(m=1,2)$ has $N_j{}^m$ $(j=1,2,\cdots j_F{}^m)$ protons as j'th equivalent nuclei, the number of elemental four-levels is

$\prod_m\prod_j(N_j{}^m+1)$. The statistical degeneracy of each four-level is calculated simply with binomial coefficients.[5] Figure 4 is an example of the calculation, which shows the reduction of the spin adduct yield as a function of the microwave pulse duration.

The effect of microwave irradiation as a function of pulse duration changes like a damped oscillation at a frequency of $\gamma B_1/2\pi$, as curve A of Fig. 4 for the present system. Since this curve is composed of many oscillating functions from all the four-levels, which are overlapping with each other, it is rather difficult to grasp the physical meaning. If we calculate this function for a system with only one proton as the magnetic nucleus and smaller reaction rates, it becomes curve B of Fig. 4, where oscillation due to the microwave field becomes apparent. The function may be approximately expressed as:

$$Y(t,t_0) = \text{const} \times \{1-\exp(-\lambda(t-t_0))\cos(\omega^*(t-t_0))\}, \quad (4)$$

where $\omega^*=\gamma B_1$ and λ is the decay rate constant of the radical pair; t and t_0 represent the pulse duration (from $t=0$, when laser pulse is irradiated) and the appearance time of the radical pair, respectively. Although the population of the triplet state oscillates at the frequency of the difference between the resonance frequencies of the two radicals,[2] this modulation almost disappears in Fig. 4 since the product yield corresponds with the integration of the triplet state density (Eq. 3). Using the time profile of the appearance of the radical pair, $A(t_0)$, the actual pulse-width dependence of the effect ($Y_{\text{total}}(t)$) becomes,

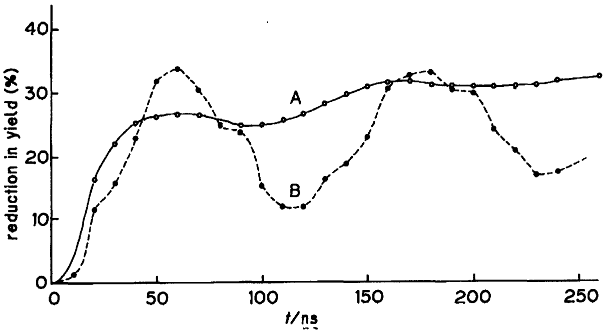

Fig. 4. Calculated dependencies of the spin adduct yield on the duration of a microwave pulse of 0.3 mT. It was postulated that the radical pair is generated at time zero. Parameters for A are: $k_T=4\times10^6$, $k_S=3\times10^7\,\text{s}^{-1}$, $B_1=0.3$ mT, $a_H(\alpha)=2.1$ mT, $a_H(\beta)=2.5$ mT for SDS radical, $a_H(1,3,7,9)=0.31$ mT for anthrasemiquinone; $\Delta g=1.2\times10^{-3}$. Curve B is calculated for a model system with only one magnetic nucleus ($I=1/2$) with parameters: $k_T=2.0\times10^6$, $k_S=7.5\times10^6\,\text{s}^{-1}$, $B_1=0.3$ mT, and $a=2.5$ mT.

$$\begin{aligned} Y_{\text{total}}(t)/\text{const} &= \int_0^t A(t_0)\{1-\cos(\omega^*(t-t_0)) \\ &\quad \times \exp(-\lambda(t-t_0))\}\,\mathrm{d}t_0 \\ &\fallingdotseq \int_0^t A(t_0)\,\mathrm{d}t_0. \end{aligned} \quad (5)$$

The oscillating term disappears when $A(t_0)$ is a dull function of time compared with $\exp(i\omega^* t)$. This relation holds well for the real system, where the response $Y(t,t_0)$ from many elementary four-level systems are overlapped. [If the curve of Fig. 4 is approximated as a sharp step function, the relation (5) is self-evident.] Thus, at a relatively high microwave power, the curve in Fig. 3B approximately represents the time profile $[A(t_0)]$ of the appearance of the radical pair. The average delay time for the appearance of the radical pair can be obtained by the following equation:

$$T_{\text{delay}} = \int_0^\infty tA(t)\mathrm{d}t \Big/ \int_0^\infty A(t)\mathrm{d}t. \quad (6)$$

Calculation of T_{delay} with Fig. 3B (4.0 W) using Eq. 6 gives 0.5 µs for the average appearance time of the radical pair ($J \ll a$). This delay time may be spent for intersystem crossing in the excited anthraquinone, hydrogen abstraction from the SDS molecule, and separation of the resulting two radicals to reduce the exchange interaction. Scaiano et al.[20] observed the time evolution of benzophenone ketyl radical in the photoreduction of benzophenone in SDS micellar solution and reported that its concentration reaches a maximum about 0.3 µs after the laser excitation.

The authors thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes for the use of the HITAC M-680H. This work was supported by Special Coordination Funds for Promoting Science and Technology.

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