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A Pulse-Product-Yield-Detected ESR Study on the Photolysis of Nitronaphthalene–Aniline Bifunctional Chain Molecule

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The effects of microwaves (MW) on the photolysis of a benzene solution of *N*-[12-(4-nitro-1-naphthyloxy)dodecyl]-aniline under a magnetic field were investigated. The reaction intermediate was identified as a biradical the ESR spectrum of which was recorded by plotting the MW effect as a function of the magnetic field under which the reaction proceeds. The kinetic parameters of the reaction system were estimated from the MW effects observed as functions of the delay period from the laser pulse for putting on/off the MW pulse.

The mechanism of a photoredox reaction between an aromatic nitro species and a reductant is rather complex except for intramolecular photoinduced redox reactions which include nitro-to-nitroso conversion in the reaction scheme. The latter, which is important in application to, e.g. photochromism and photoresists,[1—4] is well-documented for a wide variety of *ortho*-substituted nitrobenzenes. In the photolysis of an aromatic nitro compound a nitroxide radical has been postulated as an intermediate which may be produced by the hydrogen abstraction reaction. The photoredox reaction of a molecule having both an aromatic nitro group and a reductant, which are separated by a polymethylene chain, is interesting in studying this redox mechanism, because a pair of redox partners is held in a short distance and thus the reaction must be modified accordingly. In a previous study a large magnetic field effect was observed on the final product of the photolysis of *N*-[12-(4-nitro-1-naphthyloxy)dodecyl]aniline (NNDA).[5] To pursue the mechanism, we decided to study this system by using the product-yield-detected ESR (PYESR) method,[6,7] with which we can observe a transient radical pair and its dynamics. Although the laser flash-photolysis technique[8—10] is sometimes useful for detecting the excited triplet states of nitrobenzenes and the related species, it is less effective for probing nitroxides, of which detection may be indispensable for clarifying the reaction mechanism of this system. This is due to the fact that the strongest absorption band of a nitroxide may appear in the shorter wavelength region and the extinction coefficient may be much smaller than that of the parent nitro aromatic compound. The reaction mechanism shown in Fig. 1 for NNDA was suggested in previous works,[5,11] though the structure of the assumed biradical intermediate was not clearly mentioned. According to this scheme, the nitronaphthalene moiety excited to the lowest triplet state by photoirradiation abstracts a hydrogen atom from the methylene group adjacent to aniline, and a neutral triplet biradical is formed. When intramolecular radical recombination occurs, Product 1, a cage product, is formed by releasing the aniline moiety. Product 2 is formed as an escape product by the reaction of the intermediate with a parent molecule. In this study we have tried to detect the assumed intermediate biradical by the product-yield-detected ESR (PYESR) technique to establish the reaction mechanism and also to characterize the reaction kinetics by using the pulse-PYESR technique.[12,13]

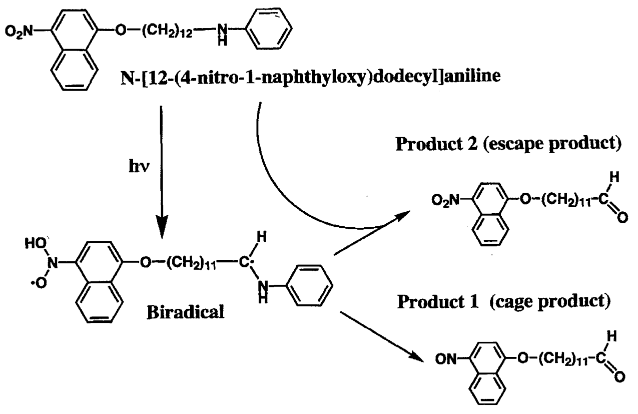

Fig. 1. Reaction scheme proposed in a previous study[5] for the photolysis of *N*-[12-(4-nitro-1-naphthyloxy)dodecyl]-aniline in benzene solution. Product 1 (cage product) is produced by the intramolecular rearrangement of the intermediate biradical. Product 2 (escape product) is produced by the reaction between the biradical and the parent compound.

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PYESR is a powerful technique for detecting the radical pair (RP) intermediate in a solution system by taking advantage of the effects of both the magnetic field and the microwave field on the photoreactions.[6,7] The ESR spectrum of the radical pair (PYESR spectrum) is obtained by plotting the yield of a final product as a function of the magnetic field, under which the reaction proceeds in the presence of a microwave field. Therefore PYESR does not need a chromophore for detection. Recently absorption-detected ESR (ABESR)[14] or optically detected ESR (ODESR)[15] have been developed as similar techniques. In these experiments the spin state of a transient radical pair (or a biradical) is modified upon inducing the ESR transition of one of the two radical centers by irradiating the system with a microwave field. If the initial spin state of the radical is triplet, the recombination is prohibited without any additional interaction since the recombination product is in the singlet state. Upon inducing the ESR transition, however, the spin state is converted into the singlet state, thus an increase in the recombination product is observed. On the other hand, "escape products" which are produced by random recombination of the free radicals escaped from the radical pair decrease upon inducing the ESR transition of the triplet radical pair. The kinetic parameters of the radical pair can be obtained by the pulse-PYESR experiment, where a reaction product is measured as a function of the delay period from the laser pulse for putting on/off the microwave-pulse.[12]

Experimental

Synthesis of *N*-[12-(4-nitro-1-naphthyloxy)dodecyl]aniline (NNDA) was reported elsewhere.[11] HPLC grade benzene purchased from Wako (Osaka) was used as solvent without further purification. A benzene solution of NNDA was deoxygenated by Ar-gas bubbling for 45 min and was introduced into a quartz flat cell (thickness 0.25 mm) set in a microwave cavity of an ESR spectrometer (JEOL, JES-RE1X), where it was irradiated by a Nd : YAG laser (Spectra-physics, GCR-170, λ = 355 nm, 20 mJ/pulse, 10 Hz). Microwave pulse (X-band, pulse width : 10 µs) irradiation was made with a timing shown in Fig. 2, which was made by a pulse programmer (Iwatsu SY8220). Simulation of the pulse-PYESR responses were made by numerical integration of the differential kinetic equations by the Runge–Kutta method. Details of the apparatus and method for the pulse-PYESR method were given elsewhere.[12] The sample solution was frozen immediately after photoreaction and kept at liq. N_2 temperature until its analysis. HPLC analysis was done by a standard procedure with a standard kit (Waters 302; Waters 996) and a normal phase column (LiChrosorb Si60, 10 µm, Cica–Merck).

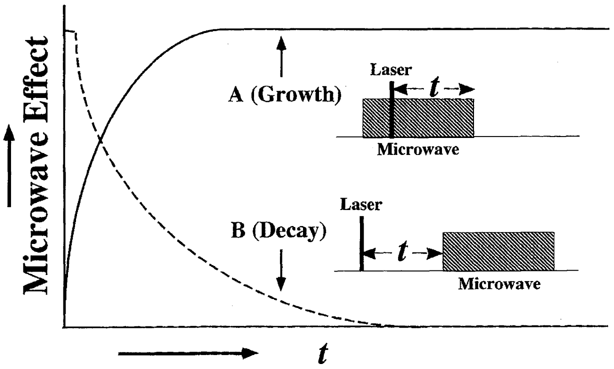

Fig. 2. Pulse sequences employed in the pulse-product-yield-detected ESR and the delay time dependence of the microwave effect. In experiment A (Growth), the microwave irradiation starts before the laser and finishes at time "*t*" after the laser pulse. If the rate of intersystem crossing is sufficiently large, this experiment gives us information on the formation process of the transient biradical. In experiment B (Decay), the microwave irradiation starts at time "*t*" after the laser and this provides information on the decay process of the biradical intermediate.

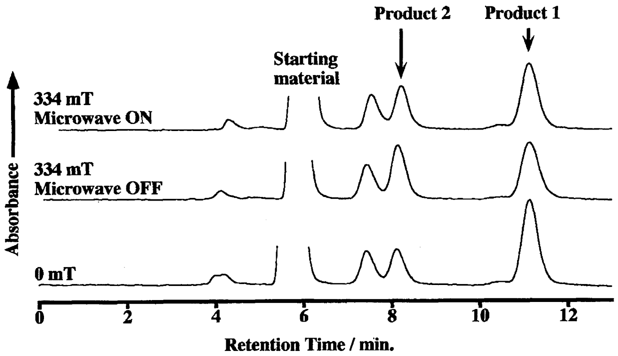

Fig. 3. HPLC of the reaction products drawn by the absorbance at 370 nm. The magnetic field and the microwave effects are shown. A mixture of benzene and tetrahydrofuran (volume ratio 400 : 1) was used for the HPLC analysis. Microwave irradiation was made at the output power of 1 kW for 7 µs after laser irradiation.

Results and Discussion

Experimental Results. Figure 3 shows the HPLC chromatograms of the products. Peaks at 11 min and 8 min were assigned to Product 1, which has an absorption maximum at 390 nm due to the nitrosonaphthalene moiety, and Product 2, having an absorption maximum at 360 nm due to nitronaphthalene moiety, respectively.[5] Product 1 was decreased by a magnetic field and increased by microwave irradiation. On the other hand, Product 2 was increased by a magnetic field and decreased by microwave irradiation. Therefore Product 1 and Product 2 are assigned naturally to a cage product and an escape product, respectively. In this study the experimental results were analyzed using the ratio between the relative change in the two products "*r*," which is defined below. This procedure is taken merely to cancel out errors due to both concentration fluctuations in the process of freezing/thawing a small amount of sample solution and fluctuation in the volume of sample injected in the HPLC apparatus.

$$r = \frac{I(\mathrm{P1})/I(\mathrm{P2})}{I_0(\mathrm{P1})/I_0(\mathrm{P2})} \tag{1}$$

I and I_0 are the peak height of the products with and without the microwave irradiation, respectively. The change in "*r*" as a function of the external magnetic field B_0 is shown in Fig. 4A. It is seen that "*r*" increases from 1 to 1.7 around 334 mT. This pattern corresponds to the ESR spectrum of the

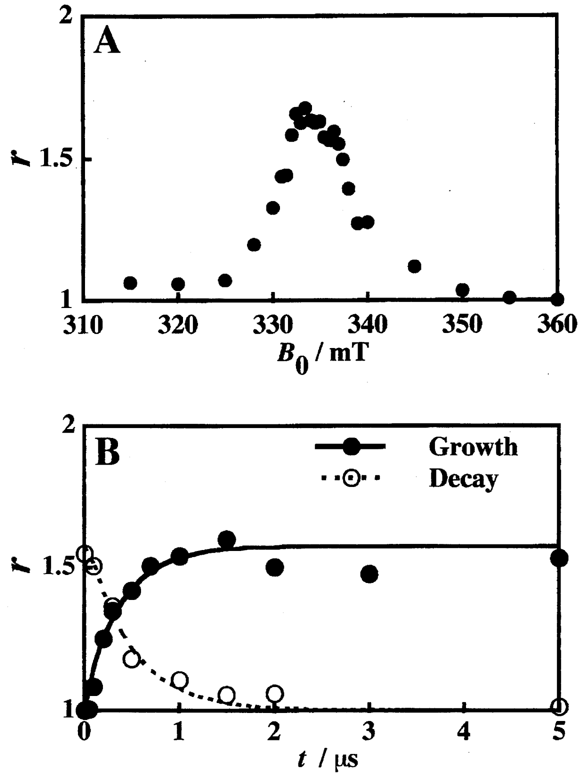

Fig. 4. PYESR spectrum (A) and pulse-PYESR responses (B) obtained from the ratio of the HPLC peaks for Product 1 and 2. For HPLC analysis a mixture of benzene and tetrahydrofuran was used and absorption at 370 nm was employed. For experiment A the microwave irradiation was made (at 1 kW for Experiment A and at 100 W for Experiment B) for 10 μs after laser irradiation. Solid (Growth) and broken (Decay) lines of B represent the simulation curves.

intermediate radical pair and is called the PYESR spectrum. This is direct evidence that a radical pair or biradical is included as an intermediate. From the frequency of the microwave field, 9.36 GHz, and the magnetic field, 334 mT, the g-value of the radical species was calculated as 2.00. The microwave-field effect was large enough to conclude that the exchange interaction between the two radical centers is small.[7] A large PYESR signal in a nonviscous solvent indicates that the two radical centers are connected to each other, since the lifetime of a usual (i.e. separated) radical pair must be too short to observe any microwave effects. From these observations we can conclude that a biradical with a small exchange interaction is the intermediate species. Since J of 10 mT decreases the PYESR amplitude seriously,[7,16] the mutual distance between the two radical centers would be as long as or larger than 1.0 nm. Therefore the structure of the intermediate in Fig. 1 is plausible from this point of view. The pulse-PYESR experiment was made at a magnetic field of 334 mT where the microwave field effect is large enough. The result is shown in Fig. 4B taking "r" (Eq. 1) as the ordinate. In the pulse-PYESR experiment, the product yield as a function of the time interval between laser irradiation and off/on of the microwave pulse (delay time) could be analyzed and the information on the dynamics of a biradical or radical pair could be obtained.[12,17,18] The time constant of growth of the microwave effect was around 200 ns. This large growth rate indicates that both the hydrogen abstraction reaction and the cage product formation rate are rapid ($\geq 1.0\times10^{7}$ s^{-1}). The decay process was also rapid and the lifetime was as short as 600 ns. This indicates either the spin lattice relaxation or the quenching process or both are very rapid.[12]

Analysis of Microwave Effects by Using "r" and the Yield Ratio of Products. Since the sum of the yields of Products 1 and 2 was constant, the relative change of the yields by microwave irradiation can be calculated by using the following equations.

$$MWE(\mathrm{P1}) = \frac{[\mathrm{P1}]-[\mathrm{P1}]_0}{[\mathrm{P1}]_0} = \frac{A(r-1)}{r+A}, \qquad (2)$$

$$MWE(\mathrm{P2}) = \frac{[\mathrm{P2}]-[\mathrm{P2}]_0}{[\mathrm{P2}]_0} = \frac{1-r}{r+A}, \qquad (3)$$

where A is given as:

$$A = \frac{[\mathrm{P2}]_0}{[\mathrm{P1}]_0}. \qquad (4)$$

$[\mathrm{P1}]_0$ and $[\mathrm{P2}]_0$ represent the yields of Product 1 and 2, respectively, without the microwave effect. Hence A is $[\mathrm{P2}]_0/[\mathrm{P1}]_0$ and it can be calculated from the relation,

$$A = \frac{I_0(\mathrm{P2})}{I_0(\mathrm{P1})}\cdot\frac{\varepsilon(\mathrm{P1})}{\varepsilon(\mathrm{P2})}. \qquad (5)$$

The ratio of the molar absorption coefficients of Product 2 and Product 1, ε(Product 2)/ε(Product 1) was estimated to be 1.14 by using the molar absorption coefficients of 1-methoxy-4-nitronaphthalene (instead of Product 2) and 1-methoxy-4-nitrosonaphthalene (instead of Product 1). From the peak heights in HPLC of Fig. 3 (Fig. 4B) and the ratio between ε's A was estimated to be 0.843.[5,11] Figure 5 shows the pulse-PYESR responses for each of the products calculated with using Eqs. 2 and 3.

Estimation of Kinetic Constants by Simulation A kinetic scheme used in the pulse-PYESR simulation for a radical pair or a biradical (this case) in a high magnetic field is depicted in Fig. 6. It is assumed that the radical pair is

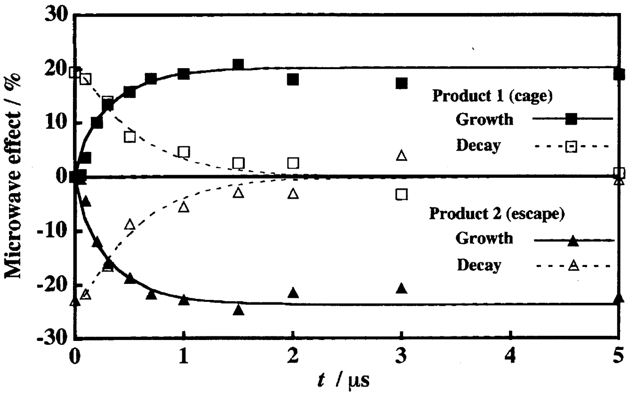

Fig. 5. Microwave effects on the individual yields of Product 1 and Product 2 calculated from r. Solid line (Growth) and broken line (Decay) represent the simulation curves by kinetic equations.

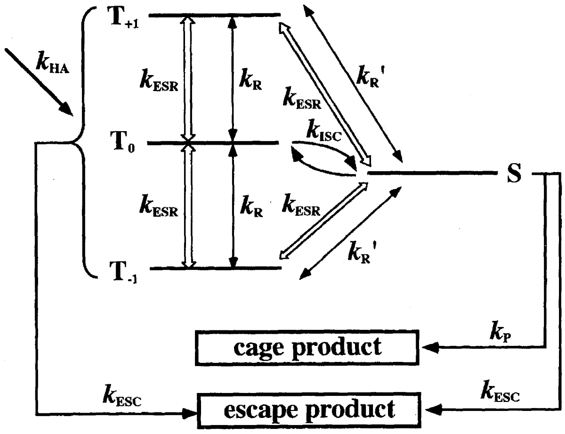

Fig. 6. Kinetic model for a biradical at a high magnetic field. The kinetic processes are shown by arrows with the rate constants. Radical pair is produced at the rate of hydrogen abstraction (k_{HA}). Spin lattice relaxation between the triplet sublebels (k_R) as well as that between the singlet and one of the triplet sublebel (k'_R) mixes the populations in these energy levels. Radical pair decays either by recombination within the pair (k_P) or by self-degradation to yield two free radicals (k_{ESC}). The rate of recombination from the triplet state is negligible in the present case. In case of a small spin exchange interaction, the interconversion between T_0 and S (k_{ISC}) is rapid.

produced by the hydrogen abstraction reaction (k_{HA}) and is distributed over all the triplet sublevels equally. A rapid intersystem crossing (k_{ISC}) is allowed only between T_0 and S in a high field. The formation of cage product (k_P) is allowed for the singlet radical pair. Escape process (k_{ESC}) occurs independently of the spin state. Upon irradiating the system with a microwave field that is resonant on the transient radical pair, the ESR transitions between $T_{\pm 1}$ and T_0 or S are induced (k_{ESR}). The results of the pulse-PYESR were simulated by numerical integration of the kinetic equations for the scheme using the Runge–Kutta method. The results are shown with solid lines (Growth) or broken lines (Decay) in Fig. 4B and Fig. 5.

Since we don't have a high-resolution ESR spectrum of the transient biradical it is difficult to determine k_{ISC} by calculation.[12] We tentatively used 5.04×10^7 s^{-1} which is related with the average separation of 1.8 mT between the ESR lines of the two radical centers. For ESR transition by microwave irradiation (k_{ESR}) we used 2.8×10^7 s^{-1}, which corresponds to the microwave amplitude of 0.9 mT (about 100 W). The rest of the rate constants, those for hydrogen abstraction, recombination, escape product formation, and spin-lattice relaxation were determined as the fitting parameters: $k_{HA} = 3.0\times10^7$ s^{-1}, $k_P = 8.5\times10^6$ s^{-1}, $k_{ESC} = 9.0\times10^6$ s^{-1}, and $k_R = 7.0\times10^5$ s^{-1}, respectively. The rates of spin lattice relaxation k_R and k'_R were assumed to be equal, and is frequently expressed as follows:

$$k_R = k'_R = \frac{\gamma^2 B_{loc}^2 \tau_c}{1+\gamma^2 B_0^2 \tau_c^2}, \tag{6}$$

where γ and B_{loc} are the gyromagnetic ratio of electron and the amplitude of the local fluctuating magnetic field, respectively.[19] τ_c is the rotational correlation time and was calculated to be 15 ps according to the Stokes–Einstein relation for a molecule with a radius of 0.3 nm in benzene (viscosity 0.564 cP, 1cP = mPa s) at 300 K. The amplitude of the local fluctuating magnetic field, which causes electron spin relaxation, was estimated as $B_{loc} = 1.75$ mT.

Kinetics of Biradical Intermediate. From the growth experiment the rate of radical pair production can be obtained as an authentic value if the recombination rate k_P is comparable to that. Therefore the value of 3.0×10^7 s^{-1} for k_{HA} may be underestimated one. According to the proposed reaction mechanism the escape process is a reaction of the biradical with a parent molecule.[5] Therefore, the pseudo-first-order rate constant k_{ESC} can be represented as a product of a second-order rate constant k_q and the concentration of the parent molecule [S] (see Fig. 1).

$$k_{ESC} = k_Q[S]. \tag{7}$$

Since [S] = 0.3 mM, k_Q was estimated as 3.0×10^9 M^{-1} s^{-1} (M = mol dm^{-3}). This value is as large as the maximum value of the rate constants reported for the reaction of nitrobenzene derivatives with some free radicals.[20,21]

The local fluctuating field B_{loc} has been reported[22,23] to be 1.2—1.4 mT and 1.7—1.8 mT for the intermediate biradicals in the photolysis of xanthone–xanthene (XH–XO) and benzophenone–diphenylamine (BP–DPA) bifunctional chain molecules, respectively.[20] The local fluctuating field, 1.75 mT, for this system is similar to that of the latter system. In XH–XO system the two radical centers are delocalized to the benzene rings, thus only a small B_{loc} is expected. On the other hand in the BP–DPA system the N-centered radical may give a large B_{loc}. Therefore, the above order for B_{loc} supports the proposed structure of the biradical intermediate, which has one alkyl radical with two β-hydrogens and one nitroxide radical. The large B_{loc} of this sytem is due to the hyperfine anisotropy of the nitroxide moiety and the hfc of the two β-protons of the alkyl radical.

Conclusion

The biradical intermediate with a *g*-factor of 2.00 and a small exchange interaction was directly confirmed in the photolysis of a benzene solution of *N*-[12-(4-nitro-1-naphthyloxy)dodecyl]aniline by using the product-yield-detected ESR technique. The local fluctuating field was estimated for the biradical as being 1.75 mT, which is plausible for the structure of the biradical intermediate in Fig. 1. From these findings the scheme of Fig. 1 has been confirmed. The rate constant for hydrogen abstraction by the nitro group (k_{HA}) and that for the intermolecular quenching reaction (k_Q) were found to be very fast and those are $k_{HA} \geq 3\times10^7$ s^{-1} and $k_Q \approx 3\times10^9$ M^{-1} s^{-1}, respectively.

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16) When J is much larger than the hfc's of the radical-pair system, the transition between the triplet and the singlet states is prohibited and thus no PYESR signal is expected. Since the maximum hyperfine interaction in the system would be 6.0 mT (due to two β-protons and one α-proton in the carbon-centered radical of Fig. 1), J should be smaller than 10 mT. According to an exponential model for J proposed by F. J. J. De Kanter, et al. (*Chem. Phys. Lett.*, **58**, 334 (1978)), J of 10 mT corresponds to the separation of 1.5 nm for the two spins.

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