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Photoconductivity Detected Magnetic Resonance Study on Photoinduced Electron-Transfer Reaction of Xanthone and *N,N*-Diethylaniline in 2-Propanol

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A PCDMR (photoconductivity detected magnetic resonance) method developed recently is applied to the study of a photoinduced electron-transfer reaction. The PCDMR spectrum of the transient radical-ion pair formed by the photochemical reaction of xanthone/*N,N*-diethylaniline in 2-propanol is observed for the first time. A peculiar PCDMR spectrum is observed by irradiation with strong microwaves. This spectrum is tentatively explained by spin−locking at the line center and by the transition at both broadened wing portions. The lifetime of the radical-ion pair is estimated to be 2×10^{-7} s at room temperature and is anomalously long.

Introduction

Study of the spin dynamics of intermediate radical-ion pairs (RIP) formed by photoexcitation is important for understanding the primary reaction mechanism of the photochemistry. RYDMR[1−6] (reaction yield detected magnetic resonance) methods are used along with a time-resolved ESR to investigate the main chemical reaction manifold or the interactions of two paired radicals that determine the direction of the chemical reaction. For the observation of the RYDMR, ADMR[1−3] (transient absorption detected magnetic resonance), FDMR[4−6] (fluorescence detected magnetic resonance), and other reaction yield detection methods have been employed by several groups so far.

Recently, we applied time-resolved photoconductivity measurements to the study of the spin dynamics of the RIP formed in the photolysis of TMPD (*N,N,N′,N′*-tetramethyl-1,4-phenylenediamine) in a mixed alcohol solvent. We succeeded in the observation of the PCDMR[7,8] (photoconductivity detected magnetic resonance) spectrum of this particular system: namely, the ESR spectrum of the RIP (TMPD cation radical and solvated electron). Photoconductivity allows the only measurement of the amount of transient ion radicals escaped from the RIP, which is the difference from the other RYDMRs. Therefore, it gives different or complementary information about the dynamics of transient species.

In the photolysis of xanthone (Xn) and *N,N*-diethylaniline (DEA) in 2-propanol, the photoinduced electron-transfer reaction from DEA to the excited triplet state of Xn (^{3}Xn*) takes place, and it is believed to form a transient RIP. The magnetic field effect (MFE) on the transient absorption of this system in 2-propanol has been reported by Igarashi et al.[9] Their data of large MFE imply a long lifetime of the transiently formed RIP.

This paper reports the observation of MFE on the photoconductivity and the PCDMR spectrum of the transient RIP formed from Xn and DEA at different microwave powers.[10] The peculiarly long lifetime of the RIP is also estimated. This report is the first observation of the ESR spectrum on the RIP composed of the Xn anion and DEA cation radicals at room temperature.

Experimental Section

Xn (Wako Pure Chemical) was repeatedly recrystallized from a 2:1 (v:v) mixture of ethanol−water. DEA (Kanto Chemical) and 2-propanol (Wako Pure Chemical) were used as received. The concentrations of Xn and DEA in 2-propanol were 1.0×10^{-3} M (mol/dm^3) and 2.0×10^{-2} M, respectively, in most experiments. Low concentration (1.0×10^{-4} M) of Xn was used to determine the lifetime of the RIP. The sample which was deoxygenated by bubbling with nitrogen gas was excited by the third harmonic light of Nd:YAG laser ($\lambda = 355$ nm) in an X-band ESR cavity (TE$_{011}$ mode) at room temperature (20 °C). Xn could be excited selectivity by this laser under present conditions.

Photoconductivity was measured in a specially designed flat quartz-flow cell (light path of 0.6 mm) with platinum electrodes. The potential between electrodes was about 150 V/mm. Experimental setup is the same as that of previous papers.[7,8] A 50 Ω resistance inserted in the observation circuit, which converts photocurrent to voltage, gives a time resolution of better than 20 ns. For the observation of MFE, a Hall-effect type gaussmeter was used to determine the absolute field. Zero field (<0.1 mT) was adjusted by the offsetting coil to compensate the residual field of the electromagnet. A proton-resonance type NMR gaussmeter was used for the PCDMR observation. The signal of the transient photoconductivity stored in a 10 bit digital oscilloscope (LecRoy 9430) was transferred to a microcomputer system for data processing. A TWT amplifier (Litton) with maximum power of 1 kW was used to boost the microwave pulse.

A digital delay/pulse generator, model DG535 (Stanford Research System), was used to adjust the timing of the laser and microwave pulses for the lifetime measurement (off−on measurement) of the RIP. The signal intensity at 800 ns after the turning on time of the microwave radiation was measured as the concentration of the RIP at the time of the microwave-on after the laser excitation.

Results and Discussion

The photoinduced electron-transfer reaction of the present system[9] takes place by way of the excited triplet state of Xn. The application of the magnetic field and the microwave

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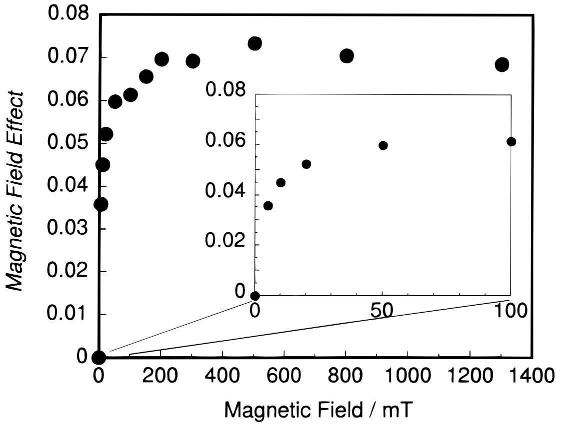

Figure 1. External magnetic field effect upon the photoconductivity observed in the photolysis of Xn/DEA in 2-propanol at room temperature (20 °C). The data of 1.0−1.5 μs after the laser pulse were time-integrated.

radiation under the ESR resonance conditions are expected to modulate the ISC rate of the intermediate RIP.

Magnetic Field Effect. Figure 1 shows the MFE on photoconductivity, where the magnetic field effect is defined as the ratio of the difference of the conductivity signals in the presence and absence (zero field) of the external magnetic field to that in the zero field. The photoconductivity increases about 7% at 200 mT compared with that in the zero field. It shows a steep curve below 20 mT and gradual increase after that point. The result is in good accordance with that reported by Igarashi et al.[9] by a transient absorption technique. The magnetic field ($B_{1/2}$) where one-half of the saturated MFE is achieved is about 5 mT. The result is explained by the typical two MFE mechanisms: hyperfine coupling mechanism and relaxation mechanism.[11−14] The increase of the photoconductivity is explained as follows: In the external magnetic field, Zeeman interaction separates the triplet sublevels, T_+, T_0, and T_- states, of the RIP. Since the T_+ and T_- states cannot perform ISC to the S state efficiently, the reaction of the RIP is decelerated compared with the zero field condition. Therefore, the concentration of the free ion radicals escaped from the unreacted RIP, namely, photoconductivity, increases. The question raised by the present data is the appearance of the large MFE in the homogeneous alcohol solution. In general, the lifetime of RIPs is believed to be in the order of or less than a few nanoseconds in homogeneous polar media[15] and is not long enough to induce the large MFE.

PCDMR Spectra at Low Microwave Power. Figure 2 presents the time-resolved PCDMR spectra observed at low microwave power (10 W) in the photolysis of Xn/DEA in 2-propanol. The photoconductivity decreases about 1% at the ESR resonance conditions. The ratio of the difference of the signals in the presence and absence of microwave radiation to that in the absence of microwaves is called "microwave effect". The decrease of photoconductivity is explained as follows: Under the ESR resonance conditions, the transitions from T_+ to T_0 and T_- to T_0 are accelerated by microwave irradiation. Consequently, the intersystem crossing is promoted, and the population of the triplet state where the escape of the ion radical mainly takes place decreases compared with that without microwave radiation under the static magnetic field. Therefore, the number of free ion radicals, namely, photoconductivity, decreases. This is called "pumping effect".

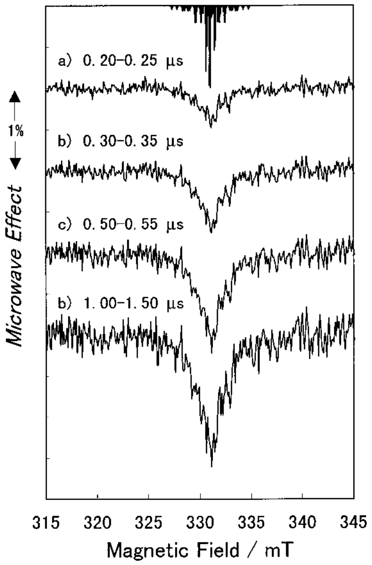

Figure 2. Time-resolved PCDMR spectra observed after laser excitation at low microwave power (10 W) in the photolysis of Xn/DEA in 2-propanol. The inset above spectrum a is the stick ESR spectrum of the Xn^- and DMA^+ (instead of DEA^+).

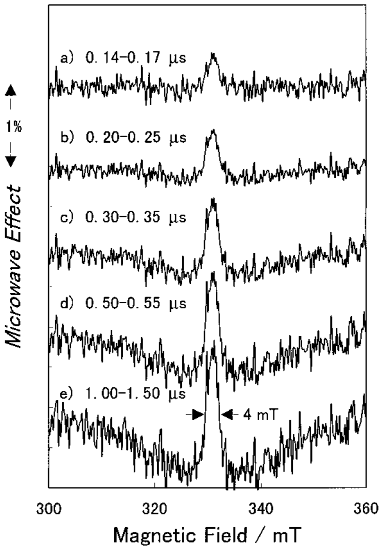

Figure 3. Time-resolved PCDMR spectra observed after laser excitation at high microwave power (1 kW) in the photolysis of Xn/DEA in 2-propanol. The upward and downward signals indicate the deceleration and acceleration of the reaction, respectively.

The shape of the PCDMR spectrum is explained by the envelope of the hyperfine structures of the component radicals. The total distribution of all the hyperfine coupling lines of DEA cation radical ($DEA^{\bullet+}$) is presumed to be nearly 10 mT from the reported data of *N*,*N*-dimethylaniline which must have similar structure to DEA cation radical, and that of the xanthone anion radical ($Xn^{\bullet-}$) is much narrower (about 2 mT).[16] The relatively strong microwave power (10 W and B_1 of about 0.3 mT), which is a few thousand times higher than the ordinary ESR method, obscures the structure.

PCDMR Spectra at High Microwave Power. In Figure 3, the time-resolved PCDMR spectra observed in the same system at a strong microwave (1 kW) are presented. These spectra show an inverted shape at the center field, and the line width of the upward spectrum is about 4 mT. This is due to the spin−locking effect at the ESR resonance center. On the contrary, a negative signal (pumping) having a broad winglike structure appears at a later time. The wing portions which show the pumping effect seem to be due to the large difference of spectral width of two radicals (DEA cation radical has about 5 times larger hyperfine distribution than that of Xn anion radical) which cannot be covered by B_1; then spin−locking does not take place. Accordingly, the T_+-T_0 and T_--T_0 transitions followed by the T_0-S mixing appear. However, the extremely broadened wing shape cannot be interpreted only by these transitions. The B_1 field broadening and the other effects should be taken into account. The similar spectral shape has been reported in the system of a long-lived polymethylene-linked biradical where the J modulation is postulated.[1] Anyway, the strong B_1 field and the long lifetime of RIP are thought to be needed for the appearance of the broad wings in the present case. The appearance of these spin effects is quite interesting, because the present system is an apparent homogeneous solution.

Analysis of the Kinetics. The kinetic model of the reaction is expressed by the following equations (eqs 1−6):

$$^3\mathrm{Xn}^* + \mathrm{DEA} \xrightarrow{k_d} \mathrm{RIP} \tag{1}$$

$$^3\mathrm{Xn}^* + \mathrm{ROH} \xrightarrow{k_a} {}^\bullet\mathrm{XnH} + {}^\bullet\mathrm{ROH} \tag{2}$$

$$\mathrm{RIP} \xrightarrow{k_e} \mathrm{Xn}^{\bullet-} + \mathrm{DEA}^{\bullet+} \tag{3}$$

$$\mathrm{RIP} \xrightarrow{k_r + k_m} \mathrm{products} \tag{4}$$

$$\mathrm{Xn}^{\bullet-} + \mathrm{DEA}^{\bullet+} \xrightarrow{k_f} \mathrm{RIP} \tag{5}$$

$$\mathrm{Xn}^{\bullet-} + \mathrm{DEA}^{\bullet+} \xrightarrow{k_q} \mathrm{products} \tag{6}$$

where k_d is the rate constant of the reaction of ^{3}Xn* and DEA, k_a is the reaction rate constant of ^{3}Xn* and alcohol, k_e is the escaping rate constant from the RIP, k_r is the reaction rate constant of the RIP to make products under X-band magnetic field, k_m is the acceleration of reaction 4 by microwave radiation, k_f is the encounter rate constant to form free radical ion pair, and k_q is the quenching rate constant of IR (ion radicals).

According to eqs 1−6, the kinetic equations are as follows (photoconductivity is proportional to the amount of IR, and [IR] is assumed to be $[\mathrm{DEA}^{\bullet+}] \approx [\mathrm{Xn}^{\bullet-}]$):

$$\frac{\mathrm{d}[^3\mathrm{Xn}^*]}{\mathrm{d}t} = -k_d[\mathrm{DEA}][^3\mathrm{Xn}^*] - k_a[^3\mathrm{Xn}^*] \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{RIP}]}{\mathrm{d}t} = k_d[\mathrm{DEA}][^3\mathrm{Xn}^*] - (k_e + k_r + k_m)[\mathrm{RIP}] + k_f[\mathrm{IR}]^2 \tag{8}$$

$$\frac{\mathrm{d}[\mathrm{IR}]}{\mathrm{d}t} = k_e[\mathrm{RIP}] - (k_f + k_q)[\mathrm{IR}]^2 \tag{9}$$

The RIP is generated by diffusion-controlled reaction of ^{3}Xn* and DEA, since k_d is reported[9] as 3×10^9 M^{-1} s^{-1}. k_a is also known to be 3.5×10^6 s^{-1} from the experiment of transient absorption.[9] Its value is very small compared with the reaction with DEA under the present experimental conditions. The diffusion-controlled rate constant 3×10^9 M^{-1} s^{-1} is used as k_f, provided that the generation of the free pair is due to a simple encounter of IR. k_q is the bimolecular quenching reaction rate of the ion radicals and is not affected by the microwave radiation.

The introduction of this quenching, k_q, elucidates the slow decay of the photoconductivity signals. We used two conditions of Xn concentration: (a) high-concentration case (1×10^{-3} M) and (b) low-concentration case (1×10^{-4} M). By comparing the two cases as shown in Figure 4 of the photoconductivity change without the magnetic field, it is clear that IR is quenched by the second-order reaction because the decay rate of high concentration is faster than that of low concentration. From the fitting of the photoconductivity data by these equations (see Figure 4), k_q is estimated to be 1.8×10^9 M^{-1} s^{-1}. The use of this second-order rate constant k_q is necessary to simulate the time profile of photoconductivity quenching.[17] It is difficult to fit the data by using the first-order decay. The result is natural because the charge-quenching reactions, such as a proton transfer between the cation and anion radicals, may take place.

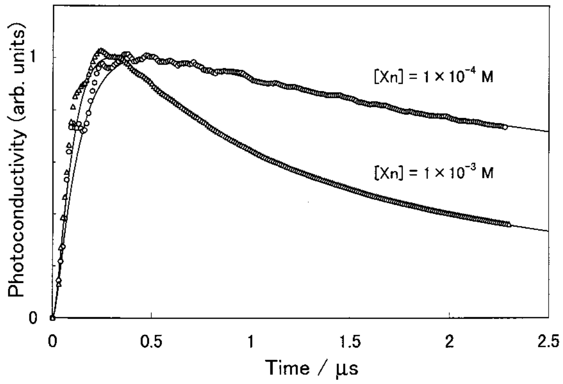

Figure 4. Time profiles of the photoconductivity observed in two different Xn concentrations under zero magnetic field and no microwave radiation. The open circles and triangles show the observed data in the diluted (1×10^{-4} M) and concentrated (1×10^{-3} M) conditions of Xn, respectively. The solid lines are respective calculations. The weak oscillation immediately after laser excitation is an artificial noise.

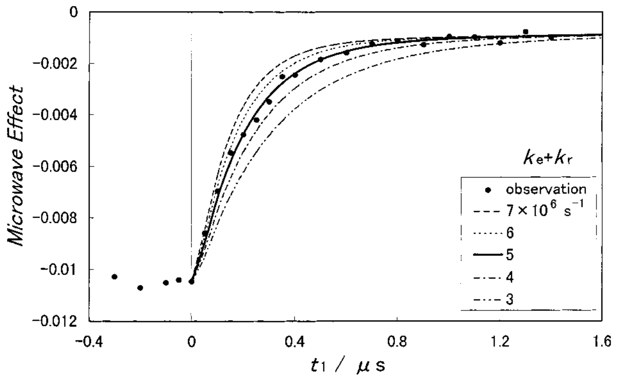

Figure 5. Photoconductivity change observed at the various turn-on times of the microwave radiation after the laser pulse. The concentration of Xn was 1×10^{-4} M. The solid and broken lines are the simulations obtained by eq 10. The closed circles are the experimental data. When $k_e + k_r = 5 \times 10^6$ s^{-1}, the simulated solid line reproduces well the experimental data.

Measurement of the RIP Lifetime. The long lifetime of the RIP is predicted by the results of the MFE and PCDMR experiments. The spectral shape observed in the strong B_1 field shown in Figure 3 implies the long lifetime of the RIP as mentioned before. The lifetime should be determined directly by the time domain observation. The intensity of the PCDMR signal after the microwave irradiation is proportional to the amount of the RIP at the turning on time of microwave. Then we tried the microwave off−on experiment that controls the delayed turning-on time of the microwave radiation. Figure 5 shows the PCDMR intensity (microwave effect) versus microwave radiation-on time t_1 (−300 to 1500 ns) after laser excitation. Here, the low-concentration condition of Xn was used to avoid the complexity of the reactions. The signal at the center field of the spectrum under low microwave power (10 W) was monitored. As shown in Figure 5, it is clear that the PCDMR intensity does not become zero even at 1 μs after the laser excitation. This implies that the contribution of the free ion radicals that repeatedly form the RIP after escaping from the geminate RIP should be taken into account.

The lifetime of this RIP was estimated by curve fitting as shown in Figure 5 using the kinetic model. When the microwave is not radiated, k_m is zero, and k_m has a finite value by the radiation. The time profile of microwave effect is expressed by eq 10, where t_2 is the observation time of the photoconductivity ($t_2 = t_1 + 800$ ns in the present case):

$$\text{microwave effect} = \frac{([\mathrm{IR}(t_0 \rightarrow t_1)]_{\mathrm{MWoff}} + [\mathrm{IR}(t_1 \rightarrow t_2)]_{\mathrm{MWon}}) - [\mathrm{IR}(t_0 \rightarrow t_2)]_{\mathrm{MWoff}}}{[\mathrm{IR}(t_0 \rightarrow t_2)]_{\mathrm{MWoff}}} \tag{10}$$

The lifetime of the RIP is expressed by $1/(k_e + k_r)$. The differential equations were solved by the Runge−Kutta method. In this fitting, the lifetime of the RIP is estimated to be about 2×10^{-7} s, $(k_e + k_r) = 5 \times 10^6$ s^{-1}, as shown in Figure 5. The other simulations of the estimation of the RIP lifetime were tried. They were the fitting of the time profile of direct photoconductivity, MFE, and PCDMR with continuous microwave irradiation. These results also provided nearly 2×10^{-7} s of RIP lifetime.[17] The lifetime of the RIP is peculiarly long compared with the general RIP system in homogeneous solvent.

If the radicals diffuse without any interaction (the case of free diffusion), the lifetime of RIP is considered to be a few nanoseconds.[15] Then, the Coulomb interaction is considered as the reason of the long lifetime. However, the relative dielectric constant ϵ_r of 2-propanol (19.8) is too large to confine RIP for a long time. Therefore, the most possible explanation of the long lifetime of the RIP may be the introduction of some properties of 2-propanol along with the Coulomb interaction that stabilize the free motion of the RIP. Then it suppresses the escaping of ion radicals from the RIP. In the simulation procedure,[17] the k_e was estimated to be 4×10^6 s^{-1}, which mainly contributes to the lifetime of RIP at X-band magnetic field. As for the 2-propanol, many peculiar phenomena like the present case are reported.[7,8,18−20] We conclude that 2-propanol may make the lifetime of the RIP long by decelerating k_e.

Conclusion

The photoinduced electron-transfer reaction between the excited triplet state of xanthone and *N,N*-diethylaniline was studied in 2-propanol by MFE on the photoconductivity and PCDMR method. The photoconductivity increased about 7% with increasing the external magnetic field from 0 to 200 mT. This magnetic field effect was explained by both the hyperfine coupling and relaxation mechanisms. Under the ESR resonance conditions, about 1% decrease of photoconductivity was observed under the magnetic field of 330 mT at low microwave power. PCDMR spectrum was in good accordance with the spectral envelope estimated from the hyperfine coupling constants of DEA$^{\bullet+}$ and Xn$^{\bullet-}$. Under the strong microwave radiation, PCDMR spectrum showed the spin−locking effect at the center and the pumping effect on both wing portions. This shape of spectrum was caused by the long lifetime of the RIP. The lifetime of this system was estimated to be 2×10^{-7} s by the microwave off-on measurement. This long lifetime of the RIP in homogeneous solvent at the room temperature (20 °C) is peculiar. The value of k_e in this system is about 4×10^6 s^{-1}, while k_e of the ordinary RIP is on the order of or larger than 10^8 s^{-1}. The property of 2-propanol and the Coulomb interaction, which strongly suppress the escaping of the ion radicals from RIP, may be the cause of the long lifetime.

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