Dynamic Process of Delayed Geminate Ion Pairs in X-Irradiated Squalane Solution of *p*-Terphenyl: An ODESR Study

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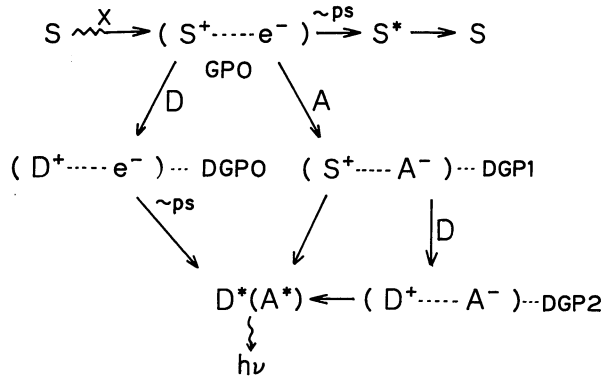
The fluorescence detected ESR (ODESR) spectrum of a squalane solution of *p*-terphenyl was observed at various temperatures, concentrations, and microwave powers. Analysis of the ODESR amplitude, the line shape, and the area under the spectrum which is normalized by the fluorescence intensity led us to conclude that two geminate pairs (one with a terphenyl anion and a hole of the solvent squalane and the other with a terphenyl anion and its cation) contribute to the ODESR spectrum. It was also concluded that the former pair has a much shorter recombination time than that of the latter. It is suggested that though the hole center hops among the solvent squalanes, the rate is much less than that for the hole in aromatic solvents.

The kinetics and charge-transfer processes of the geminate pair are essential for the subsequent processes of radiation chemical reactions.[1,2] In a multicomponent system the primary process of a radiation chemical reaction may include: (1) the formation of a geminate pair with a hole and an electron, (2) negative and positive charge transfer to an electron acceptor and to an electron donor,[3] respectively, (3) recombination of the pair to release charge neutralization energy which may be used to promote one of the components to an electronically excited state, and (4) emission of luminescence upon the transition of the excited molecule to its ground state. These processes are summarized as the following scheme:



Scheme 1.

where D and A represent the electron donor and the electron acceptor, respectively. We hereafter call the original geminate pair (S^+, e^-) GP0, and those delayed geminate pairs ((D^+, e^-), (S^+, A^-), and (D^+, A^-)) DGP0, DGP1, and DGP2, respectively. The magnetic field dependence[4] of this fluorescence intensity and the ESR spectrum observed through a modulation of this fluorescence due to the ESR transitions of transient radicals of the geminate pair (ODESR,[5] or FDMR[6]) gave detailed information about these processes and the subsequent reactions,[7–16] including cation radical formation,[7,8,15] dehydrogenation of the cation,[9,10] cation dimer formation,[11,16] electron or hole trapping,[12–14] and so on.

Molin and others found very mobile holes in the solution of 2,5-diphenyloxazole and *p*-terphenyl in aromatic solvents,[13,14] benzene and toluene, by the ODESR technique. They determined the hopping rate of a hole in the solvents by measuring the line narrowing of the ODESR spectra. Though the ODESR amplitude also depends on the parameters which are essential to characterize geminate pairs (mainly delayed geminate pairs), the fact that several delayed geminate pairs contribute to ODESR at the same time somewhat hampered us from extracting information from it. However, the geminate pairs contributing the ODESR signal can be discriminated by analyzing several series of spectra obtained with various parameters.

In the present study, the ODESR amplitude of a squalane solution of *p*-terphenyl (*p*-TP) was obtained at various concentrations, microwave powers, and temperatures. As a result, the formation of two kinds of geminate pairs (one composed of a *p*-TP anion and a hole in the solvent squalane (DGP1) and the other including a *p*-TP anion and its cation (DGP2)) has been confirmed. In addition, it has been shown that the ODESR amplitude should be treated relative to the fluorescence intensity for studying the kinetic processes in an irradiated system.

Many studies have been devoted to detecting solvent alkane cations using the ODESR technique.[7–10,15] However, at elevated temperatures (including room temperature) solvent-minus H_2 cation is observed in most cases,[9,15] and the solvent cation, itself, is rarely identified,[8,15] since the hole in alkanes (cation center) is expected to migrate at a high rate; thus, its identification is difficult.

Experimental

p-Terphenyl (*p*-TP) was obtained from Tokyo Kasei Kogyo (Tokyo) and purified by sublimation. Squalane,

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pyrene, and hexafluorobenzene were purchased from the same company as the purest-grade (>99%) reagents. The optical density of squalane at 227 nm was about 0.2, which indicates that the purity is sufficient for our experiments. These latter chemicals were used without further purification. 1.0 ml of the sample solution was packed in an ESR sample tube with a diameter of 5.5 mm (o.d.), and degassed with the freeze-pump-thaw technique. The ODESR spectra were obtained with an apparatus which was assembled with an X-ray emitter made by Rigaku Denki Co. (Osaka) with an end-on type tube (OEG-75H, Machlett), a Bitter-type magnet with poles of 10 cm (o.d.) (which was specially designed by Echo Electrics (EM-464B, Tokyo) for our use), a home-made microwave unit with a 20 W cw-TWT amplifier (Keltec Florida), and a photomultiplier (R1894, Hamamatsu Photonics, Shizuoka, Japan) connected with a photon-counting unit (C767, Hamamatsu Photonics). Magnetic field scanning as well as processing of the digital output from the photon counter were performed with a microcomputer (PC 9801-VX, NEC, Tokyo). The temperature was controlled with cold nitrogen gas by monitoring the temperature of the gas at the outlet. Details of the spectrometer have been described elsewhere.[17] The ODESR amplitude was normalized by the fluorescence (>300 nm) intensity (photon count) after subtracting the background signal.

The X-ray dose rate was estimated using a film containing methylviologen[18] and was 0.25 MR/hr at the 3 KW output. The microwave power was measured with a power meter (HP437B with a power sensor HP8481B, Hewlett Packard).

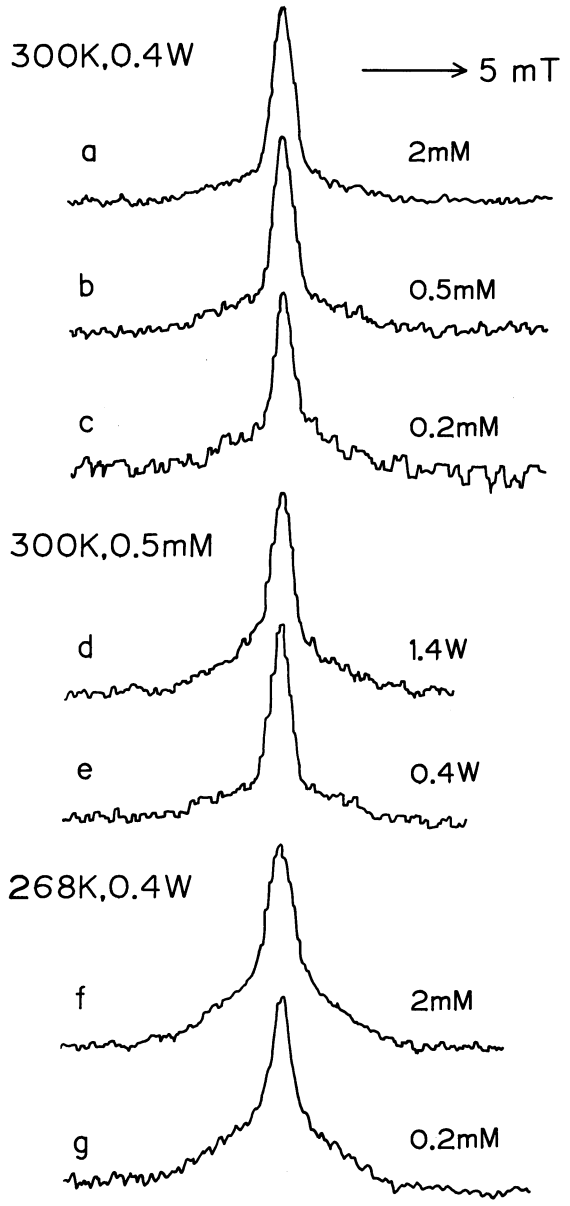

Fig. 1. ODESR spectra of squalane solution of *p*-terphenyl under various conditions: a, 2 mM; b, 0.5 mM; c, 0.2 mM, at 300 K with 0.4 W microwave power; with the microwave power of d, 1.4 W, e, 0.4 W at 300 K 0.5 mM; and 2 mM, f, and 0.2 mM, g, at 268 K with 0.4 W. The time needed for each scan was 10 min.

Results

Figure 1 shows the ODESR spectra of terphenyl in squalane under various conditions: traces a, b, and c show the concentration dependence of the ODESR specrtum, traces d and e show the dependence on the microwave power, and traces f and g show the ODESR spectra at a lower temperature. In addition to the central sharp component which is assigned to the ion radicals of *p*-terphenyl (*p*-TP) from its *g*-value, a broad component becomes prominent upon decreasing the concentration. Because squalane without a solute gave no ODESR signal, this broad component should be due to a radical pair composed of a *p*-TP ion

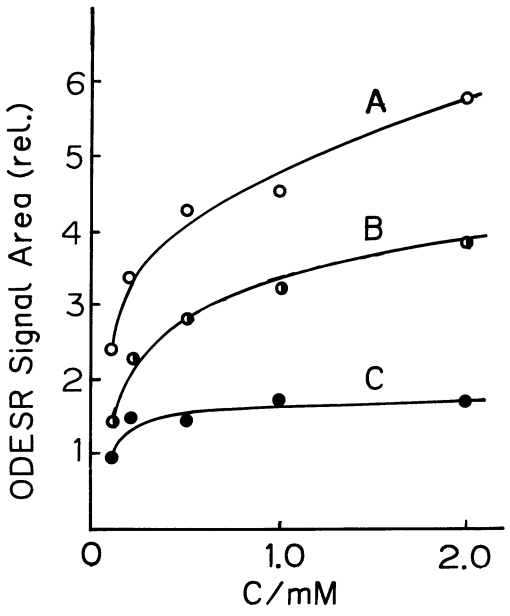

Fig. 2. ODESR signal area (relative) normalized with fluorescence intensity as the functions of concentration of terphenyl. The microwave power was 1.4 W (A) or 0.4 W (B, C) and the temperature was 278 K (A, B) or 298 K (C).

radical and a radical which gave the broad ESR signal. Besides, this broad component does not change even if hexafluorobenzene (a strong acceptor) is added to the system and is also observed in a experiment with another dye molecule, i.e. pyrene. Therefore, this broad component is assigned to the solvent-derived hole (or solvent cation) which constitutes a delayed geminate pair (DGP1) with a solute anion.

This broad component increases upon increasing the microwave power, as shown in traces d and e and with decreasing the temperature, as shown in traces f and g. This may be merely because the recombination time of DGP1 is considerably shorter than that of DGP2, but is elongated at low temperatures.

Figure 2 shows the area under the ODESR spectrum as functions of the concentration of *p*-TP. The ODESR amplitude is normalized by the fluorescence intensity. Curves A and B represent the ODESR signal area (in arbitrary unit) of a squalane solution of *p*-TP at 278 K at microwave powers of 1.4 and 0.4 W, respectively. Curve C represents the ODESR signal area at 298 K at 0.4 W. At each temperature, the ODESR signal area (relative to the fluorescence intensity) increases rather steeply in the low-concentration region and continues to increase up to 2 mM (1 M=1 mol dm^{-3}). If the fluorescence is generated from a single type of geminate pair, the ODESR amplitude normalized by the fluorescence intensity should be independent on the solute concentration. Therefore, a considerable increase in the area under the ODESR spectrum upon increasing the *p*-TP concentration is another form of evidence that several geminate pairs contribute to this fluorescence.

Figure 3 shows the microwave power dependence of the ODESR amplitude at 288 K (left) and 268 K (right). Upon increasing the microwave power, the ODESR amplitude initially increases steadily; subsequently, however, the increase is blunted, and finally starts to decrease. This decrease of the ODESR amplitude at high microwave power is due to the simultaneous flip of the spins of the radical pair,[19,20] which induces no singlet–triplet mixing. At both temperatures, the ODESR amplitude (relative to the fluorescence intensity) decreases upon reducing the concentration. At the same time, when the concentration is low, the maximum amplitude occurs at a higher microwave power than that in the case of a higher concentration. As mentioned above, at low microwave powers the ODESR amplitude, which is normalized by the fluorescence intensity, is approximately proportional to the product of the square of the microwave field strength (B_1) and the lifetime of the geminate pair (τ_g),[21]

$$\text{ODESR amp} = \text{Const}\cdot(\gamma B_1)^2 \tau_g, \qquad (1)$$

where γ is the gyromagnetic ratio of electron and "Const" is a constant dependent on other experimental parameters, such as the photomultiplier sensitivity. Therefore, the gradient of the curves in the low microwave field region in Figure 3 may be proportional to the lifetime of the radical pair. Thus, the (averaged) lifetime of the pairs increases upon increas-

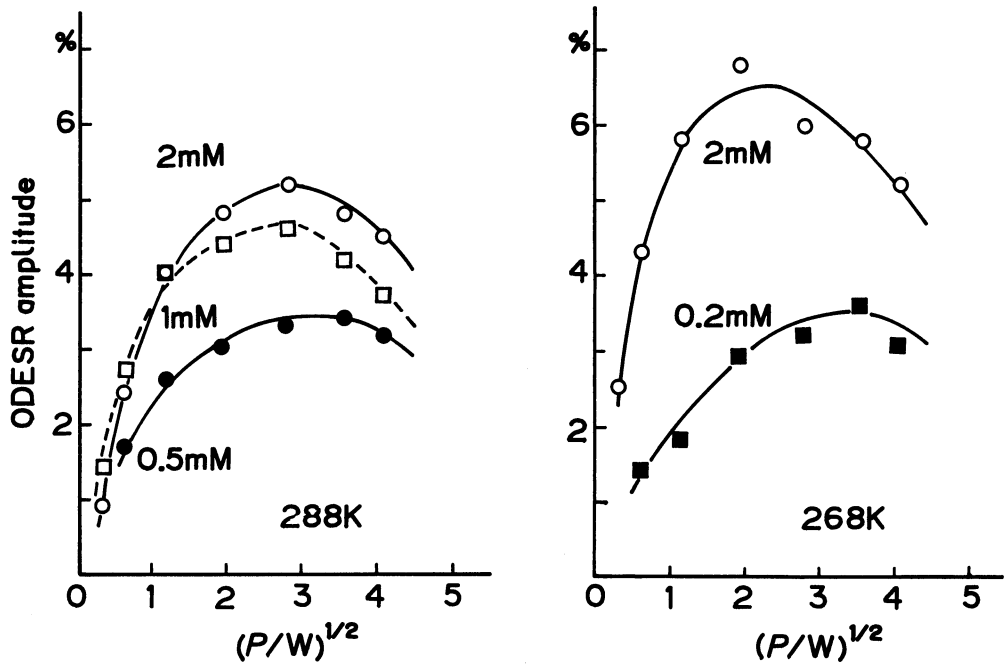

Fig. 3. Microwave dependence of ODESR amplitude (normalized to the fluorescence intensity) at two temperatures: left 288 K; right, 268 K for the samples at the concentration shown. The abscissa is graduated by the square root of the microwave power and thus proportional to the microwave field.

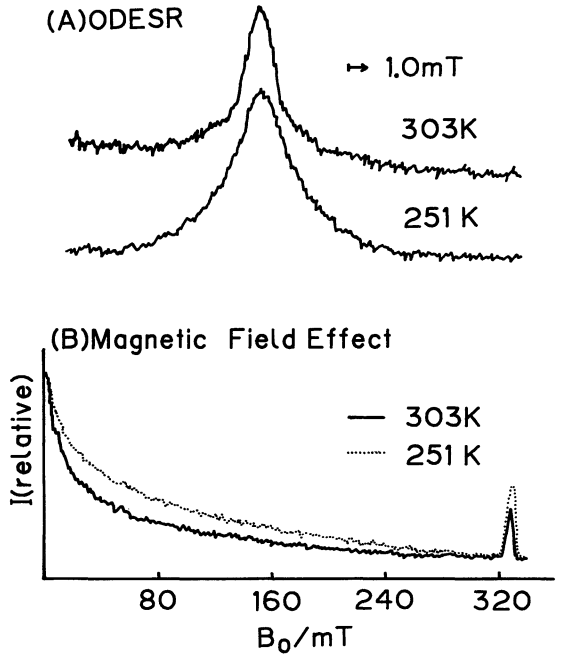

Fig. 4. ODESR spectrum of pyrene solution in squalane at 303 K and 251 K (A), and the magnetic field dependence of the fluorescence at those two temperatures; solid line, 303 K and dotted line, 251 K. The pyrene concentration was 0.3 mM and the microwave power was 1.4 W. Scanning time of the ODESR spectrum and that of the magnetic field dependence was 10 min. The negative direction of the ordinate in B corresponds to the increase in the fluorescence intensity.

ing the concentration of *p*-TP or lowering the temperature.

Figure 4(A) shows the ODESR spectrum of a 0.5 mM pyrene solution in squalane at a temperature of 303 K or 251 K and at the microwave power of 1.4 W. Upon decreasing the temperature, the broad component greatly increases. This is not due to "saturation",[22] but is due to the fact that the contribution of the broad component becomes large at lower temperatures, just in the same way as the terphenyl's case. In fact, $B_{1/2}$, at which field the magnetic field effect on the fluorescence intensity becomes half of its asymptotic value, increases by more than 50% upon decreasing the temperature from 303 to 251 K, as shown in Fig. 4(B). Since $B_{1/2}$ is approximated by the averaged hyperfine field for the radical pair,[23] this result indicates that the contribution of the geminate pair with a larger hyperfine coupling (i.e. DGP1) to the ODESR signal increases upon decreasing the temperature,

$$B_{1/2} \approx \Sigma[a_i^2 I_i(I_i + 1)]^{1/2}, \quad (2)$$

where a_i is the hyperfine coupling constant for the i'th nucleus whose nuclear spin moment is I_i. An equivalent phenomenon was observed using *p*-TP instead of pyrene.

Discussion

The ODESR spectrum of a squalane solution of *p*-terphenyl (*p*-TP) showed two components: one is a sharp absorption with $\Delta B_{1/2}$ (width at half height) of about 1.0 mT and the other is a broad absorption with $\Delta B_{1/2}$ of about 4.5 mT (Fig. 1). The broader signal increased relatively upon decreasing the concentration of *p*-TP (Fig. 1), lowering the temperature, and increasing the microwave power (Fig. 1). In addition, the area under the ODESR spectrum, the amplitude of which is normalized by the fluorescence intensity, increased upon increasing the *p*-TP concentration (Fig. 2). The microwave power dependence of the ODESR amplitude was also dependent on the *p*-TP concentration (Fig. 3), i.e. the maximum amplitude for the lower *p*-TP concentration occurred at a relatively higher microwave power. Essentially the same phenomena are observed for a pyrene solution in squalane. The increase of a component with larger hyperfine couplings in the geminate pair under the conditions mentioned above was confirmed by the fact that $B_{1/2}$, at which field the increase in fluorescence due to the magnetic field becomes half of the asymptotic value, also increases under those conditions (Fig. 4).

In the case that mechanisms other than the geminate ion recombination contribute to the fluorescence considerably, and those are very much dependent on the solute concentration or on the temperature, the following discussion becomes invalid. However, it is well known that more than 90% of the geminate pairs recombine in alkanes,[24,25] and that the excitation transfer from the solvent to the solute contributes little when the solute concentration is low.[26] Therefore, we believe that the discussion below is valid and regarding the main process.

1. Two Geminate Pairs: Because the ESR transitions of both components of a radical pair contribute to the decrease of fluorescence equally, the area of the anion signal must be equal to that of cation signal. Therefore, the fact that the broad component behaves in a different way from the sharp component indicates that there are at least two geminate pairs which contribute to the fluorescence. From Scheme 1, four radical pairs should be taken into account for an analysis of the ODESR spectrum: GP0, DGP0, DGP1, and DGP2. In the present case, S indicates squalane and both D and A represent a fluorescent molecule. The primary radical pair, GP0, and one of the delayed geminate pairs, DGP0, may recombine within a very short time due to the high electron mobility; thus no direct contribution to the ODESR spectrum considered. We therefore conclude that two radical pairs, one of which contains a squalane radical cation (or hole) and a *p*-TP anion (i.e. DGP1) and the other that contains a *p*-TP cation and its anion (i.e.

DGP2), contribute to our ODESR spectrum. Trifunac et al. assigned the broad component in their FDMR spectra of a PPO (2,5-diphenyloxazole) solution in cyclohexane to the solvent hole.[7] They also reported that the broad component comes from the radical pair with a solvent hole and a solute anion,[15] even if the hole transfer in cyclohexane is expected to be very fast.

2. Solute Concentration Dependence: If the hole and the electron captures occur independently, as shown in Scheme 1, and the fluorescence is produced only from the recombination of DGP2, the fluorescence intensity may be proportional to the product of the concentrations of D and A. Because *p*-TP works as both the donor and the acceptor in present case, the fluorescence must be proportional to the square of the *p*-TP concentration. However, the fluorescence changes linearly about the *p*-TP concentration (up to 1 mM), or less than that at still higher concentrations.[27] This can be understood by postulating that once one of the components of the original geminate pair (the electron or the hole) is captured by *p*-TP, the radical pair may contribute to the fluorescence, whether it develops to DGP2 or not.

A simple consideration on the conversion ratio of the original geminate pair to the secondary pairs (DGP1 and DGP2) may help us to grasp the approximate feature of the recombination process. Using a dose rate of 0.04 MR h^{-1} (500 W output to the X-ray tube), G=4, the fluorescence yield $\approx$1, and the ratio of the fluorescence introduced into the photomultiplier >1% (estimated roughly by the solid angle of the aperture of light guide from the fluorescent spot), it is shown that the observed photon count of 10^6 s^{-1} is less than $1/10^4$ of the estimated photon number. Therefore, only a small part of GP0 transfers its charge to a *p*-TP which, by chance, resides in the vicinity of the electron or the hole. However most of the GP0 may recombine within a short time without producing the fluorescence observable in our experiment. When the electron of GP0 is trapped by *p*-TP first, the lifetime of the ion (geminate) pair DGP1 is elongated by thousands of times due to the low mobility of molecular ions. Therefore, DGP1 can be converted to DGP2 with considerable probability. On the other hand, if the positive charge is transferred to *p*-TP to produce DGP0, it may recombine within a very short time which is not sufficient for DGP0 to be converted to DGP2, since the mobility of the electron is much higher than that of the hole. Therefore, DGP0 may contribute to the fluorescence, but not to the ODESR signal, due to the short lifetime (see Eq. 1). The concentration dependences of the ODESR spectrum and its amplitude are attributed to the fact that the conversion probability of DGP1 to DGP2 is dependent on the *p*-TP concentration. At a low concentration, as in the case of trace B in Fig. 1, DGP1 dominates in the ODESR spectrum, whereas at a higher concentration, as in the case of trace A in Fig. 1, most of the DGP1 may be converted to DGP2.

3. Microwave Power Dependence: In the case where two geminate pairs contribute to the ODESR signal and the lifetimes are different from each other, the relative ODESR amplitude (or area) is strongly dependent on the solute concentration. As shown in Fig. 3, the initial slope of the ODESR amplitude as a function of the microwave field is smaller at low concentrations than that at higher concentrations. In terms of the Eq. 1, this indicates that the (averaged) lifetime for the geminate pairs at lower *p*-TP concentration is shorter than that at higher concentration. Therefore, DGP1 must have a shorter lifetime than DGP2.

The microwave intensity at which the ODESR amplitude is maximum is also very much dependent on the composition of the geminate pair. If the ESR field of the anion and that of the cation are widely separated from each other, there should not be any maxima on these curves. On the other hand, if the two ESR transition frequencies (or fields) are close to each other, the ESR transitions of the two component radicals of the pair can be simultaneously induced at high microwave fields, which results in a decrease in the ODESR signal. Because the geminate pair DGP1 is composed of a solvent hole which has a broad ESR signal and a *p*-TP anion with a narrow ESR, as shown in Fig. 1, the probability that the two-component ESR transitions are induced simultaneously is low. On the other hand, the component radicals of the other geminate pair DGP2 have ESR transitions at positions close to each other, and the simultaneous induction of the ESR transitions occurs even at a low microwave power. This is the reason why the peak for a 2.0 mM solution appears at a lower microwave power, i.e. at higher concentrations the ratio of the geminate pair DGP2 increases, the component radicals of which have ESR fields close to each other.

Upon lowering the temperature, the peak position shifts to a lower microwave field and the peak height or maximum ODESR amplitude becomes larger, as shown in Fig. 3. At low temperatures, because the diffusion rate becomes low and the life-span of each geminate pair increases, the initial increase of the ODESR amplitude with respect to a unit increase of the microwave field becomes large and saturation of the ODESR amplitude begins at a lower microwave power.

4. Lifetime of the Radical Pair: If we postulate that all of the radicals comprise DGP1 at 0.1 mM and DGP2 at 2 mM and also that the lifetime can be estimated with a simple equation (Eq. 1), the lifetime of the former is about 1/3 that of the latter. Because the molecular volume of squalane ($C_{30}H_{62}$) is much larger than that of *p*-TP ($C_{18}H_{14}$), the diffusion rate of the squalane cation should be much smaller than that

of the *p*-TP cation. However, the experimental results indicate that DGP1 recombines three-times faster than DGP2. Therefore, the positive hole may migrate from one solvent molecule to another. According to Williams,[28] the recombination time, τ_g, as the charges diffuse within their attractive electrostatic field, is given by

$$\tau_g = r_x^3(1+4r_x/3r_c)^{3/2}/3Dr_c, \quad (3)$$

where r_x is the initial separation of the ion pair, r_c represents the Onsager radius (about 290 Å[29]) and D is the sum of the diffusion constants. When 5.9×10^{-8} $cm^2\,s^{-1}$ for *p*-TP and 4.4×10^{-8} $cm^2\,s^{-1}$ for squalane molecules (calculated using Stokes–Einstein relation with the hydrodynamic radius of 4.4 Å for *p*-TP and 6.0 Å for squalane molecules, the viscosity of 78 cp, and the temperature of 278 K) are employed for the diffusion constants, the recombination times for DGP1 and DGP2 are calculated as 5.0 μs and 4.3 μs, respectively, for an initial separation of 130 Å. At this initial separation, the G-value for the free ion may be around 0.4, which is a typical value in hydrocarbons.[30,31] Because the recombination of DGP1 is completed in a much shorter time compared with that of DGP2 against the expectation from the hydrodynamic radii of the component radicals, the charge may hop several tens times toward the counter ion in its lifetime. Thus, the hopping rate may be around $10^7\,M^{-1}\,s^{-1}$, which is not sufficient to average the hyperfine field of about 45 Gauss of the squalane cation. Therefore, the line width is almost unchanged with this hopping process. The same kind of hole migration has been reported in a benzene or a toluene solution, where the rate is sufficient to partially average the hyperfine field.[13] This is because the electron-transfer rate between the solvent hole and the solvent molecules is about $10^9\,M^{-1}\,s^{-1}$ or more, which is much larger than that in squalane. At a higher temperature of 300 K, the ODESR amplitude decreased considerably, as can be seen in Fig. 2. This may be due to a decrease in the lifetimes of the geminate pairs as well as due to a decrease of the spin lattice relaxation times.

Conclusion

A geminate pair comprising a solvent hole and a *p*-TP anion has been observed in addition to a pair with a *p*-TP anion and its cation in an X-ray irradiated squalane solution of *p*-TP at room temperature using the ODESR technique. It has also been shown that analysis of the ODESR amplitude as a function of the *p*-TP concentration gives the ratio between the recombination times of the two kinds of geminate pairs, as well as the ratio between the recombination rate and the hole-trapping rate.

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