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Recombination of 2,3,4,5-Tetraphenylpyrrolyl Radicals in Benzene Solution: Photochromism, Partially Diffusion-Controlled Reaction, and Magnetic Field Effect

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Violet-colored 2,3,4,5-tetraphenylpyrrolyl radicals (TPPRs) were remarkably long-lived (more than 10 h) in benzene solution at room temperature. Their decay obeyed the second-order kinetics; two TPPRs recombine to form a colorless dimer. The temperature dependence of the recombination rate was close to that of the reciprocal of solvent viscosity, precluding the presence of any additional activation barrier for the recombination reaction apart from that imposed on the encounter of radicals by solvent viscosity; the rate is limited solely by the steric factor. Although TPPRs come across many times by diffusion, four outspread phenyl groups limit the useful approach of the reactive sites that are on the pyrrolyl ring. In most cases, TPPRs form the nonreactive random encounter radical pair (RERP), which separates again with the diffusion rate. The reactive RERP is formed only when TPPRs approach each other with their reactive sites exactly facing each other. Useful approach is limited to only a small "favorable" solid angle, resulting in the partially diffusion-controlled recombination. A significant retarding effect caused by the external magnetic field was observed on the recombination reaction of the reactive RERP. The effect was not saturated up to 0.5 T and can be explained by the relaxation mechanism with the underlying hyperfine coupling mechanism.

Introduction

Among many types of reactions occurring between a pair of reactants, recombination of free radicals is one of the most fundamental ones. When the reactants are frequently scattered and exchange energy with the medium, the kinetic energy of the reactants is in thermal equilibrium with the medium. In such a case, motion of the reactants can be described by the diffusion equation. The theory of diffusion-influenced reaction was first formulated by Smoluchowski.[1] Since then, the theory has been refined and generalized in many aspects.[2−5]

Recombination can occur when the two reactants (free radicals) approach each other to a certain distance, which is called the encounter distance. Two extreme cases of boundary conditions of the diffusion equation are: (i) a reflecting boundary with no reaction at all, all reactants separate again; (ii) an absorbing boundary with maximum reaction rate at the boundary, in which all reactants recombine and none get back; the overall reaction rate is determined by the encounter rate. In the intermediate case (iii), the so-called "radiation" boundary, reaction occurs at a finite rate slower than the encounter rate. Tachiya[3] called such a case "partially diffusion-controlled recombination".

Magnetic field effects (MFEs) on photochemical scission of chemical bonds have been extensively studied.[6−8] However, most of these works have been concentrated on the early-time events of geminal pair recombination before escaped radicals are formed or on the relative yields of "cage" (geminal) and escaped radical recombination products. MFE on the reverse reaction, i.e., recombination of the random encounter radical pair (RERP), has scarcely been reported, except for the early trial of Margulis et al.[9] on chlorophyll a radical cation/*p*-benzoquinone radical anion pair in 1,3-propanediol, that of Sato et al.[10] on 2,4,5-triphenylimidazolyl radicals (TPIRs) in a polymer medium, Cozens and Scaiano's work[11] on benzyl radicals in micellar solution, and a recent report of Sakaguchi and Hayashi[12] on a 10-methylphenothiazine/tetrafluoro-1,4-dicyanobenzene electron-transfer pair in 2-propanol.

Nakai et al.[13] briefly reported MFE on the recombination reaction of RERPs of photochromic 2,3,4,5-tetraphenylpyrrolyl radicals (TPPRs). Partial oxidation (about 4%) of 2,3,4,5-tetraphenyl-1*H*-pyrrol (TPP) to give TPPR was originally reported by Kuhn and Kainer.[14] Then Blinder et al.[15] made spectroscopic and ESR studies to show that the oxidation product of TPP exhibits photochromism and thermochromism in solutions and that these phenomena are due to dissociation of the oxidation product into TPPRs by UV irradiation and heating, respectively. Maeda et al.[16] prepared two isomeric dimers of TPPR, the photochromic dimer (PD) and the piezochromic dimer, by oxidation of TPP by lead oxide and potassium ferricyanide, respectively. The finding that the photochromic dimer of a similar radical TPIR exhibits photochromism due to the radical dissociation of a C−N bond[17,18] led Maeda et al. to indicate that only two isomers with a C−N linkage among the dimers of TPPR are photochromic (Scheme 1).

The ESR spectrum of TPPR[16] tells its π-radical nature. Hückel MO calculation of TPPR[16] shows that most of the spin is localized on the pyrrolyl ring. Therefore, recombination of TPPRs occurs only on the pyrrolyl ring (i.e., not on peripheral phenyl groups). This significantly lowers the recombination probability because four outspread phenyl groups prevent the approach of the pyrrolyl rings of two TPPRs close enough to be able to recombine, and this makes, in turn, escaped TPPRs quite long-lived even in fluid solution. In particular, TPPRs survived more than 10 h in benzene solution at room temperature. This system is particularly interesting because (1) the colorless parent compound (dimer)/colored radical constitutes a photochromic system, (2) it provides an interesting example

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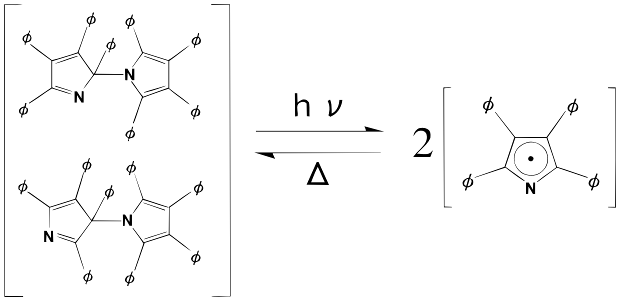
SCHEME 1



of the partially diffusion-controlled reaction, and (3) it is a very convenient system for observing MFE on the slow recombination of escaped radicals.

In the present paper, the recombination reaction of TPPRs in benzene solution was studied together with its temperature dependence in the absence and presence of the external magnetic field to elucidate the nature of the partially diffusion-controlled reaction and the MFE on the reaction.

Experimental Section

The photochromic dimer (PD) of TPPR was prepared by Kuhn and Kainer's oxidation procedure[14] of TPP, which was synthesized after Davidson.[19] Because of the air-sensitive nature of PD, its preparation was carried out under nitrogen atmosphere in the dark. The purity of TPP and PD was examined by ^{1}H and ^{13}C NMR and FTIR.

UV irradiation of a degassed benzene solution of PD (3.75×10^{-4} M) was carried out using an Ushio USH-500 high-pressure mercury lamp, equipped with a glass filter transmitting 260−380 nm UV light. Irradiation gave violet-colored TPPR with an absorption maximum at 563 nm with a shoulder near 525 nm. The solution in a 1 cm × 1 cm quartz cell was set in a temperature-controlled water jacket (kept at 21.5, 30, or 40 ± 0.2 °C) located between poles of a Tokin SEE-9G electromagnet. The diameter of the magnetic poles was 60 mm. The distance between the poles was 48 mm. The electromagnet was cooled by running water. The magnetic field strength was controlled by variation of the DC current on the electromagnet and measured by an F. W. Bell model 4048 gauss meter. The residual magnetic field was canceled by a homemade Helmholtz coil. UV irradiation was made for a total of 180 s, with intermittent (every 15 s) interchange of the irradiated surface of the quartz cell and shaking of the solution during the irradiation to attain coloration as homogeneous as possible. Then, the time evolution of the absorbance at 563 nm was monitored using a tungsten lamp (Noma 10 V, 4 A) with a cutoff filter transmitting the light above 520 nm as a probe light and a monochromator (American ISA)/photomultiplier (Hamamatsu 1P28) assembly. The intensity of the lamp was monitored simultaneously. The two outputs were fed to a split-chart recorder.

Utmost care was taken to obtain results reproducible within ca. 5% for each temperature and magnetic field strength. It was found imperative to use a "virgin" sample solution, i.e., one not irradiated before. Moreover, use of freshly prepared PD was necessary to obtain good reproducible results. Experiments with and without a magnetic field were made under a random sequence to avoid any systematic errors. The data given in this paper are those averaged over more than two or three independent runs using virgin sample solutions of fresh PD.

The ESR measurement was carried out for a UV-irradiated sample in deaerated toluene with a JEOL JES-SRE2X ESR spectrometer. The spectrum (not shown) was in good agreement with that reported by Maeda et al.[16]

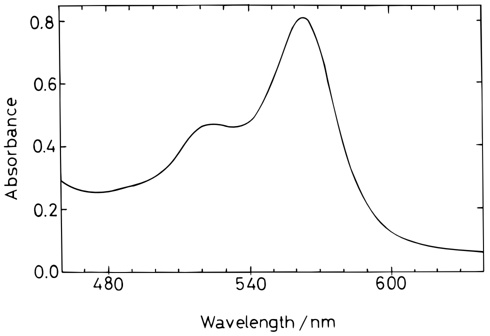


Figure 1. Absorption spectrum of 2,3,4,5-tetraphenylpyrrolyl radical (TPPR) in benzene solution.

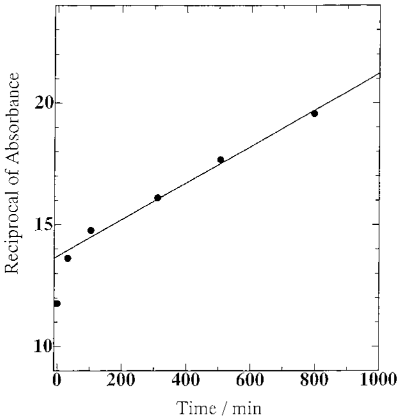


Figure 2. Reciprocal of absorbance vs time: temperature = 21.5 °C; applied magnetic field = 0 T.

Results

The absorption spectrum of TPPR in benzene solution is shown in Figure 1. A typical plot of the reciprocal of the absorbance at 563 nm ($A(t)^{-1}$) against time is given in Figure 2. As shown, the recombination reaction followed second-order kinetics,

$$2\mathrm{R}^{\bullet} \xrightarrow{k_2} \mathrm{R{-}R} \tag{1}$$

$$\frac{1}{C_R(t)} - \frac{1}{C_R(0)} = k_2 t \tag{2}$$

except for a very fast decay in the initial time range near $t = 0$. (TPPR is designated as R$^{\bullet}$. $C_{\mathrm{R}}(t)$ is the concentration of R$^{\bullet}$ at time t.)

From

$$A(t) = \epsilon C_R(t) d \tag{3}$$

$$\frac{1}{A(t)} = \frac{1}{\epsilon d}\frac{1}{C_R(t)} = \frac{k_2}{\epsilon d}t + \frac{1}{\epsilon d}\frac{1}{C_R(0)} = k_2{}'t + \frac{1}{\epsilon d}\frac{1}{C_R(0)} \tag{4}$$

the slope of the straight line in Figure 2 corresponds to $k_2{}' = \epsilon^{-1}d^{-1}k_2$ (min^{-1}), where ϵ is the unknown molar extinction coefficient (M^{-1} cm^{-1}) of the radical at 563 nm and d (the thickness of sample solution) is 1 cm. Absolute values of k_2 cannot be obtained because we have at present no convenient means to know ϵ. However, under the plausible assumption that ϵ is independent of temperature and the applied magnetic field

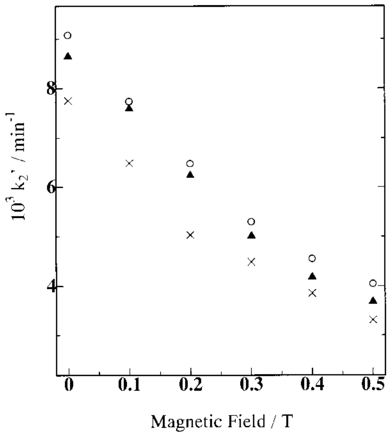


Figure 3. Dependence of $k_2' = \epsilon^{-1}d^{-1}k_2$ on the applied magnetic field: temperature = 21.5 (×), 30 (▲), and 40 °C (○).

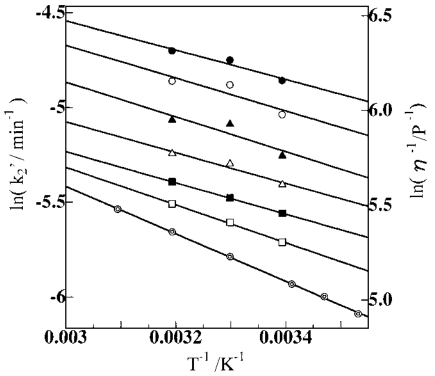


Figure 4. Temperature dependence of $k_2' = \epsilon^{-1}d^{-1}k_2$. Strengths of applied magnetic field are 0 (●), 0.1 (○), 0.2 (▲), 0.3 (△), 0.4 (■), and 0.5 T (□). The temperature dependence of reciprocal of coefficient of viscosity of benzene ($\eta(T)^{-1}$) is shown (◎) for comparison.

strength, we can discuss relative values of k_2 using the values of $k_2' = \epsilon^{-1}d^{-1}k_2$.

The values of k_2' decrease with increasing magnetic field strength and are not saturated up to 0.5 T, as shown in Figure 3.

A logarithmic plot of k_2' against the reciprocal of temperature is shown in Figure 4 for each value of the magnetic field strength. Linear relationship holds; that is, the data fit to

$$k_2' = \epsilon^{-1}d^{-1}k_2 = (\epsilon^{-1}d^{-1}A)\exp(-E/RT) \tag{5}$$

As shown, slopes ($-E/R$) for different field strengths are very close to each other. The plot of E vs magnetic field strength (Figure 5a) reveals no appreciable dependence of E on the magnetic field strength. However, the relative frequency factor $\epsilon^{-1}d^{-1}A$ decreases linearly with increasing magnetic field strength, as shown in Figure 5b.

A logarithmic plot of the reciprocal of the coefficient of viscosity, $\eta(T)^{-1}$, of benzene vs reciprocal temperature is added in Figure 4. The slope of k_2' is close to that of $\eta(T)^{-1}$.

Discussion

Partially Diffusion-Controlled Reaction. Several groups worked out kinetic equations for the radiation boundary case, with or without taking the back reaction into account. Berlin et al.[2] formulated a unified theory of the modified Smoluchowski equation with the radiation boundary condition for both of geminal and homogeneous (second-order) recombination reactions.

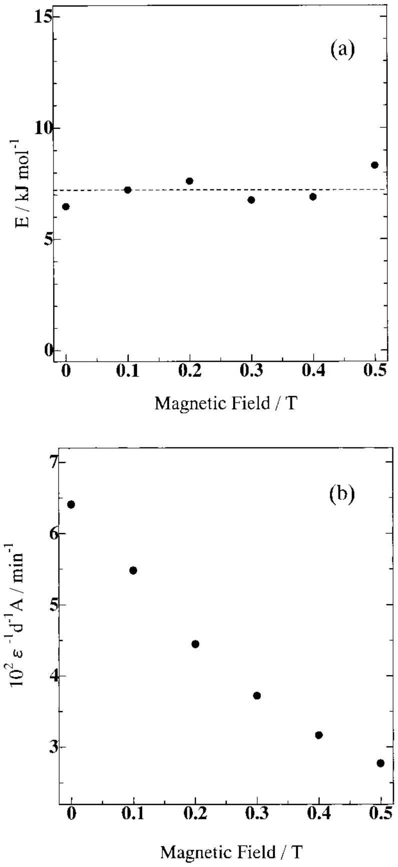


Figure 5. Magnetic field dependence of E (a) and of $\epsilon^{-1}d^{-1}A$ (b).

Following the treatment of Berlin et al.,[2] reactivity of escaped radicals can be characterized by the value of the homogeneous recombination rate constant, and it can be obtained by solving the modified Smoluchowski equation (time-integrated form of the nonstationary Smoluchowski equation)

$$\frac{D}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\frac{\mathrm{d}\tilde{C}}{\mathrm{d}r} + \lambda\frac{\mathrm{d}u}{\mathrm{d}r}\tilde{C}\right] = C(r,\infty) - C(r,0) \tag{6}$$

where $C(r,t)$ is the concentration of reactant B on the sphere with radius r around the reaction partner A at time t, D is the sum of the diffusion coefficients of reactants A and B, u is the potential energy of the particle B in the field due to the particle A, and $\lambda = (k_BT)^{-1}$, with k_B the Boltzmann's constant. In this equation, $\tilde{C}$ is the time-integrated flux of the particle B though the sphere of radius r

$$\tilde{C}(r) = \int_0^\infty C(r,t)\,\mathrm{d}t \tag{7}$$

After solution of the equation under relevant boundary conditions, we finally have for the rate constant (k_r)

$$\frac{1}{k_r} = \frac{\exp[\lambda u(R)]}{k_p} + \frac{I(\infty)}{4\pi D} \tag{8}$$

where k_p is the rate constant of chemical reaction between species A and B (in the present case recombination reaction of $R^\bullet$ with another $R^\bullet$) at $r = R$ (the radius of the partially absorbing barrier), and

$$I(r) = \int_R^r r^{-2}\exp[\lambda u(r)]\,\mathrm{d}r \tag{9}$$

In the present case, since $u(R) = 0$, we obtain

$$\frac{1}{k_r} = \frac{1}{k_p} + \frac{1}{4\pi DR} \tag{10}$$

which is very simple. When $k_p \gg 4\pi DR$ holds, we have $k_r \approx 4\pi DR$ (totally diffusion-controlled reaction), and at the limit of $k_p \rightarrow 0$, we obviously have no reaction.

Let us turn to the temperature dependence of the reaction rate. The two terms on the right-hand side (rhs) of eq 10 may have different temperature dependences. Assuming a spherical particle model with the radius r_0, the diffusion constant D is related to the viscosity coefficient $\eta(T)$ by the Einstein–Stokes relation

$$D = k_B T/[6\pi r_0 \eta(T)] \tag{11}$$

Then the second term in the rhs of eq 10

$$(4\pi DR)^{-1} = 3r\eta(T)/(2k_B RT) \tag{12}$$

varies as $\eta(T)/T$. Using the Arrhenius-type empirical relation

$$1/\eta(T) = B \exp(-E_V/RT) \tag{13}$$

with a constant B, the $(4\pi DR)^{-1}$ term varies as

$$(4\pi DR)^{-1} = B' \exp(E_V/RT) \tag{14}$$

where B' is a "constant" $3r/(2k_B RTB)$, neglecting the change in T within a small temperature range in comparison with the exponential term. E_v is the apparent activation energy due to viscosity. The first term in the rhs of eq 10 varies as

$$k_p^{-1} = A' \exp(E_R/RT) \tag{15}$$

where E_R is the activation energy of the chemical reaction. Then, k_r^{-1} must have a biexponential temperature dependence, corresponding to that of $(4\pi DR)^{-1}$ and k_p^{-1}, respectively.

The temperature dependence of k_2' in the present case shows the single-exponential behavior with an apparent activation energy (E) of only ca. 7.2 kJ mol^{-1}. Moreover, the temperature dependence of k_2' runs closely parallel to that of $\eta(T)^{-1}$ of benzene. Although the used temperature range is limited, it seems unlikely that any additional activation barrier associated with k_p is present, apart from that due to diffusion that is determined by the solvent viscosity. It is a natural conjecture then that k_p is large enough compared to the diffusion-controlled rate; that is, the very limited reaction rate observed is not due to a kinetic constraint. It must be due to the steric factor only. Four outspread phenyl groups limit the approach of reactive sites of two radicals close enough for the recombination reaction 1 to occur. Although TPPRs come across many times at the diffusion-controlled rate ($k_r = 4\pi DR$), in most of the cases TPPRs form a nonreactive random encounter radical pair (RERP) which instantaneously separates again at the diffusion rate ("touch-and-go" process). A reactive RERP is formed only when two TPPRs approach each other with their reactive sites exactly facing each other. The useful approach is limited to only a small "favorable" solid angle of approach. Remember that recombination of TPPRs is realized only when the pyrrolyl ring of one TPPR is directly attacked by that of the other TPPR. In other words, all of the reaction surface ($4\pi R^2$) of a TPPR cannot be active. $4\pi R^2$ should be multiplied by a very small limiting factor, which represents the portion of solid angle corresponding to the useful approach of the two spatially overcrowded radicals.

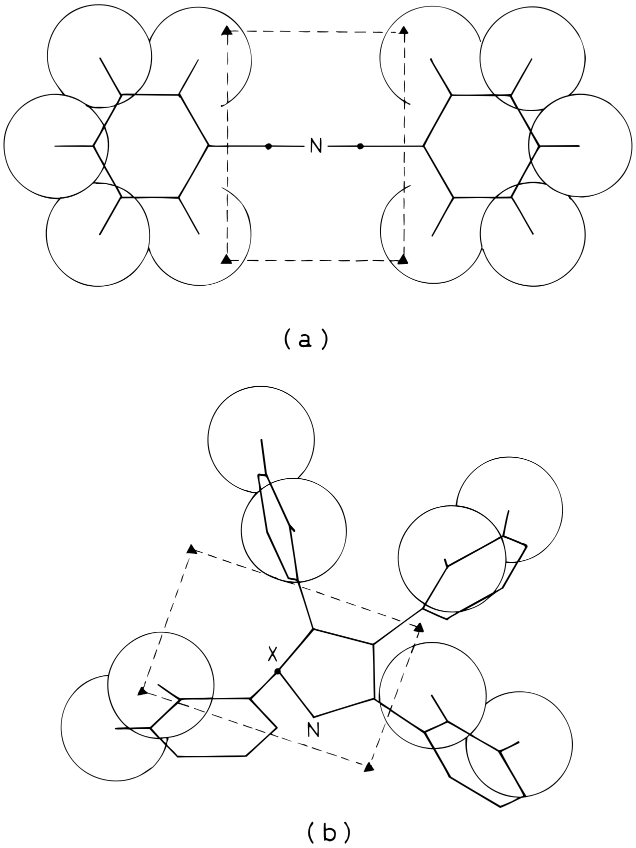


Figure 6. Image of very restricted "favorable" approach: (a) very difficult N–N approach, (b) more favorable C–N approach (X denotes the attacked sp^3 carbon atom; see text). Circles show roughly van der Waals radii of hydrogen atoms. Black triangles indicate positions of hydrogen atoms of the incoming radical. Bond lengths and angles are only schematic. As for hydrogen atoms, only those facing the incoming radical are shown.

When this limiting factor is designated as β, we can write

$$k_r\,(\text{reactive}) = 4\pi\beta DR \tag{16}$$

with $\beta \ll 1$, and

$$k_r\,(\text{nonreactive}) = 4\pi(1-\beta)DR \tag{17}$$

In the case of the radical–radical reaction reported by Margulis et al.,[9] the bimolecular reaction coefficient k_2 was nearly equal to $4\pi DR$ and radicals could be modeled as "white spheres with large black (=reactive) spots" or roughly "black spheres". In the present case, radicals are to be modeled as "white spheres with very small black spots". Margulis et al.[9] remarked that the problem becomes very sophisticated when the probability of singlet radical pair recombination is significantly lower than unity. One may note that a somewhat similar treatment of orientation-dependent reactivity is found in the use of "opacity" function in the calculation of gas-phase reaction probability of a target molecule with a projectile atom. However, the present case is far more complicated since both reaction partners are spatially overcrowded, thus severely prohibiting their facile approach.

Although the π-radical nature of TPPR is evident from its ESR spectrum, the unpaired electron of TPPR should be localized on a σ-type bond on the time of recombination. Recombination of two Nσ-radicals to form an N–N bond is spatially very difficult, even when two radicals approach with their rings perpendicular to each other as shown in Figure 6a,

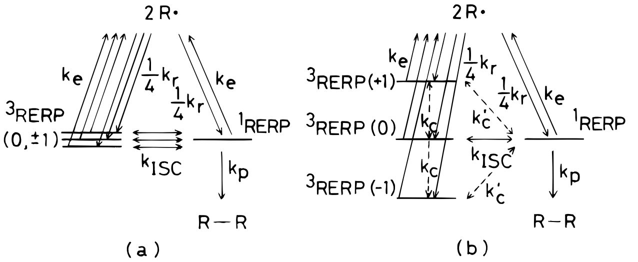


Figure 7. Schematic picture of radical recombination reaction and magnetic field effects, in the absence (a) and presence (b) of the magnetic field; see text.

because four hydrogen atoms on ortho positions highly repel each other. More facile recombination is feasible when an Nσ-radical approaches one of the two carbon atoms next to the nitrogen atom of the other radical, in a concerted way with the carbon atom changing its hybridization gradually from sp^2 to sp^3. In the latter case, four ortho hydrogen atoms on the Nσ-radical (shown by black triangles in Figure 6b) can seek empty spaces avoiding hydrogen atoms of the counter-radical. (It is to be noted that the ortho hydrogen atom on the phenyl ring on the sp^3 carbon atom, designated as X, is in a lower position compared to the other three ortho hydrogen atoms, of which the van der Waals radii are shown.) However, the solid angle of the favorable approach is very much limited. A rough estimate of the favorable solid angle can be made using a space-filling model. It leads to ca. 0.01%; that is, only some 10^{-4} portion of $4\pi R^2$ is useful. Then $\beta \approx 10^{-4} \times 10^{-4} = 10^{-8}$, since the limiting factor is applicable for both reactants.[20]

There is some possibility of temperature dependence of β in that thermally activated movement of four phenyl groups on each of the approaching radicals may cause some increase of the useful solid angle with increasing temperature. However, this effect seems to be very small, if any, in the used temperature range (21.5−40 °C). After all, the reaction is diffusion-controlled in the sense that the rate is nearly proportional to that determined by diffusion. However, the rate is smaller by a steric limiting factor (some 10^{-8}) representing the fraction of the favorable solid angle for the recombination to occur. Thus, this system provides an example of the partially diffusion-controlled reaction.

Magnetic Field Effect. The magnetic field effect (MFE) in the present case is apparently on the recombination of escaped radicals, since it is on the second-order reaction occurring on the time scale of minutes and hours. The recombination mechanism can be considered as depicted in Figure 7 (cf. ref 10). The recombination starts from two escaped radicals (doublet plus doublet). Escaped radicals come across many times at the diffusion rate. However, in most cases, they form a nonreactive RERP and two radicals separate again at the diffusion rate (the “touch-and-go” process). Only when the approach is spatially favorable, i.e., when the reactive spots (favorable solid angles) on the molecular surfaces of two radicals exactly face each other, they form a reactive RERP. The formation of the reactive RERP is realized with an overall rate constant $k_r(\text{reactive}) \approx 4\pi\beta DR$ (eq 16). Since the MFE is monitored by the recombination reaction of TPPRs, no MFE is expected for the nonreactive RERP, which does not recombine at all. MFE occurs only on the reactive RERP. Hereafter, we write k_r(reactive) as k_r and reactive RERP as RERP. The singlet/triplet ratio of RERPs immediately after the encounter is 1:3 by an a priori statistical weight. The singlet RERP recombines with a rate constant k_p to form a colorless dimer (not necessarily the original isomer) or separates again with a rate constant k_e, while the triplet RERP only separates. Intersystem crossing (ISC) between the singlet and triplet occurs within these RERPs. Once a singlet RERP is formed, the recombination rate of two R$^\bullet$’s within the RERP (k_p) must be much larger than $4\pi\beta DR$, as indicated by temperature-dependence experiments (see above).

Several types of magnetic field effects have been reported. ISC is enhanced by the applied magnetic field in the case of the electronic Zeeman or level-crossing mechanism, while it is diminished in the case of the hyperfine coupling or relaxation mechanism. The overall effect on the recombination is as follows. For an initial triplet radical pair, the magnetic field increases recombination by the electronic Zeeman or level-crossing mechanism, while it decreases recombination by the hyperfine coupling or relaxation mechanism. The reverse holds for an initial singlet radical pair. In the MFE in the present case, the initial radical pairs originate from random encounters of free radicals to give a 1:3 mixture of initial singlet and triplet pairs. However, the first encounter eliminates more of the singlet pairs by the k_p channel, and the radical pairs left after this event behave rather like initial triplet pairs.[6] Then, the observed decrease of recombination by the magnetic field must be due to the hyperfine coupling and/or relaxation mechanism. While it is known that the hyperfine coupling effect is saturated at a relatively small magnetic field strength (e.g., below 0.1 T),[21] the MFE in the present case is not saturated even at 0.5 T. Therefore, it should be due to the relaxation mechanism, in addition to the underlying hyperfine coupling mechanism.

According to the reaction scheme shown in Figure 7, the reaction rates for the escaped radical (R$^\bullet$), the singlet RERP (^{1}RERP), and three components of the triplet RERP (^{3}RERP(0), ^{3}RERP(+1), and ^{3}RERP(−1)) in the absence of the magnetic field (Figure 7a) are expressed as follows:[22]

$$-\frac{d[R^\bullet]}{dt} = k_r[R^\bullet]^2 - k_e[^1\text{RERP}] - k_e[^3\text{RERP}(0)] - k_e\{[^3\text{RERP}(+1)] + [^3\text{RERP}(-1)]\} \quad (18)$$

$$-\frac{d[^1\text{RERP}]}{dt} = -\frac{1}{4}k_r[R^\bullet]^2 + k_e[^1\text{RERP}] + k_p[^1\text{RERP}] + k_{ISC}[^1\text{RERP}] + 2k_{ISC}{}^*[^1\text{RERP}] - k_{ISC}[^3\text{RERP}(0)] - k_{ISC}{}^*\{[^3\text{RERP}(+1)] + [^3\text{RERP}(-1)]\} \quad (19)$$

$$-\frac{d[^3\text{RERP}(0)]}{dt} = -\frac{1}{4}k_r[R^\bullet]^2 + k_e[^3\text{RERP}(0)] + k_{ISC}[^3\text{RERP}(0)] - k_{ISC}[^1\text{RERP}] \quad (20)$$

$$-\frac{d[^3\text{RERP}(\pm1)]}{dt} = -\frac{1}{4}k_r[R^\bullet]^2 + k_e[^3\text{RERP}(\pm1)] + k_{ISC}{}^*[^3\text{RERP}(\pm1)] - k_{ISC}{}^*[^1\text{RERP}] \quad (21)$$

(The rate constant with an asterisk (k_{ISC}*) is the same as k_{ISC} in the absence of the magnetic field. It is to be replaced by k_c' (relaxation rate constant) in the presence of the magnetic field; see below.) Since the absorption band at 563 nm can be considered as due to the sum of R$^\bullet$, ^{1}RERP, and three components of ^{3}RERP,[23] the decay of the band corresponds to

$$-\frac{d}{dt}\{[R^\bullet] + [^1\text{RERP}] + [^3\text{RERP}(0)] + [^3\text{RERP}(+1)] + [^3\text{RERP}(-1)]\} = k_p[^1\text{RERP}] \quad (22)$$

The S−T conversion rate constant k_{ISC} is determined by hyperfine coupling and has the order of 10^9-10^8 s^{-1}. The reaction rate constant k_p of recombination (formation of R−R) from the singlet RERP has the order of $10^{10}-10^7$ s^{-1} (ref 21). The value of k_p in the present case may be rather large, because the reactive sites of two R$^\bullet$'s are close enough, once the reactive RERP is formed. The rate constant of escape (k_e) is not small because it is for the escape in fluid solution (see below for more discussion). These three are by far the larger compared to the rate constant of formation of RERP (k_r). The formation of a reactive RERP from two R$^\bullet$'s is the rate-determining step.

In other words, the spin diffusion process to form reactive RERPs is completely separated from such processes as ISC, recombination, and escape. The very slow reaction of TPPRs has made this possible. However, TPPRs do not live so long (10 h, for example) in the form of RERPs. The very long lifetime of TPPRs stems from its steric difficulty in forming reactive RERPs, and TPPRs survive through most of their lifetime as escaped radicals (R$^\bullet$'s). (However, see below for more discussion.)

When k_p, $k_e \gg k_{ISC}$ holds, ^{1}RERP immediately recombines into the product R−R or separates into R$^\bullet$'s, and ^{3}RERP separates, before ISC occurs. We have little chance of magnetic field effect. However, when $k_{ISC} > k_p > k_e$, $k_{ISC} \approx k_p > k_e$, or $k_p > k_{ISC} > k_e$ holds (it is highly likely that k_p is larger than k_e, see below), ISC occurs in the direction to reestablish the 3:1 population ratio of ^{3}RERP and ^{1}RERP. When the steady-state approximation is applied on ^{1}RERP, we have

$$k_e[^1\mathrm{RERP}] + k_p[^1\mathrm{RERP}] - \frac{1}{4}k_r[\mathrm{R}^\bullet]^2 = k_{ISC}[^3\mathrm{RERP}(0)] + k_{ISC}{}^*\{[^3\mathrm{RERP}(+1)] + [^3\mathrm{RERP}(-1)]\} - k_{ISC}[^1\mathrm{RERP}] - 2k_{ISC}{}^*[^1\mathrm{RERP}] \quad (23)$$

The right-hand side (rhs) of this equation vanishes when $[^1\mathrm{RERP}] = [^3\mathrm{RERP}(0)] = [^3\mathrm{RERP}(+1)] = [^3\mathrm{RERP}(-1)]$ holds. However, there is always a little surplus of triplet RERPs over the 3:1 ratio to the singlet ones, since the k_p channel consumes the latter. Net ISC occurs in the direction of triplet → singlet. Then, the rhs of eq 23 has a positive value. We can express it in the form of

$$S_0 = \alpha_0 k_r[\mathrm{R}^\bullet]^2 \quad (24)$$

with $0 < \alpha_0 < 1$, since all of singlet and triplet RERPs are formed through the formation of RERPs by recombination of two R$^\bullet$'s as the rate-determining step (total RERP = $k_r[\mathrm{R}^\bullet]^2$). Then,

$$[^1\mathrm{RERP}] = \frac{1}{k_e + k_p}\left(\frac{1}{4} + \alpha_0\right)k_r[\mathrm{R}^\bullet]^2 \quad (25)$$

Because the net ISC occurs from the triplet into the singlet, we have to a good approximation

$$\alpha_0 \approx \frac{3}{4}\frac{k_{ISC}}{k_{ISC} + k_e} \quad (26)$$

From eqs 22 and 25, the decay of total radicals reduces to

$$-\frac{d}{dt}\{[\mathrm{R}^\bullet] + [^1\mathrm{RERP}] + [^3\mathrm{RERP}(0)] + [^3\mathrm{RERP}(+1)] + [^3\mathrm{RERP}(-1)]\} = \frac{k_p}{k_e + k_p}\left(\frac{1}{4} + \alpha_0\right)k_r[\mathrm{R}^\bullet]^2 \quad (27)$$

Thus, the second-order rate constant k_2 can be expressed as

$$k_2 = \frac{k_p}{k_e + k_p}\left(\frac{1}{4} + \alpha_0\right)k_r = \frac{k_p}{k_e + k_p}\left(\frac{1}{4} + \alpha_0\right)4\pi\beta DR \quad (28)$$

In the presence of the magnetic field (Figure 7b), triplet sublevels of ^{3}RERP are split apart in energy in proportion to the magnetic field strength. Relaxation processes between ^{3}RERP sublevels (with a rate constant k_c) and between ^{1}RERP and ^{3}RERP(±1) (with a rate constant k_c') become progressively slower and hence less and less competitive with the other processes (ISC between^{1}RERP and ^{3}RERP(0), recombination and escape). These lead to the reduction of α_0 into α_H ($\alpha_H < \alpha_0$), which results in the reduction of k_2. Since the communication between ^{3}RERP(±1) and ^{1}RERP is progressibly reduced, as are those between triplet sublevels, we have, to a good approximation,

$$\alpha_H \approx \left(\frac{3 - a}{4}\right)\frac{k_{ISC}}{k_{ISC} + k_e} \quad (29)$$

with $2 \geq a > 0$ and $a = 2$ at the limit of no communication.

The magnetic field dependence of E and $\epsilon^{-1}d^{-1}A$ shown in parts a and b of Figure 5, respectively, clearly shows that magnetic field affects the frequency of recombination (formation of R−R) event without appreciable temperature dependence. The former point shows that the magnetic field effect is on the frequency of occurrence of singlet RERPs. The latter point indicates that the rate of relaxation among triplet sublevels changes little with temperature in the used temperature range.

For the confirmative demonstration of the relaxation mechanism, we have to show the lifetime of reactive RERPs to be long enough to be affected by magnetic-field-dependent variation of relaxation rates. However, the lifetime measurement of the RERP is not feasible in view of its extremely low steady-state concentration. The magnitude of relaxation rate constants k_c and k_c' depends on many unknown parameters. Hayashi and Nagakura[21] estimated $k_c + k_c'$ for many cases. Their values are in the range of 10^5-10^7 s^{-1} in zero magnetic field, decreasing by 1−2 orders of magnitude at 0.5 T. RERPs in our case are in fluid solution. Their lifetime is to be determined by the slower of k_p and k_e. Once a reactive RERP is formed, the reactive sites of two component radicals face each other and are close enough. The recombination reaction to form R−R is straightforward. Therefore, k_p cannot be small. One factor conceivable for making the RERP somewhat long-lived is that two R$^\bullet$'s are sterically tangled with each other in the RERP and they may need some time to separate; that is, k_e may be somewhat small even in fluid solution. Properly designed experiments are necessary to clarify these points.

Conclusion

The recombination reaction of photochromic 2,3,4,5-tetraphenylpyrrolyl radicals (TPPRs) in benzene solution was studied at 21.5, 30, and 40 °C. The radical is remarkably long-lived (more than 10 h), and its second-order recombination reaction provides a good example of the partially diffusion-controlled reaction. The temperature dependence of the recombination rate was similar to that of the reciprocal of solvent viscosity. This precludes the presence of any additional activation barrier for the recombination reaction apart from that imposed on the encounter of radicals by solvent viscosity. The very small rate is ascribable solely to steric factors. Although TPPRs come across many times by diffusion, four outspread phenyl groups limit the useful approach of reactive sites that are on the pyrrolyl ring. In most cases, TPPRs form the nonreactive random encounter radical pair (RERP), which separates again with the diffusion rate. The reactive RERP is formed only when TPPRs approach with their reactive sites exactly facing each other. In other words, all of the reaction surface ($4\pi R^2$) of a TPPR cannot be active. A favorable solid angle for the recomibination to occur is estimated to be some 10^{-4} of $4\pi R^2$ per one radical. The recombination rate is reduced by some $10^{-4} \times 10^{-4} = 10^{-8}$ compared to the diffusion rate, which makes TPPRs so long-lived. A remarkable magnetic field effect (MFE), retarding the recombination of the reactive RERP, was observed. The MFE did not show appreciable temperature dependence in the temperature range studied and was not saturated throughout the used magnetic field strength (up to 0.5 T). The MFE can be explained by the relaxation mechanism in addition to the underlying hyperfine coupling mechanism.

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References and Notes

(1) Smoluchowski, M. V. *Z. Phys. Chem.* **1917**, *29*, 129.
(2) Berlin, Yu. A.; Cordier, P.; Delaire, J. A. *J. Chem. Phys.* **1980**, *73*, 4619.
(3) Agmon, N. *J. Chem. Phys.* **1984**, *81*, 2811.
(4) Agmon, N.; Pines, E.; Huppert, D. *J. Chem. Phys.* **1988**, *88*, 5631.
(5) Tachiya, M. *J. Chem. Phys.* **1987**, *87*, 4622.
(6) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.
(7) Hayashi, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, FL, 1990; Vol. 1, Chapter 2.
(8) Grissom, C. B. *Chem. Rev.* **1995**, *95*, 3.
(9) Margulis, L. A.; Khudyakov, I. V.; Kuzmin, V. A. *Chem. Phys. Lett.* **1986**, *124*, 483.
(10) Sato, H.; Kasatani, K.; Murakami, S. *Chem. Phys. Lett.* **1988**, *151*, 97. In this reference, "increases" in line 2 from the bottom on the right column in p 98 should read "decreases (increases)".
(11) Cozens, F. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 5204.
(12) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem. A* **1997** *101*, 549.
(13) Nakai, T.; Tani, M.; Nishio, S.; Matsuzaki, A.; Sato, H. *Chem. Lett.* **1997**, 795.
(14) Kuhn, R.; Kainer, H. *Biochim. Biophys. Acta* **1953**, *12*, 325.
(15) Blinder, S. M.; Peller, M. L.; Lord, N. W.; Aamodt, L. C.; Ivanchukov, N. S. *J. Chem. Phys*. **1962**, *36*, 540.
(16) Maeda, K.; Chinone, A.; Hayashi, T. *Bull. Soc. Chem. Jpn.* **1970**, *43*, 1431.
(17) White, D. M.; Sonnenberg, J. *J. Am. Chem. Soc.* **1996**, *88*, 3825.
(18) Aldag, R. In *Photochromism, Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 714.
(19) Davidson, D. *J. Org. Chem.* **1939**, *3*, 361.
(20) When we assume $\epsilon = 10^3$ or 10^4 M^{-1} cm^{-1}, we obtain $k_2 = 0.1-2$ M^{-1} s^{-1} from $-\ln(k_2'/\text{min}^{-1}) = 4.5-5.5$ (Figure 4). Since $4\pi DR \approx 6 \times 10^9$ M^{-1} s^{-1}, β in eq 16 must be on the order of 10^{-9}.
(21) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.
(22) All [RERP]s are represented on the basis of $R^{\bullet}$'s in the pair. Otherwise, they are to be divided by 2, since two $R^{\bullet}$'s are necessary to have one RERP.
(23) The absorption must be mostly due to escaped radicals ($R^{\bullet}$'s), however, since the steady-state concentrations of ^{1}RERP and ^{3}RERP must be extremely low.