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Geminate Recombination of the *p*-Aminophenylthiyl Radical Pair Produced by the Photodissociation of *p*-Aminophenyl Disulfide in Nonpolar Solvents

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Photodissociation of *p*-aminophenyl disulfide and the following geminate recombination of the *p*-aminophenylthiyl radical pair as well as radical dimer formation in nonpolar solvents have been investigated by using picosecond transient absorption spectral measurement techniques. Temperature effects of the geminate recombination and the sandwich dimer formation were measured and compared with the results of the molecular orbital calculation. The spectral broadening of the radical band observed in the short delay times was considered to be an indication of the radical−radical interaction in the geminate pair and was analyzed to obtain the time dependence of the separation distance between the radicals. The exponential narrowing in time was found for the *p*-aminophenylthiyl radical band in *n*-hexane, which should carry information about the diffusion process in the solvent cage and is compared with the results of the simulation. The speed of the increase in the radical−radical separation distance shows a larger temperature effect than for the geminate radical recombination to form the parent molecule. The characteristic feature of the dynamic behavior of the *p*-aminophenylthiyl radical pair, the formation of the sandwich dimer, and the slow recombination of the linear dimer should be due to the large dipole moment of the radical, which not only prevents the recombination but keeps the radicals in close proximity with each other.

Introduction

We have previously reported preliminary observations on the dynamic behavior of the *p*-aminophenylthiyl geminate radical pair produced by a photodissociation of *p*-aminophenyl disulfide in nonpolar solvents at room temperature in the picosecond-to-nanosecond time scale.[1] In order to obtain a microscopic view of the diffusion process of the radical pair in solution, we have carried out a more precise study on the temperature dependence of the picosecond time-resolved absorption spectra and a more detailed analysis of the spectral broadening of the visible band of the *p*-aminophenylthiyl radical at short delay times.

p-Aminophenylthiyl radical is characterized by its unique photophysical and photochemical behavior. The radical has large dipole moments in both the ground (4.3 D) and the excited states (7.3 D),[2] a high fluorescence yield in solution,[2,3] an intense absorption band in the visible region,[2−6] and a high yield of recombination to form *p*-aminophenyl disulfide without side reactions,[7] which were revealed in the course of the extensive studies performed by many researchers. The large extinction coefficient of the radical in the visible region is quite helpful to investigate the dynamic behavior of the radical by using transient absorption measurement techniques. We should stress here that the large dipole moment makes the radical not only a good probe of the microscopic environment in solution[2,8−10] but also an excellent indicator of the radical−radical interaction through the transient absorption spectra. The latter character was extensively used in this study for elucidating geminate recombination and a diffusion process in the solvent cage.

Photodissociation and the following recombination of the radical pair are the most important photochemical primary processes in the present system. Moreover, they can provide fundamental information on the solvent cage effects as well as on the more general problem of collision pair dynamics which govern bimolecular chemical reactions in the liquid phase. In spite of their importance of elucidating reaction dynamics in the condensed phase, only a limited number of studies concerned with the direct observation of the formation and the recombination of the geminate radical pair have been found in the literature.[1,10−15] In the liquid phase, only a few large aromatic molecules which produce the radicals, diphenylaminyl,[11−14] phenylthiyl,[15,16] or their derivatives,[1,16] as primary products of photodecomposition were the subject of fast kinetic studies.

In general, it is difficult to distinguish the radical pair from the dissociated unpaired radicals due to the weak interaction between radicals. The studies described above were mainly concerned with the measurements of the time dependence of the transient absorbance, which represent the sum of the geminate radical pair and the radicals escaped from a solvent cage. If we can distinguish the interacting radical pair from the escaped radical with high time resolution, it should be quite helpful to extract knowledge about the geminate dynamics and to make great progress in this field. We have reported that *p*-aminophenylthiyl radical was the case where the geminate pair and the noninteracting radical gave different spectra in the visible region.[1] We show in the present work the dynamics of the geminate pair of *p*-aminophenylthiyl radical in detail, where two kinds of interacting radical pairs, antiparallel linear pair (linear dimer) and antiparallel sandwich pair (sandwich dimer), are observed in nonpolar solvents and only the solvated linear dimer is observed in polar solvents. We consider that the linear dimer has a conformation close to that just after photodissociation of *p*-aminophenyl disulfide in a solvent cage and the sandwich dimer is formed from the linear dimer by the diffusive motion under their dipole fields.

Experimental Section

Picosecond transient absorption spectra were measured by using a dye laser photolysis system pumped by second harmonics of a mode-locked Nd^{3+}:YAG laser (Quantel, Picochrome

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YG-503C/PTL-10). The laser was operated at 10 Hz, and a signal was typically averaged for 30 shots. The sample was excited with second harmonics of the rhodamine 6G dye laser (295 nm). Time resolution of our transient absorption measurements was about 15 ps. The details of this system were described elsewhere.[17] *p*-Aminophenyl disulfide was purified by repeated recrystallization from a mixture of benzene and *n*-hexane, while *p*-aminophenylthiol was distilled in vacuo. Spectrograde *n*-hexane, diethyl ether, methanol, and acetonitrile were used without further purification. In order to reduce an accumulation of photoproducts and a degradation of the sample, a large amount of the sample solution was flowed through a quartz cell of 2-mm optical path length. The concentrations of *p*-aminophenyl disulfide and *p*-aminophenylthiol were about 1.0 $\times$ 10^{-4} and 3.0 $\times$ 10^{-4} M, respectively. For the measurements of the temperature dependence, the temperature of the sample reservoir and the circulating tube near the inlet of the quartz cell was controlled by contacting them with temperature-controlled ethylene glycol. The temperature of the sample was monitored by using a thermocouple in the optical cell about 5 mm downstream from the point of the transient absorption measurements.

We calculated the interaction energies of the *p*-aminophenylthiyl radical pair at several inter-radical distances and geometries. For this calculation, MOPAC-6[18] on SX-3 (NEC) of the Computation Center Osaka University was used. In the case of the recombination of the linear dimer to produce the parent molecule, the two dipoles of the component radicals were kept in the same plane and in an antiparallel conformation, and the angle of $\angle$CSS was assumed to be 110°, which is taken from the most stable conformation of the parent molecule. For the calculation of the energy of the sandwich dimer, the planes of two benzene rings were kept in parallel and the line joining the centers of the benzene rings was assumed to be perpendicular to the benzene ring. All the other structures such as the structure of the component radical (bond lengths and bond angles) were optimized in the course of the calculation. As a result of the optimization of the geometry, hydrogen atoms of the amino group were not found on the plane of the benzene ring. As a comparison, a similar calculation was performed for the phenylthiyl radical which has a similar structure but a smaller dipole moment than that of the *p*-aminophenylthiyl radical.

Assuming a Lenard-Jones 6$-$12 potential, $U = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$, for a pair of radicals with a separation distance of r, with various strengths, ϵ, and ranges, σ, we carried out a Monte Carlo simulation of the geminate behavior of the radical pair in *n*-hexane solution. Mutual diffusion and a reaction at the encounter of the radical were simulated by a random walk model of the diffusion equation under the influence of the inter-radical potential. The algorithm employed here is essentially the same as that used to solve the Smoluchowski equation to obtain the survival probability of electrons produced by the ionization of nonpolar liquid.[19] One radical was fixed at the origin, and displacements of the other radical were generated randomly with a time step of $\Delta t = 1$ fs. By adding a displacement, Δr, caused by the inter-radical potential to the random displacement, we took into account the effect of the mutual potential of the radical pair on the diffusion process. Δr can be given as

$$\Delta r = (-\mathrm{d}U/\mathrm{d}r)D\Delta t/k_{\mathrm{B}}T$$

where D stands for the diffusion constant estimated from the viscosity of the solvent, k_{B} is the Boltzmann constant, and T is the temperature. In this simulation, the temperature dependence of the solvent viscosity was ignored. A HP model 712/80 computer was used for this purpose.

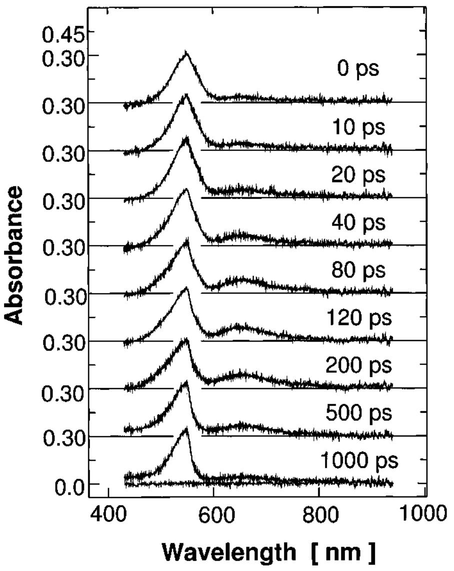

Figure 1. Picosecond transient absorption spectra of *p*-aminophenyl disulfide in *n*-hexane. Delay times after the picosecond 295-nm laser pulse excitation are indicated in the figure. The radical dimer band peaked at 650 nm was observed.

Results and Discussion

Photodissociation of *p*-Aminophenyldisulfide in Various Solvents. By using the picosecond laser photolysis system, we have measured transient absorption spectra of *p*-aminophenyl disulfide in various solvents. Figure 1 shows the time-resolved absorption spectra of the *n*-hexane solution at room temperature excited at 295 nm. Immediately after the excitation, a transient absorption band around 540 nm is observed, while at tens of picoseconds after the laser pulse excitation, two absorption bands peaking around 540 and 650 nm are observed. The 650-nm band is assigned to the *p*-aminophenylthiyl sandwich dimer,[1] while the 540-nm band is similar to that assigned to the *p*-aminophenylthiyl radical.[3,5] The width of the 540-nm band shows narrowing with increasing delay times, which gives us the recombination dynamics of the linear dimer to the parent molecule as described in the next subsection. We confirmed that the interaction between the radical and the parent molecule does not affect our measurements in the time scale of shorter than a few nanoseconds by changing the concentration of the sample.

As we reported in the previous paper,[1] the decay curve of the transient absorbance of *p*-aminophenyl disulfide in *n*-hexane measured at 540 nm was able to be analyzed as a superposition of an exponentially decaying component and an almost constant one. The constant component was the absorbance due to the free radicals that escaped from the geminate pair. The decay time of the former component, which was considered to give a rough idea about the time scale for the geminate recombination to the parent molecule, was found to increase slightly with lowering temperature. In order to eliminate the effects of a slight change of the spectral shape of the 540-nm band, which should be brought by the radical$-$radical interaction as well as the vibrational cooling, the time dependence of the intensity of the spectrum integrated between 500 and 600 nm was plotted in Figure 2. The decay function can be expressed as $A_{\mathrm{s}}\exp(-t/\tau_{\mathrm{s}}) + A_1$, where τ_{s} is the lifetime of the linear dimer and τ_{s} agrees roughly with the rise time of the 650-nm band. A_{s} is the initial intensity of the short-lived component and can be evaluated by extrapolating the short-lived component of the decay curve to the delay time of 0 ps. A_1 is the intensity of the constant component. The dissociation yield of the geminate

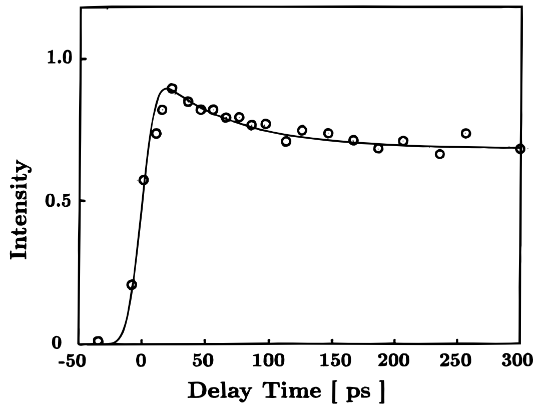

Figure 2. Time dependence of the integrated intensity of the 540-nm band of *p*-aminophenylthiyl radical in *n*-hexane.

TABLE 1: Temperature Dependence of the Decay Time, Dissociation Yield of the Geminate Pair, the Diffusion Time (k^{-1}) Estimated from the Exponential Narrowing of the Bandwidth, the Initial Value of the Bandwidth, and the Viscosity of *n*-Hexane

T/K	τ/ps	Φ_{diss}	k^{-1}/ps	$\Delta\nu(0)$/cm^{-1}	η/cP
278	80	0.71	305	610	0.38
283	70	0.70	185	640	0.355
293	60	0.73	120	520	0.320
303	55	0.71	88	520	0.290
313	42	0.72	60	570	0.264
323	38	0.71	48	530	0.241

pair can be estimated as $\Phi = A_l/(A_s + A_l)$. The temperature dependences of τ_s, Φ, and the viscosity of the solvent are listed in Table 1. The dissociation yield was found to be slightly larger than 0.7 and essentially temperature independent. The activation energy of the geminate recombination was estimated to be about 14 kJ mol^{-1}, which was larger than that of the self-diffusion of the solvent, *n*-hexane. Comparing the absorbance of the 650-nm band extrapolated to $t = 0$ ps with $A_s + A_l$, we estimated the relative yield of the sandwich dimer. Unfortunately, the extinction coefficient of the radical dimer is unknown; the absolute value of the yield was not obtained, but it was found that the yield of the sandwich dimer decreased slightly with increasing temperature.

Figure 3 shows the transient absorption spectra measured at 50 ps after the laser pulse excitation of *p*-aminophenyl disulfide in various solvents. The intensity of the sandwich dimer band at 650 nm decreased significantly with increasing solvent polarity. Even in benzene, the yield of the sandwich dimer was much smaller than that in *n*-hexane. The spectrum of the *p*-aminophenylthiyl radical shifts to the red with increasing dielectric constant of the solvent. The width of the radical band is broader in polar solvents than that in nonpolar solvents. These results should indicate the strong radical−solvent interaction in polar solvents. Within the time resolution of our measurements, neither the decay of the transient absorbance nor the spectral change was observed in polar solvents.

According to the femtosecond laser photolysis measurements of *p*-aminophenyldisulfide in polar solvents,[8,9] photodissociation seems to be a quite rapid process and occurs within their instrumental response time. Although the rapid and large spectral shifts ascribed to the solvation of the radical were observed, no decay of the radical was reported in diethyl ether[8] and in acetonitrile[9] in the femtosecond-to-tens of picosecond region. Combining these results with our observation of the constant absorbance of the radical band at times up to 6 ns after the excitation, we may conclude that essentially no geminate recombination of *p*-aminophenylthiyl radical occurs in polar solvents.

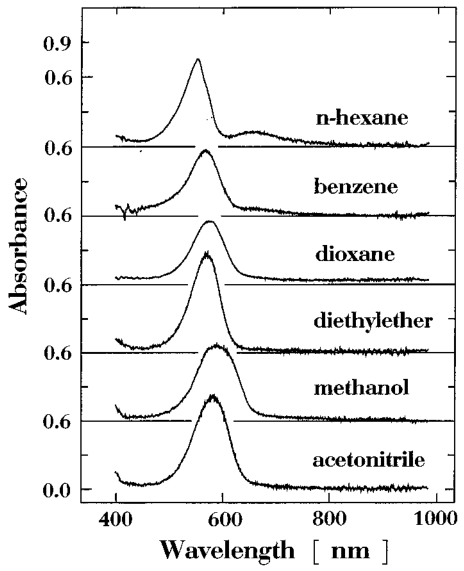

Figure 3. Picosecond transient absorption spectra of *p*-aminophenyl disulfide in various solvents measure 50 ps after the laser pulse excitation. Solvents are indicated in the figure.

The large dipole moment of the *p*-aminophenylthiyl radical, which results in the large solvation energy in polar solvents, seems to be a decisive factor to determine the fate of the geminate radical pair. By using the MNDO Hamiltonian of MOPAC-6, we calculated the energy released on the formation of the *p*-aminophenylthiyl sandwich dimer in the vacuum and obtained it to be about 2.7 kJ mol^{-1}. Under the restrictions of the geometry of the sandwich dimer given in the Experimental Section, the potential minimum appeared at a distance between two benzene rings of 0.48 nm. If we use the PM3 Hamiltonian instead of the MNDO Hamiltonian, the larger stabilization energy of 5.8 kJ mol^{-1} was obtained for the *p*-aminophenylthiyl radical at a slightly smaller inter-radical distance (0.46 nm).

The solvation energy of the separated two-point dipoles, twice the solvation energy of a point dipole of 4.3 D, in diethyl ether estimated from the Born equation was about 6.9 kJ mol^{-1}, which is larger than the stabilization energy gained by the formation of the *p*-aminophenylthiyl sandwich dimer. Since only a little solvation energy of the sandwich dimer of which the dipole moment is negligibly small can be expected, the formation of the sandwich dimer cannot be a preferable channel in polar solvents.

Only a little stabilization (0.72 kJ mol^{-1}) and a larger separation distance (0.54 nm) were obtained for the phenylthiyl sandwich dimer. When we use the PM3 Hamiltonian, the stabilization energy and the inter-radical distance of the stable conformation of the phenylthiyl sandwich dimer were found to be 1.5 kJ mol^{-1} and 0.52 nm, respectively. These results are consistent with the experimental results for the absence of the phenylthiyl radical dimer even in nonpolar solvents.[1]

According to the MO calculation (MNDO), the activation energy of the geminate recombination of the linear dimer to produce the parent molecule was estimated to be 24 kJ mol^{-1}, which appears at a inter-radical distance of about 0.7 nm. In this calculation, the effect of the solvent dielectric constant was not taken into account. The experimentally evaluated activation energy in *n*-hexane was 14 kJ mol^{-1} and was smaller than the calculated value. The difference should be due to the solute−solvent interaction and the restriction to the conformation of radicals used in the calculation. We did not perform the calculation along with the real reaction coordinate. The angle of ∠CSS was fixed to 110° and the direction of the dipole moments was kept in antiparallel throughout the calculation. In spite of these limitations, the results suggest that the repulsion between the dipole moments of the radicals makes the geminate recombination to the parent molecule slow.

Broadening of the Transient Absorption Spectra of the Geminate Radical Pair. As shown in Figure 1, the spectral shape of the 540-nm band in *n*-hexane changes in the short-delay-time region. In this figure, the spectrum measured at 1 ns after the laser pulse excitation is quite similar to the spectrum of the *p*-aminophenylthiyl radical in the literature[3] and is considered to be the spectrum of the escaped free *p*-aminophenylthiyl radical. The spectral broadening was not observed on the photolysis of *p*-aminophenylthiol in *n*-hexane, where the *p*-aminophenylthiyl radical−hydrogen atom pair was formed and the radical−radical interaction may not be expected. The vibrational cooling could not explain the spectral broadening in the short delay times, either.[1] These results strongly indicate that the broadening of the radical band at 540 nm requires two radicals in close proximity to each other.

Although it is considered in general that the radical−radical interaction should be so weak that no significant effect can be brought to the electronic spectra of the large aromatic radicals examined before, exceptionally, the large effect observed in the linear dimer should again be due to the large dipole moment of the *p*-aminophenylthiyl radical. The interaction energy between two point dipoles of $\mathbf{p}_1$ and $\mathbf{p}_2$ located at $\mathbf{x}_1$ and $\mathbf{x}_2$ ($\mathbf{x}_1 \neq \mathbf{x}_2$) is

$$E(\mathbf{p}_1,\mathbf{p}_2) = \{\mathbf{p}_1\cdot\mathbf{p}_2 - 3(\mathbf{n}\cdot\mathbf{p}_1)(\mathbf{n}\cdot\mathbf{p}_2)\}/|\mathbf{x}_1 - \mathbf{x}_2|^3$$

where $\mathbf{n}$ is a unit vector in the direction $\mathbf{x}_1 - \mathbf{x}_2$. The interaction energy can be attractive or repulsive, depending on the orientation of the dipoles. Typical example is where the maximum value of attraction (repulsion) occurs when the dipoles are colinear and parallel (antiparallel) each other.

When the stabilization energy of the dipole−dipole interaction is much larger than k_BT, we need to consider only near the potential minimum. In such cases, the interaction potential may be approximated as a harmonic. The dipole moment for *p*-aminophenylthiyl radical in the excited state was estimated to be 7.3 D[2], which is almost twice that in the ground state. Since it is not strange to consider that the direction of the dipole moment is the same for both the ground and the excited states, the potential minimum should appear at the same configuration in both states. Thus, the potential curves of the radical pair in the ground and the excited states at fixed separation distances of radicals, *r*, near the potential minimum where the two radicals are colinear and parallel to each other may be approximated as

$$U_g = V_g(q^2 - 2)$$

and

$$U_e = V_e(q^2 - 2)$$

respectively, where *q* represents the configuration coordinate. V_g and V_e are given by

$$V_g = |\mathbf{p}_g|^2/r^3$$

and

$$V_e = |\mathbf{p}_g|\cdot|\mathbf{p}_e|/r^3$$

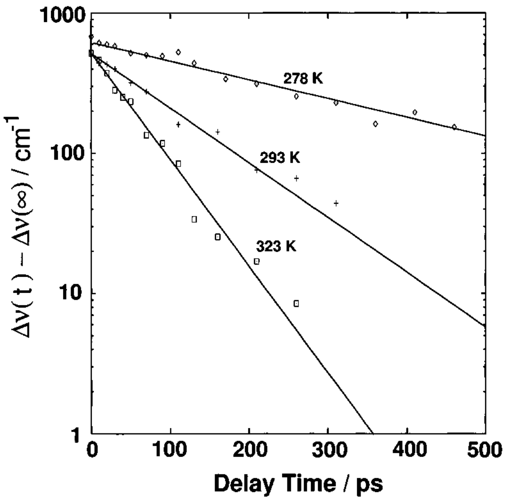

Figure 4. Logarithmic plot of the half-width at half-maximum in the long-wavelength side of the 540-nm band of *p*-aminophenylthiyl radical in *n*-hexane against the delay times after the laser pulse excitation at various temperatures.

where $\mathbf{p}_g$ and $\mathbf{p}_e$ represent the dipole moments of the radical in the ground and excited states, respectively.

Assuming the Boltzmann distribution in the ground electronic state, we can obtain the averaged shift of the transition energy and the standard deviation as

$$\langle\Delta\nu\rangle = -2(V_e - V_g) + (1/2)\{(V_e - V_g)/V_g\}k_BT$$

and

$$\langle(\Delta\nu - \langle\Delta\nu\rangle)^2\rangle^{1/2} = (1/2)^{1/2}\{(V_e - V_g)/V_g\}k_BT$$

where $\Delta\nu$ is the shift of the transition energy and $\langle\ \rangle$ denotes the average. In the case of *p*-aminophenylthiyl radical, V_e is close to twice that of V_g and $V_g > k_BT$ should be satisfied for small *q*, where the spectral broadening is observed; therefore, the results suggest that we may observe both a red shift and a broadening of the radical band.

Logarithmic plots of the half-width at half-maximum (HWHM) of the 540-nm band, $\Delta\nu(t) - \Delta\nu(\infty)$, against the delay times are shown in Figure 4. Since the spectral broadening was significant in the longer wavelength region and the transient absorption due to a photoproduct appeared in the shorter wavelength region, we took HWHM of the lower energy side instead of the full width at half-maximum. A good linear relation was obtained at various temperatures, and the slope of the plot decreased with decreasing temperature. If the inter-radical interaction is brought by the interaction between two point dipoles, the interaction decreases with increasing radical−radical separation, *r*, as r^{-3}. Because the radical cannot be treated as a point dipole, the interaction between multipoles as well as a higher order term should be taken into account. Thus, we can expect a rather complex *r* dependence of the interaction, but our experimental results may suggest that the exponential decrease of the inter-radical interaction is not a bad approximation. In this manner, we obtained a simple relation between the bandwidth, $\Delta\nu(t)$, and the averaged separation distance, $\langle r(t)\rangle$, as $\Delta\nu(t) \sim \exp(-\alpha\langle r(t)\rangle)$.

This means that *r* increases linearly with increasing delay time. Therefore, the separation distance at time *t* can be written as $\langle r(t)\rangle = \langle r(0)\rangle + kt$. If $\langle r(t)\rangle$ is simply governed by a translational diffusion, we cannot expect a linear relation with time. The inter-radical potential should affect $\langle r(t)\rangle$; thus, $\langle r(t)\rangle$ should be a rather complex function of time. In spite of these

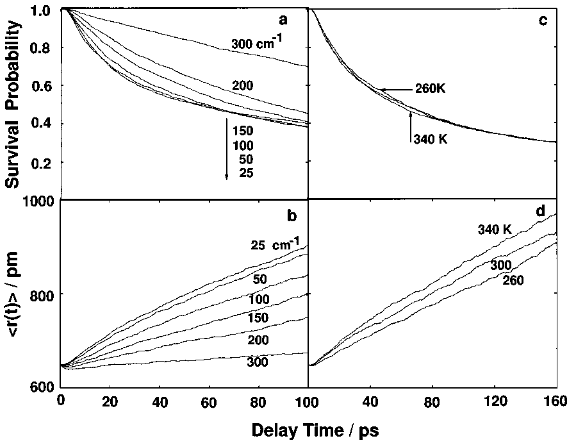

Figure 5. Simulated decay curve of the survival probability (a, c) and the averaged inter-radical distance (b, d) of *p*-aminophenylthiyl radical pair in *n*-hexane. The potential depths (ϵ) used in the simulation (a, c) are indicated in the figure, while the curves calculated for 50 cm^{-1} are shown in b and d. The temperature is 300 K for a and b, while in c and d, three curves calculated at 260, 300, and 340 K are shown.

situations, we hope that the slope, k, can give a rough idea about the rate of the effective diffusion in the microscopic region. The temperature dependences of k and $\Delta\nu(0)$ in *n*-hexane are also listed in Table 1. The temperature dependence of k was found to be larger than that of the decay time of the geminate pair. When the temperature changes from 278 to 323 K, solvent viscosity decreases about 37%, while the slope decreases more than 80%, which suggests that the diffusion in the proximity of the radicals cannot be explained only by the diffusion coefficient in the bulk. The potential which is strong enough to affect the electronic spectrum of the radical may also affect the movement of the radicals. Although $\Delta\nu(\infty)$, which we took as the bandwidth at 2 ns, decreased with decreasing temperature, $\Delta\nu(0)$ seems to be almost temperature independent.

Dynamic Behavior of the Geminate *p*-Aminophenylthiyl Radical Pair. Figure 5 shows the simulated time dependence of the survival probability (a) and the averaged inter-radical distance (b) of *p*-aminophenylthiyl linear dimer in *n*-hexane at 300 K. In this simulation, both σ and the reaction radius were assumed to be 0.55 nm. The introduction of the radical−radical interaction, ϵ, between 25 and 300 cm^{-1} makes the slope, k, small. The decay of the survival probability becomes slow with increasing potential depth, which should be due to the trapping effect of the radicals in their proximity. When the potential was shallow ($\epsilon \leq 100$ cm^{-1}), decay curves were not affected significantly by the potential.

We obtained the temperature dependence of the survival probability and the inter-radical distance as a function of time as indicated in Figure 5c and d, respectively. The decay curves calculated at 260, 300, and 340 K are almost the same, while k decreased with decreasing temperature. Under the consideration of a fixed viscosity, the temperature dependence of k should be ascribed to the temperature dependence of the detrapping of the radicals. This effect was added to the temperature dependence of the viscosity and can explain why the experimentally observed temeprature dependence of k is larger than that of the decay time of the geminate pair. The results suggest that the recombination occurs near the inner boundary of the trap and the population at the reaction zone decreases faster than the escaping of the radical from the range of the radical−radical interaction. A slight increase in the inter-radical distance may result in a significant decrease in the probability of the recombination.

Conclusion

We have carried out picosecond transient absorption measurements of *p*-aminophenyl disulfide in various solvents. The spectral broadening and the exponential narrowing in time were found for the *p*-aminophenylthiyl radical band in *n*-hexane. The former is an indication of the radical−radical interaction in the linear dimer, while the latter should carry information about the diffusion process in the solvent cage and is compared with the results of the simulation. The speed of the increase in the radical−radical separation shows a larger temperature effect than the rate constant of the recombination to form the parent molecule. The MO calculations of the radical pairs supported the experimentally observed large activation energy for the geminate radical recombination and the formation of the sandwich dimer in nonpolar solvents.

The characteristic features of the geminate process of the *p*-aminophenylthiyl radical pair in nonpolar solvents should be due to the rather strong radical−radical interaction, which was revealed as the broadening of the radical band. Although no literature we reported here concerned with geminate radical recombination touched upon the broadening of the radical band, we can expect that this phenomenon should provide us with a quite important tool for establishing a microscopic view of the dynamics of diffusion as well as chemical reaction in the solution phase.

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