J. Am. Chem. Soc. **1982,** *104,* 3711–3714

Monomer–Dimer Equilibrium of the 1-Methyl-2-methoxycarbonylpyridinyl Radical in 2-Methyltetrahydrofuran Solution. Kinetic and Thermodynamic Studies by Electron Spin Resonance Spectroscopy

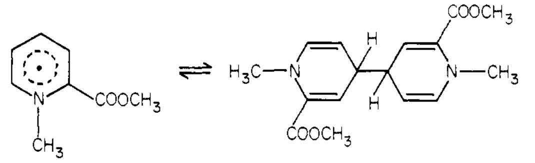
Shozo Tero-Kubota, Yutaka Sano, and Yusaku Ikegami*

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980, Japan. *Received November 17, 1981*

Abstract: The dimerization rate of the 1-methyl-2-methoxycarbonylpyridinyl radical generated by photodissociation of the dimer is measured at a wide range of temperatures by kinetic ESR spectroscopy. Intermediate formation of a radical pair of π-complex type is proposed from a two-step decay of the radical, in which the fast step is represented by reversible second and first order and the slow step is first order, respectively. Activation and stabilization energies for the radical pair formation are $\Delta E_1 = 5.0$ kcal/mol and $\Delta H_1 = -7.9$ kcal/mol, respectively. The dimerization rate is controlled by the step of σ-bond formation from the radical pair with an activation energy of 13.0 kcal/mol. The heat of the σ-bond formation (ΔH) from the radical is estimated to be −16.5 kcal/mol.

Introduction

The first isolation and identification of the 1-methyl-2-methoxycarbonylpyridinyl radical (R) were reported by Watanabe, Ikegami, and Seto in 1972.[1] For this radical species, the existence of R in equilibrium with the dimer (D) in solution was recently revealed by the following studies: (a) temperature dependences of the intensity and the line broadening of the ESR spectrum,[2,3] (b) an absorption spectral study of a thin film of R at low temperatures,[4] (c) the concentration dependence on the absorption spectrum,[5] (d) the photochemical behavior in solution and in the solid state,[2,3] (e) studies by reverse pulse polarography (RPP),[6,7] and (f) the observation of the NMR spectrum of the diamagnetic dimer D with a highly concentrated solution at low temperature.[5]



R D

This equilibrium lies in favor of the dimer. Order-of-magnitude estimates of the equilibrium constant are possible, but the exact determination is difficult by absorption spectroscopy, since the absorption band at 332 nm of D weakly overlaps with that of R. The separated band in the visible region of R has a very small and unknown extinction coefficient. Chemical titration yielded an equilibrium constant of 4×10^5 M^{-1},[2] while an electrochemical technique led to the value of 6.3×10^4 M^{-1} in CH_3CN at room temperature.[7]

A rate constant for dimerization of about 10^6 M^{-1} s^{-1} in CH_3CN was estimated from optical measurements using N_2 laser flash photolysis,[3] while the RPP technique led to the value of 1.3×10^4 M^{-1} s^{-1}.[7] Therefore, a detailed investigation on the kinetics and thermodynamics of the equilibrium is desirable and can be expected to provide reliable parameters for such a radical–dimer equilibrium system which is completely reversible to photolytic perturbation.[2]

In this work, thermodynamic parameters are completely obtained and a precise interpretation for the dimerization process of the radical is investigated. The decay rate constants of R generated by photodissociation of the dimer D are measured by kinetic ESR spectroscopy. Intermediate formation of a π complex is proposed from the observation of a two-step decay, in which each of the steps is reversible second and first order, and first order, respectively.

Experimental Section

Materials. The pyridinyl radical R was prepared from the corresponding pyridinium iodide, purified by distillation as previously described,[2] and then dissolved in 2-methyltetrahydrofuran (MTHF). Purification of solvents was also reported in the previous paper.[8]

Total Concentration of the Species. Addition of 1,1′-dimethyl-4,4′-bipyridinium dichloride (Paraquat) into a solution of R and the dimer D causes a quantitative electron-transfer reaction generating the Paraquat cation radical.[2] Total concentration of the species was determined from the absorption measurement of the cation radical (ϵ 13 000 at λ_{max} 605 nm).[2]

Radical Concentration. An electronic double integrator of ESR signals was built to determine the radical concentration. The integrator equips a low-drift chopper-stabilized OP amplifier (Teledyne 1701-01). A benzene solution of diphenylpicrylhydrazyl was used as a standard sample and the concentration was determined from its optical absorbance (ϵ 1.415×10^4 at 519 nm).[9] The ESR sensitivity variation in different solvents was calibrated with an internal standard of strong pitch in a capillary tube.

Kinetic ESR Spectroscopy. A Varian X-band ESR spectrometer E-109E equipped with field/frequency lock accessory (Varian E-272B) and using 100-kHz modulation was employed along with an optical transmission cavity. The light pulse was obtained by using an electromagnetic shutter (Copal EMS No. 0) capable of varying the shutter speed from 4 to $^1/_{125}$ s, 10 steps. A Kikusui 8700 transient memory and averaging system was used for sampling and averaging the growth and decay curve of the ESR signal at constant magnetic field. The light source was a high-pressure mercury lamp (Ushio, 500 W). A 20-mm water filter was used to shut out an infrared radiation. For kinetic experiments, the light was filtered with a Toshiba VY-44 glass filter to prevent the additional decomposition of the radical.

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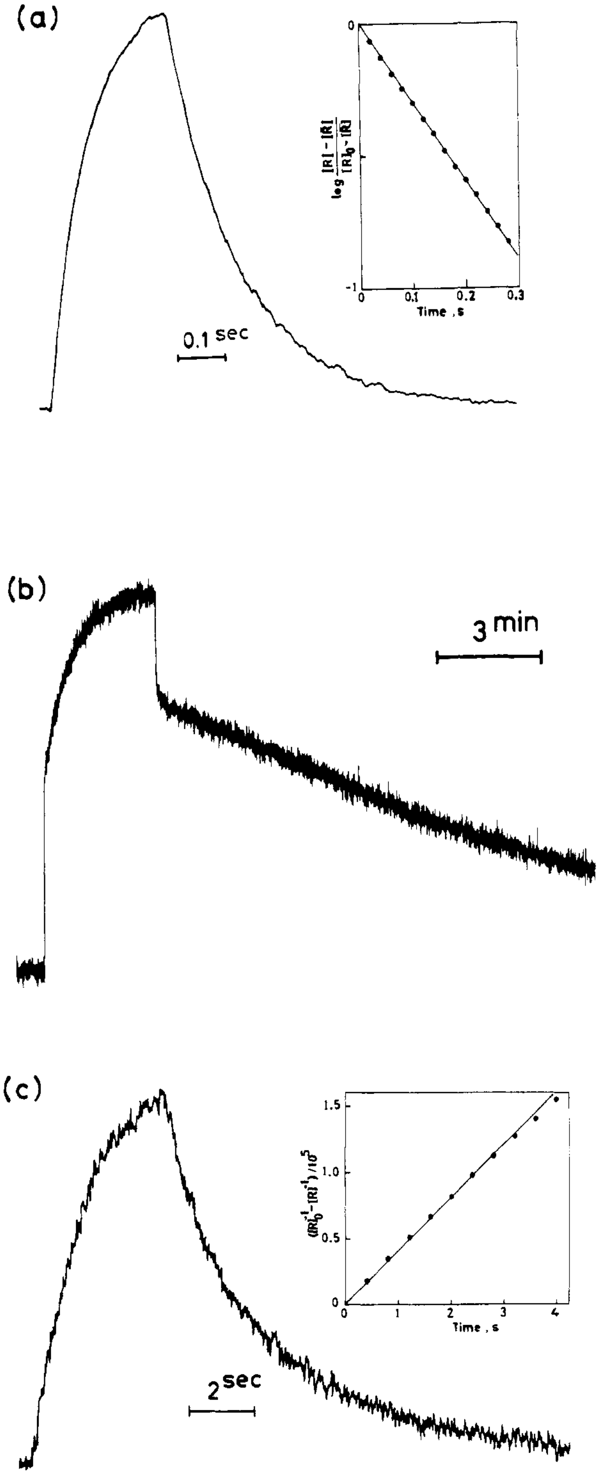

Figure 1. Growth and decay curves of 1-methyl-2-methoxycarbonylpyridinyl radical in MTHF solution with light pulse irradiation at (a) 15 °C, (b) -65 °C, and (c) -95 °C. Insert: (a) first-order plot and (c) second-order plot.

Results

Kinetic Measurements. The dimer D has a $\pi\sigma$–$\pi\sigma^*$ transition at λ_{max} 332 nm in MTHF[4] and generates R by irradiation with the light corresponding to the band.[2,6] Since the absorption band is broad and spread over the visible region, the dissociation is caused by visible light. After the irradiation pulse, the enhanced radical decays back to its equilibrium concentration. The decay rate of R in MTHF solution has been measured at a wide range of temperatures by kinetic ESR spectroscopy.

Figure 1 shows the growth and decay curves of R in MTHF observed at various temperatures. A two-step decay, as shown in Figure 1b, was observed at temperatures below -50 °C, while no change of hyperfine splitting pattern was exhibited. This indicates that there exists an intermediate in the dimerization process of R. In this paper, the decay at low temperatures is called "the fast step", and the decay of the second step in Figure 1b which is also observed at high temperatures is represented as "the slow step" reaction.

The fast step is nearly approximated with a second-order decay for the measurements in the temperature range -85 to -114 °C. On the other hand, the slow step is first-order decay in the range, 15 ~-75 °C. The reaction rates are represented as follows:

the fast step:

$$\log (k_{exp}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = [(9.9 \pm 0.2) - (4.3 \pm 0.2)](\mathrm{kcal/mol})/\theta$$

the slow step:

$$\log (k_{exp}/\mathrm{s}^{-1}) = [(10.7 \pm 0.1) - (13.0 \pm 0.1)]\ (\mathrm{kcal/mol})/\theta$$

where $\theta = 2.303RT$. These reactions should be reversible and further details will be discussed later.

The first-order decay of the slow step implies that the intermediate is a radical pair (RP), which is a π complex composed of two pyridinyl radicals. Thus, it is considered that the fast step corresponds to a radical-pair formation and the slow step to a σ-bonding process. This speculation seems reasonable, since a low activation energy is needed for radical-pair formation and a high activation energy is required for σ bonding.

Equilibrium Constant of Radical-Pair Formation, K_1. Since a two-step decay was clearly observed at low temperatures, the equilibrium constant between R and radical pair (RP), K_1, can be estimated. In the irradiation with a strong and short light pulse, the initial concentrations of R and RP immediately after the irradiation are represented, as $[\mathrm{R}]_0$ and $[\mathrm{RP}]_0$, respectively. After the pulse, the preliminary equilibrium is rapidly established and each concentration becomes $[\bar{\mathrm{R}}]$ and $[\bar{\mathrm{R}}\bar{\mathrm{P}}]$, respectively. When a strong and short light pulse was used for irradiation at low temperatures, K_1 can be determined from the following equation:

$$K_1 = \frac{[\bar{\mathrm{R}}\bar{\mathrm{P}}]}{[\bar{\mathrm{R}}]^2} = \frac{[\mathrm{R}]_0 - [\bar{\mathrm{R}}]}{2[\bar{\mathrm{R}}]^2} \qquad (1)$$

since $2[\mathrm{RP}]_0/([\mathrm{R}]_0 - [\bar{\mathrm{R}}]) \ll 1$.

The measurements were carried out with the shutter speed of $^1/_{15}$ or $^1/_{30}$ s, using a UV-29 glass filter at temperatures between -80 and -105 °C. Under these conditions, even if a shutter speed of shorter than $^1/_{30}$ s was used, the obtained K_1 value was independent of the shutter speed. The linear relationship of the observed K_1 values *vs.* $1/T$ led to the enthalpy of the radical pair formation, ΔH_1, of -7.9 ± 0.5 kcal/mol with the least-squares method.

Equilibrium Constant of the Dimer Formation, K. Stationary-state radical concentrations, $[\bar{\mathrm{R}}]$, were measured at the temperatures between 0.5 and 60.5 °C using an electronic double integrator for ESR spectra. Then, the radical-pair concentration, $[\bar{\mathrm{R}}\bar{\mathrm{P}}]$, in equilibrium at each temperature, can be estimated from the relation $[\bar{\mathrm{R}}\bar{\mathrm{P}}] = K_1[\bar{\mathrm{R}}]^2$. Since the total concentration of the species in the equilibrium was already determined by Paraquat titration, the concentration of the σ-bonding dimer, $[\bar{\mathrm{D}}]$, can be obtained. Thus the equilibrium constant of the dimer formation is determined by the equation

$$K = [\bar{\mathrm{D}}]/[\bar{\mathrm{R}}]^2 \qquad (2)$$

A good linear relation between the observed K and $1/T$ was obtained as shown in Figure 2. The enthalpy change involved in σ-bond formation between the pyridinyl radicals was ΔH = -16.5 ± 0.1 kcal/mol. The entropy change was ΔS = -29 ± 1 cal/K·mol. At 25 °C, an equilibrium constant of $7.44 \times 10^5\ \mathrm{M}^{-1}$ was obtained. Thus, it is clear that the dimer predominates over the radical in this equilibrium.

Discussion

Dimerization Mechanism. Two schemes (eq A and B) are considered to interpret the observed two-step decay, in which the radical generated photolytically decays initially in a second-order and then in a first-order process:

$$2\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RP} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{D} \tag{A}$$

$$K_1 = k_1/k_{-1} = [\bar{\mathrm{R}}\bar{\mathrm{P}}]/[\bar{\mathrm{R}}]^2 \tag{3}$$

$$K_2 = k_2/k_{-2} = [\bar{\mathrm{D}}]/[\bar{\mathrm{R}}\bar{\mathrm{P}}] \tag{4}$$

$$K = k_1k_2/k_{-1}k_{-2} = [\bar{\mathrm{D}}]/[\bar{\mathrm{R}}]^2 \tag{5}$$

The deviation from the equilibrium concentration for each species A is denoted by ξ_{A} which is defined as follows:

$$\xi_{\mathrm{A}} = ([\mathrm{A}] - [\bar{\mathrm{A}}])/[\bar{\mathrm{A}}] \tag{6}$$

We can write the kinetic equations:

$$\mathrm{d}\xi_{\mathrm{R}}/\mathrm{d}t = -2k_1[\bar{\mathrm{R}}]\{(2 + \xi_{\mathrm{R}})\xi_{\mathrm{R}} - \xi_{\mathrm{RP}}\} \tag{7}$$

$$\mathrm{d}\xi_{\mathrm{RP}}/\mathrm{d}t = (k_1/K_1)\{(2 + \xi_{\mathrm{R}})\xi_{\mathrm{R}} - \xi_{\mathrm{RP}}\} - k_2(\xi_{\mathrm{RP}} - \xi_{\mathrm{D}}) \tag{8}$$

In our case, each step can be treated independently, because the rate constants of the two steps are substantially different from each other.

(i) The Fast Step. Decrease of 1 mol of R generates 0.5 mol of RP in this step. Therefore,

$$\xi_{\mathrm{RP}} = -\xi_{\mathrm{R}}/2K_1[\bar{\mathrm{R}}] \tag{9}$$

Introducing this expression into eq 7 yields

$$\frac{\mathrm{d}\xi_{\mathrm{R}}}{\mathrm{d}t} = -2\ k_1[\bar{\mathrm{R}}]\left\{\frac{1 + 4k_1[\bar{\mathrm{R}}]}{2k_1[\bar{\mathrm{R}}]}\xi_{\mathrm{R}} + \xi_{\mathrm{R}}^2\right\} \tag{10}$$

Assuming $4K_1[\bar{\mathrm{R}}] \gg 1$,[10]

$$2k_1t = -\frac{1}{2[\bar{\mathrm{R}}]}\ln\left|\frac{[\mathrm{R}] - [\bar{\mathrm{R}}]}{[\mathrm{R}] + [\bar{\mathrm{R}}]}\middle/\frac{[\mathrm{R}]_0 - [\bar{\mathrm{R}}]}{[\mathrm{R}]_0 + [\bar{\mathrm{R}}]}\right| \tag{11}$$

(ii) The Slow Step. Since the activation energy in this step is large, we can neglect the reverse reaction. Therefore, eq 7 and 8 lead to the kinetic equation,

$$\frac{\mathrm{d}\xi_{\mathrm{RP}}}{\mathrm{d}t} = -\frac{1}{2K_1[\bar{\mathrm{R}}]}\frac{\mathrm{d}\xi_{\mathrm{R}}}{\mathrm{d}t} - k_2\xi_{\mathrm{RP}} \tag{12}$$

The preliminary equilibrium, $K_1 = [\mathrm{RP}]/[\mathrm{R}]^2$, is always established. That is,

$$\xi_{\mathrm{RP}} = \xi_{\mathrm{R}}(2 + \xi_{\mathrm{R}}) \tag{13}$$

and therefore,

$$\frac{\mathrm{d}\xi_{\mathrm{RP}}}{\mathrm{d}t} = 2(1 + \xi_{\mathrm{R}})\frac{\mathrm{d}\xi_{\mathrm{R}}}{\mathrm{d}t} \tag{14}$$

Substituting eq 14 into eq 12 yields,

$$\frac{\mathrm{d}\xi_{\mathrm{R}}}{\mathrm{d}t} = -2k_2K_1[\bar{\mathrm{R}}]\frac{(2 + \xi_{\mathrm{R}})\xi_{\mathrm{R}}}{1 + 4K_1[\bar{\mathrm{R}}](1 + \xi_{\mathrm{R}})} \tag{15}$$

If $4K_1[\bar{\mathrm{R}}](1 + \xi_{\mathrm{R}}) \gg 1$ and $\xi_{\mathrm{R}} \gg 1$,

$$k_{\mathrm{exp}}t = \frac{k_2}{2}t = -\ln\frac{[\mathrm{R}] - [\bar{\mathrm{R}}]}{[\mathrm{R}]_0 - [\bar{\mathrm{R}}]} \tag{16}$$

$$\mathrm{RP} \underset{k_{-1}}{\overset{k_1}{\leftrightharpoons}} 2\mathrm{R} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{D} \tag{B}$$

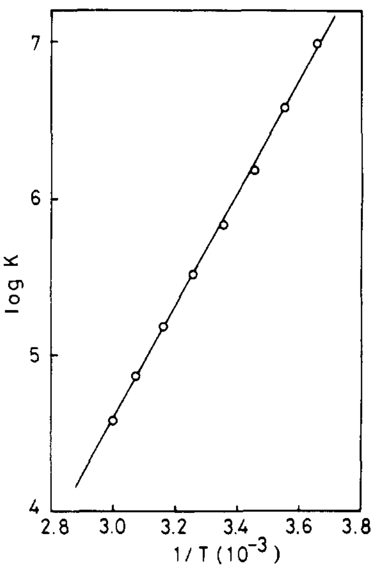

Figure 2. Monomer–dimer equilibrium constants ($K = [\bar{\mathrm{D}}]/[\bar{\mathrm{R}}]^2$) *vs.* $1/T$.

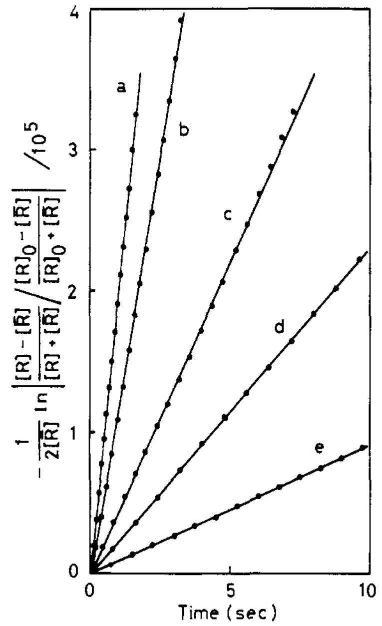

Figure 3. Reversible second- and first-order plots for the decay of the fast step: (a) −75°, (b) −85°, (c) −95°, (d) −104°, and (e) −114 °C.

(i) The Fast Step. A similar kinetic procedure is applied. By neglecting the D formation, we can obtain the same kinetic equation as that in eq A.

(ii) The Slow Step. A kinetic procedure similar to that applied in reaction A yields

$$k_{\mathrm{exp}}t = \frac{k_2}{2K_1}t = -\ln\frac{[\mathrm{R}] - [\bar{\mathrm{R}}]}{[\mathrm{R}]_0 - [\bar{\mathrm{R}}]} \tag{17}$$

As mentioned above, the same equation for radical-pair formation is obtained for both schemes (eq A and B). Figure 3 shows the reversible second- and first-order plots for the fast step. Very good linear relations are obtained for all measurements. For σ-bonding reaction, the first-order decay arises at high concentration of the radical in both schemes. Therefore, there is no kinetic method for distinguishing between these two reaction schemes. For eq A, the experimental rate constant is $k_{\mathrm{exp}} = (k_2/2)$ and, for eq B, $k_{\mathrm{exp}} = (k_2/2K_1)$.

The Arrhenius plots for each reaction, followed by calculations by the least-squares method, afforded the activation energies for the radical pair and the dimer formation: $\Delta E_1 = 5.0 \pm 0.2$ kcal/mol and $\Delta E_2(\mathrm{exp}) = 13.0 \pm 0.1$ kcal/mol, respectively.

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[10] The condition, $4K_1[\bar{\mathrm{R}}] \gg 1$, is satisfied in our measurements. At −75 °C, K_1 is 2.43×10^7 M^{-1} and $[\bar{\mathrm{R}}]$ is usually $\simeq 5 \times 10^{-6}$ M; therefore, $4K_1[\bar{\mathrm{R}}] \simeq 490 \gg 1$. The value increases with decreasing temperature.

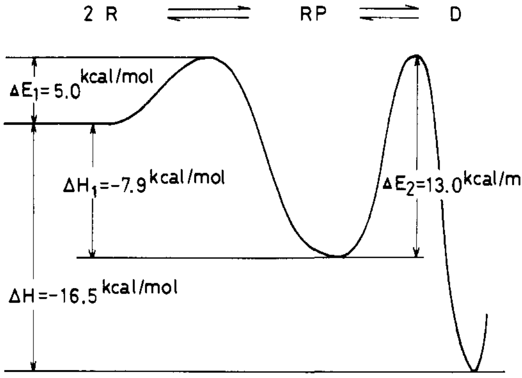

Figure 4. A potential energy vs. reaction coordinate diagram for the dimerization of 1-methyl-2-methoxycarbonylpyridinyl in MTHF solution.

If the dimerization occurred with reaction B, the experimental rate constant for σ-bonding would involve the preliminary equilibrium constant (K_1). Therefore, the true activation energy is determined as follows:

$$\Delta E_2 = \Delta E_2(\mathrm{exp}) + \Delta H_1 \qquad (18)$$

Experimentally, we obtained, $\Delta E_2(\mathrm{exp}) = 13.0$ kcal/mol and $\Delta H_1 = -7.9$ kcal/mol. The true activation energy, therefore, is derived to be $\Delta E_2 = 5.1$ kcal/mol. This value is nearly equal to ΔE_1 for radical-pair formation. It seems unreasonable that the same activation energies occurred in both reactions, because the transition state in σ-bonding accompanies the structural distortion in the radicals to form the new bond while there is no significant effect for the structure in the transition state of radical-pair formation. Therefore, reaction A is chosen as the dimerization process of the pyridinyl R.

According to the above discussion, a potential energy vs. reaction coordinate diagram can be depicted, as shown in Figure 4, summarizing the thermodynamic parameters obtained completely for this equilibrium system. It is considered that the existence of an intermediate radical pair is responsible for the discrepancy among the rate and equilibrium constants so far obtained from the measurements by flash photolysis, chemical titration, and electrochemical methods.

For some radicals, such as diethyl nitroxide,[11] phenoxy,[12] and iminoxy,[13] the intermediate formation of an unstable dimer has also been proposed in the dimerizations. From the point of view that the kinetics of these intermediates are significantly influenced by substituents and solvent, pyridinyl radicals are interesting materials to investigate those effects, because various derivatives can be prepared and the measurements can be carried in a "clean system" which contains only the solutes and solvent.

Rate Constants. Since reaction A is indicated for the dimerization mechanism, the following rate constants are given.

radical-pair formation:

$$\log\,(2k_1/\mathrm{M^{-1}\,s^{-1}}) = [(10.88 \pm 0.21) - (5.0 \pm 0.2)](\mathrm{kcal/mol})/\theta$$

σ-bond formation from the radical pair:

$$\log\,(k_2/\mathrm{s^{-1}}) = [(10.98 \pm 0.11) - (13.0 \pm 0.1)]\ (\mathrm{kcal/mol})/\theta$$

The rate constant of radical pair formation at 25 °C is 7.8×10^6 $\mathrm{M^{-1}\,s^{-1}}$. This value is three orders of magnitude smaller than that of a usual diffusion-controlled reaction. This is mainly due to the low preexponential factor, A. The low A value means that the stabilized radical pair is formed only by the collision of radicals in stereospecific orientation. The comparatively high activation energy may reflect both the steric factor to form singlet radical pair and the interaction between the isolated radical and solvent.[14] The large activation energy required for the formation of a σ bond is ascribed to the stabilization of the intermediate radical pair.

The reverse reaction rates are estimated from the decay rates and the equilibrium constants:

$$k_{-2}(25\ ^\circ\mathrm{C}) = k_2K_1/K = 1.15\ \mathrm{s^{-1}}$$

Structure of the Intermediate. When a solution of R in MTHF was irradiated at 77 °K, a triplet radical pair was clearly observed exhibiting the photodissociation of the diamagnetic dimer D within the solvent cavity. An average spin separation of 5.5 Å has been evaluated from the zero-field splitting constant of $D = 0.0155$ $\mathrm{cm^{-1}}$.[3,4] For this radical pair observed in MTHF glass, it seems that there is only a small overlap between the π orbitals of two pyridinyl rings and no stabilization, since the stable conformation of D is assumed to be a s-trans form, which would produce the radical pair retaining the conformation in the solvent cavity.

On the other hand, the radical pair observed intermediately in solution seems to be a singlet π complex having a sandwich-like structure, because it shows a large stabilization. This is consistent with the result of thin-film spectroscopy, in which a strong charge-transfer (CT) absorption was observed.[4] Although no CT absorption has been observed in the present photolytic study, the absorption is expected to be detected by further examination. In the series of 4-substituted 1-alkylpyridinyl radicals, a singlet π-complex formation has been also suggested in solution at low temperatures.[15-17]

Thermodynamic Parameters for Dimerization. The enthalpy change ΔH involved in σ-bond formation between the pyridinyls is −16.5 kcal/mol. This value is comparable to that of C–C bond formation between the phenoxy rings[18] and is larger than those for the dimerization of triphenylmethyl (−11.2 kcal/mol)[19] and $(\mathrm{CF_3S})_3\mathrm{C}$ (−13.7 kcal/mol)[20] radicals. The entropy change of −29 ± 1 cal/K·mol seems reasonable for dimerization reactions.

Acknowledgment. The authors thank Dr. M. Kumano and Associate Professor T. Ikenoue for valuable advice concerning the instrumentation. We are grateful to Dr. H. Hayashi of the Institute of Physical and Chemical Research for information on the electromagnetic shutter. We are also indebted to Professor T. Abe of the College of General Education, Tohoku University, for helpful discussions. Part of this work was supported by a Grant-in-Aid for Scientific Research No. 56540245 from the Ministry of Education, Science and Culture, Japan.

Registry No. R, 37342-90-8; D, 76318-30-4.

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[14] A referee questions why the activation energy is so high and the A value so low for the fast step. The ease of radical-pair formation of pyridinyl radicals is affected considerably by the kind and number of substituents on the ring. A recent result shows that the difference in k_1 (for the fast step) for the 1-methyl-, 1-ethyl-, and 1-isopropyl-4-phenylpyridinyl radicals originates from different A values rather than activation energy. Kinetic studies on the pyridinyl radicals with various substituents are under way.

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