in Figure 11. It shows the excitation profiles of the bands at 553 [ν_s(Fe–O) of the peroxo-bridged species], 572 (out-of-plane porphyrin deformation), 639 (phenyl mode), and 888 cm^{-1} (in-plane porphyrin deformation). It is seen that the intensities of these four bands maximize at 415–410 nm. Therefore, we conclude that the Soret π–π^* transition is responsible for resonance enhancement of the ν_s(Fe–O) of the peroxo-bridged dimer.

Oxidation of Other Iron Porphyrins. Similar experiments were carried out using several other porphyrins such as Fe(OEP), Fe(α^4-$\mathrm{T_{PIV}}$PP),[9] Fe(*cis*-$\alpha^2\beta^2$-$\mathrm{T_{PIV}}$PP), and Fe(T(2,6-MeO)$_4$PP) in order to observe five-coordinate dioxygen adducts of the FePO$_2$ type containing bulky porphyrins that might sterically hinder the formation of the peroxo-bridged species. In all cases, only the bands characteristic of the peroxo-bridged species were observed in solution at -80 °C and these solutions exhibited ferryl bands upon warming. In contrast to the NMR studies,[9] we could not observe the Raman spectra of "base-free" O$_2$ adducts of these porphyrins in toluene solution at -80 °C. This may be due to local heating caused by the laser beam. However, the Raman spectra of their O$_2$ adducts were observed in O$_2$ matrices at 15–30 K.[3,4,36] Table III lists the ν(Fe–O)/ν(FeO) of all the complexes thus far determined in our laboratory.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMB-8613741). The Raman spectroscopic equipment used for this investigation was purchased with funds provided by a National Science Foundation grant (CHE-8413956). We thank Prof. J. R. Kincaid, Dr. L. M. Proniewicz, and Dr. R. Czernuszewicz (University of Houston) for their valuable comments.

Spin Polarization Conservation during Triplet–Triplet Energy Transfer in Fluid Solution As Studied by Time-Resolved ESR Spectroscopy

Kimio Akiyama,* Atsuko Kaneko, Shozo Tero-Kubota, and Yusaku Ikegami

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980, Japan. *Received September 5, 1989*

Abstract: Electron spin polarization of pyridinyl radicals generated from the photosensitized dissociation of the dimers was studied. Addition of triplet sensitizer to the dimer solution induced drastic change in the CIDEP spectrum. Examinations of the dependence of spectral change on the T$_1$ state energy level and the spin alignment in the T$_1$ sublevels of sensitizers lead to the conclusion that energy transfer between the pyridinyl dimer and the sensitizer occurred and that the spin polarization was conserved during the process. From a series of triplet donors, nonphosphorescent T$_1$ states of two types of pyridinyl dimers were estimated to be 2.43 eV for the 2,2′-dimer of 1-methyl-4-*tert*-butylpyridinyl and 2.65 eV for the 4,4′-dimer of 1-methylpyridinyl.

Time-resolved ESR (TRESR) method has played an important role in studying photochemical reaction mechanisms because the CIDEP spectra give information about the character of the excited state associated with the reaction as well as the radical intermediate with short lifetime.[1]

Recently, we first proposed the conservation of electron spin polarization during the triplet–triple (T–T) energy transfer in fluid solution,[2] although the possibility had been demonstrated in single crystals[3-6] and glassy matrices.[7-9] In our study, the dimer of the 1,4-dimethylpyridinyl radical (**2**) was used as the energy acceptor, since direct photochemical excitation induced homolytic cleavage from the S$_1$ state, showing a pure RPM (radical pair mechanism) with A/E (absorptive/emissive) polarization in the ESR spectrum of the produced radical.[10] Addition of triplet sensitizers, such as 2-acetonaphthone and benzophenone, to the dimer solution caused a significant change of the CIDEP spectrum from A/E to all E polarization. In these sensitizers, the intersystem crossing (ISC) occurs preferentially to the highest triplet sublevel in the T$_1$ state with a high quantum yield. It was found that the occurrence of the polarization transfer depends on the energy level of T$_1$ state of the sensitizer. These results provide us a new field in the application of the CIDEP method to determine the T$_1$ state energy level in fluid solution.

In the present study, we examine the T–T energy transfer in detail using a series of sensitizers as the donor and the dimers of 1-methylpyridinyl (**1**) and 1-methyl-4-*tert*-butylpyridinyl (**3**) radicals as the acceptor.

These radicals each couple at 2- and 4-positions to form dimers, and the equilibrium between the radical and dimers tends overwhelmingly toward the dimers in the dark. The structure of the dimers depends on the bulkiness of the substituent at the 4-position of the pyridine ring. According to ^{1}H NMR measurements, the solution of **3** contains dl- and meso-2,2′-dimers (**5**)[11] and, for **2**, there are four kinds of isomers, dl- and meso-, 2,2′-, 2,4′ and 4,4′-dimers. Only the 4,4′-dimer was observed for the solution of **1**. The ^{1}H NMR spectrum of the 4,4′-dimer (**4**) of **1** showed lines at δ_H values of 2.76 (6 H, NCH$_3$), 2.83 (2 H, 4,4′-H), 4.23 (4 H, 3,3′; 5,5′-H), and 5.79 (4 H, 2,2′;6,6′-H) in CD$_3$CN with the Me$_4$Si standard at δ 0.00. All these dimers are photosensitive and generate the corresponding monomeric radicals from the S$_1$ states.[10,11] Positions of coupling in dimer formation have also been

---

(1) For a recent review, see: Trifunac, A. D.; Lawler, R. G.; Bartles, D. M.; Thurnauer, M. C. *Prog. React. Kinet.* **1986**, *14*, 43, and references therein.

(2) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Ikenoue, T. *J. Am. Chem. Soc.* **1984**, *106*, 8322.

(3) El-Sayed, M. A.; Tinti, D. S.; Yee, E. M. *J. Chem. Phys.* **1969**, *51*, 5721.

(4) Clarke, R. H. *Chem. Phys. Lett.* **1970**, *6*, 413.

(5) Scharnoff, M.; Hurbe, E. B. *Phys. Rev. Lett.* **1971**, *27*, 576.

(6) Kim, S. S.; Weissman, S. I. *Rev. Chem. Intermed.* **1979**, *3*, 107.

(7) Weir, D.; Wan, J. K. S. *J. Am. Chem. Soc.* **1984**, *106*, 427. Wan, J. K. S.; Dobkowski, J.; Turro, N. J. *Chem. Phys. Lett.* **1986**, *131*, 129. Wan, J. K. S. *Electronic Magnetic Resonance*, Weil, J. A., Ed.; Canadian Chemical Society: Ottawa, Canada, 1987; 599.

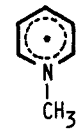
(8) Imamura, T.; Onitsuka, O.; Murai, H.; Obi, K. *J. Phys. Chem.* **1984**, *88*, 4028. Imamura, T.; Onitsuka, O.; Obi, K. *J. Phys. Chem.* **1986**, *90*, 6741. Obi, K.; Imamura, T. *Rev. Chem. Intermed.* **1986**, *7*, 225.

(9) Murai, H.; Yamamoto, Y.; I'Haya, Y. J. *Chem. Phys. Lett.* **1986**, *129*, 201.

(10) Akiyama, K.; Tero-Kubota, S.; Ikenoue, T.; Ikegami, Y. *Chem. Lett.* **1984**, 903.

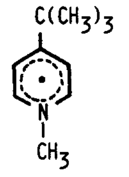
(11) Akiyama, K.; Ishii, T.; Tero-Kubota, S.; Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3535. Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Ikenoue, T. *J. Phys. Chem.* **1985**, *89*, 339.

0002-7863/90/1512-3297$02.50/0

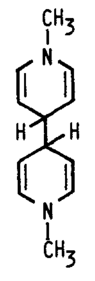


1

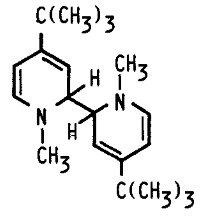
2



3



4



5

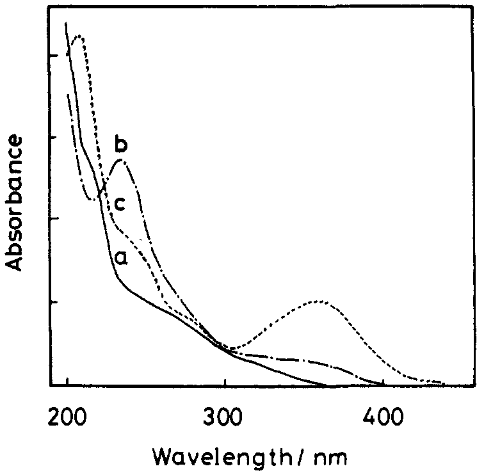


Figure 1. Absorption spectra of pyridinyl dimers in CH$_3$CN at 25 °C: (a) 4,4′-dimer of 1-methylpyridinyl; (b) mixture of 2,2′-, 2,4′-, and 4,4′-dimers of 1,4-dimethylpyridinyl; (c) 2,2′-dimer of 1-methyl-4-*tert*-butylpyridinyl radicals.

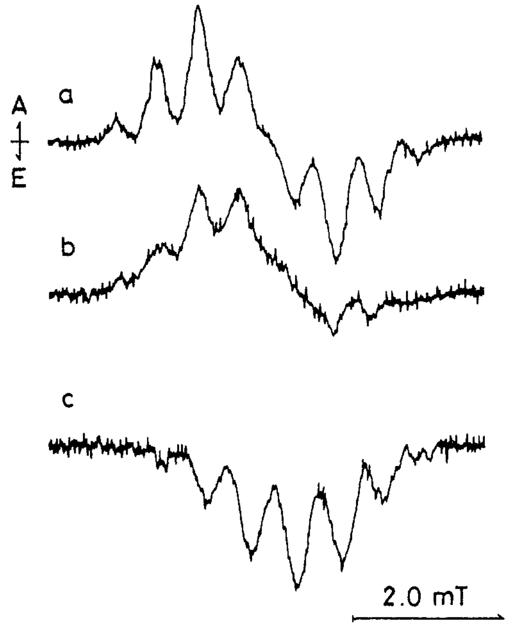


Figure 2. CIDEP spectra of the 1-methyl-4-*tert*-butylpyridinyl radical observed 1 μs after the laser pulse photolysis of the dimer (0.01 M) at −40 °C in toluene: (a) without sensitizer; (b) in the presence of pyrido[2,3-*b*]pyrazine (0.1 M); (c) in the presence of 2-acetonaphthone (0.1 M).

discussed from the viewpoint of chemical–electrochemical study.[12] It can be easily deduced that 4,4′- and 2,2′-dimers have different energy levels of the T_1 states, since the former has a 1,4-diene structure while the latter is a 1,3-diene. The energy levels, however, are unknown because of the nonphosphorescent behavior. It is also difficult to observe S–T absorption with O_2 or other molecules containing a heavy metal, since the dimers are reactive to these molecules. This paper deals with the energy level of the T_1 states of the 4,4′- and 2,2′-dimers of pyridinyl radicals as a reesult of the CIDEP observations associated inherently with the T–T energy transfer.

Experimental Section

Sample Preparation. 1-Methyl 4-substituted pyridinyl radicals were prepared by a one-electron reduction of the corresponding pyridinium bromide with 3% sodium amalgam in deoxygenated water and extracted with toluene or *n*-hexane.[13] Deoxygenated solvents by argon bubbling were used for the preparation because the samples are reactive to O_2. For NMR measurements, the solvent was replaced by CD_3CN by vacuum line techniques.

ESR and NMR Measurements. Time-resolved ESR spectra were observed with a Varian E-109E X-band EPR spectrometer without field modulation. The ESR signal from the preamplifier output of the microwave bridge was amplified to 40 dB by a handmade wide-band amplifier. Microwave power was 1 mW for measurements of spectra. The signal was taken at arbitrary times, after the laser pulse, into a two-channel boxcar integrator (NF BX-531) with a gate width of 100 ns. An excimer laser (Lumonics HE-420, XeCl, 308 nm) was used as the light pulse source. The power of the pulse (50 mJ/pulse) was monitored with power meter to maintain constant incident power.

The sample solution, deoxygenated with bubbling of pure Ar gas for 2 h, flowed slowly through the quartz tube in the ESR cavity. The temperature was controlled by a conventional variable-temperature apparatus. NMR spectra were measured with a Varian XL-200 NMR spectrometer.

Results

Absorption Spectra. In Figure 1 are shown absorption spectra of the dimers of these pyridinyl radicals in toluene. As reported previously,[11] the solution of **3** contains only 2,2′-isomer because of the bulky substituent at the 4-position. The 2,2′-dimer has absorption maxima at 360 ($\epsilon \cong 3000$) and 247 nm (34 000).[12] On the other hand, the solution of **1** exhibits a monotonous spectrum in the near-UV region, and the species is assigned to the 4,4′-dimer by ^{1}H NMR measurement. These absorption spectra show a difference from the corresponding dihyropyridines, which have the $S_1(\pi\pi^*)$ transitions at 325 nm for 1-methyl-1,2-dihydropyridine and at around 280 nm for 1,4-dihydropyridine.[14] The absorption bands of the present dimers in the UV region are assigned to $(\sigma\pi) \rightarrow (\sigma\pi)^*$ transition.[15] The absorption spectrum of **2** in toluene (Figure 1b) indicates the presence of several isomers in this system. According to analysis of the ^{1}H NMR spectrum, this solution contains 2,2′-, 2,4′-, and 4,4′-dimers in a ratio of 4:4:2 at room temperature, and the ratio varies slightly with the conditions of sample preparation.

Photolysis of these dimer solutions generates the corresponding pyridinyl radicals, which subsequently dimerize in the dark.[11] The homolysis–dimerization reaction is completely reversible for irradiation of the light with wavelengths longer than 300 nm, though light of shorter wavelengths induces a partial decomposition. Molar absorption coefficients (ϵ) were estimated for the representative dimers at 308 nm to be 700 and 1200 for **4** and **5**, respectively.

Triplet Sensitization. Figure 2a shows the CIDEP spectrum generated from direct excitation of the 2,2′-dimer (**5**) of **3** (0.01

---

[12] Raghavan, R.; Iwamoto, R. T. *J. Electroanal. Chem.* **1978**, *92*, 101; **1979**, *102*, 85.

[13] Cairns, J. F.; Corran, J. A. *Chem. Abstr.* **1969**, *71*, 8142g.

[14] Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1.

[15] Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4801. Kosower, E. M. *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer: Berlin, **1984**; p 117.

Table I. Physical Parameters of Triplet Sensitizers and the Phase of Polarization of 1-Methylpyridinyl and 1-Methyl-4-*tert*-butylpyridinyl Radicals 1 μs after the Laser Pulse in Toluene

sensitizer	E_S[a]	E_T[a]	ϕ_{ISC}	ϵ_{308}	phase[b]	phase[c]
pyrazine	3.82	3.30	0.33	630	A*/E	A*/E
benzophenone	3.30	2.99	1.00	100	A/E*	A/E*
pyrido[2,3-*b*]pyrazine		2.73		4000	A*/E	A*/E
quinoline	3.95	2.69	0.31	2000	A/E*	A/E*
1-bromonaphthalene	3.86	2.56	1.00	450	A/E*	A/E, E[d]
2-acetonaphthone	3.34	2.56	0.84	870	A/E*	A/E
1-acetonaphthone	3.30	2.47	1.00	6500	A/E*	A/E
biacetyl	2.60	2.39	0.98		A/E	A/E
benzil	2.56	2.30	0.92	640	A/E	A/E

[a] Energy of lowest singlet and triplet levels in electronvolts.[28] [b] Phase of CIDEP due to the 1-methyl-4-*tert*-butylpyridinyl radical. [c] Phase of CIDEP to the 1-methylpyridinyl radical. [d] Phase of CIDEP due to the methylviologen cation radical.

M). The spectrum was observed 1 μs after the laser pulse irradiation. The A/E polarization spectrum due to monomer pyridinyl **3** indicates that the precursor of the radical is a singlet radical pair formed from the S_1 state of the dimer.[10] Addition of the triplet sensitizers induced a striking change of the polarization pattern. In the presence of 0.1 M pyrido[2,3-*b*]pyrazine (E_T = 2.99 eV), solution of a 0.01 M 2,2′-dimer gave an A*/E pattern (Figure 2b). The spectrum is essentially due to radical **3**. The spectral pattern indicates the contribution of A-TM (triplet mechanism) to the original A/E-RPM. A similar pattern of polarization was observed in the presence of pyrazine (E_T = 3.30 eV). It has been established by time-resolved ESR[16] and ODMR[17] studies that the lowest sublevel of the T_1 state in these sensitizers is preferentially populated in the ISC. Keeping of the spin alignment in fluid solution is supported from the observations of A-CIDEP in the photochemical hydrogen abstractions of these azaaromatic molecules.[18,19] Therefore, the spectrum of A-TM observed in the present study certainly reflects the polarized T_1 state of the sensitizers and is understood as a phenomenon of spin polarization conservation during the T–T energy transfer.

We examined the effects of other sensitizers. The CIDEP spectrum with an A/E* pattern was observed in the presence of 2-acetonaphthone (E_T = 2.56 eV) as shown in Figure 2c. The sensitizer has a large quantum yield of the ISC (ϕ_{ISC} = 0.84)[20] and $\pi\pi^*$ character in the T_1 state. Addition of benzophenone (E_T = 3.30 eV), 1-bromonaphthalene (E_T = 2.56 eV), and 1-acetonaphthone (E_T = 2.56 eV) gave similar CIDEP patterns, though the ratio of TM and RPM was different in each case. It has been known that preferential ISC occurs to the highest sublevel in these sensitizers.[21-23]

Apparent spin relaxation of the E polarization was different from that of the A/E signal. Figure 3 shows the transient ESR spectra of **3** observed at indicated times after laser pulse irradiation in the presence of 0.1 M benzophenone at −40 °C. The A/E-polarized component of the spectrum rapidly disappeared within 3 μs, while the E polarization gradually decreased. Then, only the E polarization was observed 3 μs after the laser pulse. Similar behavior was observed in the CIDEP spectra for systems containing other sensitizers and has also been demonstrated for the photochemical reduction of camphorquinone, in which A/E polarization was exhibited from the reaction of the excited singlet state and E polarization from the T_1 state.[24] This is probably due to the difference in relaxation times between the multiplet and net effects in the CIDEP, as proposed previously.[25] The relaxation of the hyperfine dependent polarization is accelerated by the spin-exchange mechanism.

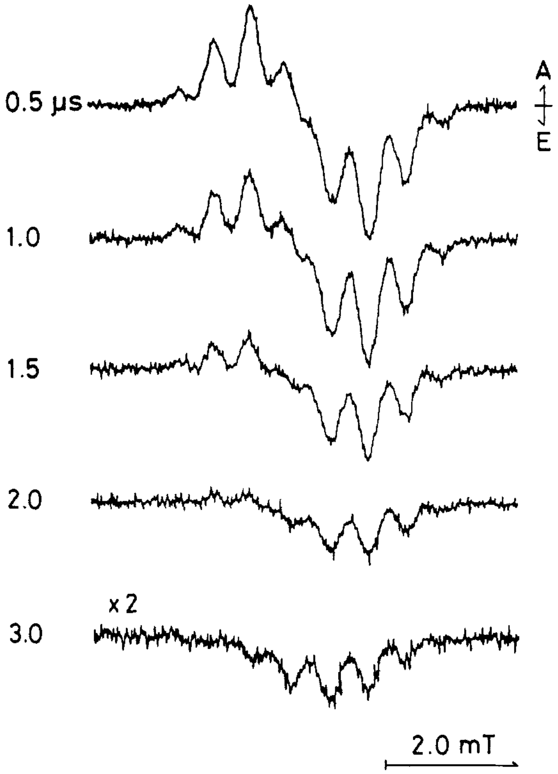


Figure 3. CIDEP spectra of the 1-methyl-4-*tert*-butylpyridinyl radical generated by irradiating the dimer (0.01 M) in the presence of benzophenone (0.1 M) at −40 °C in toluene. The spectra were taken at the indicated times after the laser pulse.

In contrast with the above results, addition of biacetyl (E_T = 2.92 eV) or benzil (E_T = 2.56 eV) to the dimer solution induced the intensity reduction of the CIDEP spectrum without a change in the pattern. As shown in Figure 4, quenching depends on the concentration of benzil. The presence of equimolar benzil completely quenched the A/E spectrum of **3**. This clearly indicates that benzil and biacetyl act as the singlet quencher because their S_1 and T_1 states lie at the relatively low energy level.

The present results are summarized in Table I. Electron spin polarization transfer depends on the T_1 state energy level of the sensitizers. Therefore, it can be deduced that acceptor **5** has an excited-state energy level lower than 2.43 eV.

Similar sensitizer effects were observed on the CIDEP spectrum from **4**, though dependence on the T_1 state energy level of the sensitizer was different from the case of 2,2′-dimer. The well-resolved CIDEP spectrum of **1** produced from the photolysis of the dimer without sensitizer showed A/E polarization (Figure 5a)

---

(16) Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1987**, *91*, 1754.

(17) Nishi, N.; Kinoshita, M.; Nakashima, T.; Shimada, R.; Kanda, Y. *Mol. Phys.* **1977**, *33*, 31.

(18) Basu, S.; McLauchlan, K. A.; Sealy, G. R. *Chem. Phys. Lett.* **1982**, *88*, 84. Buckley, C. D.; McLauchlan, K. A. *Mol. Phys.* **1985**, *54*, 1.

(19) Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1984**, *88*, 4631.

(20) Pitts, J. N.; Johnson, H. W.; Kuwana, T. *J. Phys. Chem.* **1962**, *66*, 2456.

(21) Yamauchi, S.; Pratt, D. W. *Mol. Phys.* **1979**, *37*, 541.

(22) Murai, H.; Imamura, T.; Obi, K. *Chem. Phys. Lett.* **1982**, *87*, 295.

(23) The time-resolved ESR spectra of the T_1 states of 1-bromonaphthalene (D = 0.099 and E = −0.009 cm^{-1}) and 1-acetonaphthone (D = 0.089 and E = −0.009 cm^{-1}) showed the E EEA/EAA polarization pattern, suggesting preferential population at the highest sublevel.

(24) Depew, M. C.; Wan, J. K. S. *J. Phys. Chem.* **1986**, *90*, 6597.

(25) Syage, J. A. *J. Chem. Phys.* **1987**, *87*, 1022. Adrian, F. J. *Ibid.* **1988**, *88*, 3216.

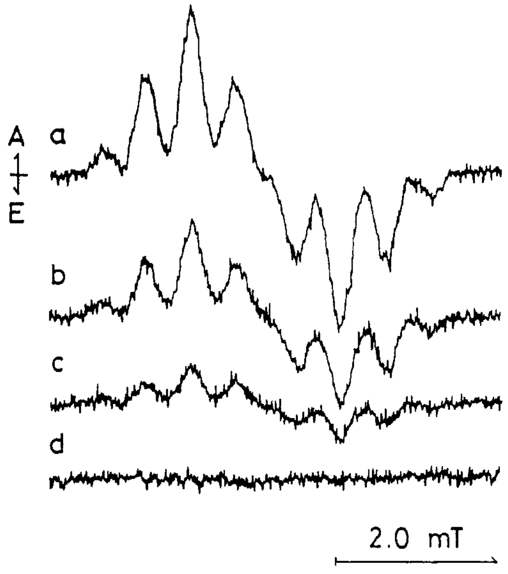


Figure 4. Benzil concentration dependence of CIDEP spectra of the 1-methyl-4-*tert*-butylpyridinyl radical observed 1 μs after the laser pulse irradiation of the 2,2′-dimer (0.05 M) at −40 °C in toluene. Concentration (M) of benzil: (a) 0; (b) 0.01; (c) 0.02; (d) 0.05.

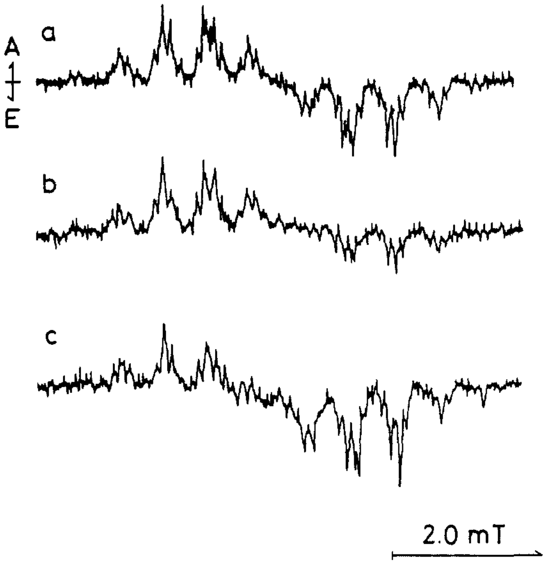


Figure 5. Transient ESR spectra of 1-methylpyridinyl radical produced by photolysis of the 4,4′-dimer (0.01 M) in toluene at −40 °C: (a) without sensitizer; (b) in the presence of pyrazine (0.1 M); (c) in the presence of quinoline (0.1 M).

as observed for the other pyridinyl radicals. Addition of pyrazine to this system as the sensitizer afforded A*/E polarization of the spectrum of **1** (Figure 5b), indicating the contribution of A-TM to the A/E-RPM. A similar polarization pattern was obtained in the presence of pyrido[2,3-*b*]pyrazine. However, 2-acetonaphthone did not lead to any change in the CIDEP pattern, besides a slight decrease in intensity, while benzophenone induced a change to the A/E* polarization. In the presence of quinoline (E_T = 2.69 eV), the transient ESR spectrum showed an A/E* pattern as shown in Figure 5c. It has been reported for this sensitizer that the electron spin is mainly populated in the highest sublevel of the T_1 state through ISC.[26,27]

On the other hand, addition of 1-bromonaphthalene (1-BrNp) to the 4,4′-dimer solution caused an unusual change in the CIDEP spectrum, as shown in Figure 6. The E-polarized broad signal appeared, together with the A/E signal of **1**. This broad signal can be assigned to the methylviologen cation radical ($MV^{\bullet+}$) from the spectral width and the *g* value. This is supported by the observation of a well-resolved conventional ESR spectrum due to $MV^{\bullet+}$ and a characteristic blue color after the photolysis. Since $MV^{\bullet+}$ can be produced by dehydrogenation from the 4,4′-dimer cation, the present result would be interpreted as arising from electron transfer between the dimer and the sensitizer, as follows.

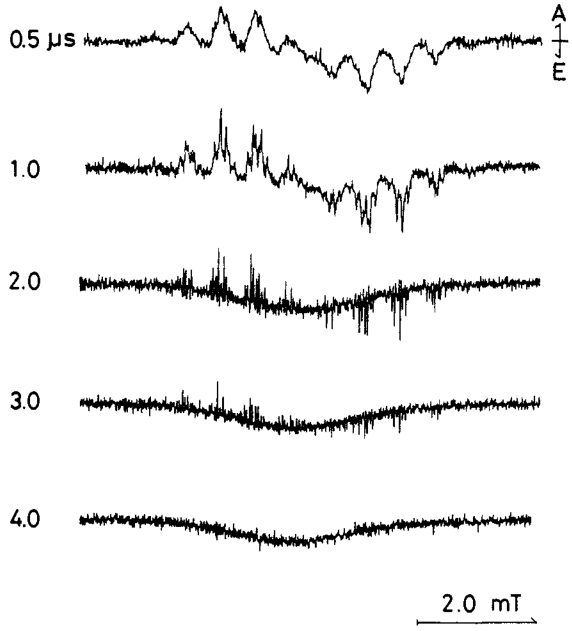


Figure 6. Transient ESR spectra of the 1-methylpyridinyl radical generated from laser photolysis of the dimer (0.05 M) in the presence of 1-bromonaphthalene (0.2 M) in toluene at −40 °C. The signals were taken at the indicated times after the laser pulse.

The free energy of electron transfer in various solvents can be estimated by applying the equation[29,30]

$$\Delta G = 23.05\left[E^{\mathrm{ox}}{}_{1/2}(\mathrm{D}) - E^{\mathrm{red}}{}_{1/2}(\mathrm{A})\right] - E_{\mathrm{exc}} + \frac{Ne^2}{4\pi\epsilon_0 a}\left(\frac{1}{\epsilon_r} - \frac{2}{37.5}\right)$$

where $E^{\mathrm{ox}}{}_{1/2}(\mathrm{D})$ and $E^{\mathrm{red}}{}_{1/2}(\mathrm{A})$ are oxidation potential of the donor and reduction potential of the acceptor, respectively, E_{exc} is excitation energy, and the last term is due to Coulomb interaction and solvation energy derived from the Born model. This relation has been successfully used for many systems.[31,32] In toluene (ϵ_r (relative permittivity) = 2.38), the value of the last term is 0.75 eV at a = 0.7 nm. For the free energy difference in the **4** ($E^{\mathrm{ox}}{}_{1/2}$ = −0.1 V vs SCE)[12]–1-BrNp ($E^{\mathrm{red}}{}_{1/2}(\mathrm{A})$ = −1.96 V vs SCE)[33]–toluene system, a nearly zero ΔG value (0.061 eV) is obtained from the above equation. The electron transfer would proceed with a rate of 2 or 3 orders of magnitude less than the diffusion-controlled rate. The anion radical of 1-BrNp is dissociative and generates the reactive intermediate radical ($\mathrm{Np}^{\bullet}$),[34] which has the ability to abstract hydrogen from the 4,4′-dimer cation radical.

$$^{3}(1\text{-BrNp})^{*} + 4,4'\text{-dimer} \rightarrow 1\text{-BrNp}^{\bullet -} + 4,4'\text{-dimer}^{\bullet +}$$
$$\rightarrow \mathrm{MV}^{\bullet +} + \mathrm{Br}^{-} + \mathrm{NpH}$$

---

(26) Kinoshita, M.; Iwasaki, N.; Nishi, N. *Appl. Spectrosc. Rev.* **1981**, *17*, 1.

(27) Atkins, P. W.; Topping, G. S. *Mol. Phys.* **1982**, *46*, 941.

(28) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, **1973**.

(29) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 791.

(30) Taniguchi, Y.; Nishiya, Y.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 764.

(31) Arimitsu, S.; Masuhara, H.; Mataga, N.; Tsubomura, H. *J. Phys. Chem.* **1975**, *79*, 1255. Mataga, N.; Shioyama, H.; Kanda, Y. *Ibid.* **1987**, *91*, 314.

(32) Mattay, J. *Tetrahedron*, **1985**, *41*, 2393, 2405. Mattay, J.; Gersdorf, J.; Buchkremer, K. *Chem. Ber.* **1987**, *120*, 307.

(33) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Dekker: New York, **1970**.

(34) M'Halla, F.; Pinston, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

The result suggests that in the present system the electron transfer can be clearly distinguished from the energy transfer, since $MV^{\bullet+}$ is obtained from the former while the monomer radical formed from the latter. To summarize from Table I, no polarization transfer was observed for **4** from sensitizers with triplet energy lower than 2.69 eV. Therefore, the energy level of the excited state of the acceptor would be lower than this value.

Discussion

Electron spin polarization conservation was observed during the energy transfer between different molecules. In the present study, direct generation of the pyridinyl radicals from the S_1 state of the dimer is unavoidable, though the concentration of the dimers is one-tenth that of the sensitizer. The molar absorption coefficients of the sensitizers at 308 nm are listed in Table I. Irradiated light substantially excites the sensitizer except for the case of benzophenone, in which the ϵ value at 308 nm is very small (ϵ_{308} 100). Selective excitation of the donor was attempted by the use of several sensitizers such as 1,4-naphthoquinone and 4,4′-bis(dimethylamino)benzophenone, which have relatively lower S_1 energies than the dimers. The attempt, however, was unsuccessful because low oxidation potentials of the present dimers (4,4′-dimer, −0.10 V; 2,4′-dimer, −0.48 V vs SCE)[12] induced a thermal electron transfer. Therefore, we must consider two possible mechanisms of triplet–doublet (T–D) energy transfer and T–T energy transfer with electron exchange. Obi and his co-workers[35] found that the spin polarization transfer in the T–D system can be interpreted in terms of electron- and/or spin-exchange mechanism. Recently, they drew the conclusion that the polarization is due to the T–D energy transfer with exchange mechanism.[36]

The T–D energy transfer is considered to be minor in the present system since only a very low concentration ($<10^{-6}$ mol/dm^{-3}) of the pyridinyl radical may be generated by the direct excitation in the presence of sensitizers except benzophenone. Furthermore, the lowest excited states of the monomer radicals are lower than those of the acceptors determined in the present study. They have a broad absorption band at around 500 nm, extending to about 600 nm.[37] Therefore, it may be concluded that the monomer radical showing the TM in the present CIDEP spectra was produced, from the T_1 state of the dimer generated by intermolecular T–T energy transfer.

According to the flash photolysis studies,[38,39] the rate of T–T energy transfer will be close to a diffusion-controlled one for an exothermic energy difference greater than 0.13 eV. If the energy difference approaches zero, the efficiency of energy transfer is drastically reduced because of the back-reaction. No energy transfer occurs from molecules with triplet energy lower than that of the acceptor so efficiently. However, it has been also reported that when the lifetime of the acceptor is much smaller than that of the donor, the rate of energy transfer will be diffusion-controlled even if the energy difference is about zero or more.[40]

In the present system, lifetime of the excited acceptor would be very short since the dimer is dissociative in the T_1 state. Then, the T–T energy transfer is deduced to be a diffusion-controlled rate in the systems, which leads to the contribution of TM in the present CIDEP spectra. Energy levels in the T_1 states were estimated to be 2.43 eV for the 2,2′-dimer and 2.65 eV for the 4,4′-dimer.

Both energy transfer and electron transfer are thermodynamically allowed in the cases exhibiting the TM in the present systems. In both reactions, spatial overlap between donor and acceptor orbitals is required.[41,42] The discrimination is sometimes very difficult, but electron transfer usually predominates.[43] Irrespective of the difficulty, the reactions were readily distinguished in the present cases, since they gave different intermediate radicals. Preferential contribution of energy transfer was clearly observed.

Conclusion

Electron spin polarization conservation was observed in the system of photosensitized dissociation of the dimers of pyridinyl radicals in fluid solution. The process was concluded as a T–T energy transfer since the polarization depends on the T_1 energy level and the anisotropic population in the T_1 states of sensitizers. The T_1 state energy levels were determined to be 2.43 and 2.65 eV for the 2,2′- and 4,4′-dimers of pyridinyl radicals, respectively. Preferential energy transfer was observed in the condition that both electron transfer and energy transfer were allowed. Electron transfer from the 4,4′-dimer to the T_1 state of 1-bromonaphthalene induced the generation of the $MV^{\bullet+}$ by dehydrogenation from the cation radical of the dimer. The present results promise further application of the CIDEP method to studies on energy and electron-transfer systems in fluid solution.

Acknowledgment. The present work was partially supported by Grants-in-Aid for Developmental Scientific Research No. 63840012 and for Scientific Research No. 01540356 from the Japanese Ministry of Education, Science and Culture.

---

(35) Imamura, T.; Onitsuka, O.; Obi, K. *J. Phys. Chem.* **1986**, *90*, 6741.

(36) Okutsu, T.; Obi, K. *Nippon Kagaku Kaishi* **1989**, 1339.

(37) Akiyama, K.; Kaneko, A.; Ito, O.; Tero-Kubota, S.; Ikegami, Y. To be published.

(38) Porter, G.; Wilkinson, F. *Proc. R. Soc.* (*London*) **1961**, *A264*, 1.

(39) Sandros, K.; Backstrom, H. L. J. Acta *Chem. Scanad.* **1962**, *16*, 958. Sandros, K. *Ibid.* **1964**, *18*, 2355.

(40) Stevens, B.; Walker, M. S. *Proc. Chem. Soc.* **1964**, *26*, 109.

(41) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

(42) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(43) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.