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MONOMER-DIMER EQUILIBRIUM AND PHOTOCHEMICAL BEHAVIORS OF THE 1-METHYL-4-PHENYLPYRIDINYL RADICAL

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A neutral free radical, 1-methyl-4-phenylpyridinyl radical, can be isolated by distillation under a vacuum. Equilibrium between the radical and the diamagnetic radical dimer, photochemical dissociation of the dimer with visible light, and photochemical decomposition of the radical with ultraviolet light to generate the phenyl radical have been demonstrated.

Pyridinyl radicals so far prepared have an electron-withdrawing substituent, such as methoxycarbonyl and acetyl groups, at 4- or 2-position and the introduction of such a substituent has been considered to be indispensable to the stabilization of a pyridinyl ring.$^{1-3)}$ We found that an introduction of the phenyl substituent which is less electron-withdrawing is also effective to stabilize the pyridinyl ring. This paper reports the preparation of 1-methyl-4-phenylpyridinyl, the equilibrium between the radical and the diamagnetic radical dimer in solution, and some photochemical behaviors of the radical-dimer solution.

Treatment of 1-methyl-4-phenylpyridinium iodide, mp 164-165°C, with 3 % sodium amalgam in degassed acetonitrile at 0°C for 2 h afforded a greenish solution. After the insoluble substances were filtered off and then the solvent was removed, the residue distilled (∿100°C) onto the Dewar surface at 77 K as a beautiful violet film on an appearance. 2-Methyltetrahydrofuran (MTHF) or acetonitrile was distilled onto the film and the greenish-orange solution produced after warming was sealed off with that portion of the apparatus bearing the cells for measurements.

The solution prepared above exhibited the ESR spectrum with well-resolved hyperfine structure at moderate concentrations as shown in Fig. 1. Hyperfine structure of the spectrum was reasonably analyzed with seven splitting constants on simulation with a computer. The constants were assigned tentatively according to the type of splitting and by comparing them with the calculated spin densities by the McLachlan procedure in a similar manner to that for other pyridinyl radicals.$^{2)}$ No conformational twisting between the two aromatic rings was assumed in the calculation. The constants and the assignments are given with the structure in Fig. 1.

Signal intensity of the ESR spectrum decreased with a lowering of temperature and the intensity at -40°C was about one tenth of that at 20°C. The intensity change was completely reversible against the change in temperature and this phenomenon is ascribed to that the radical species is in equilibrium with the diamagnetic radical dimer in solution. Accordingly, the result of titration with

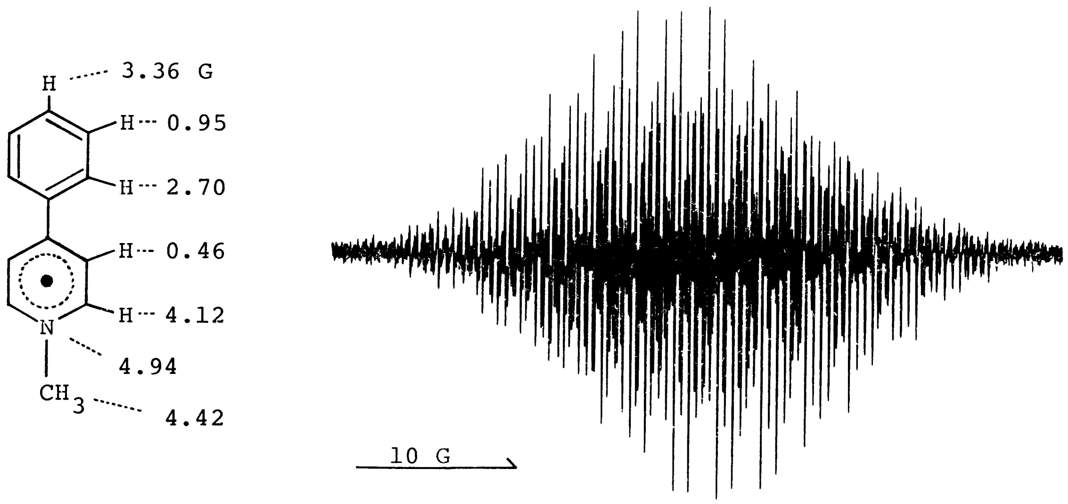

Fig. 1. ESR spectrum and hyperfine splitting constants of the 1-methyl-4-phenylpyridinyl radical in MTHF at room temperature. $\underline{c}$(as Py·) = 2 × 10^{-3} mol/dm^3.

1,1'-dimethyl-4,4'-bipyridinium (MB^{2+}) dichloride in acetonitrile could be interpreted as a quantitative oxidation of both radical and dimer in the solution. The concentration, $\underline{c}$(as Py·), was thus determined from the absorption intensity of the $MB^{\dot{+}}$ cation radical at 605 nm (ε = 13000) as that of species reactive to MB^{2+}. The equilibrium is supported by the temperature dependence of the absorption spectrum as shown below.

Fig. 2 shows the absorption spectra of the solution prepared above at various temperatures. As the temperature is lowered, intensity of the absorption band at 390 nm increased, while the bands at 365- and 530-nm weakened, disappearing below -40°C. This reversible spectral change is reasonably interpreted as arising from the monomer-dimer equilibrium with the assignments of the two bands at 365- and 530-nm to the monomeric radical and of the band at 390 nm to the dimer.

The following demonstrates the reversible photodissociation of the dimer with visible light and the photodecomposition of the radical with ultraviolet light. Irradiation of the solution placed in the cavity of ESR spectrometer with the light of wavelengths longer than 400 nm at around 0°C caused the rise in the intensity of the ESR spectrum. The rate of the reversible change in signal intensity was very rapid for both turning on and turning off the light at this temperature.[4] The solution immersed in liquid nitrogen in the dark showed no

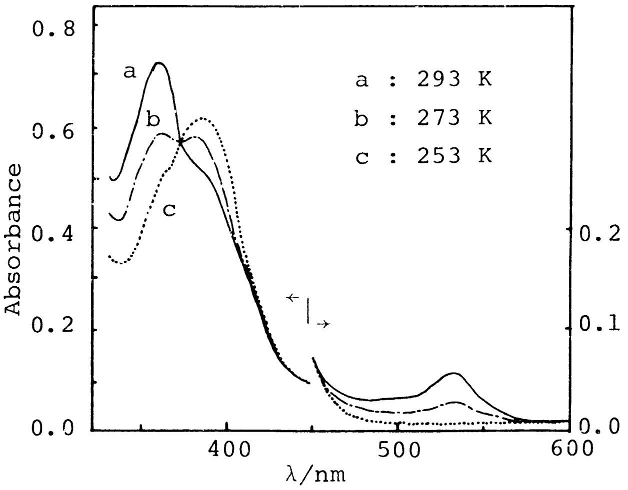

Fig. 2. Absorption spectra of the radical-dimer solution in MTHF at various temperatures. $\underline{c}$(as Py·) = 1 × 10^{-3} mol/dm^3.

Fig. 3. ESR spectrum of the radical pair of 1-methyl-4-phenylpyridinyl generated by photolysis of the dimer in MTHF at 77 K.

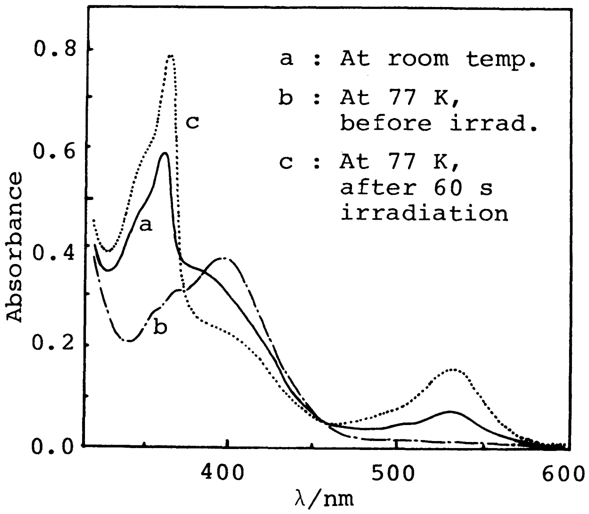

Fig. 4. Spectral change of the radical-dimer solution in MTHF on light irradiation at 77 K. c(as Py•) = 8.5×10^{-4} mol/dm^3.

ESR signal as expected from the temperature dependence above-mentioned. Irradiation of the solution at 77 K with wavelengths longer than 400 nm resulted in an appearance of the new signal shown in Fig. 3. The signal was persistent for a long period after turning off the light. This spectrum is readily assigned to the triplet transition due to the radical pair generated by photolysis of the diamagnetic dimer. Appearance of the $\Delta M = 2$ transition at 1650 G supports the triplet transition. The zero-field parameters, $D = 0.0151$ and $E = 0$ cm^{-1} with $2D = 322$ G, correspond to the spin-spin interaction for an average separation of 5.7 Å, which is larger than that for the radical pair of 1-benzyl-4-methoxycarbonylpyridinyl.[5)]

The change of absorption spectrum of the radical-dimer solution on light irradiation at 77 K is shown in Fig. 4. The solution in the dark has a broad absorption band at 390 nm (Fig. 4b). The irradiation in a similar manner to that in the ESR experiment caused an appearance of two bands at 365- and 530-nm, being accompanied by a disappearance of the 390-nm band. Referring to the temperature dependence of the spectrum of Fig. 2, the spectral change in Fig. 4 can be explained by the photodissociation of the dimer to generate the radical pair, in accordance with the result of ESR experiment.

On the other hand, irradiation of the radical-dimer solution with ultraviolet light caused the irreversible decomposition of the radical, as a long standing of the solution in the light resulted in a disappearance of the radical species. The photolysis is demonstrated by the ESR spectrum shown in Fig. 5a, which was measured after 10 min irradiation of the solution in MTHF at 77 K with wavelengths longer than 300 nm. Hyperfine structure of the spectrum is interpreted to be that of the phenyl radical.[6)] To confirm this interpretation, the ESR spectrum of the phenyl radical in a similar condition to that of the measurement of Fig. 5a

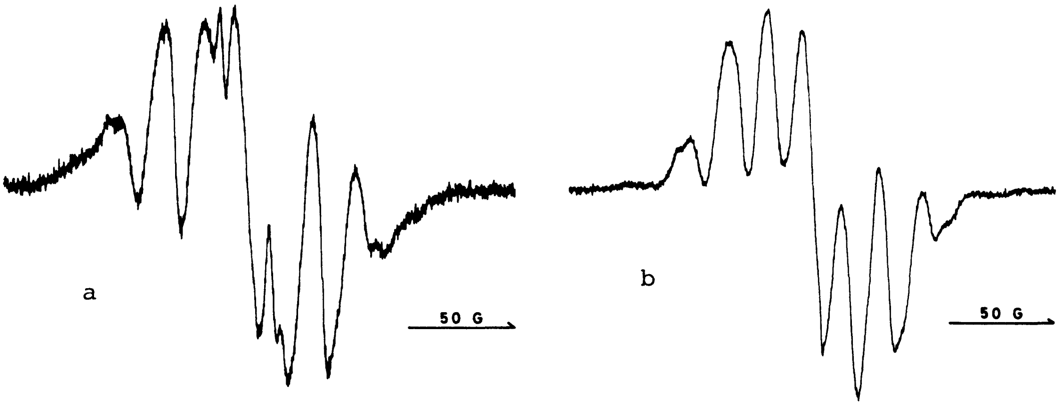

Fig. 5. ESR spectra of the phenyl radical generated (a) by the photochemical decomposition of 1-methyl-4-phenylpyridinyl and (b) by the photolysis of phenyl iodide, both in MTHF at 77 K.

was measured. Fig. 5b is the spectrum of the radical generated by the photolysis of phenyl iodide with ultraviolet light in MTHF. A good agreement of both spectra of Figs. 5a and 5b proved the generation of the phenyl radical by a cleavage of the C-C bond between pyridine and benzene rings.

No definite structure has been given to the diamagnetic dimer in equilibrium with the 1-methyl-4-phenylpyridinyl radical. However, we can assume tentatively the structure to be that coupled covalently at each 2-position of two radicals, based on two facts: One is that the absorption spectrum of the dimer is in contrast with that of the radical and shows no absorption characteristic of the π-π interaction of two pyridinyl rings, and the other is that the similar equilibrium, as well as the photodissociation of the dimer, has been established for the 1-methyl-2-methoxycarbonylpyridinyl radical, in which the 4-position is most reactive to the coupling to form the dimer.7)

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References and Note

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