Bull. Chem. Soc. Jpn., 58, 3535—3539 (1985)

Photolytic Generation and the Subsequent Dimerization of 4-Alkyl-1-methylpyridinyl Radicals in Solution as Studied by Steady-state and Kinetic ESR Spectroscopy

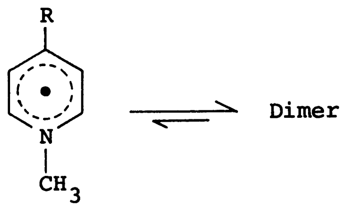
Kimio Akiyama, Toru Ishii, Shozo Tero-Kubota,† and Yusaku Ikegami*
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980
†Institute for Molecular Science, Myodaiji, Okazaki 444

(Received July 18, 1985)

1-Methylpyridinyl and 4-alkyl-1-methylpyridinyl (alkyl=methyl, ethyl, isopropyl, and *t*-butyl) radicals were generated photolytically from their dimers in solution. Hyperfine splitting constants for these radicals were assigned and the temperature dependence was discussed. Absolute dimerization rates of these radicals in the range of −50—−100 °C were determined by analyzing the ESR signal decay during the dark period. A nearly constant activation energy of dimerization was observed for five radicals, while the frequency factor decreased with the bulkiness of 4-substituent, which are discussed in terms of the steric hindrance for the dimerization.

Electron spin resonance (ESR) spectra of the neutral pyridinyl radicals prepared by one-electron reduction of the corresponding pyridinium salts have been successfully analyzed.[1] However, the isolable radicals in solution are restricted to those having electron-withdrawing and delocalizing group at 2- or 4-position of the pyridine ring. In our recent studies,[2] it was established that some pyridinyl radicals are equilibrated with the dimers and the interconversion between the radical and the dimer is completely reversible for an intermittent photolysis or a temperature change. A kinetic ESR method was applied to such equilibrium systems and elucidated the dimerization mechanism showing a two-step decay of the ESR signal due to the radical generated photolytically. Further, the time-resolved ESR studies revealed that the precursor of the radical generated upon light irradiation was singlet radical pair for the reason that the A/E polarized transient ESR spectra were observed in solution.[3,4]

Based upon these results, we attempted the generation of simple 4-alkyl-substituted pyridinyl radicals which might be produced by photoirradiation of the corresponding dimers. In spite of the radical formation from the singlet radical pair, the pair has relatively long lifetime enough to cause ST_0-mixing and to escape from the primary cage. The ESR spectra of five pyridinyl radicals, **1**—**5**, were then observed during the continuous irradiation and analyzed to obtain the hyperfine splitting (hfs) constants. The kinetic ESR study was also carried out to determine the activation parameters of the second-order dimerization.



1 R=H
2 R=CH_3
3 R=CH_2CH_3
4 R=$CH(CH_3)_2$
5 R=$C(CH_3)_3$

Experimental

Vacuum line technique was standard in the preparation and purification of the radicals and solvents. Each pyridinyl radical was prepared from the corresponding pyridinium iodide by the reduction with 3% sodium-amalgam in degassed acetonitrile at about −30 °C and extracted with a nonpolar solvent such as methylcyclohexane. All pyridinium iodides were obtained by treating the pyridines with methyl iodide without solvent, and recrystallized from ethanol. Solvents for the measurements were transferred by the trap-to-trap method using a vacuum system. Steady-state ESR measurements were carried out with a Varian E-109E EPR spectrometer. A high pressure Hg-lamp (Ushio 500 W) as a light source was equipped with a UV-31 glass filter to prevent undesirable decomposition of radicals. Spectral simulation and McLachlan calculation were performed by using a Sharp MZ-80C microcomputer. Kinetic ESR technique was described previously.[2]

Results and Discussion

Hfs Constants of 4-Alkyl-1-methylpyridinyl Radicals. The 4-alkyl-1-methylpyridinyl radicals dimerize in solution at room temperature forming covalently-bonded dimers, which show a broad absorption band in the near UV region. As the radical-dimer equilibrium is in favor of the dimer side, no ESR signal was observed at room temperature for all radicals examined. Either photolysis or rise in temperature of a dimer solution led to exhibit the ESR spectrum. The interconversion between the radical and the dimer was completely reversible at temperatures below 80 °C. Figure 1a shows the ESR spectrum observed during a continuous irradiation to the dimer of 1-methylpyridinyl radical (**1**) in 2-methyltetrahydrofuran (MTHF) at −40 °C. Hyperfine structure of the spectrum was reasonably analyzed on the computer simulation (Fig. 1b). The hfs constants were assigned tentatively according to the types of splitting and by comparing them with the spin density calculations by the McLachlan procedure. The constants and assignments are given in Table 1 together with those of the other alkyl-substituted pyridinyl radicals. As seen in Table 1, changes in the constants with the substitution of 4-alkyl group are negligibly small compared with the substitution of electron-withdrawing or delocalizing groups.[5] Relatively large

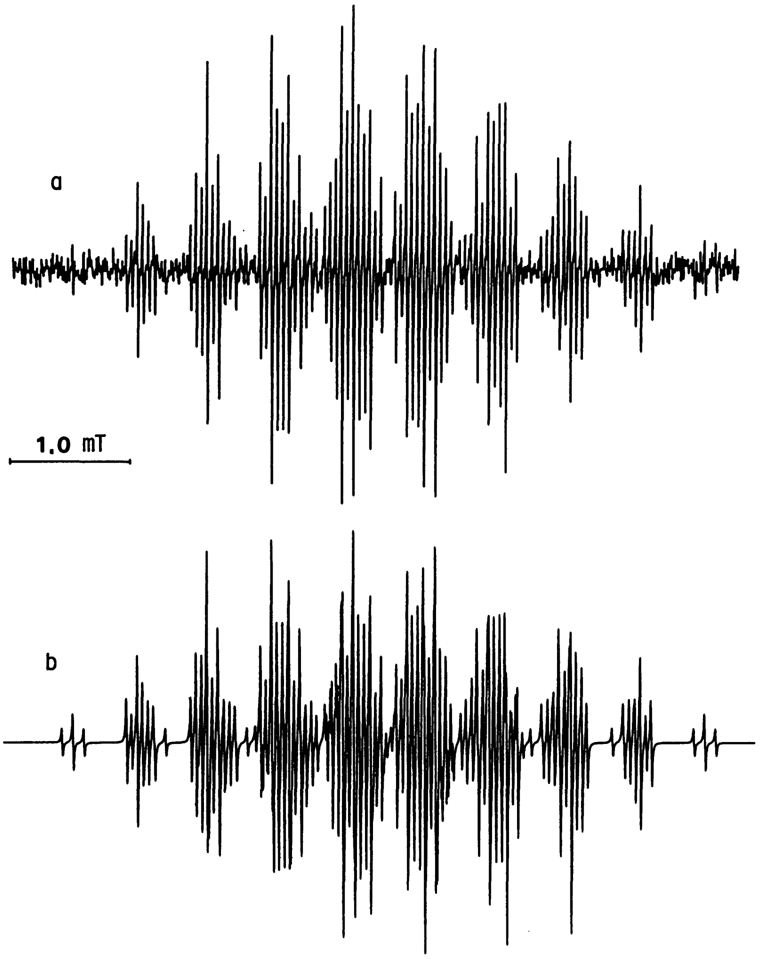


Fig. 1. ESR spectrum of the 1-methylpyridinyl radical generated by light irradiation of the dimer solution in MTHF at −40 °C. (a) Measured and (b) simulated.

Table 1. Hyperfine splitting constants (*a* in mT) for the 4-alkyl-1-methylpyridinyl radicals in MTHF at −40 °C

Position	R at 4-position				
	H	CH_3[a]	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
1	0.678	0.639	0.647	0.663	0.665
2, 6	0.577	0.584	0.586	0.584	0.585
3, 5	0.092	0.113	0.108	0.107	0.106
N	0.535	0.491	0.495	0.494	0.494
4	1.118				
R (β-H)		1.168	0.871	0.566	
R (γ-H)			b)	0.018	0.022

a) Measured in toluene. b) Unresolved.

hfs constants were observed at 4-, 2-, and 6-positions, where would apt to couple in the dimerization.

The hfs constants of β-protons of 4-alkyl groups, ring nitrogen, and *N*-methyl protons showed dependence on temperature, while the other constants were almost independent. Temperature dependence of the hfs constants of pyridinyl radicals having polarizable groups has been discussed in terms of polarity change of the solvent and the restricted rotation of substituents.[5,6] On the other hand, the temperature dependent hfs constants of 1-hydropyridinyls have been analyzed using the model of localized out-of-plane vibration of the protons.[7] For the present radicals, the comparatively large dependence was found with temperature coefficients of 5.4×10^{-4} and 8.3×10^{-4} mT/°C for the β-protons in **3** and **4**, respectively. These values can be interpreted by the existence of restricted rotation of the alkyl groups. This is supported by the small hfs constants, 0.871 mT for **3** and 0.566 mT for **4**, compared with 1.168 mT for **2** in which the methyl group rotates freely in temperature range examined (−80—+40 °C). After the usual manner to interprete the internal rotation of alkyl groups by ESR spectroscopy, we found that the conformation of the alkyl groups is similar to those of 1-alkyl-4-methoxycarbonylpyridinyl radicals reported previously.[6]

The hfs constant of the *N*-methyl protons reflects the spin density on the bonded nitrogen atom and the conformational change around this atom. The nitrogen spin density also correlates with the spin densities on the adjacent atoms with the Karplus-

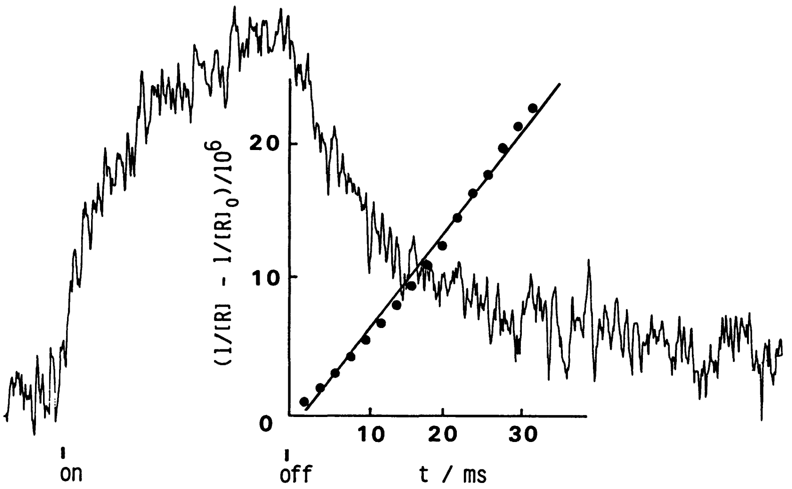


Fig. 2. Growth and decay curve of the 1-methylpyridinyl radical in MTHF solution at −76 °C. Insert is the second-order plot.

TABLE 2. KINETIC PARAMETERS FOR THE DIMERIZATIONS OF THE 4-ALKYL-1-METHYLPYRIDINYL RADICALS IN MTHF

No.	R at 4-position	k_{exp}[a] mol^{-1}dm^{3}s^{-1}	log A mol^{-1}dm^{3}s^{-1}	E_a kJ mol^{-1}
1	H	5.4×10^7	10.2	8.79
2	CH_3	4.3×10^7	10.0	8.37
3	CH_2CH_3	3.0×10^7	9.8	8.79
4	$CH(CH_3)_2$	1.4×10^7	9.5	8.75
5	$C(CH_3)_3$	1.3×10^7	9.4	8.37

a) Observed value at −80 °C.

Fraenkel relation.[8] In the present radicals, since the spin densities at 2- and 6-positions were independent of temperature, the latter contribution to the change of the nitrogen spin density with temperature can be ignored, though the overlapping between the $p\pi$-orbital of the nitrogen and the 1s orbital of the bonded methyl protons may vary with the structural change. It is rather indicative of the presence of the out-of-plane vibration of the *N*-methyl group that the temperature coefficients for a^N and $a^H_{N\text{-}CH_3}$ showed the opposite signs each other. With a lowering of temperature, $a^H_{N\text{-}CH_3}$ would decrease and a_N increases, because the out-of-plane vibrational amplitude decreases. Sander and Dohrmann[7] reported the temperature dependent hfs constants of protons and nitrogen for 1-hydropyridinyl radicals and estimated the frequencies of the out-of-plane vibrations of the protons. Das and Fraenkel[9] suggested that the out-of-plane vibration of the N–H proton probably contributes to the temperature dependent hfs constants of the dihydropyrazine cation radical. In our case, the observed temperature coefficient of 1.3×10^{-4} mT/°C for nitrogen is small for the conformational change with temperature, compared with those of 1-hydropyridinyl radicals. This may be due to the low vibrational frequency and the small displacement of N–CH_3 group from the π-plane.

Kinetic Treatment of the Dimerization. The dimers of the 4-alkyl-substituted pyridinyl radicals have a dihydropyridine type structure and show each a broad absorption band in the near UV region. Light irradiation to this band causes a homocentric C–C bond cleavage, resulting the appearance of ESR signal of the monomeric radical. After the pulse irradiation, the radical dimerizes and then the signal decays in the intermittent dark period. Figure 2 shows a growth and decay of the ESR signal measured during the photolysis of the dimer of 1-methylpyridinyl in MTHF at −76 °C. The signal was accumulated 2000 transient times. Although the signal-to-noise ratio is rather poor, the decay curve could be analyzed in terms of a second-order kinetics. The straight line inserted in Fig. 2 represents a least squares fit to the points according to the equation:

$$1/[R] = k_{exp}t + 1/[R]_0 \qquad (1)$$

where $[R]_0$ is the concentration of the radical at time t=0 after an onset of the dark period. This equation is best explained by the C–C bond formation of two radicals. The dimerization rate constants (k_{exp}) were estimated by obtaining values from three independent measurements at −80 °C. The constants are listed in Table 2.

The rates were also measured in the temperature range −50— −100 °C. Figure 3 presents the Arrhenius plots for the dimerization of **1**—**5**. The activation

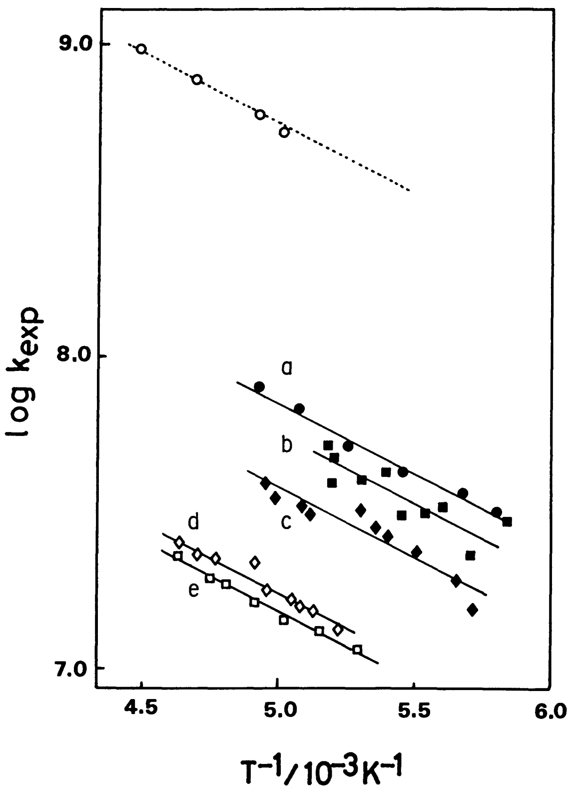


Fig. 3. Dimerization rate constants *vs.* 1/*T* for a: **1**, b: **2**, c: **3**, d: **4**, and e: **5**. A dotted line represents the diffusion-controlled rate constants (see text).

energies (E_a) and frequency factors (A) were each estimated by the least squares method from the plots, as summarized in Table 2. Because of the low yield of **2** from the dimer, the integrated signal intensities of ESR showed a poor reproducibility, leading to a significant deviation of the plot. The rates observed for **5** were slightly larger than those reported reviously.[4] This is caused by that, in the previous study, the concentration ($\approx 10^{-4}$ mol dm^{-3}) of the standard 2,2-diphenyl-1-picrylhydrazyl (DPPH) solution used to evaluate the initial concentration of radical was far different from the radical concentration ($\approx 10^{-6}$ mol dm^{-3}) produced by light irradiation.[10] In the present work, a standard DPPH solution of *ca.* 10^{-6} mol dm^{-3} was used.

A dotted line in Fig. 3 represents the diffusion-controlled second-order rate constants estimated by use of the Smoluchowsky-Stoles-Einstein relation:[11]

$$k_{\rm diff} = 8RT/3 \times 10^3\eta(T) \qquad (2)$$

where $\eta(T)$ denotes the temperature-dependent viscosity of solvent MTHF.[12] From the slope of the line, we obtain the activation energy of 8.98 kJ mol^{-1} for a diffusion in MTHF and the frequency factor of log A=11.1 mol^{-1}dm^{-3}s^{-1}. It is implied from Eq. 2 that the diffusion-controlled rate constants for a bimolecular reaction are independent of the size of the reactants. This may be true to the radicals in which the electron is completely delocalized so that the reaction is equally probable at any direction, but it would be unadaptable to saturated or σ-type radicals, in which the unpaired electron is localized and the reaction therefore occurs at a particular site on the radical.

The radical **5** forms only the 2,2′-dimer composed of its diastereoisomers.[4] On the other hand, **1** forms the 4,4′-dimer at the temperature range 30—−70 °C.[11] Since the highest spin density is located at 4-position, as discussed on the basis of the steady-state ESR experiments, this position would be the most active site for dimerization. However, when a sterically large group such as *t*-butyl is substituted at this position, the dimerization occurs at the position having next higher spin density, *i.e.* 2- or 6-position, forming 2,2′-dimer. In spite of the delocalized unpaired electron, the coupling reaction of pyridinyls proceeds in a site-selective manner like σ-type radical. Even if the above factor shifts the diffusion rates for the present radicals from that expressed by Eq. 2, the observed rates are two or three orders of magnitude smaller than that of diffusion encounter. The slow rate is ascribed to the small frequency factor. The activation energies in Table 2 agree well with that of diffusion in the MTHF solution within experimental error limit. Although the frequency factors are small compared with that of diffusion, the values of 10^{9-10} mol^{-1}dm^{3}s^{-1} are larger than those in the dimerizations of spin-delocalized π-radicals such as triphenylmethyl and triphenylimidazolyl.[14,15] The values for the present radicals are rather comparable to those of spin-localized alkyl radicals.[16]

Although the activation energy is nearly constant for the dimerizations of **1**—**5**, the rate constant and the frequency factor are significantly affected by the size of 4-substituent. Since the bulky substituent prevents the bond formation at 4-position, the dimerization occurs at 2-position. Thus, with a decrease in the probability of 4,4′-dimer formation, the frequency factor and the rate decreased. In order to extend further discussion, the thermodynamic parameters of the monomer-dimer equilibria for **1**—**5** should be obtained. Determination of the parameters, however, has been unsuccessful, because the radical concentrations could not be determined by reason of that each equilibrium inclines overwhelmingly toward the dimer side even at 70 °C.

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