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DECAY MECHANISM OF THE 1-HYDRO-4-PHENYLPYRIDINYL RADICAL

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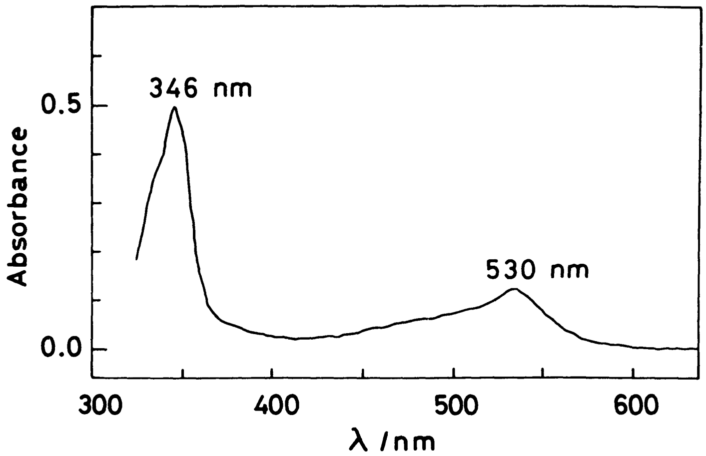
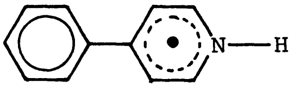
Intermediate formation of radical pair has been proposed in the dimerization of 1-hydro-4-phenylpyridinyl radical from the observation of two-step decay of the radical, in which the fast step is represented by second-order and the slow step is first-order. The activation parameters were determined.

Substituent effect on the stabilization of pyridinyl radicals is so large that some pyridinyls such as 1-ethyl-4-methoxycarbonylpyridinyl are isolable by distillation under vacuum[1)] while 1-methylpyridinyl dimerizes rapidly.[2)] On the other hand, it has become apparent from the absorption and ESR spectroscopic studies that 1-methyl-2-methoxycarbonylpyridinyl (I) and 1-methyl-4-phenylpyridinyl (II) are in equilibrium with each σ-bonding dimer.[3-5)] Recent studies by kinetic ESR spectroscopy revealed intermediate formation of the radical pair in the dimerization processes of I and II.[6,7)] A series of 1-hydropyridinyl radicals are appropriate to study the substituent effect since the various derivatives can be readily generated by photolysis of the corresponding pyridine in acetone/2-propanol.[8)] Kinetics of the decay of 1-hydro-4-phenylpyridinyl (III) is reported here.

Photolytic reduction of 4-phenylpyridine (0.1 M) in acetone/2-propanol (1:1 by volume) solution showed a well-resolved ESR spectrum which was reasonably assigned to III.[9)] The radical formation was also confirmed by the observation of the absorption spectrum by flash photolysis. Figure 1 shows the spectrum measured with a multichannel-photodetector (Union Giken Co. Ltd.) at 8 ms after the flash. It has the bands at 346 and 530 nm and is quite similar to that of II.



Growth and decay curve of III was measured in a wide range of temperatures by kinetic ESR



III

Fig. 1. Transient absorption spectrum due to 1-hydro-4-phenylpyridinyl observed at 8 ms after flash photolysis.

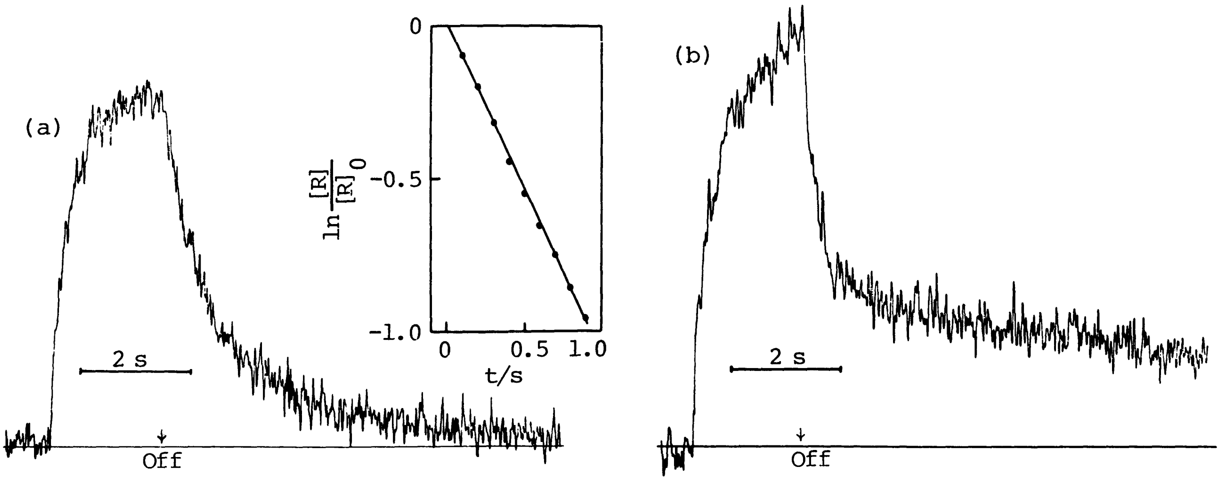
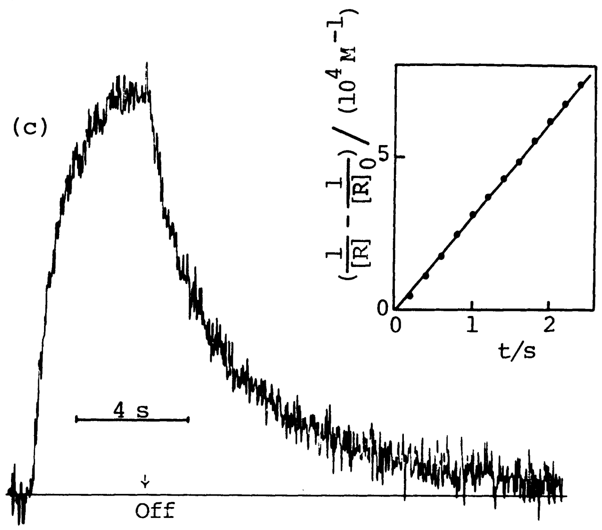


Fig. 2. Growth and decay curves of 1-hydro-4-phenylpyridinyl with light pulse irradiation at (a) 31, (b) -10, and (c) -50°C. Inserts: (a) first-order plot and (c) second-order plot.



spectroscopy. An averaging technique was used to obtain a good signal to noise ratio (Kikusui 8700 transient memory and averaging system). Light pulse was generated by an electromagnetic shutter, using a high pressure mercury lamp. A glass filter (UV-29) was used to prevent the additional decomposition of the radical. Radical cencentration was determined by an electronic double integrator of ESR signal. In the integration, a solution of diphenylpicrylhydrazyl in benzene was used as a standard sample. The system will be reported elsewhere.

As shown in Fig. 2a, radical III shows a simple first-order decay at the temperatures above 10°C. On the other hand, a two step decay (Fig. 2b) was observed at the temperature range from 10 to -15°C, while no change of the hyperfine pattern was exhibited. In this letter, the decay appeared at low temperatures is called the "fast step" and the decay of the second step in Fig. 2b, which is also observed at high temperatures, is represented as the "slow step" reaction. The fast step is a second-order decay in the temperature range, -45 — -64°C (Fig. 2c). These results seem to indicate that III decays initially in a second-order and then in a first-order process. When the initial concentration of III was very low ($< 5 \times 10^{-6}$ M) , the two-step decay was also observed in the same temperature range shown above, but a simple second- or first-order decay was not exhibited for each step. This means that the reaction with solvent molecule is in competition with dimerization reaction at low radical concentrations. In any event, we can neglect the reaction with solvent molecule under the condition of high initial concentrations.

A similar two-step decay has been observed in the dimerization processes of radicals I and II, to which intermediate formation of the radical-pair of π-complex type was proposed.[6,7] We suppose a similar scheme for the present dimerization process as follows,

$$2\,R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RP \xrightarrow{k_2} D$$

where R, RP, and D denote radical monomer, radical pair, and σ-bonding dimer, respectively. Since the rate constants of the two steps are very different from each other, we can treat each step independently.

a) The fast step: A simple second-order decay is obtained by neglecting the reverse reaction.

$$k_{exp}t = 2k_1t = [R]^{-1} - [R]_0^{-1} \qquad (1)$$

b) The slow step: We can write the following equation for the above scheme.

$$d[R]/dt = -2d[RP]/dt - 2k_2[RP] \qquad (2)$$

Since the preliminary equilibrium is always established in this step,

$$[RP] = K_1[R]^2 \qquad (3)$$

where K_1 is a preliminary equilibrium constant. Substituting eq. 3 and its differentiating equation in eq. 2 yields the following one.

$$d[R]/dt = -2k_2K_1[R]^2/(1 + 4K_1[R]) \qquad (4)$$

If $4K_1[R] \gg 1$, eq. 4 becomes a simple first-order reaction. Therefore,

$$k_{exp}t = (k_2/2)t = -\ln[R]/[R]_0. \qquad (5)$$

The above treatment implies that, when some conditions are satisfied, a first-order decay of the radical would be observed in the slow step in spite of bimolecular reaction. Thus, the two-step decay in the present system can be well explained by the above scheme. Arrhenius plots for the two steps are shown in Figs. 3 and 4. The reaction rates are represented as follows,

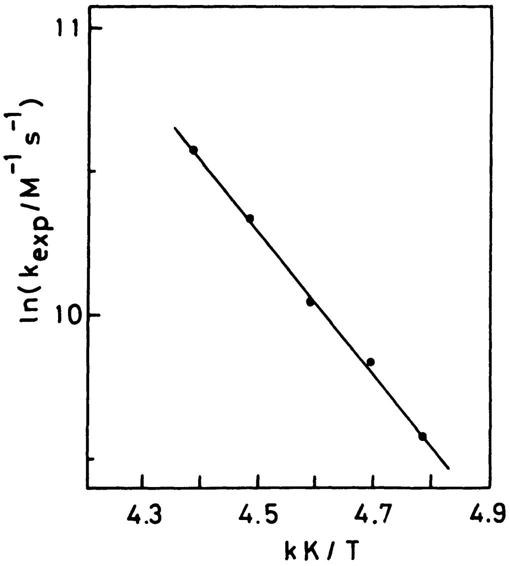


Fig. 3. Arrhenius plots for the decay of the fast step.

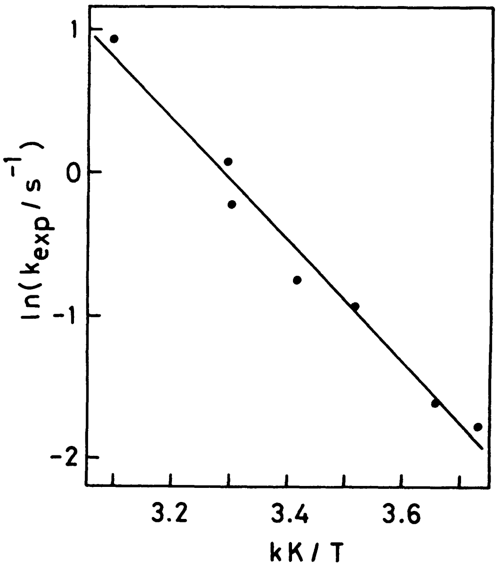


Fig. 4. Arrhenius plots for the decay of the slow step.

the fast step: $k_{exp}/M^{-1}s^{-1} = (2.3 \pm 0.5) \times 10^{9}\exp[(-5.0 \pm 0.1)^{kcal/mol}/RT]$,

the slow step: $k_{exp}/s^{-1} = (1.4 \pm 1.0) \times 10^{6}\exp[(-8.5 \pm 0.4)^{kcal/mol}/RT]$.

The activation energies of 5.0 and 8.5 kcal/mol were obtained for the fast and slow steps, respectively. Both values are smaller than those for the dimerization of radical II in MTHF, in which they are 6.7 and 11.3 kcal/mol, respectively. This indicates that the substituent at nitrogen affects the rates of both intermediate and σ-bond formation processes though the precise comparison is impossible because of their different solvent systems. The frequency factor for the slow step is very low as compared with that of the dimerization of II for which the value of 2.4×10^{8} has been obtained.7) Since the factor seems to reflect the stability of the intermediate, further examinations for the various derivatives would make possible to interprete the very low frequency factor of the above slow step.

An attempt to detect the intermediate radical-pair by absorption spectroscopy has been unsuccessful. This may be ascribed to that the spectrum of the radical pair resembles that of the radical monomer and, moreover, the concentration of the pair is low at room temperature. Examination of time dependence of the absorption spectrum showed that the dimer is also unstable even in the dark, yielding the final product with a very slow rate.

Recently, kinetic measurement of the decay of 1-hydro-4-acetylpyridinyl was reported by Krohn et al.,10) showing a simple second-order decay. It is noteworthy that the dimerization occurred at the acetyl carbon, since the unpaired electron is significantly localized at the position.

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