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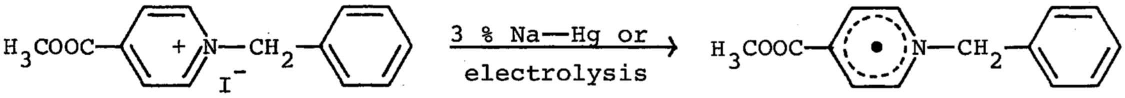
PHOTOLYSIS AND ASSOCIATION OF 1-BENZYL-4-METHOXYCARBONYLPYRIDINYL

Yusaku IKEGAMI and Hidetoshi WATANABE*
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira 2-1-1, Sendai 980

A neutral free radical, 1-benzyl-4-methoxycarbonylpyridinyl is stable in the dark, but decomposes by light irradiation to generate benzyl radical. Association of the radical at low temperature has been investigated.

1-Alkyl-4(or 2)-methoxycarbonylpyridinyls associate intermolecularily to form both the diamagnetic singlet (A_S) and paramagnetic triplet (A_T) dimers at low temperature. Another triplet species (B_T) is generated from A_S by irradiating the solution at 77 K with visible light.1,2) In order to investigate the effect of N-substituent on the stability and association of pyridinyls, 1-benzyl-4-methoxycarbonylpyridinyl (I) has been prepared. The preparation and characteristics of the radical will be reported. Generation of I was preliminarily examined by the electrochemical reduction of the corresponding pyridinium iodide in degassed acetonitrile or N,N-dimethylformamide.



II I

Treatment of 1-benzyl-4-methoxycarbonylpyridinium iodide3) (II, 1.5 mmol) with 3 % sodium amalgam (1.7 mmol) in degassed acetonitrile (18 ml) at around 5°C in the dark afforded a green solution. After stirring for about 50 min, insoluble materials were filtered off and removal of the solvent gave blue crystals composed of radical I and sodium iodide. Yield of the radical based on the spectroscopic estimation was over 85 %. The radical is slightly soluble in hydrocarbons and soluble in ethereal or aprotic dipolar solvents. The radical solution is stable for a long period at room temperature in the dark, but decomposes gradually in the light and immediately in contact with alcohols, water, or air. The radical is not distillable under vacuum in contrast to the 1-methyl and 1-ethyl homologs.1,4)

The radical concentration of the solution for spectroscopic studies was determined spectroscopically by the following electron-transfer reaction.

$$\text{Methylviologen dichloride} + \text{I} \longrightarrow \begin{array}{c}\text{Methylviologen radical cation}\\ \text{chloride}\end{array} + \begin{array}{c}\text{1-Benzyl-4-methoxycarbonyl-}\\ \text{pyridinium chloride}\end{array}$$

The reaction of an excess of solid methylviologen dichloride with the dilute solution of I (concn < 5×10^{-3} M) in acetonitrile in the dark proceeded rapidly to form the methylviologen radical cation. The absorption intensity of the resulting cation at 605 nm (ε = 10060)[5)] was converted into the concentration of I.

The ESR spectrum of the radical solution is shown in Fig. 1. The hyperfine structure is interpreted reasonably as arising from the structure I with five splitting constants indicated in the figure. The assignments to the constants were given tentatively according to the type of splitting and by comparing them with the assignments to the constants of 1-methyl-4-methoxycarbonylpyridinyl.[6)]

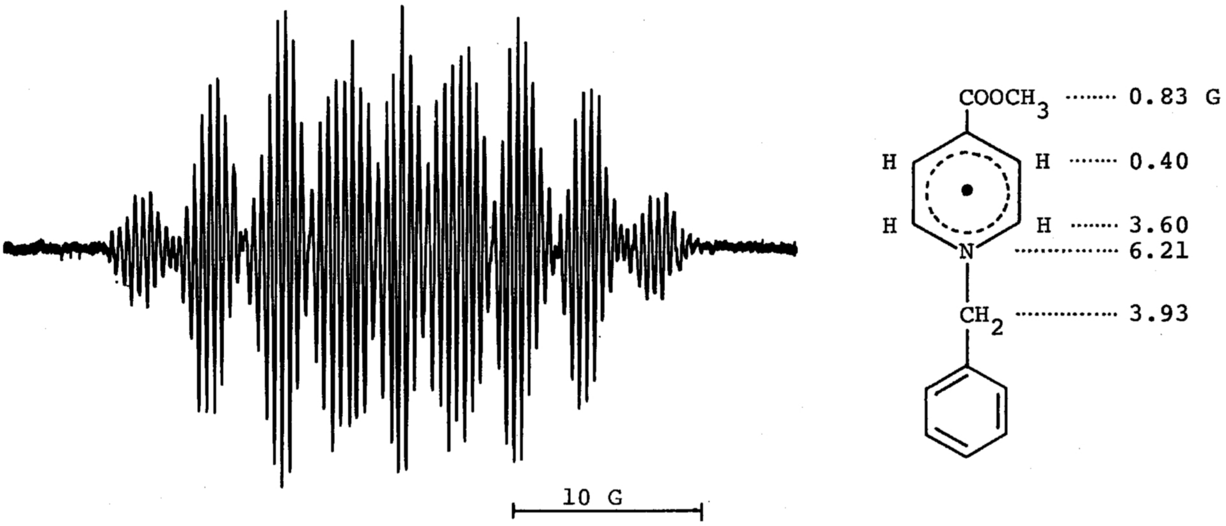
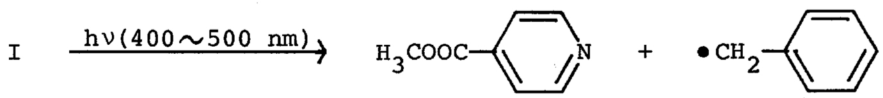


Fig. 1. ESR spectrum and hyperfine splitting constants of 1-benzyl-4-methoxycarbonylpyridinyl in MTHF at room temperature (6 × 10^{-4} M).

The radical shows absorption bands at 246, 302, 393, and 630 nm (Fig. 2). When the radical solution was irradiated with visible light, the last three bands disappeared as a result of the photolysis. The effect of the irradiation on the spectrum is shown in Fig. 2. The photolysis of I occurred also in 2-methyltetrahydrofuran (MTHF) glass at 77 K. The change in the spectrum is shown in Fig. 3, in which the disappearance of absorption bands at 286, 372, and 616 nm on irradiation accompanied the appearance of new bands at 260, 306, and 319 nm. The new bands coincide in their wavelengths with those of the benzyl radical generated in 3-methylpentane at 77 K.[7)] Thus, the photolysis may be explained by the following C-N bond cleavage.



The band at 260 nm is referred to both the benzyl radical and methyl isonicotinate.

The absorption spectrum of I at 77 K has an intense band at 616 nm, while the absorption in this region at room temperature is very weak. As the absorption intensity at 616 nm was dependent on the radical concentration, the dimeric association[1,2)] of the radical can account for the strong absorption in this region of Fig. 3. Since the solution contains a considerable amount of sodium iodide, the strong intensity may be partially due to the complex formation of I with sodium iodide. The complex formation may also explain the hypsochromic shifts of the bands at 302 and 393 nm (Fig. 2a) to 286 and 372 nm (Fig. 3a),

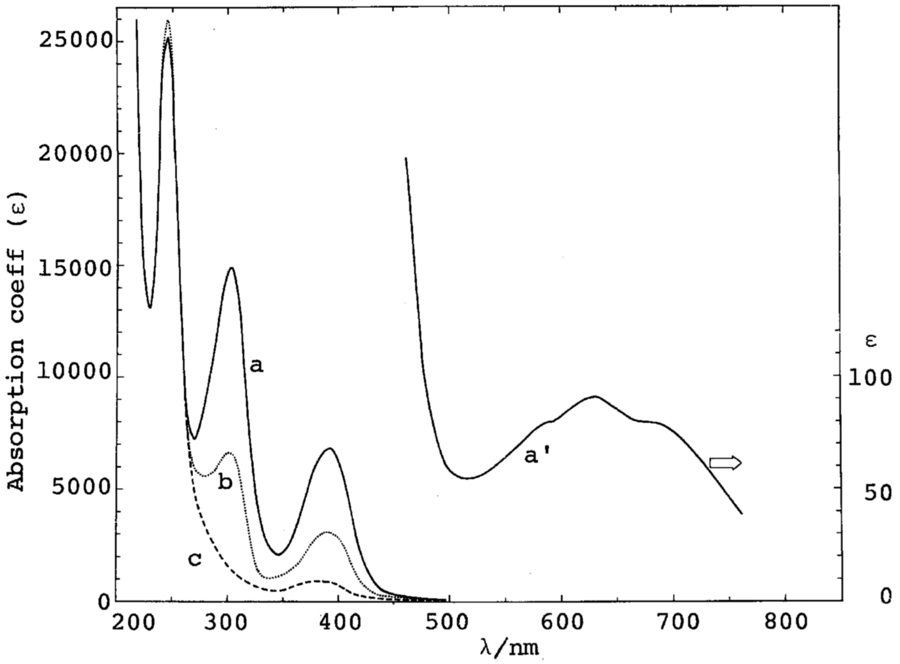


Fig. 2. Absorption spectrum of I and the spectral change on light irradiation in acetonitrile at room temperature: (a), 3.9×10^{-3} M, and (a'), 2.6×10^{-2} M, before irradiation; (b), after 100-sec irradiation of (a) with visible light; (c), after sufficient irradiation. A 500 W tungsten lamp equipped with a Toshiba filter UV-39 was used for the irradiation.

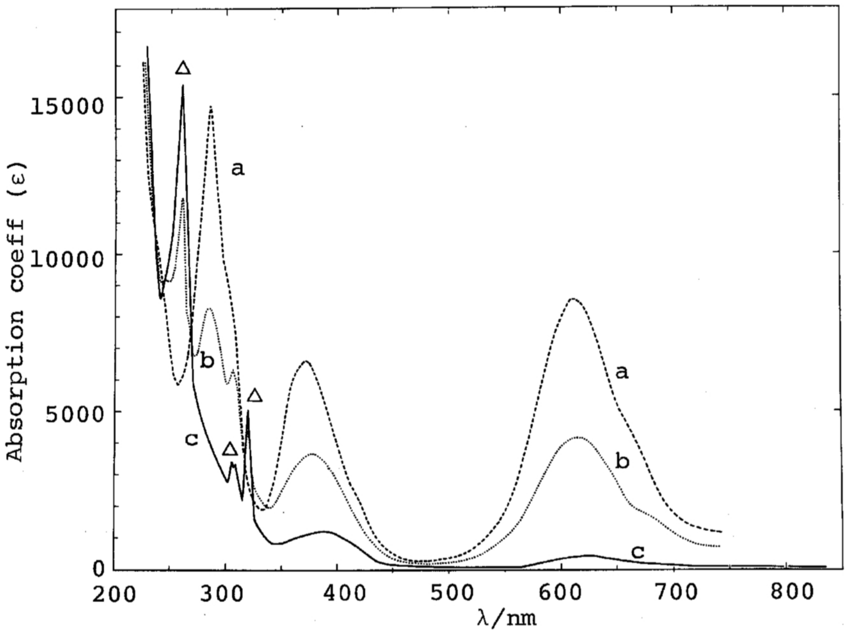


Fig. 3. Absorption spectrum of I and the spectral change on light irradiation in MTHF at 77 K: (a), 8.8×10^{-3} M, before irradiation; (b), after 1 min irradiation; (c), after sufficient irradiation with a 500 W tungsten lamp. △ indicates the bands due to the products.

respectively, by lowering temperature.

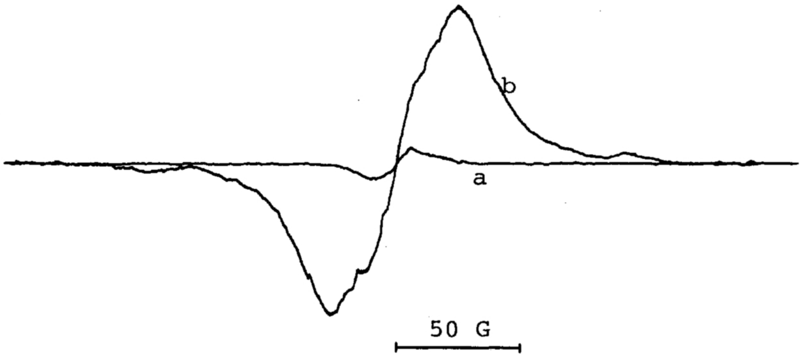


Fig. 4. ESR spectra of I in MTHF glass at 77 K, before (a) and after (b) 3 min irradiation with visible light (1.4×10^{-2} M).

An ESR study at low temperature presented information about the radical association. The signal intensity due to the radical decreased gradually with lowering temperature. The intensity at -150°C was less than 2 % of that at room temperature at the concentration of 1.4×10^{-2} M in MTHF. This decrease is ascribed to the formation of diamagnetic radical dimer at low temperature.$^{1)}$ Irradiation of the solution with visible light at 77 K resulted in the spectral change shown in Fig. 4. Although this change may be partly explained by the generation of benzyl radical, the large extent of signal and the appearance of two wings with $\Delta H = 195$ G in Fig. 4 would be interpreted as arising from the generation of triplet radical dimer B_T.$^{1)}$ Appearance of the $\Delta M = 2$ transition at the half-field proved the triplet. The zero-field parameters estimated roughly are $\underline{D} = 0.0091\ \mathrm{cm}^{-1}$ and $\underline{E} \approx 0$. The $\underline{D}$ value is consistent with a spin-spin dipolar interaction for an average separation of 6.7 Å, which is larger than those in the triplet associations of 1-methyl- and 1-ethyl-4-methoxycarbonylpyridinyls by 1.2 Å.$^{1)}$

The above results indicate that the irradiation of the solution at 77 K caused both the singlet-triplet transformation in the dimeric association of I and the photolytic generation of benzyl radical from I. Since both occurred with visible light, an electronic excitation in the radical may bring about both phenomena.

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* Present address: Sankyo Co. Ltd., 1-2-58 Hirocho, Shinagawa-ku, Tokyo 140.

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