Tetrahedron Letters No.2, pp. 227-231, 1966. Pergamon Press Ltd.
Printed in Great Britain.

pi-COMPLEX BETWEEN THE SUBSTITUTED PYRIDINYL RADICALS

Michiya Itoh
Faculty of Pharmaceutical Sciences
The University of Tokyo, Hongo, Tokyo, Japan
Saburo Nagakura
The Institute for Solid State Physics
The University of Tokyo, Azabu, Tokyo, Japan

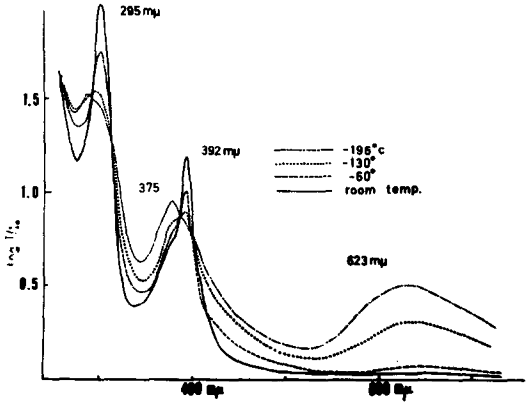
(Received 22 November 1965)

In the course of the spectroscopic studies of pyridinyl radicals, the 1-methyl-4-carbomethoxypyridinyl radical was found to exist as the dimer at low temperature. Therefore, a quantitative study of the monomer-dimer equilibrium of the pyridinyl radical in the iso-pentane solution has been undertaken.

The acetonitrile solution of the 1-methyl-4-carbomethoxypyridinyl radical was prepared by the same method as described in previous papers[1]. The solvent was completely removed from the solution. Only the pyridinyl radical was extracted from the residue with iso-pentane. All these procedures were performed in high vacuum. The electronic absorption spectra of the iso-pentane solution of the pyridinyl radical were measured at various temperatures with a Cary recording spectrophotometer Model-14M. The results are shown in Fig. 1.

A new band appears at 623 mμ at 77°K. The temperature dependence of the absorption spectra is completely reversible.

FIG. 1



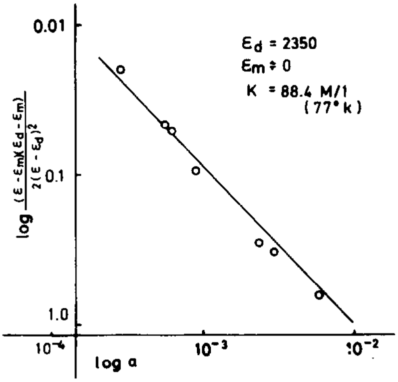
Hausser and Murrell[2] reported that the 9-ethylphenazyl radical and tetramethyl-p-phenylenediamine cation radical form the dimer in ethanol at low temperature, and that a charge transfer band associated with the π-π interaction between the radicals can be observed at about 800 mμ. Hirota and Weissman[3] studied electronic interaction in ketyl radicals. They observed a charge-transfer band at the 600-700 mμ region, which may be ascribed to the sodium benzophenone ketyl dimer.

By analogy with the above-mentioned studies, we supposed that the 1-methyl-4-carbomethoxypyridinyl radical in iso-pentane forms the dimer at low temperature, and the 623 mμ band may be regarded as the charge-transfer band. In order to check quantitatively this problem, we have undertaken to obtain the monomer-dimer equilibrium constant K of the pyridinyl radical in iso-pentane. K can be determined by the following equation;

$$K = (\varepsilon - \varepsilon_m)(\varepsilon_d - \varepsilon_m)/2a(\varepsilon - \varepsilon_d)^2 \text{ -------} (1)$$

where ε is the observed molar extinction coefficient at a certain wave-length (now 623 mμ); ε_m and ε_d are the molar extinction coefficients of the monomer radical and the radical dimer, respectively; a is the concentration of the pyridinyl radical as the monomer in iso-pentane. By assuming that the pyridinyl radicals in the iso-pentane solution of low concentration ($10^{-4} \sim 10^{-2}M$) are mostly in monomer form at room temperature, the value of a can be determined from the observed optical density of the radical solution. The absorption spectra of the iso-pentane solutions of various concentrations of the radical were measured at 77°K, and the values of ε at 623 mμ were accurately determined. The values of K, ε_m and ε_d were evaluated by inserting the observed a and ε values into Eq. 1. The least squares method was applied to the actual evaluation of K, ε_m and ε_d. Furthermore, it was shown that the value of the

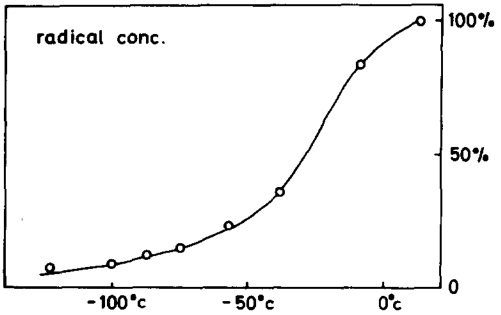
FIG. 2



$\log\left\{(\varepsilon - \varepsilon_m)(\varepsilon_d - \varepsilon_m)/2(\varepsilon - \varepsilon_d)^2\right\}$ is proportinal to logarithum of the radical concentration, $\log a$ (see Fig. 2). The slope of the straight line is about -1. This means[4] that the concentration dependence of the absorption spectrum of the 1-methyl 4-carbomethoxypyridinyl radical at 77°K can be explained by the equilibrium between the monomer and dimer. K was determined to be 88.4 M/l in 77°K.

The diluted acetonitrile solution of the 1-methyl-4-carbomethoxypyridinyl radical showed the ESR spectrum with the well resolved hyperfine structure, as reported in the previous papers[1]. In the present paper, the temperature dependence of the intensity of the ESR spectrum was observed with the isopentane solution. From the experimental result shown in Fig. 3, it is clear that the diamagnetic dimer of the pyridinyl radical are formed at low temperature. From these electronic absorption and ESR studies, there is no doubt that the diamagnetic dimer of the pyridinyl radical is formed in equilibrium with the monomer. The diamagnetic radical dimer may probably be

FIG. 3



the $\pi-\pi$ complex between the neutral paramagnetic pyridinyl radicals, in which the two radicals lie in parallel planes one above the other. The details will be discussed in the full paper.

REFERANCE

1) M. Itoh and S. Nagakura, Tetrahedron Letters, 8, 417 (1965); idem., Bull. Chem. Soc. Japan, in press.

2) K. H. Hausser and J. N. Murrell, J. Chem. Phys., 27, 500 (1957).

3) N. Hirota and S. I. Weissman, J. Am. Chem. Soc., 86, 2538 (1964).

4) H. Hosoya, J. Tanaka and S. Nagakura, J. Mol. Spectroscopy, 8, 257 (1962).