SHORT COMMUNICATIONS

Electron Spin Resonance and Electronic Absorption Spectra of the Radical Anions of Pyridine and Acridine

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(Received December 20, 1960)

Recently a number of radical anions of aromatic hydrocarbons have been studied[1-3] extensively and their electronic structures have been elucidated to some extent. As for anions of conjugated heterocyclic compounds, however, the phenazine anion was the only one studied hitherto[4]. It seems to be interesting, therefore, to study the electronic structures of anions of heterocyclic compounds, giving special attention to hyperfine interaction between unpaired electron spins and nuclear moments of hetero-atoms, and to compare the results with those of aromatic hydrocarbons. In the present communication a study on the anions of pyridine and acridine is reported briefly. The method of preparation of the anions was the same as reported in the previous paper[3]; that

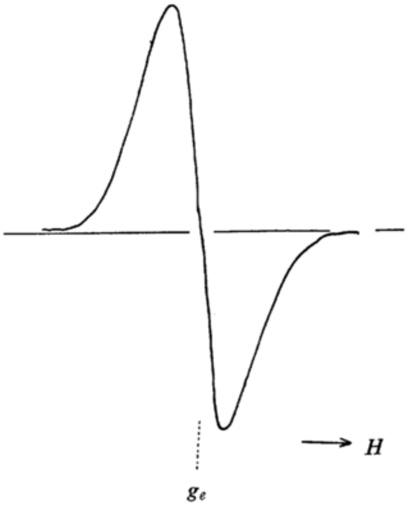

Fig. 1. ESR spectrum of the THF solution of the adduct of pyridine with sodium (H_{msl}= 10 gauss).

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[1] D. E. Paul, D. Lipkin and S. I. Weissman *J. Am. Chem. Soc.*, **78**, 116 (1956); T. R. Tuttle, Jr. and S. I. Weissman, ibid., **80**, 5342 (1958).

[2] G. J. Hoijtinks and W. P. Wiyland, *Molecular Physics*, **1**, 231 (1958).

[3] K. Morigaki, K. Kuwata and K. Hirota, This Bulletin, **33**, 952, 958 (1960); K. Kuwata, K. Morigaki and K. Hirota, ibid., **32**, 895 (1959).

[4] Y. Fellion and J. Uebersfeld, *J. Arch. Sci.*, Geneve, **10**, 95 (1957); cf. D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance", Butterworths Scientific Publication, London (1955), p. 167.

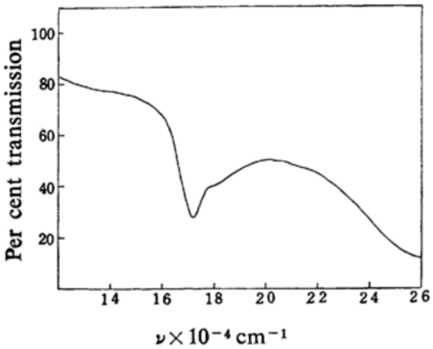

Fig. 2. Absorption spectrum for the THF solution of the adduct of pyridine with sodium.

is to say, all the procedures were carried out in an extremely evacuated system.

On heating pyridine with metallic sodium in tetrahydrofuran solution, a brownish yellow solution was obtained after evolution of a definite amount of gas[5]. This solution exhibited an ESR spectrum of a broad singlet as shown in Fig. 1. On continuing the procedure a red solution was obtained. Its absorption spectrum in the visible region is shown in Fig. 2, and the ESR spectrum obtained in this reaction stage was the same as that obtained in the early stage.

In the case of acridine a red solution of diamagnetic adduct was formed at the early stage of the reaction with sodium. The color of the solution changed to blue on heating it with sodium, and the ESR spectrum of a broad singlet was observed, the g-facter and the line width (H_{msl}) of which were 2.003 and 13 gauss, respectively.

In the previous investigation on the reaction of pyridine with alkali metals[6], formation of " sodium bipyridyl " was proposed on the basis of the results of chemical analysis of its decomposition product. However, according to our experiment described above, it is highly probable that radical anions of pyridine and also of acridine were formed.

Further studies will be published elsewhere.

The authors wish to express their sincere thanks to Professor M. Nakagawa of Osaka University for his helpful discussions.

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[5] In the case of dimethoxyethane solution, a main part of the gas evolved was methane which may be formed from decomposition of the solvent.

[6] B. Emmert, *Ber.*, **50**, 31 (1917).