NOTES

The Electron Spin Resonance Absorption of the Complexes of Aromatic Sulfur Compounds with Lewis Acids

By Minoru KINOSHITA and Hideo AKAMATU

(Received December 14, 1961)

The origin of the unpaired electrons which are responsible for the electron spin resonance (ESR) absorption of the complexes of aromatic compounds with Lewis acids has not been clarified. The ESR absorption of aromatic hydrocarbons, such as tetracene and perylene, in a sulfuric acid solution has been observed. Also, the ESR absorption of the complexes of these hydrocarbons with antimony pentachloride[1,2] and aluminum chloride[3,4] has been investigated, both in solids and in solutions in phosphorus oxychloride or carbon disulfide. In solutions the complexes display hyperfine structures which are similar to those of the corresponding hydrocarbon solutions in sulfuric acid. Thus the same organic radicals are likely responsible for the ESR absorption of the complexes and the sulfuric acid solutions. On the other hand, it is known that the radicals produced from compounds containing sulfur atoms show absorption lines which are characterized by relatively large g-values, because of the localization of unpaired electrons on the sulfur atoms. The ESR absorption of aromatic sulfur compounds, such as thio-phenol, thio-β-naphthol and thianthrene, in a sulfuric acid solution has been reported[3,5,6]. The characteristic features in the absorption of these radicals are large g-values in comparison with those of other organic free radicals and the appearance of two absorption bands[5]. Hence, the similar characteristic features in the ESR absorption of the complexes of aromatic sulfur compounds with Lewis acids can be expected. This short report is concerned with these.

The solid complexes with antimony pentachloride were made by mixing the solutions of sulfur compound and antimony pentachloride in dried chloroform. The solutions of the complexes with aluminium chloride were prepared in the same way by the use of nitrobenzene as a solvent. The concentration of these solutions and of the sulfuric acid solutions of the compounds was about $10^{-2}\sim10^{-3}$ M.

The solid complexes are deeply colored; thio-β-naphthol and 2, 2′-dinaphthyl disulfide give dark green compounds, while thianthrene forms a brownish purple compound. These colorations are identical with the colors of the sulfuric acid solutions of the corresponding compounds. When once dried completely in vacuum, the complexes with antimony pentachloride are very stable even in exposure to the air, but the complex of dibenzothiophene seems to be rather unstable.

The ESR absorption was examined at a frequency of 9.4 kMc./sec. at room temperature with a Hitachi MPS-1 spectrometer. As shown in Table I, the g-values of these complexes, estimated by a comparison with DPPH ($g=2.0036$), were found to be large, coinciding with those of the sulfuric acid solutions of these compounds.

In the sulfuric acid solution, thio-β-naphthol and 2, 2′-dinaphthyl disulfide showed two absorption lines. The peak of the lower field side was very weak. This weak peak was not observed in the dried complexes, but when an excess of antimony pentachloride was added to the complexes, the weak line at the lower field could be detected; on removal of the exceses of the reagent, this peak disappeared.

In the solid complexes with antimony pentachloride, the ESR absorption lines were found to be very broad in contrast to those of the complexes of aromatic hydrocarbons[2]. In Table II, the line widths are shown by the distances between the points of maximum slope. The broadness and the large g-values of the ESR absorption of the radicals containing sulfur atoms can be interpreted by the localization of an unpaired electron on the sulfur atom[7]. In the powdered thianthrene complex with

---

[1] S. I. Weissman, E. deBoer and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957).

[2] Y. Matsunaga, This Bulletin, **34**, 893 (1961).

[3] J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).

[4] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, **1961**, 142.

[5] J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955).

[6] A. Fava, P. B. Sogo and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

[7] For example, Y. Kurita and W. Gordy, *J. Chem. Phys.*, **34**, 1285 (1961).

TABLE I. THE OBSERVED g-VALUES OF THE COMPLEXES

Donor	Acceptor		
	$SbCl_5$ (powder)	$AlCl_3$ (solution)	H_2SO_4 (solution)
Thio-β-naphthol	2.0076±0.0002	2.0074±0.0002	2.0074±0.0002 2.0139±0.0002
2,2′-Dinaphthyl disulfide	2.0074±0.0001	2.0076±0.0002	2.0076±0.0001 2.0140±0.0002
Thianthrene	2.0080±0.0001	2.0080±0.0002	2.0083±0.0001
Dibenzothiophene	2.0044±0.0002	—	—

TABLE II. THE OBSERVED LINE WIDTHS[a] OF THE COMPLEXES

Donor	Acceptor		
	$SbCl_5$ (powder)	$AlCl_3$ (solution)	H_2SO_4 (solution)
Thio-β-naphthol	8.5	3.0	2.9
2,2′-Dinaphthyl disulfide	8.2	3.1	3.0
Thianthrene	Three lines[b]	Five lines[c]	Five lines[c]
Dibenzothiophene	4.5	—	—

a) Distance between the points of maximum slope in gauss.
b) Over-all width of about 45 gauss.
c) Over-all width of about 10 gauss.

antimony pentachloride, the absorption was found to consist of three broad lines, which may be ascribed to the anisotropy of g-value. In other complexes studied here, no structure in the ESR absorption was observed, but thio-β-naphthol and 2,2′-dinaphthyl disulfide seemed to form two kinds of complexes; one of them had a g-value of 2.0076 and 2.0074 respectively and the other 2.0051, for both compounds. When the antimony pentachloride solution was dilute, a complex with a higher g-value was resulted, but if a somewhat concentrated solution was used, a complex with $g=2.0051$ and a line width of 5.6 gauss, or the mixture of these two kinds of complexes, which gave an asymmetric or two absorption lines, was obtained. The presence of two kinds of complexes has been already found in the system of tetracene and antimony pentachloride[2].

The solutions of these compounds as well as of the complexes displayed sharp absorption lines compared with the solid complexes; however, no hyperfine structures were observed other than in the solutions of thianthrene and its complex. For dibenzothiophene we could not obtain any ESR absorption in the dissolved state, but in a fuming sulfuric acid solution it showed a weak and sharp absorption.

Since the thianthrene complex with antimony pentachloride was found to show an interesting behavior in the ESR absorption, we shall describe it in detail shortly.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo