The Electron Spin Resonance Absorption of the Complex of Thianthrene with Antimony Pentachloride

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In a previous note[1] we presented some preliminary results of the ESR absorption study of the complexes of some aromatic sulfur compounds with strong Lewis acids, in both the solid and dissolved states. In the course of the study it was found that thianthrene, when treated with antimony pentachloride, formed a very stable complex which showed a very strong ESR absorption. Its absorption consists of three broad lines in the powdered state, while in the dissolved state the complex shows the hyperfine structure which has been known to be characteristic of the sulfuric acid solution of thianthrene[2,3]. In the case of aromatic hydrocarbons such as anthracene, tetracene and perylene, it has been observed that a complex with antimony pentachloride[4] or aluminum chloride[5] shows the hyperfine structure in the dissolved state similar to that of the sulfuric acid solution of the corresponding hydrocarbon; meanwhile, in the solid state the absorption is only a single sharp line[6]. In this report, the system of thianthrene and antimony pentachloride is investigated; the results will be discussed with reference to the case of aromatic hydrocarbons.

Experimental

Preparation and Composition of the Complex.— Similarly to the case of aromatic hydrocarbon[6,7], the complex of thianthrene with antimony pentachloride was prepared by mixing the dilute solutions of both the components in dried chloroform. When the solutions were mixed, a brownish purple precipitate was formed immediately. This precipitate was filtered, washed with dried chloroform, and then dried in a vacuum for about 30 min. The dried complex is very stable and has a definite melting point of 152∼153°C. For the determination of the composition, it was decomposed in boiling water, and the concentration of the free chlorine ion was determined by titration with silver nitrate solution. It was estimated that the complex consists of one mole of thianthrene and 0.93 mol. of antimony pentachloride. The complexes of thianthrene with aluminum chloride and titanium tetrachloride were prepared in a similar way. These complexes were not so stable as the complex with antimony pentachloride. Stannic chloride did not seem to form any solid complex with thianthrene in a dried condition.

Measurements.—The ESR absorption spectra of the complexes were examined at 9.4 kMc./sec. by the use of a Hitachi MPS-1 spectrometer. The unpaired spin concentration and the *g*-value of the complex were estimated by comparison with a standard piece of diphenylpicrylhydrazyl, for which the *g*-value of 2.0036 had been decided upon.

The magnetic susceptibilities of thianthrene and its complex were measured by the Gouy method, and the electronic absorption spectra were obtained in association with a Cary model-11 spectrophotometer. All the mesurements in this work were carried out at room temperature.

Results

The complex formed by the reaction of thianthrene with antimony pentachloride was a brownish purple powder. When examined by an X-ray diffractometer, it gave a sharp crystalline pattern which was quite different from that of thianthrene itself. The complex remained unchanged after being exposed to the air for about one year, but when boiled with water, it decomposed completely, leaving thianthrene.

The ESR Absorption Spectra. — The ESR absorption spectrum of the complex in its powdered state was found to consist of three broad lines which were distributed asymmetrically (Fig. 1). The separations between the three lines increased in proportion to the resonance frequency (Fig. 1b). The *g*-value for the main center line was found to be 2.0080 ± 0.0001, and the spin population was estimated as 1.3×10^{21} per gram, with an error of about 10%. Similar ESR absorption patterns were obtained for the complexes with aluminum chloride and titanium tetrachloride, but, as they were very weak, they were not investigated further.

In the nitrobenzene solution, the complex showed, in contrast to the spectrum of the

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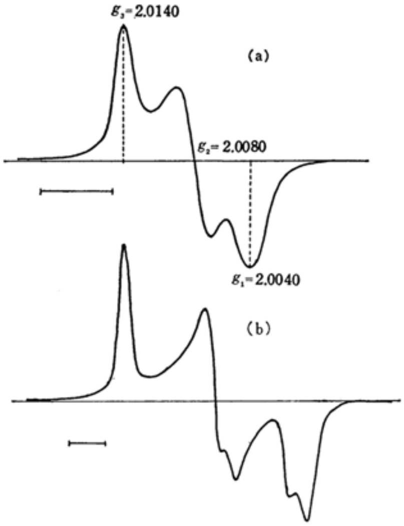

Fig. 1. The derivative curves of the ESR absorption for the powdered complex of thianthrene-$SbCl_5$, at the frequencies of 9.4 kMc./sec. (a), and of 23 kMc./sec. (b). The scale (10 gauss) is indicated in the spectra. The magnetic field increases from left to right.

solid, a hyperfine structure consisting of five equally spaced lines with an intensity ratio of about 1 : 4 : 6 : 4 : 1 (Fig. 2a). This hyperfine structure is identical with that of thianthrene or thianthrene disulfoxide in a concentrated sulfuric acid solution (Fig. 2b and c), which has been investigated by previous workers³⁾. The g-value for the center of the structure was found to be $g=2.0080\pm0.0001$, while the spacing of the five lines was about 1.2 gauss.

The Electronic Absorption Spectra. — The solutions of the complex in nitrobenzene and in o-dichlorobenzene displayed identical spectra, characterized by an absorption band with a maximum at 547 mμ, which was in coincidence with the band at 546 mμ observed in the sulfuric acid solution of thianthrene³⁾. In these solutions the complex decomposed slowly. The spectrum of the complex in the solid state was obtained by the KBr-disk method. This spectrum was similar to that of the solution, but the absorption band was shifted by about 30 mμ to the longer wavelength side. In the KBr-disk, the complex was also unstable.

The Magnetic Susceptibilities.—The observed susceptibilities are as follows:

Thianthrene: $\chi_g=-0.601\times10^{-6}$ per gram, or $\chi_M=-129.8\times10^{-6}$ per mole.

This molar susceptibility is in good agreement with the value of -129.3×10^{-6} reported by Banerjee⁸⁾.

The complex of thianthrene with antimony pentachloride: $\chi_g=1.74\times10^{-6}$ per gram, or $\chi_M=897\times10^{-6}$ per mole.
The molar susceptibility of the complex was calculated assuming the composition to be one to one in mole ratio.

Discussion

The facts that identical ESR patterns can be observed in the powdered complexes of thianthrene with antimony pentachloride, with aluminum chloride and with titanium tetrachloride, and that in solution the complex with antimony pentachloride shows the hyperfine structure which has been found in the sulfuric acid solution of thianthrene suggest that the paramagnetism of these complexes originates from thianthrene, presumably its monopositive ion, and not from the chlorides. From this investigation only, the form of these chlorides in complexes can not be deduced. However, it has been suggested, in the case of the complexes of diphenylamine derivatives

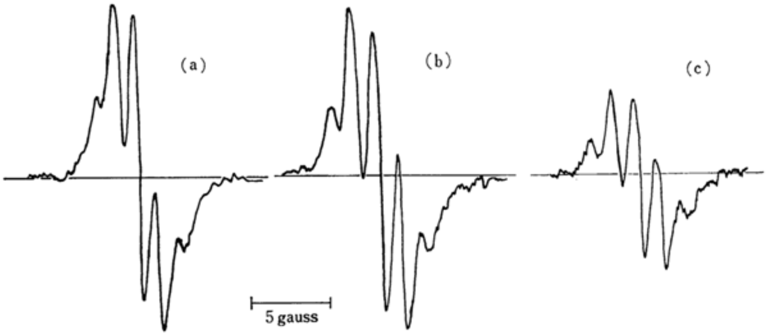

Fig. 2. The ESR hyperfine structures of the solutions of (a) the complex of thianthrene with $SbCl_5$ in nitrobenzene, (b) thianthrene in conc. H_2SO_4, and (c) thianthrene disulfoxide in conc. H_2SO_4.

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8) S. Banerjee, *Z. Krist.*, **100**, 316 (1939).

with antimony pentachloride, that the diamagnetic form of $(SbCl_6^- + SbCl_4^-)/2$ might result[9].

The three absorption lines may be attributed to the g-factor anisotropy because of the proportionality of their spacing change to the microwave frequency. Such an anisotropy has been found in some organic free-radicals, e. g., the irradiated proteins[10] and amino acids[11] containing sulfur. In the case of the organic free-radicals containing sulfur atoms, the anisotropy is often observed very clearly, but it can only with difficulty be obtained so clearly in many other free-radicals in powdered or glassy states. This fact has been interpreted qualitatively by the localization of an unpaired electron on the sulfur atom, which can be expected because of the large g-values and broad absorptions in free radicals containing sulfur. Recently this explanation has been confirmed to be valid in the quantitative treatment of the γ-irradiated single crystal of thiodiglycolic acid[12]. The principal g-values, g_1, g_2 and g_3, of the complex with antimony pentachloride, shown in Fig. 1a, are obtained by the method described by Kneubühl[13], who has made a theoretical treatment of line shapes for the powdered samples. This method has given results agreeing well with the single crystal work when applied to copper chloride powder which shows very broad anisotropic lines.

Another explanation for the three absorption lines is that they might be due to the coexistence of three kinds of paramagnetic species. In the case of the mixture of tetracene and antimony pentachloride, it has been shown that there are two kinds of paramagnetic compounds which give the two ESR absorption lines in its powdered state, the intensity ratio of which is dependent on the amount of antimony pentachloride[6]. Also, the presence of two kinds of paramagnetic species has been suggested in the systems of thio-β-naphthol and 2, 2′-dinaphthyl disulfide with the same reagent[1]. In the present complex, it was found that the absorption line shape was not changed by repeated evacuations, but the addition of a small amount of the chloride to the dried complex generated new lines at the near position of the peak with $g=2.0040$.

Although the possibility of the presence of some kinds of compounds could not be excluded completely, the suggestion of the g-factor anisotropy for the dried complex may be supported by the facts that the isotropic hyperfine structure, which is characteristic of the sulfuric acid solution of thianthrene, can be observed in a nitrobenzene solution of the complex, and that the optical absorption spectra for both solid and solution are identical (that is, the same species is responsible for the paramagnetism in both the solid and dissolved states). In the case of some polycyclic aromatic hydrocarbons, it has been shown that the same species is formed in the complex with antimony pentachloride and in the sulfuric acid solution, and identical ESR hyperfine structures[4] and optical absorption spectra[14,15] can be observed. This seems to hold in the present case also.

The concentration of 1.3×10^{21} spins/g. obtained from the ESR absorption intensity indicates that there are 6.7×10^{23} unpaired electrons in one mole of the complex, assuming that the complex is formed by each mole of thianthrene and antimony pentachloride. Since the measurements of the ESR absorption intensities have errors of about 10%, it may be considered likely that each thianthrene molecule has one unpaired electron in the complex. If so, the paramagnetic part of the molar susceptibility of this system can be calculated as about 1250×10^{-6} at room temperature. On the other hand, the observed magnetic susceptibility of the complex is 897×10^{-6}. This leads to 1150×10^{-6} as the paramagnetic part of the susceptibility after the diamagnetic correction is made, assuming that the susceptibility of thianthrene is not altered in the course of the complex formation and that antimony pentachloride takes the diamagnetic form mentioned above, for which the susceptibility is estimated as -124×10^{-6}[9]. The paramagnetic part derived from the susceptibility measurement shows a somewhat large depression below that of the ESR method. This may be ascribed to the unsuitable diamagnetic correction, the experimental error, or other elements such as the Weiss constant, if any. Among these factors, the diamagnetic correction of thianthrene is of especial interest.

In the thianthrene molecule there may be no π-electron conjugation between the two benzenoid rings through the lone pair electrons on sulfur atoms, because of the non-planarity of the molecule. This can be demonstrated from the magnetic susceptibility of thianthrene. From the values of the molar susceptibilities of thianthrene and benzene, $\chi_M=-129.8\times10^{-6}$

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and $\chi(\text{Benz.}) = -55.6 \times 10^{-6}$ respectively, and the atomic susceptibility of hydrogen, $\chi(\text{H}) = -2.93 \times 10^{-6}$, the atomic susceptibility of sulfur, $\chi(\text{S})$, can be calculated as:

$$\chi_{\text{M}} = 2\chi(\text{Benz.}) - 4\chi(\text{H}) + 2\chi(\text{S})$$

$$\chi(\text{S}) = -15.2 \times 10^{-6}$$

This value agrees with Pascal's constant, $\chi(\text{S}) = -15.0 \times 10^{-6}$, within the range of experimental error. If the conjugation can cover the whole molecule of thianthrene, the atomic susceptibility of sulfur must become more diamagnetic by the above treatment. In the complex, however, it may be suggested that the thianthrene molecule, which is presumably presented as a monopositive ion, may be capable of taking a more diamagnetic planar (or nearly planar) form and that the diamagnetism may be increased by π-electron conjugation over the whole molecule. This suggestion is supported by the stability of the complex and by the ESR hyperfine structure which can be assigned to the four equivalent protons.

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