Electron Spin Resonance of Tetracene-Antimony Pentachloride

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It has been known that aromatic hydrocarbons give deeply colored unstable molecular compounds with antimony pentachloride[1]. Brass and his coworkers have reported the isolation of some compounds consisting of two molecules of hydrocarbon and one of antimony pentachloride[2,3]. Recently Weissman and his coworkers have observed the ESR of some of these molecular compounds both in the solid and in the dissolved states. They have suggested that singly charged hydrocarbon positive ions, which are formed by oxidation with antimony pentachloride, are responsible for, at least, part of the observed paramagnetism[4]. Hoijtink and Weijland have also pointed out the fact that the electronic absorption spectrum of perylene with antimony pentachloride in chloroform is closely similar to that of perylene monopositive ion produced in concentrated sulfuric acid[5]. Here we wish to report our preliminary ESR experiments on the products given by the reaction of antimony pentachloride with tetracene and also some other aromatic hydrocarbons.

Small amount of powdered hydrocarbon was put into a sample tube for the ESR measurements, then a dried chloroform solution of antimony pentachloride was added. After the solvent and excess of the reagent were quickly removed by evacuation, the ESR of the product in vacuum was recorded at room temperature and at a frequency of 9 kMc./sec. The rapid decrease of intensity of ESR was observed in many cases. The line width was given by the distance between the points of maximum slope. All of *g*-values were found to be near 2.004.

A sharp resonance absorption peak was detected from the products prepared with the following hydrocarbons; 1, 2-benzanthracene, width 2.0 gauss, perylene 1.2, 1, 12-benzperylene 0.6, mesonaphthodianthrence 1.5, bianthryl 1.2, pyranthrene 1.6, and violanthrene 1.7. In

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1) S. Hilpert and L. Wolf, *Ber.*, **46**, 2215 (1913).

2) K. Brass and E. Tengler, ibid., **64**, 1650 (1931).

3) K. Brass and K. Fanta, ibid., **69**, 1 (1936).

4) S. I. Weissman, E. de Boer and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957).

5) G. J. Hoijtink and W. P. Weijland, *Rec. trav. chim.*, **76**, 836 (1957).

the other case the spectrum was found to consist of two or three absorption peaks. The product from anthracene gives two peaks. The widths of the two may be in the range from 3.5 to 5.5 gauss. Three peaks were observed from the mixture of chrysene and antimony pentachloride. The peak in the highest magnetic field has a width of 0.9 gauss, the central one about 2.5 gauss, and the last 2.5 gauss. The separation between the first and the last is about 5.5 gauss. The estimation of these widths can not be accurate because of overlapping of the peaks. It is not yet clear whether the appearance of two or three peaks in the present cases is due to the coexistence of two or three kinds of paramagnetic species or due to the anisotropy of *g*-value in one species. However, the formation of two kinds of compounds could be definitely shown in the case of tetracene.

The spectrum obtained from the mixture of tetracene and antimony pentachloride consists of one sharp peak with a *g*-value of 2.0045 and one broad one with a *g*-value of 2.0056. Their intensities were found to depend on the ratio of antimony pentachloride to the hydrocarbon. As shown in Fig. 1a, a sharp peak appeared in the presence of an excess of antimony pentachloride. On the removal of some amount of the reagent this peak with a width of 1.1 gauss decreases its intensity and the broad peak with a width of 5.3 gauss becomes stronger as seen in Figs. 1b and c. The reverse change could be observed on addition of antimony pentachloride. We observed also that the intensities of two peaks with *g*-values of 2.0039 and 2.0048 respectively from the mixture of triphenylene and antimony pentachloride depend similarly on the condition of preparation.

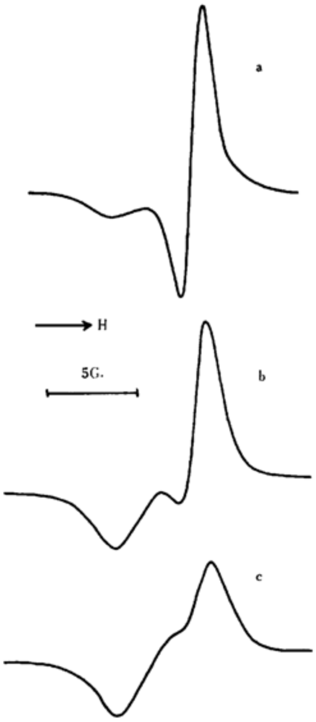

Fig. 1. Derivatives of ESR from tetracene and antimony pentachloride. a; tetracene with excess of antimony pentachloride, b and c; after removal of some amount of the reagent.

One of the two peaks, probably the broad one, appeared on addition of antimony pentachloride to tetracene may arise from the fairly stable molecular compound $2C_{18}H_{12}\cdot SbCl_5$ described by Brass and Fanta[3]. It is apparent that the species, which gives the peak with a *g*-value of 2.0045, is formed by the further addition of the complex-forming agent to the species which gives the broad peak with a *g*-value of 2.0056. The shift of *g*-value found here seems to be consistent with Wahler and Thon's observation that the magnitude of *g*-value of diarylnitrogen oxide in solution shows a marked decrease by the addition of *m*-dinitro- or *s*-trinitrobenzene[6]. The *g*-value of hydrocarbon monopositive ions in sulfuric acid has been reported to be 2.0028[7] and that of perylene perchlorate 2.0025[8]. It is unlikely that the *g*-value of paramagnetic tetracene ion becomes as high as 2.0056 by the interaction with antimony compound. Therefore, the species observed here may be not the salts of tetracene monopositive ion but the molecular compounds between the hydrocarbon and antimony pentachloride as reported by Brass[2,3]. The paramagnetic molecular compounds where the ground-state is supposed to be chiefly of non-bonding have been found in the case of aromatic hydrocarbons with halogens[9,10].

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7) A. Carrington, F. Dravnieks and M. C. R. Symons, *J. Chem. Soc.*, **1959**, 947.

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9) Y. Matsunaga, ibid., **28**, 475 (1955).

10) Y. Matsunaga, *J. Chem. Phys.*, **30**, 855 (1959).