Magnetic Susceptibilities of Aromatic Compounds Dissolved in Sulfuric Acid

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Various authors have reported that a number of aromatic compounds dissolved in concentrated sulfuric acid exhibit electron spin resonance absorption. In the case of bianthraquinon and perylene, the fraction of the radical form has been estimated as ten percent or more[1,2]. On the other hand, the static susceptibility measurement is available only for bianthraquinone, and this result does not support such a high fraction of the radical form[3].

In Table I the molar susceptibilities are presented, observed for ten compounds dissolved in 96% sulfuric acid together with the values in the solid state. The concentration of the compounds in sulfuric acid ranged from four to nine percent. The values for dissolved materials were calculated by the application of Wiedemann's additivity rule. The apparent molar susceptibilities of perylene and bianthraquinone in solution are undoubtedly less than those in the solid state. If we assume that the decrease of molar susceptibility is due to the partial compensation of diamagnetism by the paramagnetic contribution of the radical form and the diamagnetic contribution of the paramagnetic species is equal to that of the diamagnetic molecule, the fraction of the molecules with a single unpaired electron is given by $\Delta\chi \times 10^{-6}/1270 \times 10^{6}$. The estimated fraction for perylene is found to be 13.2 percent. This value is only one third of that given by Yokozawa and Miyashita[2]. As Selwood and Dobres[4] pointed out in the case of triarylmethyl radicals, the disagreement may be due, at least in part, to the enhanced diamagnetic contribution of the radical form. Although Theilacker, Kortüm and Elliehausen[3] could not find any appreciable change in the diamagnetic susceptibility of bianthraquinone, our measurement shows that 4.6 percent of the molecules are in the paramagnetic state. However, our value is still about one half of that estimated by resonance absorption[1]. Anthraquinone and fluorenone were reported to be paramagnetic in sulfuric acid and the fraction of the radical form was estimated as five percent or less[1]. Our results show that the last eight compounds in Table I including anthraquinone and fluorenone do not form any radical or the fraction of the paramagnetic species is less than one percent.

TABLE I
MAGNETIC SUSCEPTIBILITIES OF AROMATIC COMPOUNDS IN SULFURIC ACID AND IN THE SOLID STATE

Substance	Molar Suscept. in H_2SO_4	$(-\chi_M \times 10^6)$ in Solid
Perylene	0 ± 8*	168[5]
Bianthraquinone	161 ± 11	220[6]
Anthraquinone	103 ± 6	114[6]
1-Aza-anthraquinone	102 ± 6	109
Phenanthraquinone	102 ± 6	105[5]
Anthrone	122 ± 6	118[6]
Bianthrone	231 ± 11	229[6]
Fluorenone	90 ± 5	99.4
Benzanthrone	141 ± 7	143[5]
Bis(anthronylidene)-ethane	232 ± 12	232

* Estimated experimental error.

As to the nature of the paramagnetism, a triplet state[2] and a positive ion[7] were suggested for perylene and conjugated

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acid ions[1] for anthraquinone and bianthraquinone etc. These compounds are markedly protonated in solutions of strong acids like sulfuric acid[8,9], however, it has been pointed out that protonation is not sufficient condition for radical formation[10]. As shown in this paper, the fraction of the radical form is not high, so the structure of the paramagnetic species without protonation cannot be excluded. Although we cannotdiscuss in detail the nature of the radical form based on our own data, it must be noted that the appearence of the paramagnetic species in sulfuric acid depends greatly on the structural feature of the aromatic molecule.

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