Electron Spin Resonance in Solid State Samples of Phenothiazine and Oxazine Dyes

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It has been shown by Chernyakovskii *et al.*[1] that several compounds from the series of triphenylmethane dyes exhibit electron spin resonance (ESR) in the solid state. The intensity of the signal varied from compound to compound and amounted to $10^{16}-10^{18}$ paramagnetic particles per gram sample. In all cases a narrow solitary absorption line without any hyperfine structure was observed. It was suggested that the ESR-signal of the triphenylmethane dyes was not related to the structure of the molecule itself but to the crystalline state as the signal disappeared on solution and reappeared when the sample was dried. The hypothesis was expressed that the presence of unpaired electrons depended on a highly conjugated system which extended through the crystal structure, and which permits a high degree of delocalization of the π-electrons.

It this laboratory we have found that the phenothiazine dyes methylene blue, thionine and toluidine blue, and the oxazine dyes capri blue, resazurin and nile blue have an ESR-absorption in the solid state.
(i). The intensity of the ESR-absorption was within the same limits as those reported for the triphenylmethane dyes, *i.e.* 10^{15} to 10^{18} spins per gram substance corresponding to about one paramagnetic particle per 10^4 and 10^2 molecules respectively.
(ii). The spectra exhibited a single line of a width about 15 gauss except of nile blue sulphate. The g-value was close to that of DPPH.
(iii). The intensity of the ESR-signal increased when the samples were kept at a moderately elevated temperature. Thus, powdered sample of methylene blue chloride recrystallized from water was found to have about 10^{16} spins per gram. Kept in an open vessel overnight at 75°C, this sample had lost about 5 molecules of crystal water. At the same time the intensity of the ESR-signal had increased by a factor of 100. The high signal was found to persist unchanged for many days. Further treatment at a pressure of 0.05 mm Hg at 75°C for an hour involved an increase of the ESR-signal by a factor about two and a simultaneous reduction of the line width from 16 to 6 gauss. Evacuation of the sample at room temperature did not change the line width.
(iv). Nile blue chloride was found to have an ESR-signal corresponding to about 10^{15} spins per gram substance. After being kept at 75°C for two days, the signal increased about 10 times. No crystal water is present in nile blue chloride. Evacuation at 75°C reduced the line width as described for methylene blue.

Nile blue chloride exhibits polymorphism and has a melting point at about 159°C, where the dark-green substance transforms to a brown-red modification with an almost metallic lustre. At the same time the signal increases by a factor of 100 as compared with an unheated sample.
(v). Nile blue sulphate recrystallized from cold diluted sulphuric acid * has a signal corresponding to about 5×10^{15} spins per gram. The signal strength seems to be rather unaffected by heat treatment. Contrary to the other compounds here investigated the spectrum of nile blue sulphate exhibits an asymmetrical shape with four incompletely resolved lines (Fig. 1).
(vi). The ESR-signals of the compounds here studied seem to be mainly a solid state phenomenon as only a small signal ($< 10^{14}$ spins per gram substance) could be detected in concentrated water solutions.

Discussion. The presence of unpaired electrons in solid state specimens of phenothiazine and oxazine dyes is not wholly understood. It is possible that the mechanism of the origin is similar to that suggested for the triphenylmethane dyes [1]. Considering the primary process of unpairing the electrons involved, it may be pointed out that the phenothiazine and oxazine dyes constitute redox systems in aqueous solution. A possible mechanism is that an

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* Due to their high solubility the nile blue compounds are difficult to crystallize from aqueous solutions. Nile blue sulphate A (G. T. Gurr, London) was crystallized as follows. 0.5 g substance was dissolved in 10 ml water. To the chilled solution 1 ml concentrated H_2SO_4 was slowly added under vigourous stirring. After being kept at + 4°C overnight the crystals (dark-green small needles) were collected and washed with cold diluted H_2SO_4 and finally with ether in order to remove H_2SO_4.

intermediate free radical is formed and trapped at the crystallization process.

As regards the increase of the signal when heating the samples a carbonization process is ruled out as the temperatures used are low compared with those necessary to obtain charred products. It is possible that the increase to a minor extent is due to removal of paramagnetic oxygen. Another factor of importance seems to be an increase of some kind of lattice imperfections. This suggestion is supported by the increase of the signal in connection with the removal of crystal water (methylene blue) and a phase transition (nile blue chloride). In both cases there is a change in the original arrangement with breaking of intermolecular bonds.

The spectrum of nile blue sulphate has certain features in common with that obtained from phenothiazine radicals when adsorbed on a cation exchanger[2]. Both spectra are highly asymmetrical and exhibit four incompletely resolved lines. The asymmetrical shape of the phenothiazine spectrum was suggested to depend on a g-value anisotropy and a hindered rotation of the adsorbed radical. The four lines were interpreted as a hyperfine structure due to the combined interaction of one nitrogen and one hydrogen nucleus in the central ring of the phenothiazine radical. It is possible that a similar interpretation is valid also for the spectrum of nile blue sulphate. The hyperfine interaction is not wholly understood, however, as the formula given for nile blue compounds (Fig. 1) does not involve a hydrogen attached to the ring nitrogen as in phenothiazine. The presence of more than one radical species or the possibility of different g-values in different parts of the crystal structure could not be excluded without an ESR-investigation at another frequency than that used here (9 500 Mc). A hyperfine interaction in the spectrum of nile blue sulphate would indicate that the unpaired electrons are more localized and trapped in this compound than in the other dyes investigated.

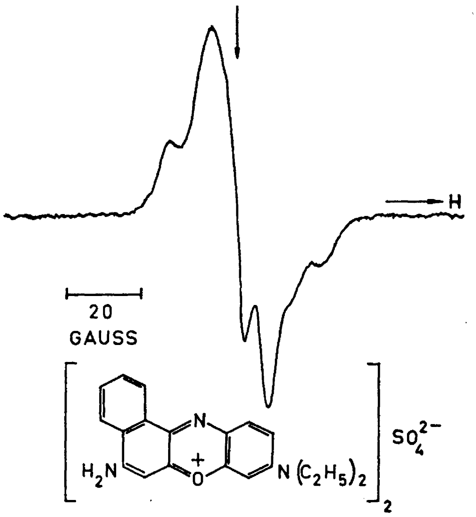

Fig. 1. The ESR-spectrum of a polycrystalline sample of nile blue sulphate (unheated). The vertical arrow gives the position of the g-value of a polycrystalline sample of DPPH.

Besides in the triphenylmethane dyes[1] and the compounds here concerned, an ESR-absorption has recently been reported in phthalocyanine complexes of diamagnetic metals by Neiman and Kivelson[3]. It is possible that the presence of varying amounts of unpaired electrons in solid state specimens is a common phenomenon in organic dyes. If this phenomenon is restricted to dyes only is unknown so far.

The ESR-spectra were obtained at room temperature using a Varian 100 kc spectrometer.

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