

## ELECTRON SPIN RESONANCE STUDIES OF PORPHYREXIDE SOLUTIONS

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Electron spin resonance (ESR) spectra of a stable organic free radical porphyrin have been recorded using a varian E-12 ESR spectrometer at 9.538 GHz frequency and 25°C temperature for two concentrations. It is seen that a three line spectrum at 0.05 M concentration splits to a nine line spectrum for 0.005 M concentration. Isotropic hyperfine coupling constants and  $g$ -value etc. are determined for the two concentrations.

### 1. Introduction

The magnetic properties of stable organic free radicals have been the subject of considerable attention in recent years, in addition to their role in polymer chemistry and other branches of chemistry. These radicals show interesting photo-conducting [1], semiconducting [1] and magnetic exchange properties [2], the origin of which is not yet understood. A precise understanding of these properties, however, might have important consequences, for example, for the search for organic semiconductors [3] or even for a further understanding of electrical and optical stimulations in biological systems. In addition, these compounds are extensively used for enhancement of weak NMR signals. All these properties and high chemical stability of these radicals are believed to be related to their paramagnetism. These compounds have, therefore, been extensively studied by magnetic resonance techniques. Though, much of the attention has been centered upon 1,1'-diphenyl-2-picryl hydrazyl (DPPH), other free radicals like picryl-N-amino carbazyl, porphyrin etc. have also been studied. The study of electron spin resonance hyperfine spectra in liquid solutions has been undertaken by various workers [4-11]. The study of hyperfine structure in the electron spin resonance spectra plays a very important role in studying the nature and strength of interactions of the electron with its surrounding media. In the present paper the hyperfine structure studies of porphyrin solution in ethyl alcohol (0.05 and

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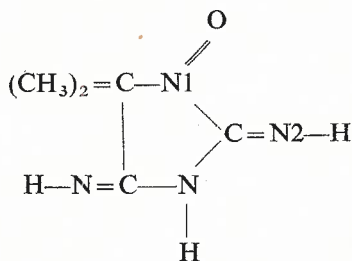
0.005 M strength) have been presented. Nucleus electron coupling constant, linewidth and separation between the lines have been determined. *g*-factor for the two concentrations is also determined. The study of the width of the hyperfine lines and the separation between them has been used to study the mechanism of spin exchange in liquids.

## 2. Experimental procedure

The ESR absorption study of solution of porphyraxide in Anal. R. Grade ethyl alcohol of 0.05 and 0.005 M strength has been made at 9.538 GHz and at 25°C. Precautions were taken to avoid the impurity and modulation broadening effects. A varian E-12,  $\alpha$ -band ESR spectrometer was used.

## 3. Results and discussions

The hyperfine structure in electron spin resonance spectrum of porphyraxide in ethyl alcohol was previously studied by MacLean et al. [12]. These authors studied the hyperfine structure (hfs) of porphyraxide in ethyl alcohol in concentrated solution (of strength 0.02 M). From the ESR spectra they could only find out hyperfine structure coefficient due to nitrogen no. 1 shown by N1 in the following structure of porphyraxide free radical



Hyperfine structure due to nitrogen no. 2 (shown by N2 in above structure) was not resolved in their spectrum because in concentrated solution linewidth of hyperfine lines, due to nitrogen N1, was more than the hyperfine coupling coefficient due to N2. In present investigations the authors have taken ESR spectra of porphyraxide in ethyl alcohol in dilute solution. At 0.005 M hyperfine structure, due to other nitrogen i. e. N2, is quite well resolved. Figs 1, 2 contain ESR spectra at 0.05 and 0.005 M dilutions. Fig. 1 contains only a triplet which is undoubtedly caused by  $\text{N}^{14}$  nucleus which has a spin one. Neither carbon nor oxygen have abundant isotopes with a nuclear spin. In Fig. 2 each line of the triplet due to N1 is further splitted into a triplet due to N2. This inference has been confirmed by molecular orbital (MO) calculations. Simple Hückel Molecular orbital (HMO) calculations were done for porphyraxide radical and they show that further splitting is due to N2 and not to other protons or nitrogens because electron spin density is more on N2 than on other nitrogen atoms or protons.

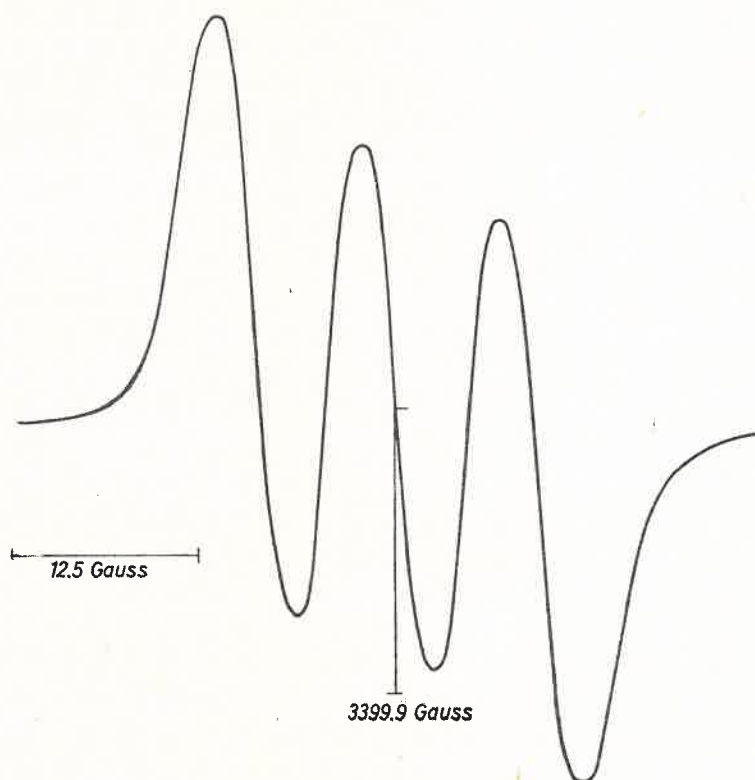


Fig. 1. ESR absorption curve of 0.05M strong porphyrexide solution

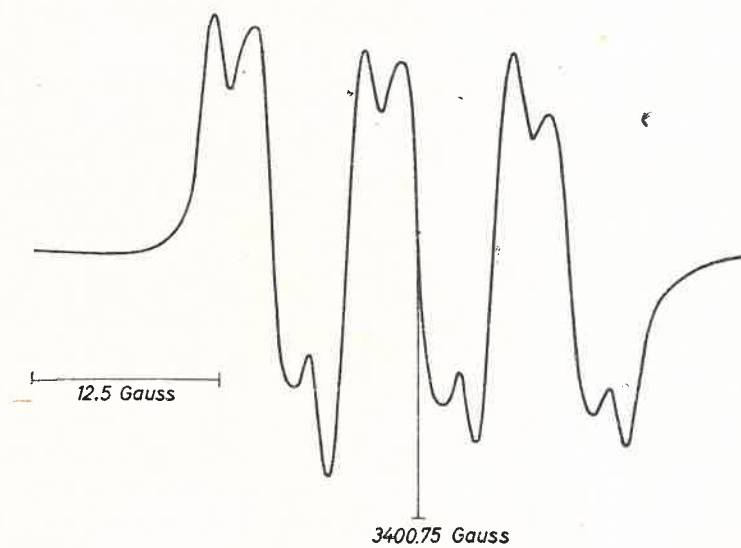


Fig. 2. ESR absorption curve of 0.005M strong porphyrexide solution

The Hamiltonian of the system, taking into account the interaction responsible for the hyperfine structure, is of the form

$$H = g\beta H + A_1 I_1 S + A_2 I_2 S,$$

where  $I_1$  and  $I_2$  are nuclear spins and  $A_1$  and  $A_2$  are hyperfine coupling coefficients between the unpaired electrons and nuclei N1 and N2. The mutual interaction of the two nitrogen nuclei  $I_1 I_2$  is neglected. In ordinary condition, the spectrum obeying this form of Hamiltonian should give nine hyperfine structure components which is the case with porphyrin. The observed hyperfine records for both the concentrations of porphyrin free radical have been analysed by assuming that all the hyperfine lines are of equal width and have equal separation. Line-width of each hyperfine component and the spacing between them (i. e.  $A_1$  and  $A_2$ ) at room temperature (298 K) and 9.538 GHz frequency for 0.05 and 0.005 M strong solution of porphyrin are given in Table I. Extreme hyperfine splitting and  $g$ -value of 0.05 and 0.005 M strong solution of porphyrin in the ethyl alcohol are given in Table II.

TABLE I

Linewidth\*  $\Delta H_{pp}$  of each hyperfine component and the spacing between them at room temperature (298 K) and 9.538 GHz for solution of porphyrin in ethyl alcohol

| Dilution (mol.) | $\Delta H_{pp}$ (Gauss) | $A_1$ (Gauss) | $A_2$ (Gauss) |
|-----------------|-------------------------|---------------|---------------|
| 0.05M           | 5.0                     | 9.5           | —             |
| 0.005M          | 1.5                     | 9.9           | 3.2           |

\* Peak to peak width of each hyperfine line.

TABLE II

Extreme hyperfine splitting\* and  $g$  of solution of porphyrin in ethyl alcohol at room temperature (298 K) and at 9.538 GHz

| Dilution (mol.) | Extreme hyperfine splitting (Gauss) | $g$    |
|-----------------|-------------------------------------|--------|
| 0.05M           | 27.5                                | 2.0050 |
| 0.005M          | 24.3                                | 2.0046 |

\* Distance between extreme maximum slope points.

It is seen from Table I that hyperfine coupling coefficient due to N2 is quite small in comparison with that due to N1 showing that electron spin density on N2 is smaller than that on N1. This is confirmed by HMO calculations done for porphyrin free radical. It is also seen from Table I, that peak to peak linewidth  $\Delta H_{pp}$  of each hyperfine component for 0.05 M strong porphyrin solution is larger than hyperfine coupling coefficient due to N2, hence hyperfine structure due to N2 is not resolved for 0.05 M strong porphyrin solution. From Table I it is also clear that hyperfine coupling coefficient due to

N1 (i. e.  $A_1$ ) is slightly increased with dilution. From Table II, it is seen that  $g$ -value is slightly decreased with dilution which may be due to decreased viscosity in the solution. From Table II, one can also see that extreme hyperfine splitting decreases with dilution. Thus, one can infer like Hausser [13] that the change in electron spin resonance parameters, like hyperfine component linewidth, separation between hyperfine lines and  $g$ -value depend upon the viscosity of the medium. These are various other factors like the effect of dissolved oxygen [14] and other impurities [15] which are found to be more effective in changing the values of various electron spin resonance parameters of most of the free radicals.

#### 4. Conclusions

From Fig. 2 it can be concluded that the hyperfine structure due to N2 can be very easily resolved by diluting the solution of porphyrin to 0.005 M strength. The conclusion drawn by MacLean et al. [12], that the unpaired electron spends most of the time on N1, seems to be wrong since splitting due to N2 is about one third of the splitting due to N1 which is not too small. If oxygen and other impurities are removed and the solution is further diluted, then using a highly sensitive electron spin resonance spectrometer one can resolve the hyperfine splitting due to other protons and nitrogen atoms which are not resolved in the spectra taken by the authors because from molecular orbital calculations it is seen that the unpaired electron spin density on other protons and nitrogen atoms is very small, and 0.005 M dilution is not too small a concentration for the resolution of the splitting of hyperfine structure of other protons and nitrogen atoms.

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