ELECTRON SPIN RESONANCE LINEWIDTH STUDIES OF VANADYL TETRAPHENYLPORPHYRIN

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The linewidths of the hyperfine components of the ESR spectra of vanadyl tetraphenylporphyrin in liquid toluene have been measured as a function of temperature and analyzed in detail. This has allowed the separate contributions to the observed ESR linewidths from spin rotational, g tensor anisotropy, hyperfine anisotropy and unresolved nitrogen hyperfine coupling to be evaluated. These results have been used to estimate the size of the nitrogen isotropic hyperfine coupling constant and thus the extent of delocalization of the unpaired electron onto the nitrogen atoms.

It was suggested in the previous investigation of the electron spin resonance of vanadyl and copper tetraphenylporphyrin[1,2] that the unpaired electron in these complexes are delocalized onto the nitrogen atoms. In the case of copper tetraphenylporphyrin, the unpaired electron is strongly delocalized and causes a resolution of extra superhyperfine structure in the ESR spectrum with $B_N = 1.6$ mT arising from the interaction of the unpaired electron with the four pyrrol nitrogens. On the other hand, no superhyperfine structure has been observed in the ESR spectrum of the analogous vanadyl tetraphenylporphyrin complex so that the extent of the delocalization could not be estimated. However, it is still possible to estimate the size of the nitrogen hyperfine coupling from the contribution which it makes to the width of the lines in the ESR spectra of this compound in solutions. It was therefore decided to analyze in detail the ESR linewidths of vanadyl tetraphenylporphyrin as a function of temperature in order to separate the unresolved nitrogen hyperfine structure contribution from the various other effects which contribute to the linewidths. The estimated value of the nitrogen hyperfine coupling obtained in this way is then used to estimate independently the extent of delocalization of the unpaired electron into nitrogen orbitals.

EXPERIMENTAL

The ESR spectra were recorded on a Varian E-109 spectrometer equipped with temperature control accessory and the temperature was measured with a copper constantan thermocouple. Vanadyl tetraphenylporphyrin was prepared and purified according to literature methods[1,2] and the linewidths of this compound in toluene were measured as a function of temperature. The toluene solvent was repeatedly fractionated and dried with P_2O_5 and the dissolved oxygen was removed by degassing employing successive freezing and thawing of the solution. The viscosity coefficient η of toluene as a function of temperature were taken from ref.[3]. In order to prevent intermolecular interactions from effecting the linewidths of the ESR spectrum, the solution concentrations were reduced until the linewidths ceased to depend on the concentration. This was achieved at 10^{-3} mol dm^{-3}.

RESULTS AND DISCUSSION

The spin Hamiltonian parameters for vanadyl tetraphenylporphyrin were obtained from analysis of the ESR spectra of the compound in liquid and solid solutions by using method already described[4].

The parameters obtained by this method are:

$$g_{\parallel} = 1.9637 \pm 0.0005;\ g_{\perp} = 1.9798 \pm 0.0005;\ g_0 = 1.9744 \pm 0.0005$$

$$A_{\parallel} = 0.0158 \pm 0.0001\ \mathrm{cm}^{-1};\ A_{\perp} = 0.0051 \pm 0.0001\ \mathrm{cm}^{-1};\ A_0 = 0.0087 \pm 0.0001\ \mathrm{cm}^{-1}.$$

These values agree well with those reported by Assour[1] for this compound. Typical ESR spectra for this compound recorded at room temperature and at 77 K are shown in Figs 1 and 2, respectively.

In order to evaluate the isotropic nitrogen hyperfine coupling, it is neccessary to calculate all the other contributions to the linewidths of the ESR spectra. To achieve

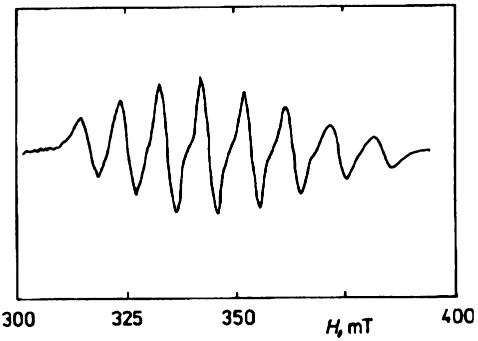

FIG. 1
The ESR spectrum of 10^{-3} mol dm^{-3} solution of vanadyl tetraphenylporphyrin in toluene at 298 K (microwave power 50 mW, magnetic modulation 0.8 mT, microwave frequency 9.52 GHz)

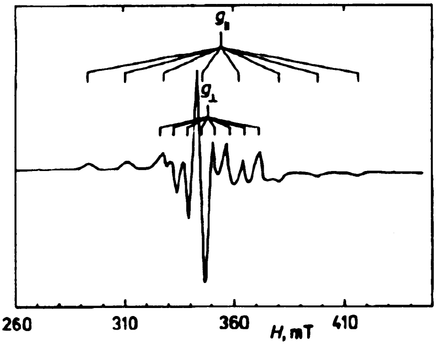

FIG. 2
The ESR spectrum of 10^{-3} mol dm^{-3} solution of vanadyl tetraphenylporphyrin in toluene at 77 K (microwave power 50 mW, magnetic modulation 0.63 mT, microwave frequency 9.38 GHz)

this, the linewidths (ΔH) of the ESR spectra are fitted to the following polynomial equation and the various parameters $\alpha + \alpha' + \alpha''$, β, γ, and δ are in turn obtained by a least squares procedures[5 – 9]

$$\Delta H = \alpha + \alpha' + \alpha'' + \beta m_I + \gamma m_I^2 + \delta m_l^3 , \tag{1}$$

where the parameters α'', β, γ, and δ are given by:

$$\begin{aligned}\alpha'' = {} & (\tau_c /360) (\pi \sqrt{3}\, g_0 B_e /h)^{-1} \{8 (H_0 \Delta\gamma)^2 [4 + 3 (1 + w_0^2 \tau_c^2)^{-1}] \\ & + 9 I (I + 1) b^2 [3 + 7 (1 + w_0^2 \tau_c^2)^{-1}]\}\end{aligned} \tag{2}$$

$$\beta = (\tau_c /15) (\pi \sqrt{3}\, g_0 B_e /h)^{-1} b H_0 \Delta\gamma [4 + 3 (1 + w_0^2 \tau_c^2)^{-1}] \tag{3}$$

$$\gamma = (\tau_c /40) (\pi \sqrt{3}\, g_0 B_e /h)^{-1} [5 - (1 + w_0^2 \tau_c^2)^{-1}] b^2 \tag{4}$$

$$\delta = (\tau_c /10) (\pi \sqrt{3}\, g_0 B_e /h)^{-1} (b^2 A_0 / \frac{h}{2\pi} w_0) , \tag{5}$$

where $\Delta\gamma$ and b are now redefined by

$$\Delta\gamma = (g_{\|} - g_{\perp})\, \beta_e \frac{h}{2\pi} \quad \text{and} \quad b = 2 (A_{\|} - A_{\perp}) / 3 \frac{h}{2\pi} .$$

The parameter α' of the above equation arises from modulation of both anisotropic g and hyperfine tensors; β from a cross correlation between these two; γ and δ from modulation of the anisotropic hyperfine tensor; α'' from the spin-rotational interaction; and α from the unresolved hyperfine coupling, plus any other small contributions which have not been considered above. The values of these parameters at different temperatures are listed in Table I.

According to the kivelson linewidth theory[10,11], the values of γ are usually more precise than the values of β and γ should be proportional to η/T, so it is necessary to check that before using γ in further calculations. This parameter is plotted as a function of η/T in Fig. 3, and it can be seen from the graph that γ provided a good straightline, passing close to the origin, in a good agreement with the theory. By using the spin Hamiltonian parameters obtained for this compound together with the values of γ at each temperature, the rotational correlation times, τ_c, can be calculated from Eq. (*4*). The values of τ_c were then used to calculate α'' from Eq. (*2*). Thus the values of the residual linewidth $\alpha + \alpha'$, could then be calculated since the values of $\alpha + \alpha' + \alpha''$, were already known. The values of τ_c calculated by this way are listed in Table I.

Since the values of α' are proportional to η/T, the contribution of the nitrogen nuclear hyperfine structure, α, to the linewidth can be obtained by fitting the values of $\alpha + \alpha'$, to an equation of the form

$$\alpha + \alpha' = \alpha + kT/\eta ,$$

where k is constant, and the resulting least square fit, which is shown graphically in Fig. 4 is given by

$$\alpha + \alpha' = (1.8 + 0.000139\, T/\eta) \,.\, 10^{-1} \qquad (\text{S. D.} = 0.03)\,.$$

TABLE I
Linewidth parameters in unites of 10^{-1} mT for vanadyl tetraphenylporphyrin in toluene at various temperatures

T, K	$\alpha + \alpha' + \alpha''$	β	γ	δ	$\tau \,.\, 10^{-11}$, s rad^{-1}
338.5	19.85	0.70	0.46	−0.008	3.0
331.0	20.26	0.81	0.62	−0.002	4.1
324.0	20.69	0.92	0.75	−0.010	4.9
315.0	21.10	1.02	0.92	−0.011	6.3
309.0	20.70	1.21	0.98	−0.021	7.0
302.5	21.88	1.32	1.09	−0.012	7.8
295.5	22.00	1.50	1.29	−0.011	8.8
283.5	22.34	1.71	1.47	−0.081	10.0

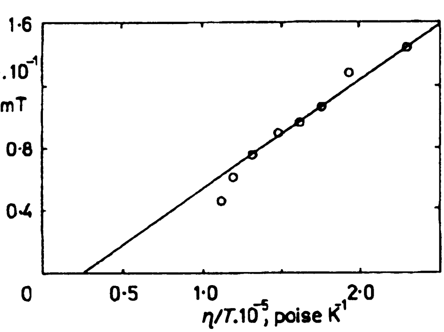

FIG. 3
γ vs η/T for vanadyl tetraphenylporphyrin in toluene

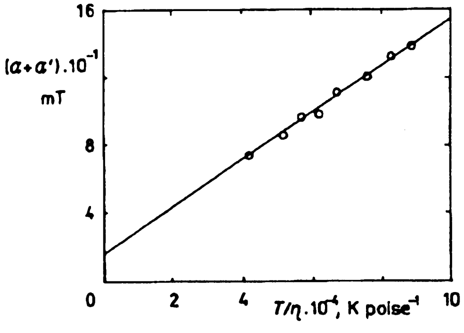

FIG. 4
$\alpha + \alpha'$ vs T/η for vanadyl tetraphenylporphyrin in toluene

As shown in Fig. 4, the contribution to the linewidths from unresolved nitroged nuclear hyperfine structure is 0.18 mT.

Each of the lines in the ESR spectra of vanadyl tetraphenylporphyrin consists of an unresolved 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 multiplet, and so to estimate the size of the nitrogen hyperfine coupling which give rise to a particular contribution to the linewidths, a computer programme has been used to plot out the single line arising from the superposition of the ninth peaks of this type. The spacing between the constituent peaks was simply varied until the width of the single composite line was larger than that of the constituent lines by 0.18 mT. In this way the nitrogen nuclear hyperfine was estimated to be 0.16 mT. Now this value could be used to estimate the extent of delocalization of the unpaired electron available in the complex onto nitrogen atoms.

By setting the value of the nitrogen isotropic coupling constant roughly equal to the largest principal value of the nitrogen spin dipolar interaction $4/7p\ \beta_2^{*2(1)}$, where $\beta_2^{*2(1)}$ is the coefficient of the nitrogen p-orbital in the molecular orbital containing the unpaired electron, and $4/7p$ is the largest principal value of the spin dipolar interaction for one electron in a nitrogen p-orbital which is estimated to be 3.3 mT (refs[12,13]), the value of $\beta_2^{*2(1)}$ was estimated to be 0.048, corresponding to a delocalization of the unpaired electron in the complex of about 4.8%. Thus the linewidth analysis of vanadyl tetraphenylporphyrin confirms that the unpaired electron is in metal ion orbital and very weakly delocalized by about 4.8% onto the nitrogen atoms, in close agreement with the results reached from the ENDOR experiment carried out on this complex[14]. Therefore, it may be concluded that the existence of this very weak delocalization of the unpaired electron in this compound accounts for the absence of the nitrogen superhyperfine structure in the ESR spectrum of vanadyl tetraphenylporphyrin.

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