

1.31, the experimentally determined net total change in frequencies in going from the ground state to transition state is $375 \pm 111 \text{ cm.}^{-1}$. The experimentally measured change is a little more than half of the 565 cm.^{-1} total change.

Badger¹⁶ has devised rules relating the stretching force constant to the equilibrium distance between two atoms. Equation 19, where k is the

$$1/\sqrt{k} = a_{ij} (D_e - b_{ij}) \quad (19)$$

force constant, a_{ij} and b_{ij} are constants depending on the nature of the atoms involved, and D_e is the equilibrium internuclear distance, is valid for the normal as well as the excited states of molecules. Since the frequency of vibration is directly proportional to the square root of the force constant, the internuclear distance is then inversely proportional to the frequency. A set of rules, having the same form, have not, as yet, been shown to be valid for bending frequencies. However, if it is assumed that a similar relationship exists for bending frequencies (in this case, as the carbon-sulfur bond length decreases the carbon-hydrogen bending frequency increases), then one might position the transition state as lying a little more than halfway

(16) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

between the ground state and a fully formed tetrahedral carbon atom having a normal carbon-sulfur bond length.

Now that frequency increments have been determined the $(1 - e^{-u})$ terms can be evaluated. If both the in-plane and out-of-plane bending frequencies are used and calculated separately for 15 and 80°, the products of the ratios are 1.025 and 1.035, respectively. This term changes relatively little in this temperature range and an average value of 1.030 for C can be used to evaluate $(\nu_{\text{H,L}}^{\pm}/\nu_{\text{D,L}}^{\pm})$. The antilogarithm of the intercept is 1.032 ± 0.05 so the ratio of the imaginary frequencies along the reaction coordinate is essentially 1.00 ± 0.05 as expected.¹ Calculation of this term using reduced masses of the fragments involved¹⁷ leads to 1.003. The data are in agreement but unfortunately not precise enough to verify the theoretical calculation of the ratio of imaginary frequencies along the reaction coordinate.

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(17) Ref. 15, p. 30.

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Electron Spin Resonance of Copper Phthalocyanine^{1a}

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The electron spin resonance spectrum of copper phthalocyanine in sulfuric acid was studied at low temperatures. The nitrogen hyperfine structure was observed, and it was found that the nitrogen splitting was smaller in the region near H_{\parallel} than the splitting in the H_{\perp} region. An explanation for this observation is proposed and a bonding parameter reflecting the nature of the copper-nitrogen bond is evaluated. The values of g_{\parallel} and g_{\perp} were determined as 2.180 and 2.037, respectively.

Introduction

A few years ago the paramagnetic resonance of crystalline copper phthalocyanine was reported.² Although the copper hyperfine structure was observed, no evidence of the nitrogen hyperfine structure appeared. It was supposed that the absence of nitrogen hyperfine structure was due either to poor resolution and the small magnetic moment of nitrogen or to a copper-nitrogen bond of high ionic character. Recently we have observed the nitrogen hyperfine structure in copper etioporphyrin II when the compound is dissolved in a suitable solvent such as benzene.³ It was therefore of interest to re-examine the phthalocyanine problem and this report is a summary of our results.

(1) (a) This investigation was supported in part by research grant RG-5144 from the division of General Medical Science, Public Health Service, National Institutes of Health. (b) Socony Mobil Field research, Dallas, Texas.

(2) J. F. Gibson, D. J. E. Ingram and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

(3) E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).

Experimental

The electron spin resonance measurements were made with a Varian model V 4500 epr spectrometer utilizing 100 kc. modulation. The magnetic field was monitored with a Harvey-Wells Model 501 nuclear magnetic resonance gaussmeter. Each spectrum was generally preceded by a spectrum of a benzene solution of DPPH. All measurements of the copper phthalocyanine were made on 0.001 molar solutions in concentrated sulfuric acid. The value of g_{\parallel} could be readily evaluated from the observed spectrum; however, difficulty was experienced in evaluating g_{\perp} because of the overlap of the two patterns. The value of g_{\perp} was obtained therefore from polycrystalline samples using the procedure outlined by Sands⁴ and Kneubühl.⁵

Results and Discussion

Figure 1 shows a typical spectrum of sulfuric acid solution of copper phthalocyanine at -137° . This spectrum is very similar to the spectrum of copper etioporphyrin II in castor oil,³ and it will be noted that the nitrogen hyperfine structure is readily observable. In each case the total spread

(4) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(5) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

of the spectrum is about 800 gauss. The spectra must be analyzed according to the theory of Sands⁴ and Kneubühl.⁵ Due to improved resolution over that obtained in ref. 3, we observe interesting variations in the nitrogen splittings in copper phthalocyanine. The splittings on the copper hyperfine lines near $H_{||}$ are smaller than the splittings on the copper components near H_{\perp} . The

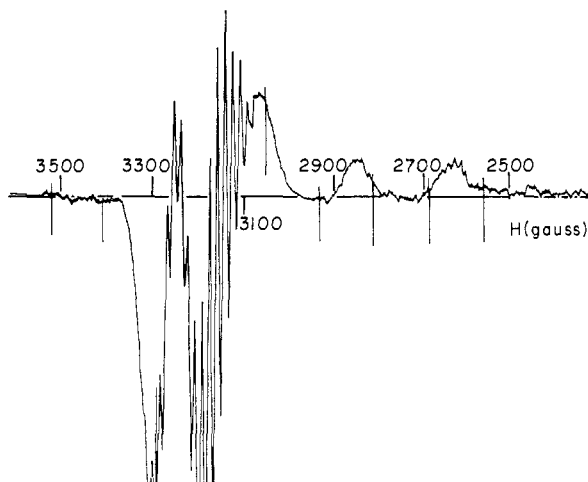


Fig. 1.—Electron spin resonance spectrum of copper phthalocyanine in sulfuric acid at -137° .

difference is undoubtedly due to the anisotropic coupling between nuclear spin and electronic spin since this coupling depends on molecular orientation. We have found the above two spacings in the nitrogen hyperfine structure to be $\Delta\nu_{||} = 13.6$ gauss and $\Delta\nu_{\perp} = 15.4$ gauss, respectively.

The procedure used in the copper porphyrin is followed and the odd electron is placed in the antibonding B_{1g} orbital

$$|B_{1g}\rangle = \alpha |d_{x^2-y^2}\rangle - \frac{\alpha'}{2} [|h_1\rangle - |h_2\rangle - |h_3\rangle + |h_4\rangle]$$

where the $|h_i\rangle$ are hybrid orbitals constructed from appropriate combinations of the nitrogen 2s and 2p atomic orbitals, and $d_{x^2-y^2}$ is the copper 3d atomic orbital. Overlap is included in the B_{1g} orbital and is related to the coefficients α and α' by

$$\alpha' = \frac{1}{2}\alpha S + \sqrt{1 - \alpha^2}$$

S has been calculated as 0.1 for the copper porphyrin complex and a similar value is being assumed for the present case.

Using the same notation as in ref. 3, the hyperfine interaction has the form

$$H = \sum_{n=1}^4 \gamma_n \beta_n \vec{h}(n) \cdot \vec{I}_n$$

where the nitrogen nuclei considered are those of the pyrrole rings and are counted clockwise. $\vec{h}(n)$ is

$$\vec{h}(n) = 2\beta_e \left\{ \frac{8\pi}{3} \delta(r_n) \vec{S} - \frac{1}{r_n^3} \left[\vec{S} - \frac{3(\vec{S} \cdot \vec{r}) \vec{r}_n}{r_n^2} \right] \right\}$$

\vec{r}_n is the vector connecting the n 'th nucleus with the electron. Making the strong field approximation and neglecting the contribution from metal orbitals, we find that the average value of $h_z(n)$ in the ground electronic state is

$$\langle h_z(n) \rangle = 2\beta_e \left(\frac{\alpha'}{2} \right)^2 \left\{ \frac{8\pi}{9} |\rho_n(0)|^2 + \frac{8}{15} \langle r_n^{-3} \rangle P_2^0(\cos \theta_H) \right\} S_z$$

θ_H is the angle between the copper nitrogen bond and the magnetic field. If the magnetic field is directed along the fourfold symmetry axis, the four nitrogen nuclei experience the same h_z and

$$\Delta\nu_{||} = \beta_e \beta_n \gamma_n (\alpha')^2 \left\{ \frac{4\pi}{9} |\rho(0)|^2 - \frac{2}{15} \langle r_n^{-3} \rangle_p \right\}$$

If the magnetic field is in the plane of the molecule, the nitrogen nuclei may be considered to occur pairwise according to $\theta_H = 0$ and $\pi/2$.

The spacings for this case are approximately

$$\Delta\nu_{\perp} = \beta_e \beta_n \gamma_n (\alpha')^2 \left\{ \frac{4\pi}{9} |\rho(0)|^2 + \frac{2}{15} \langle r_n^{-3} \rangle_p \right\}$$

Using the values of $g_{||}$ and g_{\perp} of 2.180 and 2.037, respectively, obtained from these measurements and $|\rho(0)|^2 = 33.4 \times 10^{24} \text{ cm.}^{-3}$,³ we obtain $\alpha = 0.85$ and $\langle r_n^{-3} \rangle_p = 10 \times 10^{24} \text{ cm.}^{-3}$. It is interesting to note that this latter value is significantly lower than the corresponding $\langle r_n^{-3} \rangle_p$ of $21 \times 10^{24} \text{ cm.}^{-3}$ calculated from Hartree numerical wave functions for the free atom case. This probably reflects the covalent character of the copper-nitrogen bond.

It will be noted that our values of $g_{||}$ and g_{\perp} differ from the corresponding values of 2.165 and 2.045, respectively, published by Gibson, *et al.*² We have examined our procedures carefully and could find no reasons for this discrepancy.

Theoretical expressions for $g_{||}$ and g_{\perp} depend on detailed knowledge of various energy differences and on ground and excited state bonding parameters. In order to remove the dependence on excited state bonding parameters, we define an average excitation energy $\overline{\Delta E_i}$ such that

$$\langle 0 | L_i^2 | 0 \rangle / \overline{\Delta E_i} = \sum_{n=0}^{\infty} \frac{| \langle 0 | L_i | n \rangle |^2}{E_n - E_0}$$

$\overline{\Delta E_i}$ will be the average excitation energy, ΔE_{π} , to states whose wave functions have maxima out of the plane of the molecule if $L_i = L_3$ and will be ΔE_{σ} , the average excitation energy to states whose wave functions have their maxima in the plane of the molecule, if $L_i = L_1$. We then obtain

$$g_{||} = 2.023 \left\{ 1 - \frac{\lambda}{\Delta E_{\sigma}} [4\alpha^2 + 0.331 \alpha'^2] \right\}$$

$$g_{\perp} = 2.0023 \left\{ 1 - \frac{\lambda}{\Delta E_{\pi}} \left[\alpha^2 + \frac{1}{3} \alpha'^2 \right] \right\}$$

The choice of ΔE_π or ΔE_σ is now the major problem. The first suggestion to come to mind is to choose ΔE_π as the center of gravity of the optical spectrum. For copper etioporphyrin this choice leads to 24,560 cm^{-1} for ΔE_π .⁶ Using the data of ref. 3, we calculate 0.88 for α compared to an experimental value of 0.86.

In the optical spectrum of copper phthalocyanine⁷ there are two peaks that could be associated with ΔE_π , one at 33,300 cm^{-1} and another at 38,000 cm^{-1} . The former leads to an α of 0.73

(6) J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.*, **98**, 1885 (1946).

(7) P. E. Fielding and F. Gutman, *J. Chem. Phys.*, **26**, 411 (1957).

and the latter to 0.81. The last value is in better agreement with the more reliable value of α obtained from the nitrogen hyperfine splitting. It is of interest to make this comparison of the α 's obtained by these two methods since an estimation of this bonding parameter cannot be made if the nitrogen hyperfine splitting is not observed, as was the case in vanadyl porphyrins.⁸ Consequently, another method such as the evaluation of α from optical data would be welcome if it were reliable.

We are indebted to Professor A. H. Corwin and the E. I. du Pont de Nemours and Company for a pure sample of copper phthalocyanine.

(8) E. M. Roberts, W. S. Koski and W. S. Caughey, to be published.

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Riboflavin as an Electron Donor in Photochemical Reactions¹

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The anaerobic photobleaching of riboflavin, in the absence of added electron donor, has been studied in detail. The photolysis first yields leuco deuteroflavin where the two hydrogens added to the aromatic nucleus have been supplied by the side chain. The leuco deuteroflavin can reduce various substances, being itself oxidized to deuteroflavin. The amount of substrate that can be reduced is limited by the amount of riboflavin initially present. Analysis of the kinetic data indicates that the photoprocess leading to leuco deuteroflavin involves a long-lived excited state which is strongly quenched by the photoproduct itself. The formation of the leuco deuteroflavin involves acid-base catalysis as shown by the increase in quantum yield with increasing buffer concentration. Leuco deuteroflavin is autoxidizable to yield the highly light-sensitive deuteroflavin. The photolysis of this compound also passes through a long-lived state but is not retarded by the presence of its photoproduct, namely, lumichrome.

Introduction

Riboflavin is notoriously unstable under illumination with visible light. Despite the practical importance of this property very few photochemical kinetic studies have been carried out with riboflavin.³ There exists however a considerable body of work on the examination of the organic chemistry of the photoproducts and of other compounds related to riboflavin (see, for example, ref. 4-6).

Riboflavin, like many other dyes,⁷ will undergo photoreduction in the presence of a mild reducing agent or of a tertiary amine. Riboflavin is unique however in that it will also undergo photoreduction even in the absence of an added electron donor for the light excited dye. This behavior has been interpreted to mean that hydrogens are donated by water in the photochemical reaction.⁸⁻¹⁰

Such a reaction occurring under the stimulus of visible light would be energetically unfavorable.¹¹ Furthermore, the practical implications of the postulated reaction are so far reaching that we cannot leave the question unexamined.

It is the purpose of the present paper to present support for the alternative hypothesis for the source of electrons. We suggest that hydrogens are supplied from within the light excited riboflavin molecule itself.

Experimental

Riboflavin in the form of the 5' phosphate ester monosodium salt dihydrate was supplied by Hoffmann-LaRoche, Inc. Other reagents were of Reagent Grade obtained from Fisher Scientific Company. Deionized water was used throughout. Prepurified nitrogen (Matheson) with a reported oxygen content of less than 8 p.p.m. was used for flushing the solutions free of oxygen.

The light source used was a 500 w. tungsten projector (TDC) with a heat absorbing filter and usually fitted with a Corning glass No. 3-74 filter which cuts off light below 400 $\text{m}\mu$. The reaction cell had an optical path length of 1 cm. and a volume of 20 ml. It had provision for bubbling gases through the solution. From the transmitted light the desired wave length band was isolated with the suitable interference filter (Bausch and Lomb) and the light intensity was continuously determined using a silicon solar cell (Hoffman Electronics, Type 2A) as the detector and recorded on a Varian G-10 recorder with 10 mv. full deflection. It was found that the response of the silicon cell was linear only at low intensities and hence the intensity of the light beam was decreased by means of neutral density filters. Those experi-

(1) (a) Presented at the Meeting-in-Miniature of the American Chemical Society, New York, N. Y., March 11, 1960. (b) This research was supported by the Air Research and Development Command under contract number AF 19(604)-3065.

(2) On leave from the Institute of Physical Chemistry, Uppsala, Sweden, and in part supported by the Swedish Natural Science Research Council.

(3) For review of the photochemistry of riboflavin, see G. Oster and B. Holmström, to be published.

(4) R. Kuhn and Th. Wagner-Jauregg, *Ber.*, **66**, 1577 (1933).

(5) P. Karrer, H. Salomon, K. Schöpp, E. Schlittler and H. Fritsche, *Helv. Chim. Acta*, **17**, 1010 (1934).

(6) H. Theorell, *Biochem. Z.*, **279**, 186 (1935).

(7) G. Oster and N. Wotherspoon, *J. Am. Chem. Soc.*, **79**, 4836 (1957).

(8) H. R. Merkel and W. J. Nickerson, *Biochim. et Biophys. Acta*, **14**, 303 (1954).

(9) W. J. Nickerson and G. Strauss, *J. Am. Chem. Soc.*, **82**, 5007 (1960).

(10) L. P. Vernon, *Biochim. et Biophys. Acta*, **36**, 177 (1959).

(11) See for example, E. I. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, Chap. 4, Sec. B5.