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Models of the Cytochromes *b*. 3. Prediction of the Orientation of the In-Plane Heme Symmetry Axis In Unsymmetrically Substituted Low-Spin Hemins from the Temperature Dependence of Their Proton Isotropic Shifts

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The temperature dependence of the isotropic shifts of the one to four pyrrole-H resonances of several symmetrical tetrasubstituted, a series of unsymmetrical para-substituted, and several mono-ortho-substituted tetraphenylporphyrin complexes of low-spin Fe^{III} with *N*-methylimidazole as the axial ligands has been investigated. It has been found that although the Curie plots of individual pyrrole-H resonances of each unsymmetrically substituted complex have unique slopes and intercepts, the average slope and intercept of all symmetrically and unsymmetrically substituted complexes vary linearly with the sum of the Hammett σ constants of the substituents. An analysis of the observed nonzero intercepts of the Curie plots suggests that the deviation of the intercepts from zero is mainly due to the dipolar interaction, with the deviation of the average intercept from zero being a measure of the "tetragonal magnetic anisotropy", which is quite similar for all complexes. The difference between the average and each individual intercept is thought to be a measure of the "in-plane" or "rhombic magnetic anisotropy", and varies greatly among the unsymmetrically substituted complexes of this study. The in-plane angular dependence of the latter term is consistent with our previous assignment of the individual pyrrole-H peaks of the para-substituted complexes. This approach has been successfully extended to an analysis of the isotropic shifts of metmyoglobin cyanide, for which variable-temperature NMR data are available, and in which the axial ligand plane is expected to produce the "in-plane magnetic anisotropy". It appears that, with the methods outlined herein, the direction of the axial ligand planes can be determined from room temperature isotropic shifts of heme proteins, if all four methyl resonances can be observed and assigned.

The NMR spectra of synthetic²⁻⁴ and natural^{2,5-7} porphyrin complexes of high- and low-spin iron(III) have been investigated in detail for some time in the hope of shedding light on the reasons for the unique patterns of methyl resonances observed for the heme proteins.⁸⁻¹⁸ Because

iron(III) is paramagnetic, the porphyrin proton resonances are shifted, generally outside the normal diamagnetic region. For low-spin Fe^{III}, the isotropic shifts have been shown to be due to a combination of contact (through bonds) and dipolar (through-space) contributions²

$$(\Delta H/H)^{\text{iso}} = (\Delta H/H)^{\text{con}} + (\Delta H/H)^{\text{dip}} \quad (1)$$

each of which, in simple cases, has inverse first-order temperature dependence (Curie behavior). That low-spin Fe^{III} porphyrins are not simple cases has been known for some time, for although their Curie plots ($(\Delta H/H)^{\text{iso}}$ vs. $1/T$) are linear, their extrapolated isotropic shifts at infinite temperature are not zero.^{2-4,19,20}

We have recently shown²¹ that unsymmetrically *m*- and *p*-phenyl-substituted tetraphenylporphyrin complexes of low-spin iron(III) have their pyrrole-H resonance split into a pattern of three or four peaks which is fully consistent with the expected electron density distribution in one of the 3e(π) orbitals,²² when modified by the electron-donating or -withdrawing character of the substituent(s). We have also shown²¹ that the extent of this splitting of pyr-

- (1) Recipient, NIH Research Career Development Award, 1976-81.
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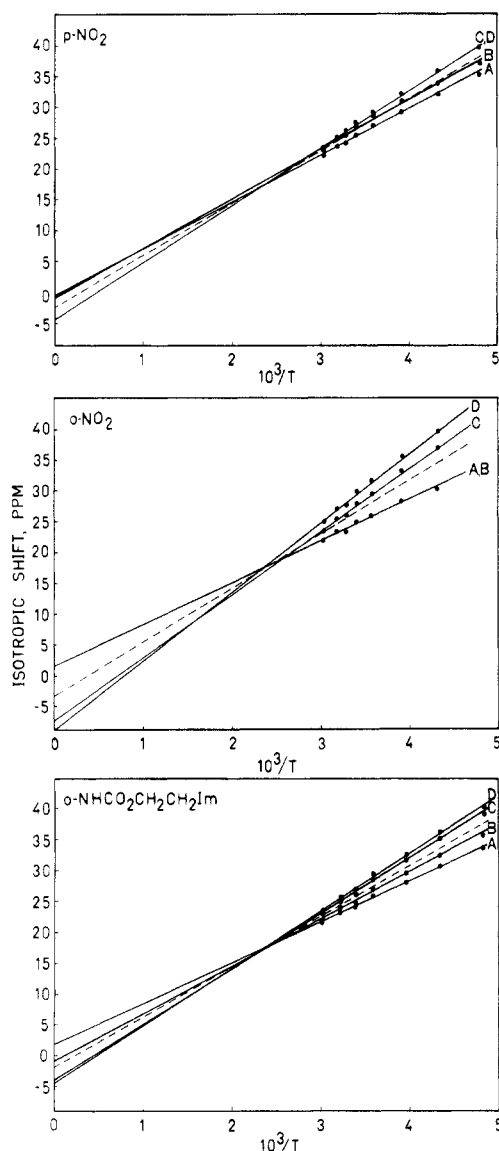


Figure 1. Curie plots for $(p\text{-NO}_2)_2\text{TPPFe}(\text{N-MeIm})_2^+\text{Cl}^-$, $(o\text{-NO}_2)_2\text{TPPFe}(\text{N-MeIm})_2^+\text{Cl}^-$, and $(o\text{-NHCO}_2\text{CH}_2\text{CH}_2\text{Im})_2\text{TPPFe}(\text{N-MeIm})_2^+\text{Cl}^-$. The labels A, B, C, and D are given in order of increasing magnetic field position at ambient temperature. The dotted line shows the temperature dependence of the average isotropic shift of A-D. The sign convention employed is that normally used for paramagnetic complexes, i.e., upfield isotropic shifts are positive and downfield shifts negative.

role-H resonances is dependent upon the difference in Hammett σ constants for the substituents involved. *o*-Phenyl-substituted complexes exhibit a more complex behavior.^{21,23}

In order to more fully explain the effects of unsymmetrical substitution on the pattern of pyrrole-H resonances observed, we have investigated the temperature dependences of the isotropic shifts of the pyrrole protons of a series of symmetrical, unsymmetrical para-substituted, and mono-ortho-substituted tetraphenylporphyrin complexes of Fe^{III} in the presence of *N*-methylimidazole. Several examples of the resulting Curie plots are shown in Figure 1. As can be seen, the individual pyrrole-H resonances have quite different temperature dependences, with different slopes and intercepts for each line. Interestingly, if one plots the average isotropic shift (dashed lines of Figure 1) of the pyrrole-H peaks for each compound against $1/T$, the Curie plots for para-substituted unsym-

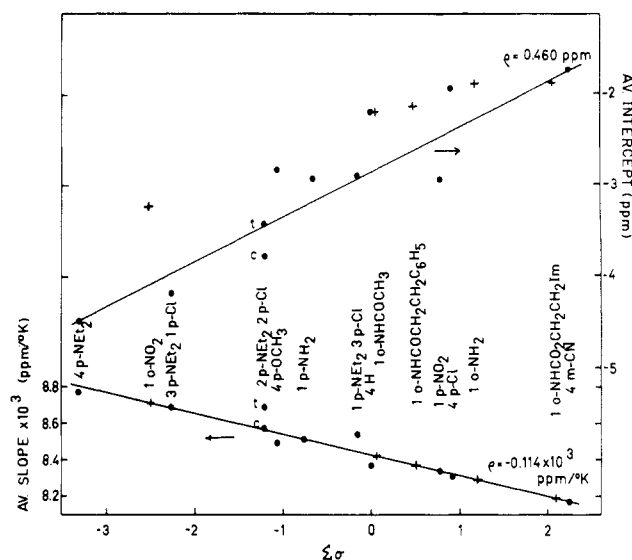


Figure 2. Plot of the average intercept and average slope of each meta- or para-substituted (circles) $\text{TPPFe}(\text{N-MeIm})_2^+$ complex of this study against the sum of the Hammett σ constants²⁴ of the substituents. The average slopes of ortho-substituted complexes (Table I) were used to define "apparent" σ constants for these substituents (crosses). Average intercepts of all complexes show more scatter than do the average slopes, as expected.

metrical and all symmetrical $\text{TPPFe}(\text{N-MeIm})_2^+$ complexes vary systematically in slope and intercept as the sums of the Hammett σ constants of the substituents²⁴ vary, as shown in Figure 2 and Table I.²⁵ This suggests that these low-spin iron(III) porphyrins all have the same basic magnetic characteristics in terms of contact and dipolar interactions, but that in unsymmetrically substituted complexes different portions of each of these are allotted to individual pyrrole positions, depending upon the nature of the phenyl substituent(s) present. To explain this more clearly, let us consider more carefully the contact and dipolar parts of the isotropic shift of eq 1.

The contact contribution to the isotropic shift is more completely written as²⁶

$$(\Delta H/H)^{\text{con}} = -\frac{a_N}{6h\gamma_N\beta} \left\{ \frac{\chi_{xx}g_{xx}}{g_{xx}} + \frac{\chi_{yy}g_{yy}}{g_{yy}} + \frac{\chi_{zz}g_{zz}}{g_{zz}} \right\} \quad (2)$$

where a_N is the Fermi contact coupling constant and the g_{ii} are the spin contributions to the g tensor components g_{ii} .

In systems having a low-lying excited state, such as the low-spin d^5 porphyrins^{19,20} or the high-spin d^4 Cr^{II} symmetrical mixed ligand complexes,²⁷ significant thermal population of the excited-state orbital is expected to make the value of a_N temperature dependent. This could lead to curvature in the Curie plots of such systems if the splitting between ground and first excited states is small. For the cytochromes *b* this splitting has been estimated

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(25) The linear relationships observed for the average slopes and intercepts of symmetrically and unsymmetrically para-substituted $\text{TPPFe}(\text{N-MeIm})_2^+$ derivatives can be used to assign apparent σ constants to the ortho substituents. Those are shown in Figure 2 and listed in Table I in parentheses. The fact that the apparent σ constants do not appear reasonable in terms of expected electronic effects is further confirmation of the fact that hindered rotation of the axial ligand on the same side of the plane as the ortho substituent plays an important role.

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TABLE I: Average Slopes and Intercepts of Curie Plots of *N*-Methylimidazole Complexes of Symmetrically and Unsymmetrically Phenyl-Substituted Fe^{III}TPPs

phenyl substituent	$\Sigma \sigma^a$	av slope, ^{b,c} 10 ⁻³ ppm K	av int, ^{b,c} ppm	individual dev from av int. ^{b,c}			
				A - av	B - av	C - av	D - av
4- <i>m</i> -CN	+2.240	8.17	-1.75				
4- <i>p</i> -Cl	+0.908	8.31	-1.94				
1- <i>p</i> -NO ₂	+0.778	8.34	-2.94	+2.20	+1.69	-1.93	-1.93
4- <i>H</i>	0.000	8.37	-2.20				
1- <i>p</i> -NEt ₂ , 3- <i>p</i> -Cl	-0.15	8.51	-2.90	+1.30	+1.30	-1.58	-1.01
1- <i>p</i> -NH ₂	-0.66	8.52	-2.94	+0.43	+0.43	-0.66	-0.19
4- <i>p</i> -OCH ₃	-1.072	8.49	-2.85				
<i>t</i> -2- <i>p</i> -NEt ₂ , 2- <i>p</i> -Cl ^d	-1.21	8.69	-3.79	+2.08		-2.07	
<i>c</i> -2- <i>p</i> -NEt ₂ , 2- <i>p</i> -Cl ^e	-1.21	8.57	-3.43	-0.17		+0.17	
3- <i>p</i> -NEt ₂ , 1- <i>p</i> -Cl	-2.26	8.69	-4.20	+0.76	+1.09	-0.69	-1.13
4- <i>p</i> -NEt ₂	-3.32	8.77	-4.50				
1- <i>o</i> -NHCO ₂ CH ₂ CH ₂ Im	(+2.1) ^f	8.19	-1.90	+3.80	+1.00	-2.22	-2.51
1- <i>o</i> -NH ₂	(+1.2) ^f	8.29	-1.90	-1.09	-0.94	+0.50	+1.56
1- <i>o</i> -NHCOCH ₂ CH ₂ Ph	(+0.5) ^f	8.37	-2.15	+4.38	+4.24	-4.88	-3.72
1- <i>o</i> -NHCOCH ₃	(+0.1) ^f	8.42	-2.20	+3.73	+3.77	-2.72	-4.76
1- <i>o</i> -NO ₂	(-2.5) ^f	8.71	-3.23	+5.07	+5.07	-4.42	-5.69

^a Sum of the Hammett σ constants of the substituents.²⁴ ^b Chemical shifts in ppm. The sign convention used is that for paramagnetic complexes: Upfield shifts are positive, downfield negative. ^c Calculated from observed chemical shift (-8.93 ppm), the latter diamagnetic correction taken from ZnTPP (F. A. Walker, unpublished work). ^d Trans isomer. ^e Cis isomer. ^f Apparent σ constant, obtained from Figure 2.²⁵

to be ca. 615 cm⁻¹,²⁰ yielding a first excited-state population of 0.049 at room temperature,²⁸ probably small enough to make curvature of the Curie plots of cytochrome *b* models undetectable. However, all contact shifts should converge to Curie behavior as the temperature is raised,²⁷ and at the limit of infinite temperature, where the orbitals are equally populated, all structurally equivalent protons should have the same a_N . This would suggest that, if only the contact term differed for the protons A-D of Figure 1, all lines should intersect at $T^{-1} = 0.0$. In each of the systems of this study, the lines do tend to intersect at a point, but at $T^{-1} \sim (2.0-2.3) \times 10^{-3} \text{ K}^{-1}$, or 430-500 K. Thus, while temperature-dependent a_N values may contribute to the individual slopes of the Curie plots for the protons A-D of Figure 1, we must look to the dipolar shift, eq 3, for an explanation of the observed intercepts.

The dipolar contribution to the isotropic shift is usually written as²⁹

$$(\Delta H/H)^{\text{dip}} = -\frac{1}{3N}\{\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})\}\left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle - \frac{1}{2N}\{\chi_{xx} - \chi_{yy}\}\left\langle \frac{\sin^2 \theta \cos 2\Omega}{r^3} \right\rangle \quad (3)$$

where θ and Ω are the familiar polar coordinate angles relating the line of length r , which connects the metal center and the proton of interest, to the z axis (θ) and its projection on the x,y plane (Ω), and χ_{zz} , χ_{yy} , and χ_{xx} are the magnetic susceptibilities along the three principal axes. This equation is often reduced to the familiar

$$(\Delta H/H)^{\text{dip}} = \frac{-\beta^2 S(S+1)}{9kT}(g_{\parallel}^2 - g_{\perp}^2)\left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle$$

in cases where the complex possesses axial symmetry and there are no thermally accessible excited states so that g^2 is directly proportional to χ . However, Horrocks and Greenberg^{19,20} have shown that, for low-spin Fe^{III} por-

phyrins, χ contains both first- and second-order Zeeman (FOZ, SOZ) contributions which lead to the nonproportionality of g^2 and χ and produce nonzero intercepts for the Curie plots such as those of Figure 1. In particular, the FOZ contributions are expected to be very temperature dependent and lead to very negative intercepts and the SOZ contributions to be only weakly temperature dependent and have positive intercepts. Additional dipolar contributions from thermal depopulation of the ground state and population of the first excited state Kramers doublets may also be involved.²⁰

Whatever the detailed contributions to the dipolar shift may be, the similar average slopes and average intercepts (with slight dependence on $\Sigma \sigma$) observed for the compounds of Table I and Figure 2 suggest that the contact term (eq 2) and the first term of eq 3, which we will call the "tetragonal magnetic anisotropy term", make similar contributions to the temperature dependence of each of these low-spin hemins. The difference in dipolar shift contributions to each line A-D must therefore come from the second term of eq 3, which we will call the "rhombic magnetic anisotropy term". These differences are probably most clearly manifested by the intercepts of the Curie plots, since the differences in slopes are probably largely due to the contact contribution^{2-4,20} (eq 1,2).

In addition to the average slopes and intercepts of the Curie plots, Table I also lists the deviations of each individual line (A-D) from the average intercept for that particular unsymmetrical compound. We note first that these individual intercepts for pyrrole-H types A-D vary significantly from compound to compound, indicating that the "in-plane" or "rhombic magnetic anisotropy" varies greatly among the unsymmetrical compounds of this study. Furthermore, the magnitude of the deviations of A-D from the average intercept is in some cases comparable to the ambient temperature calculated dipolar contribution to the isotropic shift of TPPFe(Im)₂⁺ (ca. 5.8 ppm at 29 °C).²⁻⁴

The second point to be noted about the intercepts of the individual lines A-D presented in Table I is that they are "symmetrical", with A and B of the same sign and similar magnitude and the same for C and D, with the net intercepts of A, B of opposite sign to C, D. This provides further confirmation of our previous assignment²¹ of the

(28) Reference 20 lists a first excited-state population of 0.029 at 294 K, but for $\Delta E = 615 \text{ cm}^{-1}$ we calculate the exponential term to be 0.049 at 294 K.

(29) Jesson, J. P. In "NMR of Paramagnetic Molecules"; LaMar, G. N.; Horrocks, W. D.; Holm, R. H., Ed.; Academic Press: New York, 1973; p 18.

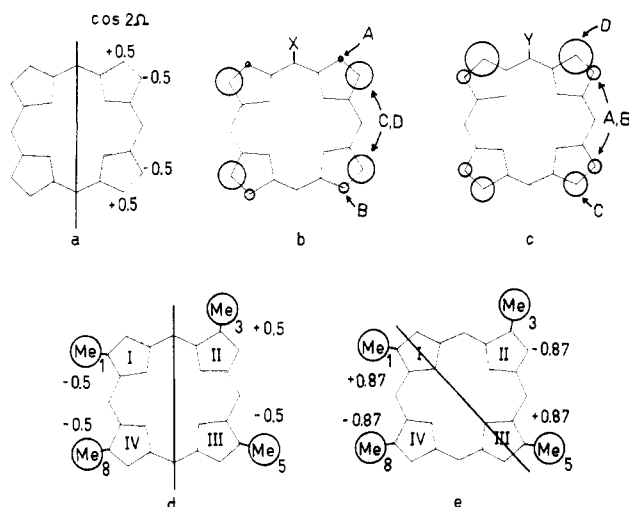


Figure 3. (a) Angular dependence of $\cos 2\Omega$ for meso-substituted TPPs. (b) Assignment of pyrrole-H resonances for unsymmetrical TPPs having one electron-withdrawing group at a meso position;²¹ (c) assignment of pyrrole-H resonances when one electron-donating group is present at a meso position;²¹ (d) Signs of $\cos 2\Omega$ for methyl groups of protoporphyrin IX when the $3e(\pi)$ nodal plane passes through the meso positions (all signs reverse if the nodal plane passes at 90° to that shown); (e) signs of $\cos 2\Omega$ for methyl groups when the $3e(\pi)$ nodal plane passes through the nitrogens of rings I and III (all signs reverse if the nodal plane passes through II and IV).

pyrrole-H peaks for the para-substituted complexes, since the in-plane angular dependence, $\cos 2\Omega$, has the predicted signs of A and B opposite those of C and D (Figure 3a). This suggests that it may soon be possible to assign the location of protons of types A–D in the ortho-substituted complexes.²⁵ Further work is in progress toward this end, as well as toward the calculation of the magnitude of dipolar and contact contributions to the slopes and intercepts of the individual lines A–D in order to test quantitatively the conclusions reached thus far.

The present work points out an important feature concerning the natural porphyrins and the heme proteins: Since the methyl groups of protoporphyrin IX are unsymmetrically distributed, the net intercepts of the four methyl resonances, obtained from a study of the temperature dependences of their isotropic shifts, should allow definition of the position of the nodal plane of the porphyrin orbital involved in unpaired electron delocalization. If the nodal plane, as defined by axial ligand planes and/or porphyrin substituents, lies through the meso positions, then the temperature dependence of the isotropic shifts of methyls 1, 5, and 8 should extrapolate to similar intercepts, on one side of the average intercept calculated from $I_{av} = 1/2[(I_1 + I_5 + I_8)/3] + I_3$, while methyl 3 should extrapolate to a different intercept, on the other side of the average, since $\cos 2\Omega$ is of opposite sign at this position (Figure 3d). If the nodal plane lies through the nitrogens of opposite pyrrole rings, for example I and III, then the Curie plot intercepts of methyls 3 and 8 should lie on one side of the average intercept calculated from $I_{av} = 1/4(I_1 + I_3 + I_5 + I_8)$, while those of 1 and 5 should lie on the other (Figure 3e). Since the intercepts of all four methyls of (protoporphyrin IX)Fe(CN)₂⁻ (where there are no axial ligand planes) are very similar,^{2,30} but are in the order $3 < 1 < (5, 8)$ looking upfield, it appears that the inherent $3e(\pi)$ orbital nodal plane passes through the meso positions, probably vertically. There is only a small "rhombic magnetic anisotropy" in this molecule, as evidence by the

small spread in methyl peak intercepts.^{2,30}

The temperature dependence of the methyl resonances is available for only one heme protein, to our knowledge, for which a related molecular structure is known: porpoise myoglobin cyanide.⁹ Since Wüthrich's original report,⁹ three of the methyl resonances have been assigned,¹¹ and it has been shown that the fourth peak attributed to a porphyrin methyl group by Wüthrich⁹ is due to some other protein residue.¹¹ More recently it has been shown³¹ that the fourth methyl resonance is slightly upfield from HDO (isotropic shift of ca. -0.5 ppm) and is nearly independent of temperature. This fact, combined with the temperature dependence of the other three methyl groups, from Figure 23 of ref 9, leads to a Curie plot in which all of the methyl isotropic shifts cross close to $1.2 \times 10^{-3} \text{ K}^{-1}$, or ca. 830 K.³² This extrapolation predicts that the average isotropic shift of the four methyls at infinite temperature should be +2.1 ppm if the nodal plane passes through the meso positions (Figure 3d) or +4.1 ppm if the nodal plane passes through the nitrogens (Figure 3e). The extrapolated shifts are quite different: +10.0(5), +5.9(1), +2.2(8), and -1.9(3) and are paired 5,1 and 8,3. Unfortunately, there is not a good model system with which to compare these results, since it is likely that the imidazole plane of model PFe(Im)CN and PFe(Im)₂⁺ complexes, where P is a natural porphyrin, takes up preferred orientations with respect to the porphyrin substituents as the temperature is lowered.³⁴ If the only available model, PPF(CN)₂,^{2,30} is used, the average extrapolated isotropic shift is -2 ppm. If we allow several ppm leeway for the difference in one of the axial ligands, it would still seem that the myoglobin data are more consistent with the axial imidazole plane lying over the meso positions, in terms of extrapolated isotropic shift. However, the wide spread of the intercepts makes this conclusion suspect, and indeed, recent X-ray crystallographic studies have shown that, at least in the solid state of oxymyoglobin,^{35,36} the axial imidazole plane lies over pyrrole ring II (90° rotation from that shown in Figure 3e). Thus it would appear that widely spaced intercepts, with methyls 5 and 1 on one side of the average and 3 and 8 on the other, rather than their numerical average, are a better clue to the orientation of the axial ligand plane.

To test this hypothesis on other heme proteins for which the temperature dependence of the methyl resonances has not been reported, we have taken the room temperature isotropic shifts for the ferric forms of cytochrome *b*₅¹⁶ and cytochrome *c* cyanide,³⁹ assumed that the lines of all four methyl resonances cross at $T^{-1} = (1.0\text{--}1.5) \times 10^{-3} \text{ K}^{-1}$ at an isotropic shift which is similar to that of the appropriate model compound, and extrapolated the isotropic shifts to $T^{-1} = 0.0$. (It is likely that PPF(CN)₂ is a reasonably appropriate model for all low-spin Fe^{III} heme proteins.³⁴)

(31) Budd, D. L., Ph.D. Dissertation, University of California, Davis, 1978.

(32) The difference in the temperature of the crossing point from that of the cytochrome *b* models of the present study may reflect the difference in electronic effects of the protoporphyrin IX substituents as compared to tetraphenylporphyrins, since the nitrogens of protoporphyrin IX are somewhat stronger bases than those of tetraphenylporphyrin.³⁴

(33) Hambright, P. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 234–8.

(34) LaMar, G. N., personal communication.

(35) Phillips, S. E. V. *Nature (London)* 1978, 273, 247–48.

(36) The structures of aquometmyoglobin³⁷ and deoxymyoglobin³⁸ both show the imidazole plane to be rotated 19° from the N_{II}–N_{IV} line, but both of these proteins contain high-spin iron which is shifted out of the porphyrin plane in the direction of the imidazole ligand. Thus it would seem that the oxymyoglobin structure provides the more reliable comparison to that of metmyoglobin cyanide.

(37) Takano, T. *J. Mol. Biol.* 1977, 110, 537–68.

(38) Takano, T. *J. Mol. Biol.* 1977, 110, 569–84.

(39) Smith, M.; McLendon, G. *J. Am. Chem. Soc.* 1981, 103, 4912–21.

(30) Viscio, D. B., Ph.D. Dissertation, University of California, Davis, 1977.

For cytochrome b_5 the intercepts are widely spaced (with methyls 1 and 3 having very similar intercepts), and the average of the four is ca. -2.4 ppm, similar to that predicted for $\text{PPFe}(\text{Im})_2^+$ in CDCl_3 ⁶ if it also crosses the b_5 lines at the same value of T^{-1} (-1.2 ppm). This suggests that the ligand planes lie over the pyrrole nitrogens, as they are known to do in the solid state.⁴⁰ For cytochrome c cyanide, however, the intercepts of methyls 5, 8 and 1 are clustered together and centered at ca. +0.6 ppm, while methyl 3 has an intercept of ca. -6.7 ppm. The average thus calculated is -3 ppm. The histidine imidazole plane is thus predicted to lie through the meso positions, in

agreement with the solid-state structure of cytochrome c .⁴¹ Thus it appears that the orientation of the axial ligand planes in heme proteins can be predicted by the methods outlined above.

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(41) Dickerson, R. E.; Takano, T.; Eisenberg, D.; Kallai, O. B.; Samson, L.; Cooper, A.; Margoliash, E. *J. Biol. Chem.* 1971, 246, 1511-35.

Interaction of Gas-Phase Deuterium Atoms with Silica Surfaces

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Two silica surfaces, Cab-O-Sil and porous Vycor glass, were exposed to D atoms cleanly generated in the absence of ions and electrons in a flow system, and the surfaces followed by infrared spectrometry. While it was established some time ago that hydrogen atoms adsorb on silicates, we report here evidence for a chemical reaction of D atoms with these surfaces, resulting in the formation of SiO-D bonds. In the case of Cab-O-Sil, the existing SiO-H groups decreased simultaneously, indicating that the mechanism of formation of SiO-D was an exchange reaction. However, in the case of porous glass the existing SiO-H did not decrease significantly, indicating that a different mechanism of formation of the SiO-D must be operative.

Introduction

Since 1912 it has been known¹ that gas-phase atoms and free radicals can be removed at the borosilicate glass surfaces of conventional laboratory reactors. Such heterogeneous processes can be especially significant, for example, in fast flow discharge systems² where species such as H and OH are observed to decay at the walls along the length of a flow tube having untreated "clean" glass surfaces.

Silica surfaces, especially porous Vycor glass, are thought to be similar in many respects to the borosilicate glass surfaces of conventional laboratory reactors. A great deal of work³ has been carried out on the reactions of stable molecules with various types of silica⁴ and, in particular, with the surface hydroxyl groups which can be readily followed by using infrared absorption spectroscopy.³ The

interactions of atoms and free radicals with such surfaces have also been studied, primarily by ESR, and the physical adsorption of such reactive species on these surfaces has been firmly established.⁵

In several studies, silica surfaces have been exposed directly to plasmas in various carrier gases and the surface itself observed with IR. For example, Tiller et al.⁶ exposed pressed silica pellets to an H_2 plasma. The formation of stable surface Si-H bonds was observed when the pellet had been preheated to drive off adsorbed water, suggesting that some reactive species produced in the plasma was reacting with the surface. Exposure of an unheated pellet led to new IR bands in the 2100-2300- cm^{-1} region (which disappeared on extinguishing the plasma) as well as a decrease in the bands due to adsorbed water. The reaction of free radicals or ions to produce an unstable surface species was suggested as an explanation of the 2100-2300- cm^{-1} bands. Low and co-workers⁷ applied an rf discharge in H_2 to a Vycor surface and followed the surface SiO-H by IR; no change in the absorption band was ob-

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(4) The silica surfaces commonly used in these studies are porous glass and pressed disks of silica powder. Porous glass has a gross composition on the basis of its ignited weight of 96% SiO_2 , 3% B_2O_3 , 0.4% R_2O_3 + RO_2 (mainly Al_2O_3) and traces of Na_2O and As_2O_3 . Silica powders such as Cab-O-Sil are a nonporous powder containing only silicon oxide and are usually prepared by the flame hydrolysis of tetrachlorosilane.

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