of **3** by treatment with trifluoroacetic acid, the activated porphyrin ester **5**[8] was reacted with the peptide segment in DMSO–DMF for 2 days at 50 °C. The precipitated products were collected (57%), treated with TMSOTf/thioanisole/trifluoroacetic acid reagent[9] in order to remove all protecting groups, and then subjected to reverse phase HPLC (Vydac C18 column, 20 mM Et_3N/H_3PO_4 pH 6.5, 30%–80% acetonitrile linear gradient for 30 min). A major peak at 63% acetonitrile was collected (37%) and was found to be the desired compound.[10]

Helichrome **1** is very soluble in buffer (over 1 mM in 20 mM phosphate, 0.16 M KCl pH 7.5) and is practically insoluble below pH 3 as expected from its peptide sequence. One of the most remarkable characteristics of **1** is the high α-helical content (ca. 70%) indicated by its CD spectrum in the aqueous buffer solution, whereas single peptide **2** alone exhibited a typical CD pattern of a disordered conformation[11] under identical experimental condition as shown in Figure 3. Helichrome **1** was found to be monomeric under the condition of the CD measurement based on both gel filtration on Sephadex G-50 and sedimentation equilibrium experiments (MW_{app} = 7200 ± 500); in accord with an intramolecularly folded state of the molecule. These observations strongly suggest that the close proximity of porphyrin-linked peptide segments induces the amphiphilic α-helical structure and then facilitates a spontaneous formation of the folded tertiary structure. Buffer solution of **1** showed a red-shifted fluorescence maximum at 617 nm, which indicated a moderately hydrophobic environment around the porphyrin ring[12] and provided further experimental support for the proposed structure of **1** in solution.

We next examined the aniline hydroxylase activity of the Fe(III) complex **1a**[13] of helichrome **1**. The formation of *p*-aminophenol was monitored[14] at varying aniline concentration and fixed concentrations of **1a** (3.1 μM), 7-acetylflavin (0.24 μM), and NADPH (2.5 mM) in 20 mM $N\alpha$-acetyl histidine buffer pH 7.0. A double-reciprocal plot of the rates for various concentrations of aniline was linear and provided $k_{cat} = 0.02$ min^{-1} and $K_m = 5.0$ mM. A series of control experiment showed that every component except 7-acetylflavin[15] in the reaction mixture was essential to the hydroxylase activity. Fe(III) coproporphyrin I (4.7 μM) showed negligible aniline hydroxylase activity[16] under the same conditions, demonstrating a significant contribution of the peptide segments to catalysis by **1a**, most probably by providing binding pocket(s) for the substrate(s). Furthermore, the observed hydroxylase activity of **1a** was completely inhibited by catalase (100 units) but not by superoxide dismutase (SOD) (10 units). Several hemeproteins[17] such as hemoglobin, indoleamine 2,3-dioxygenase, and L-tryptophane 2,3-dioxygenase have been reported to catalyze the hydroxylation of aniline in the presence of oxygen and an appropriate reducing system with k_{cat} and K_m values ranging from 0.02 to 0.65 min^{-1} and from 3.7 to 5.4 mM, respectively. Their activities are inhibited by both catalase (completely at 100 units) and SOD (ca. 50% with 10 units), suggesting possible involvement of peroxide type intermediates in the catalytic cycle.[17] Although our system requires further experimentation to define its catalytic mechanism, the above results clearly demonstrate that **1a** has a hydroxylase activity quite similar to that of native hemeproteins.

In conclusion, our preliminary work has established that helichrome **1** and its iron complex are a first generation model hemeprotein based on a synthetic peptide. It is worth noting that the folding process of such a synthetic protein could be simplified by the introduction of an appropriate organic compound as seen in the present system. Detailed mechanistic investigation of the catalysis by **1a** and further structural characterizations of **1** are now in progress.

Acknowledgment. This work was funded in part by National Science Foundation Grant CHE8418878 (E.T.K.). We thank Dr. Toshio Kokubo for many useful discussions and performing preliminary experiments for the synthesis of the activated esters of coproporphyrin I. We also thank Professor Stephen J. Benkovic for providing helpful suggestions for writing the manuscript and Dr. Mark A. Findeis for valuable discussions and reading the manuscript. All mass spectra were taken by Dr. Brian Chait at the Rockefeller University Biotechnology Mass Spectrometric Research Resources, supported by National Institutes of Health Grant RR-00862-14. CD spectra were measured on an Aviv 60DS supported by National Science Foundation Grant PCM8400268 in the laboratory of Dr. David Cowburn.

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(8) Coproporphyrin I **4** was converted to the corresponding tetrahydroxysuccinimide ester **5** which was characterized by IR, MS, HPLC, and NMR after reacting with excess L-Ala-*tert*-butyl ester and was sufficiently pure (over 90%) for the next coupling reaction with the protected peptide segment.

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(10) **1**:UV (20 mM phosphate, 0.16 M KCl, pH 7.5) 397, 499, 534, 564, and 616 nm; amino acid analysis (hydrolysis in 1:1 propionic acid–HCl for 3 h) yielded the following (calibrated to Leu) (Glu + Gln) 33.3 (32), Ala 8.48 (8), Leu 20.0 (20); MS (^{252}Cf fission fragment ionization) m/z for $(M + H)^+ = 7598.9$, theoretical 7598.7.

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(12) Coproporphyrin I exhibited fluorescence maxima at 611, 616, and 620 nm in a buffer (1 mM phosphate, pH 7.0), 20% dioxane, and 50% dioxane, respectively.

(13) (a) Iron was incorporated by a reported procedure[13b] with slight modifications. Helichrome (**1**, 3 mg) was dissolved in AcOH–TFE (6:4, 1 mL) and reacted with excess $Fe(OAc)_2$ at 70 °C for 30 min. Solvent was removed under reduced pressure, and the residues were taken up with a buffer (5% $NaHCO_3$, 0.1 M EDTA, 0.5 mL). Excess iron and salts were removed by gel filtration on Sephadex G-25. Purity was confirmed by reverse phase HPLC, and no starting material was detected. **1**a: UV (20 mM $N\alpha$-acetylhistidine, pH 7.0) 394, 491, 518 (sh); and 610 nm. (b) Sano, S. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. VII, p 377.

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Molecular Recognition of Alcohols by Layered Compounds with Alternating Organic and Inorganic Layers

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Vanadyl alkylphosphonates are a new family of compounds that can recognize primary alcohol molecules and selectively discriminate among various branched isomers. They are examples of layered solids with alternating inorganic and organic layers, intriguing materials that can exhibit useful sorptive and catalytic properties and can serve as microcrystalline bulk models for interfacial systems.[1-10] Vanadium alkylphosphonates undergo

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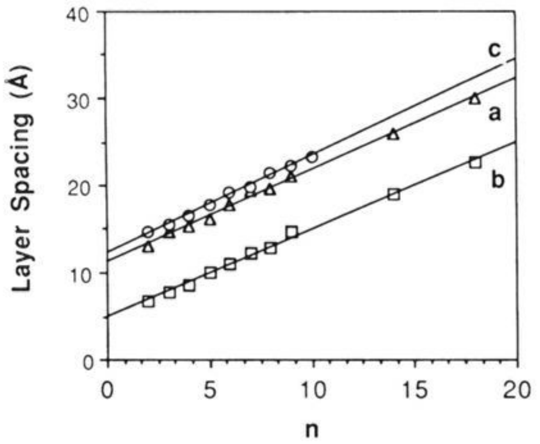


Figure 1. Layer spacings of vanadyl alkyl phosphonates as a function of either alkyl phosphonate chain length or intercalated alkanol chain length: (a) $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$, (b) $VO(C_nH_{2n+1}PO_3)\cdot H_2O$, (c) $VO(C_6H_{13}PO_3)\cdot H_2O\cdot C_nH_{2n+1}OH$. Slopes and intercepts of the lines from least-squares fits are (a) 1.05 Å/CH_2, 11.27 Å; (b) 1.01 Å/CH_2, 4.92 Å; and (c) 1.11 Å/CH_2, 12.32 Å.

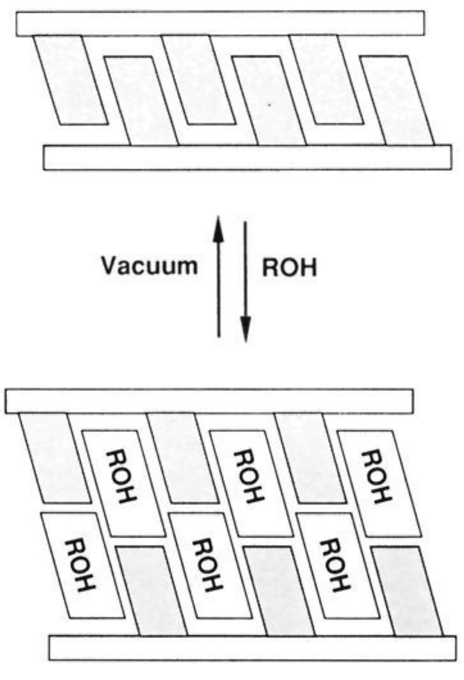
coordination intercalation reactions with alcohols R′OH rapidly at room temperature. The intercalated phases with composition $VO(RPO_3)\cdot H_2O\cdot R'OH$ have alkyl groups (R′) from alcohol molecules coordinated to vanadium atoms in the layers packed in the interlayer space with the R groups attached to phosphorus. The relative sizes and shapes of R and R′ can generally be used to influence the selectivity and the rate of alcohol intercalation.

The vanadyl alkylphosphonates are synthesized by stirring powdered V_2O_5 with a hot alcoholic solution of alkylphosphonic acid to which a small amount of aqueous mineral acid catalyst has been added.[11]

$$V_2O_5(s) + 2RPO(OH)_2(soln) + 3C_6H_5CH_2OH \xrightarrow[85\ °C]{H^+} 2VORPO_3\cdot H_2O\cdot C_6H_5CH_2OH(s) + C_6H_5CHO + H_2O$$

The benzyl alcohol serves not only as a solvent for the phosphonic acid but also as a reductant for $V^{(V)}$ to $V^{(IV)}$ and an intercalant in the solid product. Microcrystalline products are produced with well-defined X-ray diffraction patterns which can be indexed with orthorhombic cells having *a* and *c* axes of ~10 Å and *b* axes that vary with the size of the alkyl group. From the similarity in the lattice constants, the crystal structure of the vanadyl alkylphosphonates is expected to be analogous to that proposed for the vanadyl arylphosphonates[10] in which VO_6 octahedra in each layer have the connectivity indicated in the formula $VO_{1/1}O_{3/2}$-$(H_2O)_{1/1}(R'OH)_{1/1}RPO_{3/2}$ and share corners with the three oxygens of the phosphonate group. Water is coordinated in the fourth planar equatorial position of the vanadium atoms in the layers, while the vanadyl oxygen and R′OH complete the octahedral coordination of vanadium in the axial positions with the R′ group extending away from the layer. The P–C bond of the alkylphosphonate is also approximately perpendicular to the inorganic layer. The topology of this proposed layer structure is identical with that of the mineral newberyite,[12] $MgHPO_4\cdot 3H_2O$, with two trans water molecules replaced by the vanadyl oxygen and the coordinated alcohol molecule in $VORPO_3\cdot H_2O\cdot R'OH$.

Scheme I



Thermogravimetric analyses indicate that the intercalated alcohols may be removed by heating the solids in an inert atmosphere at 50–150 °C, depending on the volatility of the alcohol, and that the compounds contain 0.7–1.0 alcohol molecule per formula unit. The exact alcohol content depends on the drying conditions used prior to the analysis. The upper limit confirms that the intercalated alcohols are associated with specific sites on the interlayer surface. In contrast, the water molecule is not lost until the sample is heated beyond 180 °C, consistent with its equatorial coordination to the vanadium atom. The removal of the equatorial water molecule is irreversible and causes the structure to become amorphous.

In Figure 1, the layer spacings of $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$ (**1**) for $n = 2$–9, 14, and 18 are plotted as a function of the alkyl chain length *n* in line a. The benzyl alcohol can be removed from these compounds by heating in vacuo at 110 °C. The resulting $VO(C_nH_{2n+1}PO_3)\cdot H_2O$ compounds are crystalline, and their powder X-ray diffraction patterns can be indexed on unit cells in which the *a* and *c* axes are unchanged from those of the $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$ precursors, while the *b* axes, which correspond to the layer spacings, are reduced by ~6.3 Å. In line b of Figure 1, the layer spacings of the vacuum dried compounds are plotted. Lines a and b are parallel with slopes of 1.00 and 1.05 Å/CH_2 unit, respectively. From these slopes the arrangement of the alkyl groups in the interlayer space can be inferred. An all *trans*-polymethylene chain has a repeat distance of 1.27 Å/CH_2. Hence, if the alkyl chains attached to the phosphonate groups which project into the interlayer space were perpendicular to the layers and were arranged in a bilayer, we would expect the slope of the lines in Figure 1 to be 2.54 Å. Since the slope is less than half of this value, the alkyl groups from one

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(11) For example, finely ground V_2O_5 (273 mg, 1.5 mmol) is added to a solution of *n*-hexylphosphonic acid, $(C_6H_{13})PO(OH)_2$ (548 mg, 3.3 mmol), in 30 mL of benzyl alcohol, $C_6H_5CH_2OH$ plus 0.9 mL of 1 M HCl (50 mmol H_2O, 0.9 mmol HCl). While stirring and heating at 85 °C for 6 h, the orange V_2O_5 suspension becomes green and then blue as the reaction proceeds. Without the addition of mineral acid, the reaction takes 3–14 days. The product (95%) is isolated by filtration, washed with ether, and dried under a stream of nitrogen. Lattice constants for the orthorhombic cell determined by least-squares refinement of X-ray powder diffraction data are $a = 10.06$ (1) Å, $b = 18.81$ (2) Å, $c = 9.84$ (1) Å. Anal. Calcd for $VO(C_6H_{13}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$: C, 43.71; H, 6.49; V, 14.26; P, 8.67. Found: C, 41.71; H, 6.30; V, 14.50; P, 9.19. The P/V ratio is 1, but the values of P and V found are high while C and H are low, implying that there is less than one alcohol molecule per vanadium.

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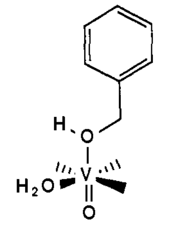
layer must interpenetrate those of the adjacent layer. Furthermore, the chains must not be perpendicular to the layer but must be slanted at an angle equal to $\sin^{-1} 1.05/1.27$ or 56°. This is the angle expected for a P–C bond that is perpendicular to the inorganic layers. A schematic representation of the packing of the alkyl chains and the alcohol molecules in the interlayer region is given in Scheme I.

Alcohol molecules are readily reabsorbed into the interlayer region of $VO(C_nH_{2n+1}PO_3)\cdot H_2O$ by contacting the dried precursor with alcohol at room temperature. Not only can benzyl alcohol be reabsorbed to regenerate the initial compounds, but a variety of other alcohols can intercalate as well. When treated with *n*-pentanol, the $VO(C_nH_{2n+1}PO_3)\cdot H_2O$ compounds expand to give a series $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_5H_{11}OH$ (**2**) that has layer spacings very similar[13] to those of the $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$ (**1**) series. The length of a benzyl alcohol and an *n*-pentanol molecule are similar as depicted in the conformations of the line drawings.



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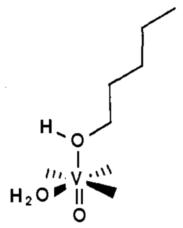

2

Vanadyl hexylphosphonate hydrate, $VO(C_6H_{13}PO_3)\cdot H_2O$, was treated with a series of linear 1-alkanols with carbon number from 2–10. The layer spacings of the resulting $VO(C_6H_{13}PO_3)\cdot H_2O\cdot C_nH_{2n+1}OH$ compounds are plotted in line c of Figure 1. In this case the layer separation is controlled by the length of the alcohol chain not by the length of the alkyl group on the phosphonate which is held constant at C_6. The slope of the line is 1.1 Å/CH_2 unit, very similar to that of the lines generated by varying the length of the alkylphosphonate chains, reinforcing the structural model suggested by Scheme I.

In their alcohol intercalation reactions, vanadyl organophosphonates can distinguish between groups of alcohol molecules. This selectivity can be controlled by the steric constraint around the absorption site, which in turn is determined by the nature of the organic group bound to phosphorus. For example, vanadyl phenylphosphonate absorbed primary *n*-alkanols over a period of hours at elevated temperature. The same alcohols are intercalated rapidly at room temperature into vanadyl alkylphosphonates, because the more flexible alkyl groups surround the coordination site. Vanadyl hexylphosphonate hydrate, $VO(C_6H_{13}PO_3)\cdot H_2O$, intercalates the primary alcohols *n*-butanol and isobutyl alcohol but does not react with *sec*-butanol or *tert*-butyl alcohol. In general, primary alcohols can be separated from secondary and tertiary alcohols with high selectivity by using vanadyl alkylphosphonates as sorbents. However, sufficiently bulky primary alcohols like neopentanol do not intercalate into $VO(C_6H_{13}PO_3)\cdot H_2O$.

We have shown that the alternating inorganic/organic layer compounds $VORPO_3\cdot H_2O$ can discriminate among isomeric alcohols. This discrimination arises because the vanadium coordination site on the intralayer surface is sterically restricted by the organic groups which surround it. In addition, reaction rates are also controlled by varying the organic group bound to phosphorus. Thus vanadyl *p*-biphenylphosphonate does not react with alcohols at all,[10] whereas the vanadyl alkylphosphonates rapidly intercalate primary alcohols at room temperature. Further work extending the synthetic and intercalation chemistry of vanadyl organophosphonates by exploring the effects of steric constraints in the organic layer will be reported in future publications.

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(13) Layer spacings of $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_5H_{11}OH$ for n = 2, 4, 6, 8: slope = 1.18 Å/CH_2; intercept = 10.85 Å.

Halogen Promoted Selective Carbonylation of Propane in Superacid Media

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Since the pioneering work of Olah and his group in the late sixties it is known that small alkanes do react with a large variety of electrophiles in superacid media under mild temperature and pressure conditions.[2] For industrial applications a major problem to solve is the lack of selectivity due to side reactions such as cracking and isomerization. We report here our results on selective carbonylation of propane in $HF\text{-}SbF_5$, the first step of an alternative method for preparing methacrylates via isobutyric acid derivatives.[3]

Earlier reports of direct carbonylation of saturated alkanes in superacid media include the reactions of C_6 cycloalkanes[4] and C_5–C_8 alkanes[5] as well as adamantane,[6] whereas in the classical Koch–Haaf synthesis[7] the intermediate carbocation is obtained by protonation of an alkene; in the superacid media it is generated directly from the alkane via the protolytic ionization process.

Two main pathways must be considered: cleavage of a secondary C–H bond or cleavage of a C–C bond. In the presence of excess carbon monoxide the initial cations are trapped giving the much more stable oxocarbenium ions[8] which can then be observed as long living species by NMR. Further titration can also be made by quenching the oxo ions in excess methanol and GC analysis of the resulting methyl esters. Our results show that the selectivity of propane carbonylation can be remarkably modified by adding catalytic amounts of halide ions. When a propane–carbon monoxide mixture ($CO:C_3$ molar ratio = 3) was bubbled during 1 h at a rate of 220 mL per hour through 1.5 mL of a $HF:SbF_5$ solution (4:1 molar ratio) in a Kel-F reactor at −10 °C, the 400 MHz proton NMR spectrum of the resulting solution showed only two ions: the isopropyloxocarbenium ion (IPOC) and the ethyloxocarbenium ion (ETOC) in a relative ratio of 2:3 (calcd conversion of propane: 4%).

All our experiments carried out with an excess of carbon monoxide showed the predominant formation of the propionyl ion resulting from the preferential C–C bond cleavage in the initial attack. This is in agreement with the observation made by Olah

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