SUPRAMOLECULAR EFFECTS IN THE REDOX AND COORDINATION CHEMISTRY OF SUPERSTRUCTURED IRON Porphyrins

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INTRODUCTION

Enzymatic systems exhibit quite remarkable properties as far as the efficiency, smoothness and selectivity of the chemistry they can carry out is concerned. These are most probably related to a common feature of their structures, i.e., the existence of a reacting center, the prosthetic group, surrounded by protein chains. The latter offer a microenvironment able to modulate the reactivity of the prosthetic group without participating directly to the reaction. Such organized structures are correlatively expected to function with minimal entropy losses. The concept of supramolecular chemistry, and electrochemistry, derives from attempts to imitate, even remotely, these structures and their functions.

In this context, the purpose of the following discussion is to examine the possibility of modifying the reactivity of a central reactant by relatively simple carbon chains superstructures, some of them containing secondary amide groups, a group known to be an essential component of protein chains. As reacting centers we chose iron porphyrins. These have the advantage of exhibiting properties that are relative to aromatic organic chemistry, coordination chemistry and organometallic chemistry. The influence of the above mentioned superstructures, if significant, will thus provide a good model for the modulation of the reactivity of molecules belonging to various different areas of chemistry. Another interest of iron porphyrins is that they serve as prosthetic groups in a number of natural metalloproteins (hemoglobin, myoglobin, cytochromes, cytochrome oxidases). The superstructured porphyrins investigated in the work described below\(^1-9\) are of the "basket-handle" type as shown in Figures 1, 7 and 9 (for the sake of comparison the Collman's picket fence porphyrin\(^10\) was also investigated). They derive from tetraphenylporphyrins (TTP) by grafting, at the ortho-positions of the phenyl rings, by means of ether or amide linkages simple carbon chains (Figure 1), carbon chains containing additional secondary amide groups (Figure 2), or carbon chains containing a hanging nitrogen base (Figure 3). The basket-handle superstructures may also be varied, not only by the nature of the chains but also by their spatial arrangement (cross-trans "CT", adjacent-trans "AT", adjacent-cis "AC") (Figure 1).
The questions we wish to address upon investigation of the redox and coordination properties of this set of superstructured iron porphyrins are the following. Do the superstructures exert a significant influence on the reactivity of the central iron porphyrin? What is the nature of the reactivity modulation brought about by the presence of the basket handle chains? Does it derive from a single effect or from the superposition of several different effects? What is the order of magnitude of each of these different effects? We will see that the presence of secondary amide groups in the chain is particularly important leading to a built-in "local solvation". In this connection, does "local solvation" build up when increasing the number of secondary amide groups included in the chains? What is the exact nature of this "local solvation" as revealed by the separation of its energetic and entropic aspects?

The modulation of the reactivity by the basket-handle superstructures was mostly investigated for reactions involving a one-unit increase of the negative charge of the porphyrin complex: Fe(II)(Fe(I)^-, Fe(I)^-(Fe("O")_2^-) redox reactions, complexation of iron(II) by anionic ligands. However, we will see that significant supramolecular effects also exist for the complexation of iron(II) by neutral nitrogen bases.

EXPERIMENTAL

Chemicals

The synthesis and characterization of the ether-linked and amide-linked basket-handle porphyrins of Figure 1 are described in References 12 and 13, respectively (for the picket fence porphyrin see Reference 13). For the superstructured porphyrins containing an increasing number of NHCO groups (Figure 7) see Reference 14 and for the hanging-base basket-handle (Figure 9) porphyrins References 6, 12, 15.

Reactivity Measurements

They were derived from the electrochemistry of the various investigated porphyrins starting with the iron(III) complex. Iron(III) porphyrins exhibit three successives one-electron reduction waves or groups of waves corresponding to the reduction of Fe(III)^+ into Fe(II), Fe(II) into Fe(I)^- and Fe(I)^- into Fe("O")_2^- (for an overview on the electrochemistry of iron porphyrins see Reference 16). Iron(III) and iron(II) porphyrins are five or six coordination complexes, one of the axial ligands possibly being the solvent. Fe(I)^- is the dominant mesomeric form of the complex resulting from the injection of one electron into an iron(II) porphyrin^{17-24}. What we note as Fe("O")_2^- is probably a combination of two dominant mesomeric forms, the iron(0) porphyrin and the anion radical of the iron(I) porphyrin^{7-23}. Both the iron(I) and iron("O") porphyrins bear no axial ligand at room temperature. For this reason the Fe(I)^-/Fe("O")_2^- wave is reversible showing no coupling with homogeneous chemical reactions and thus allowing the simple determination of the standard potential as the middle of the cyclic voltammetric cathodic and anodic peak potentials. The situation is more complex with the Fe(III)/(Fe(II) and Fe(II)/Fe(I) waves which show coupling of the electron transfer with homogeneous ligation/deligation reactions in a number of cases. Cyclic voltammetry and thin-layer spectroelectrochemistry were then used jointly for obtaining the characteristic standard potentials and equilibrium constants as well as the rate constants for the complexation of iron(II) by chloride ions. The procedures employed in this purpose have been described in detail^{11,14}, requiring in several cases an extension of the available theory^{25,26} of