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Anaerobic Oxidation of Cobalt(II) Protoporphyrin IX Dimethyl Ester[1] in Basic Methanolic Solution

Sir:

In alcoholic solutions, in the presence of molecular oxygen, and in the presence of various amine ligands (L), the oxidation of cobalt(II) protoporphyrin IX dimethyl ester,[1] [$Co^{II}P$], proceeds readily[2,3] by way of the reaction intermediate [$Co^{II}P(L)(O_2)$], the involvement of which has been widely recognized.[4-7] Even in absence of amine ligands [$Co^{II}P$] in methanol undergoes oxidation yielding mainly [$Co^{III}P(CH_3O)(CH_3OH)$] at a rate 10^2–10^3 times smaller than that with amine ligands.[8,9] In this case coordinated methanol acts as a weak electron donor, promoting electron transfer from cobalt to molecular oxygen. We now report that the best electron donors for promoting oxidation of [$Co^{II}P$] are coordinated alkoxides (methoxide < isopropoxide < *sec*-butoxide) dissolved in aliphatic alcohols. We noticed earlier[8,9] that the methoxide group in the [$Co^{III}P(MeO)$] intermediate strongly increases the electron density in the *trans* axial position, which favored the entry of the least basic amine ligand (not the most basic, as usually observed). But the most unexpected consequence of the excellent electron-donor ability of the methoxide ligand is the fact that a methanolic solution of [$Co^{II}P$] in presence of CH_3O^- yields [$Co^{III}P(CH_3O)_2$]$^-$, even in the absence of oxygen. The spectra of methanolic solutions of [$Co^{II}P$] and of [$Co^{III}P(CH_3OH)(CH_3O)$] are known.[9] The latter complex can be prepared either by the reaction of [$Co^{II}P$] with methanol and molecular oxygen in methanolic solution, or by solvolysis of [$Co^{III}P(Cl)$] in methanol.[9] If methoxide is added to the methanolic solution of [$Co^{III}P(CH_3OH)(CH_3O)$], in air, the dimethoxide complex, [$Co^{III}P(CH_3O)_2$], is formed. (The latter complex tends to slowly μ-dimerize. The rate of dimerization depends on the methoxide concentration. The dimer might be μ-methoxo-bridged cobalt(III)—analogous with μ-hydroxo-bridged iron(III) porphyrins.[10]) Curve 2 in Figure 1 shows the spectrum of methanolic solutions of [$Co^{III}P(CH_3O)_2$]$^-$ (Soret, 423 nm; α, 573 nm; β, 537 nm); curve 1 is the spectrum of [$Co^{III}P(CH_3OH)(CH_3O)$]. If methoxide is added to a methanolic solution of [$Co^{III}P$], several reactions will take place, which was inferred from the rates of [$Co^{III}P$] disappearance. At zero methoxide concentration k_{obsd} for the formation of [$Co^{III}P(CH_3OH)(CH_3O)$] from [$CO^{II}P$] is 0.8×10^{-4} s^{-1} at 25 °C. The first addition of sodium methoxide reduces the reaction rate, and the minimum rate is achieved at 5×10^{-4} mol dm^{-3} CH_3O^-. At this methoxide concentration the methanolic solutions of [$Co^{II}P$] show no spectral changes during several days.

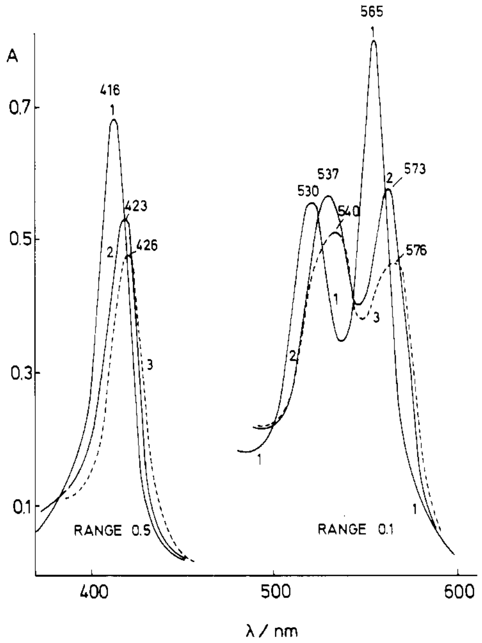

Figure 1. Absorption spectra of 5×10^{-6} mol dm^{-3} [$Co^{III}P(CH_3O)(CH_3OH)$] (1) and of [$Co^{III}P(CH_3O)_2$]$^-$ (2) in methanol (+3% v/v chloroform). Spectrum 2 changes to the dashed spectrum (3), supposedly corresponding to the cobalt(III) μ-methoxo-bridged dimer (N.B.: the β peak is larger than the α peak).

The rate decrease is expected since protons are needed for elimination of coordinated O_2 as $HO_2^{\bullet}$. The "directing" ligand is still coordinated methanol. Further increase of CH_3O^- concentration causes replacement of coordinated methanol with methoxide, and the rate goes up, in spite of the decrease of proton concentration, because coordinated alkoxides are among the best electron donors known. In strongly basic solutions (concentration of CH_3O^- > 1.0 mol dm^{-3}) the rates of aerobic and anaerobic oxidation tend to become equal, suggesting that at this methoxide concentration the same mechanism operates in both cases. The saturation rates are obtained when all coordinated methanol is replaced by methoxide. The spectrum of the reaction product is that of [$Co^{III}P(CH_3O)_2$]$^-$.

We are much surprised to find that [$Co^{II}P$] (5×10^{-6} mol dm^{-3}) and CH_3O^- (0.5 mol dm^{-3}), under oxygen-free argon, produced exactly the same spectrum as that of [$Co^{III}P(CH_3O)_2$]$^-$. Figure 2 shows the spectral changes of a solution of [$Co^{II}P$] (5×10^{-6} mol dm^{-3}) and methoxide (0.5 mol dm^{-3}) in methanol (3–5% v/v of benzene) in oxygen-free argon. The Soret maximum moves, in about 5 h, from 402 to 423 nm; the α and β peaks move simultaneously from 557 and 528 to 573 and 537 nm, respectively. The peaks at 423, 573, and 537 nm are absorption maxima of [$Co^{III}P(CH_3O)_2$]$^-$; see Figure 1. No doubt, in the absence of oxygen, it is the methoxide that is responsible for the electron transfer from Co(II), because we found the same spectral changes with isopropoxide and *sec*-butoxide. The electron-donating strength of the coordinated (directing) ligand must be important since several other investigated ligands (pyridine, imidazole, piperidine, azide, thiocyanate) did not cause any spectral changes of methanolic solutions of [$Co^{II}P$] under oxygen-free argon. For kinetic measurements, in the absence of oxygen, very pure argon (99.999%) was further purified by passing it through a cylindrical glass column, inside diameter 7 cm and height 90 cm, filled with chromium(II) salts dispersed on silica. An Oxi 9 apparatus with an E 090 WTW O_2-membrane electrode (provided by Labor Center, Nürnberg) could not detect any O_2 in a water sample saturated with argon purified as described; on the basis of instrument sensitivity it was inferred that the O_2 concentration was <10 μg dm^{-3}. The apparatus for the work in oxygen-free argon was previously described.[9] Because the concentration of O_2 in the solution was $\leq 3 \times 10^{-7}$ and the concentration of the complexes were 5×10^{-6} mol dm^{-3}, there was not enough oxygen for Co(II)

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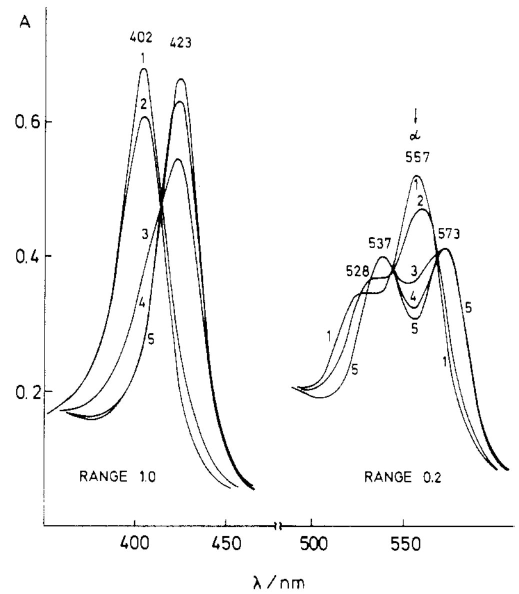

Figure 2. Spectral changes of a solution of [Co^{II}P] (5×10^{-6} mol dm^{-3}) and CH_3ONa (0.5 mol dm^{-3}) in methanol (+5% v/v benzene), in oxygen-free argon at 25 °C. Spectral changes occur within about 5 h. The product shows a spectrum practically the same as that of [Co^{III}P$(CH_3O)_2$]$^-$; see Figure 1.

oxidation. This is why pyridine, imidazole, etc. (see above) did not cause any spectral changes in the methanolic solution of [Co^{II}P]. Moreover, since the rate of oxidation depends on partial pressure of oxygen[9] the measured rate of [Co^{II}P] → [Co^{III}P] conversion in argon cannot be explained by reaction of [Co^{II}P] with traces of oxygen, because the rate would be exceedingly small, which is not the case: the conversion is completed in about 5 h at 25 °C.

The reactions were allowed to run in the dark (in the absorption cell under argon, in the closed spectrophotometer compartment. The light beam was passed for a few seconds during each measurement).

The reaction solutions were analyzed for peroxide impurities. By use of the known procedure,[11] it was found that peroxides are present only in concentration less than 1×10^{-8} mol dm^{-3}.

We have previously shown[9] that a freshly prepared methanolic solution of [Co^{II}P] (1×10^{-5} mol dm^{-3}, presence of air, 77 K) gives an EPR signal, but the reaction product, [co^{III}P$(CH_3O)(CH_3OH)$], does not. The methanolic solution of [Co^{II}P] (1×10^{-4} and 5×10^{-4} mol dm^{-3}) containing sodium methoxide (5×10^{-1} mol dm^{-3}) under argon gave no ESR signal, indicating that cobalt is already in the form of Co(III).

Discussion. Tsutsui et al.[12] observed that addition of unsaturated hydrocarbons to a solution of cobalt(II) mesoporphyrin IX dimethyl ester (presence of air) in various solvents results in an immediate shift of the Soret band from 393 to 411 nm. The α and β bands also shift from 518 and 553 to 528 and 558 nm, respectively. We observed an analogous bathochromic shift, indicative of Co(II) Co(III) oxidation. These shifts have been explained by electronic,[13] steric,[14,15] and stereoelectronic[16] factors. Tsutsui et al. observed only one isosbestic point for the Soret shift, as we also did (Figure 2), an observation which suggests that only the two species, Co(II) and Co(III), are present in solution.

The ease of oxidation of Co(II) complexes is found to be directly proportional to the base strength of the bound axial ligand, and a plot of $E_{1/2}$ vs pK_a yields a linear relationship for both π- and σ-donating bases.[17] The authors concluded that the half-wave potential gives a measure of the electron density on the cobalt as a composite of σ, π, and steric phenomena. A similar relationship is observed between the half-wave potentials for oxidation of Co(II) to Co(III) and the coordinating ability of the aprotic solvents.[18] The lowering of the potential due to good electron-donating ligands is substantial.[19,20] Thus alkoxides, which coordinate strongly along the *z* axis of cobalt(II) porphyrins, decrease tetragonal distortion of the d^7 Co(II) species and facilitate the approach to octahedral symmetry, which promoted the anaerobic oxidation in our case.

The question remains what happened to the Co(II) electron in the absence of oxygen. The electron is obviously not "hidden" within the π system of the porphyrin ring. If so, the absorption spectrum of such a complex could not be identical with that of [Co^{III}P$(CH_3O)_2$]$^-$ obtained under oxygen. In addition we could not observe any EPR signal in a methoxide-containing methanolic solution of [Co^{II}P] (under argon) upon addition of *N-tert*-butyl-α-phenylnitrone (PBN), as a spin trap. It remains as the most reasonable assumption that the electron is transferred to solvent methanol. Small quantities of H_2 produced in this manner are difficult to detect.

We mentioned that a small amount of benzene (3–5% v/v) was added to methanol to assure the complex solubility. On the other hand when, instead of benzene, 5% (v/v) chloroform was used the reaction with methoxide, in absence of oxygen, first yielded [Co^{III}P$(CH_3O)_2$]$^-$, but after some time the [Co^{II}P] spectrum was fully restored. It is well-known that the weakly acidic chloroform reacts with methoxide,[21-23] decreasing the solution basicity, which might cause the reverse reaction. In addition chloroform, or its degradation products in basic media,[23] might also function as reducing agents. The reduction of cobalt(III) tetrapyridylporphyrin bis(*N*-methylimidazole) by chloroform has been observed elsewhere.[24] There is also a possibility that two vinyl groups of protoporphyrin IX are reduced. If so this would mean that such reduction, at the periphery of the porphyrin core, does not cause a change in positions of the Soret, α, and β absorption maxima of [Co^{III}P$(CH_3O)_2$]$^-$. This is being investigated.

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Registry No. [Co^{II}P], 14932-10-6; [Co^{III}P$(CH_3O)(CH_3OH)$], 94509-07-6; [Co^{III}P$(CH_3O)_2$]$^-$, 113403-34-2; methoxide, 3315-60-4; isopropoxide, 15520-32-8; *sec*-butoxide, 35730-33-7.

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