

Unexpected Alkyl Complex Formation and Correlation of Porphyrin Basicity with Alkyliron(III) Homolytic Stability

Byung Ho Song*, Dong Kyu Park, Eui Je Cho, and Tae Woo Kwon†

*Department of Chemistry, University of Iowa, Iowa city, IA52242, U.S.A.

†Department of Chemistry, Kyung Sung University, Pusan 726-036

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The σ -bonded alkyl and aryliron(III) porphyrins are usually obtained from the reaction of the chloroiron(III) porphyrin with Grignard reagents or alkyllithium.¹ An alternative route involves reaction of the iron(I) porphyrin anion derivative with alkyl halides. The resulting (Por)Fe(III)R (R=alkyl, aryl) complexes exist as pentacoordinate, low-spin ($S=1/2$) iron(III) complexes in noncoordinating solvents.²

This work addresses examination of relative stabilities of alkyliron(III) porphyrins depending upon the phenyl ring substituents and verification of unexpected alkyl group transfer from triethylborohydride to chloroiron(III) porphyrin, which may provide another route for formation of the alkyl complexes of iron(III) porphyrins.³ The reaction was discovered in attempts to make unprecedented hydride iron porphyrin complexes. The NMR (Bruker WM-360 FT) methodology was used here to detect the products of the triethylborohydride reaction, and to monitor the relative stabilities of ethyliron(III) tetraarylporphyrins as a function of aryl substituents of a β -pyrrole resonance of Fe(II) product in case of fluorinated phenyl iron porphyrins. Ethyliron(III) porphyrin complex was prepared both by stoichiometric addition of NaEt_3BH to a solution of (Por)Fe(III)Cl and by combination of NaEt_3BH and sulfur with a 2.0-6.0 mM solution of (Por)Fe(III)Cl at room temperature.

Addition of 1.0 equiv. of NaEt_3BH in THF to toluene solutions of chloroiron(III) porphyrins results in ethyl complex formation with a corresponding β -pyrrole proton resonance ranging from -17.5 ppm to -20.05 ppm as porphyrin phenyl substituents are varied from para-methoxy to pentafluoro. The β -methyl resonance of the coordinated ethyl group ranges from -115 ppm to -126 ppm due to porphyrin substituent effects. At room temperature chemical shift of β -pyrrole and a coordinated β -methyl for (*p*-OCH₃)Fe(III)Et are -17.5 and -115 ppm, for (TPP)Fe(III)Et are -17.6 and -117 ppm, for (F₃-TPP)Fe(III)Et are -19.5 and -124 ppm, and for (F₂₀-TPP)Fe(III)Et are -20.1 and -126 ppm, respectively. The ethyl α -methylene proton resonance is not seen (located at 554 ppm) in the ¹H-NMR spectrum due to large linewidth.⁴

The triethylborohydride reagent also serves as a reducing agent, and variable amounts of iron(II) products are seen along with the alkyliron(III)porphyrin. In the 0.4% THF-toluene reaction medium the iron(II) exists as a mixture of square-planar $S=1$ and THF-ligated $S=2$ species in rapid exchange. The resulting pyrrole phenyl protons are in the downfield region, and the chemical shift values are sensitive

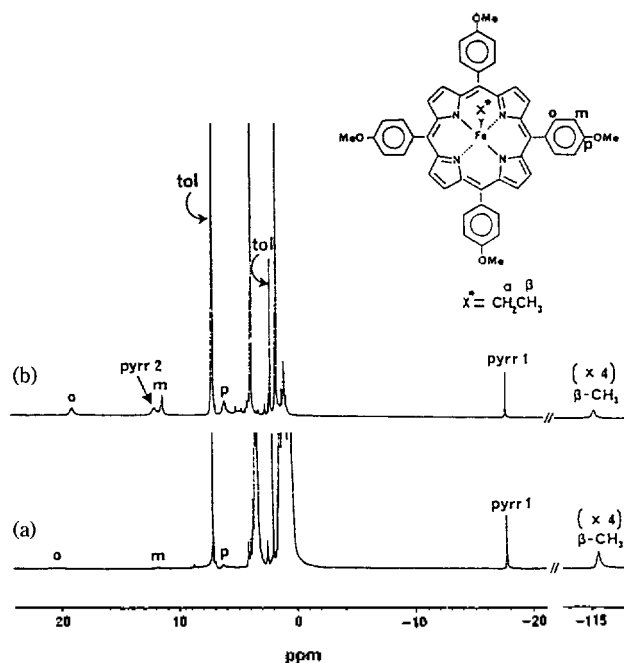


Figure 1. Proton NMR spectra of ethyliron(III) porphyrin, 360 MHz, at 298 K. The pyrrole signal of ethyliron(III) porphyrin complex is denoted "pyrr 1", coordinated methyl proton signal " $-\text{CH}_3$ ". The pyrrole and phenyl proton resonances for (*p*-OCH₃)TPPFe(II)(THF) \times as "pyrr 2", "ortho as o", "meta as m", and "para methoxy as p". (a) reproduced result of ref. 8 with concentration of 4 mM. (b) addition of 1.0 eq. NaEt_3BH to a toluene solution of (*p*-OCH₃)TPPFe(III)Cl with concentration of 2 mM.

to the iron(II) porphyrin/THF ratio and phenyl substituents. Use of substoichiometric quantities of triethylborohydride anion also produces both ethyliron(III) and iron(II) products. Equivalent results were obtained with the LiEt_3BD analogue.

Ethyliron(III) porphyrins are relatively unstable, and several hours after generation the ratio of iron(II) to ethyliron(III) porphyrin increases, presumably as a result of Fe-C bond homolysis. Porphyrins with different basicities were examined and we varied phenyl ring substituents from electron-releasing OCH₃ group to electron-withdrawing group such as F. The apparent half life for Fe-C bond homolysis is on the order of day for (*p*-OCH₃)TPPFe(III)Et, TPPFe(III)Et and with a qualitative decrease in stability. The (F₂₀-TPP)Fe(III)Et shows a remarkably short half life of 45 minutes. Hence, the relatively electron-deficient iron porphyrins show the greatest tendency to give the ultimate iron(II) homolysis product. This is surprising in that the electron-deficient iron(III) porphyrins have a higher affinity for axial ligand coordination. We initially expected that electron-deficient porphyrins would have a higher affinity than less electron-deficient porphyrins. However the opposite result was obtained, which can be explained by the extent of iron(II) porphyrin stabilization. The electron-withdrawing substituents in the porphyrin-phenyl ring stabilize the iron(II) by delocalization through conjugated macrocycle. An explanation for this apparent discrepancy for effective homolysis may be found in the relative stabilization of the iron(II) product. Hence a variety of evidences suggest homolysis is reversible⁵⁻⁷: (TPP)Fe(III)-R \rightleftharpoons (TPP)Fe(II)+R \cdot .

Homolysis of the Fe-C depending on ring basicity

Types of porphyrins	Half life for Fe-C homolysis
(F ₂₀ -TPP)Fe(III)Et	45 min.
(F ₈ -TPP)Fe(III)Et	2 days
TPPFe(III)Et	3.5 days
(p-OCH ₃)TPPFe(III)Et	4 days



F₂₀-TPP: dianion of tetrakis (pentafluorophenyl) porphyrin

F₈-TPP: dianion of tetrakis (o,o'-fluorophenyl) porphyrin

TPP: dianion of tetrakis (tetraphenyl) porphyrin

(p-OCH₃)TPP: dianion of tetrakis (p-methoxyphenyl) porphyrin.

Diminished reactivity of the iron(II) product for electron deficient iron(II) porphyrins would slow the reverse reaction and cause loss of R· by disproportionation, coupling, solvent hydrogen atom abstraction, etc. Alkyl complex formation is verified from carbon monoxide insertion reaction, which ended up to forming (F₂₀-TPP)Fe(II)CO complexes at 8.8 ppm and (F₂₀-TPP)Fe(III)C(=O)CH₂CH₃ complex formation at -10.5 ppm of characteristic pyrrole resonances, presumably via radical process. After injection of carbon monoxide at 1 atm for 10 seconds into a 5 mm NMR tube containing ethyl complex, the integrated signals of the products result in 91% (F₂₀-TPP)Fe(II)CO and 9% (F₂₀-TPP)Fe(III)C(=O)CH₂CH₃. Resulting large portion of (F₂₀-TPP)Fe(II)CO complexes can be attributable to the square-planar (F₂₀-TPP)Fe(II) (85%), which was already produced from Fe-C bond homolysis. A β-pyrrole resonance of electron-deficient (F₂₀-TPP)Fe(III) acyl complex shows upfield shift by 2.0 ppm as compared with that of TPPFe(III)C(=O)R with pyrrole at -8.6 ppm.⁶ Another set of experiment was carried out by CS₂ insertion reaction into a possible alkyliron(III) porphyrin complex. Assuming the formation of alkyl porphyrin complex, the insertion product for CS₂ revealed the same result described elsewhere.⁷ The product was a dithiocarboxylatoiron(III) porphyrin complex, TPPFe(III)CS(=S)CH₂CH₃. Reaction of (p-OCH₃)TPPFe(III)Cl with NaEt₃BH was investigated further be-

cause product identification is not consistent with an earlier literature report.⁸ Retrospective interpretation of other spectroscopic results⁸ also points to the unusual alkyl group transfer to the iron(III) porphyrin.

The "strong g-max" EPR signal reported for the product⁸ matches that known for low-spin alkyliron(III) porphyrins. Optical spectra are also consistent with the alkyliron(III) formulation. Optical spectra bands at 412 (soret), 523, and 612 nm resemble those for known alkyliron(III) tetraarylporphyrins. An ethyl group and SH⁻ are isoelectronic. A disordered ethyl group could well emulate SH⁻ ligand electron density in the reported crystal structure. A signal at 6.7 ppm assigned to the coordinated S-H group is not seen in our spectra. On the basis of r⁻⁶ dipolar relaxation (comparison with pyrrole proton linewidth) the S-H signal (ca. 1250 Hz) would not have been detected by high resolution NMR (360.13 MHz) due to large line broadness.

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