

Heme/hydrogen peroxide reactivity: formation of paramagnetic iron oxophlorin isomers by treatment of iron porphyrins with hydrogen peroxide.

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Treatment of iron(II) porphyrins, $(py)_2Fe^{II}(OEP)$, $(py)_2Fe^{II}(EtioP)$, $(py)_2Fe^{II}(DeuteroP)$, $(py)_2Fe^{II}(MesoP)$, and $(py)_2Fe^{II}(ProtoP)$, where OEP are the dianions of octaethylporphyrin, etio-1 porphyrin, deuteroporphyrin-IX dimethyl ester, mesoporphyrin-IX dimethyl ester, and protoporphyrin-IX dimethyl ester, with hydrogen peroxide in pyridine- d_5 at $-30\text{ }^{\circ}\text{C}$ in the strict absence of dioxygen is shown to result in clean oxygenation of the heme and the formation of oxophlorin complexes, $(py)_2Fe(OEPO)$, $(py)_2Fe(EtioPO)$, $(py)_2Fe(DeuteroPO)$, $(py)_2Fe(MesoPO)$, and $(py)_2Fe(ProtoPO)$. Reactions have been monitored by ^1H NMR spectroscopy. The product oxophlorin complexes are stable as long as the samples are protected from exposure to dioxygen. The hyperfine shift patterns and the relative intensities of the individual resonances have been analyzed in terms of a model in which the location of the meso oxygen substituent dominates the pattern of spin density distribution. The resulting ^1H NMR spectra obtained from oxidation of the unsymmetrically substituted hemes, $(py)_2Fe^{II}(DeuteroP)$, $(py)_2Fe^{II}(MesoP)$, and $(py)_2Fe^{II}(ProtoP)$, with hydrogen peroxide have been analyzed. These spectra show that the four isomeric oxophlorin products are formed in a nonrandom fashion. Solvent effects can produce a significant alteration in the regiospecificity of heme oxygenation.

Słowa kluczowe

Alkyls, Bioinorganic chemistry, Carbene compounds, Oxides, Pyrroles

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