Oxidation of iron(III) tetramesitylporphyrin with dimethyldioxirane.

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Streszczenie

The oxidation of $(TMP)Fe^{III}ClO_4$ in solution with dimethyldioxirane-d_6 has been examined by ^1H NMR spectroscopy. The reaction of $(TMP)Fe^{III}ClO_4$ with dimethyldioxirane-d_6 in a solvent mixture of dichloromethane-d_2/methanol-d_4 (4:1 v/v) produced two intermediates: $(TMP)Fe^{IV}(CD_3O)_2$ and $X(TMP^{\bullet})Fe^{IV}O$, which could be directly observed at low temperatures. When the $(TMP)Fe^{III}ClO_4$−dimethyldioxirane-d_6 reaction was carried out in dichloromethane-d_2, the loss of iron(III) tetramesitylporphyrin resonances was accompanied by growth of resonances due to $(TMP)Fe^{IV}(CD_3O)_2$ and $X(TMP^{\bullet})Fe^{IV}O$. A set of ferryl porphyrin cation radicals $X(TMP^{\bullet})Fe^{IV}O$ (X − ligands available) was identified. The formation of a variety of ligands resulted from side reaction pathways which include dioxirane and dichloromethane-d_2. Addition of dimethyldioxirane-d_6 to the acetone-d_6 solution of $(TMP)Fe^{III}ClO_4$ gave mainly iron(III) porphyrin cation radical $[(TMP^{\bullet})Fe^{III}((CD_3)_2CO)_2]^+$ and a small amount of ferryl porphyrin cation radicals $[(CD_3)_2CO(TMP^{\bullet})Fe^{IV}O]^+$. Typically, in the $(TMP)Fe^{III}ClO_4$−dioxirane systems the formation of one-electron oxidation product (iron(IV) porphyrin or iron(III) porphyrin radical) predominates, rendering such an approach less effective in generation of green ferryl porphyrin cation radicals than use of iodozobenzene, peroxyacids, or ozone.

Słowa kluczowe

Cations, Chemical reactions, Ligands, Oxidation, Pyrroles

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