

Dioxygen reactivity of a heme-nitrosyl: A peroxynitrite intermediate

Biplab Mondal[‡], Kenneth D. Karlin[†]

[†]*Department of Chemistry, The Johns Hopkins University, Baltimore, USA*

Peroxynitrite, an exceptional strong oxidizing and nitrating agent is of significant biological interest and is considered as a possible mediator of nitric oxide biochemistry and nitrosative stress injury. The dioxygen reactivity of the heme-nitrosyl, [(F₈TPP)Fe^{II}-NO], {F₈TPP = tetrakis(2,6-difluorophenyl)porphyrin} at low temperature in THF solvent, has been studied and spectroscopic measurements (UV-Vis, IR) reveal that a thermally unstable heme-peroxynitrite species, [(F₈TPP)Fe-ONOO] is formed. The same complex can also be generated by the reaction of a heme-superoxide [(THF)(F₈TPP)Fe^{III}-O₂⁻] with nitric oxide. The intermediate, even at low temperature, undergoes a first order isomerization to the corresponding heme-nitrate, [(F₈TPP)Fe^{III}-NO₃]. Such a peroxynitrite transformation is known to take place either through internal rearrangement or via the hemolytic cleavage of the O-O bond leading to a high-valent heme-oxo species and [•]NO₂ formation, which in turn recombine to give the heme-nitrate. Further evidence for the formation of [(F₈TPP)Fe-ONOO] is demonstrated by its reactions with activated phenols to give either ring nitration or oxidatively coupled bis-phenol products.