Visible Light Generation of High-Valent Iron-Oxo Intermediates

High-valent iron-oxo porphyrin intermediates are central oxidants in enzymatic and synthetic catalysts. In this work, we have explored the photochemical approach to generate these important oxidizing transients. Irradiation of photo-labile bromate non-electron deficient porphyrin-iron (III) salts gave iron (IV)-oxo porphyrin radical cations termed compound I. These compound I species bear resemblance to the oxidizing transient in cytochrome p450 enzymes. In contrast, visible light irradiation of electron-deficient porphyrin bromate salts gave an iron (IV)-oxo neutral porphyrin, termed compound II, and was determined to be much more stable than the compound I species. The photochemical reactions are ascribed to a heterolytic cleavage of the O-Br bond to form a putative iron (V)-oxo species, which will either relax by internal electron transfer to form the compound I radical cation or react with residual iron III porphyrins through comproportionation to form the neutral compound II. This distinction was found to be determined by the electronic nature of the porphyrin ligand. Our kinetic studies show the more oxidized compound I reacted 2-3 orders of magnitude faster than the compound II species.