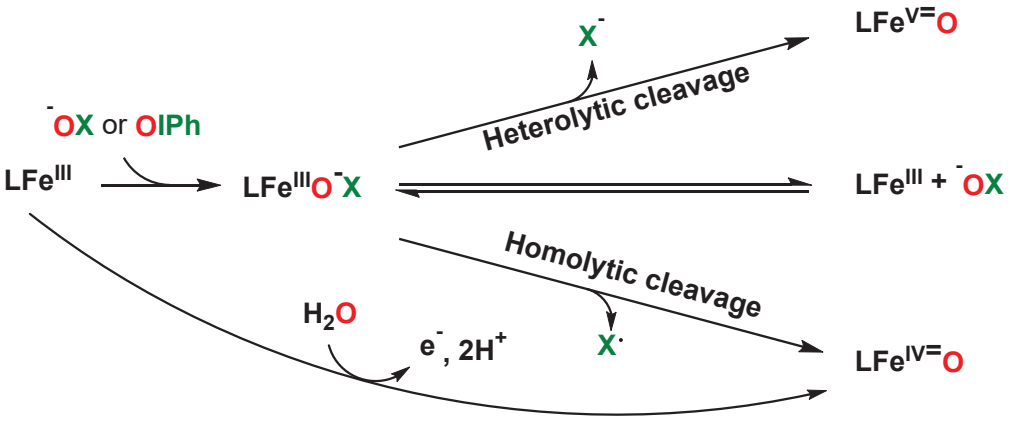
Abstract

The work presented in this thesis focuses on the activation of terminal oxidants (PhIO, NMO, H_2O_2, ^tBuOOH, cumylOOH, *m*-CPBA, ClO^-) in organic and aqueous solutions by the mononuclear non-heme iron complex $[Fe(tpena)]^{2+}$, i.e., detection and characterization of transient $[Fe(tpena)]^{2+}$-based oxidants (scheme A) as well as elucidation of mechanisms and reactivity patterns important for the use in oxidation catalysis. (tpena = *N,N,N'*-tris(2-pyridylmethyl)ethylene diamine-*N'*-acetate)



Scheme A. Simplified and unified schematic illustration of the iron chemistry presented in this PhD thesis. Changes of the oxidant (XO^- or PhIO) and/or the ligand (L) around the iron centre in non-heme iron complexes control the formation of the possible iron-based oxidants and hence the catalytic activity. X = OH, O^tBu, Ocumyl, *m*-CBA, Cl, NM(O). L = ethylenediamine backboned ligand: *N*-R-*N,N',N'*-tris(2-pyridylmethyl)ethane-1,2-diamine, (R = CH_3 (metpen), CH_2CH_3 (ettpen), $CH_2C_6H_5$ (bztpen), $CH_2C_6H_4N$ (tpen), CH_2CH_2OH (tpenOH) and CH_2COOH (tpenaH)).

$[Fe(tpena)]^{2+}$ is a germane biomimetic system for iron non-heme O_2 activating enzymes due to the presence of a carboxylate donor in the first coordination sphere and a second coordination sphere base. The carboxylate donor induces a significantly lower Fe^{II}/Fe^{III} reduction potential for $[Fe(tpena)]^{2+}$ compared to the many non-heme iron complexes without this functional group reported over the past three decades. As a consequence an iron(III) resting state rather than an iron(II) resting state is stabilized, which creates a catalyst with a remarkable diversity: the reactivity is controlled by the choice of terminal oxidant and can be switched between the paradigms of HAT- and OAT-based oxidations.

The HAT-mediated reactivity of the iron-tpena system is ascribed to the iron(IV)oxo species $[Fe^{IV}O(Htpena)]^{2+}$ generated upon homolytic bond cleavage of $[FeO\text{-}X(tpenaH)]^{2+}$. The combination of enhanced lability of the FeO-X bond and greater oxyl radical character of $[Fe^{IV}O(Htpena)]^{2+}$ is identified as the key reason for a more aggressive reactivity compared to other non-heme iron model complexes, which is demonstrated through rapid hydrogen, alkyl and acylperoxide disproportionation, greater second order constants in C-H abstraction and larger catalytic product yields. The drawback of using peroxides is that free and promiscuous radicals, $X^{\bullet}$, are subsequently formed alongside $[Fe^{IV}O(Htpena)]^{2+}$. The radicals can also work as oxidants, and thereby decrease selectivity of the substrate oxidations and cause ligand degradation, if favourable experimental design has not been made. This loss of selectivity can however be avoided by the direct generation of the iron(IV)oxo species from its iron(III)

precursor with a one electron acceptor in aqueous solutions. Within the series of ethylenediamine based iron(IV)oxo species, $[Fe^{IV}O(Htpena)]^{2+}$ and $[Fe^{IV}O(HtpenO)]^{2+}$ indeed perform best in oxidation of C-H (both in aqueous and organic solutions) and O-H bonds, respectively.

In contrast to the use of peroxides, radical chemistry is not observed when the oxidant PhIO is employed. Rather selective and catalytic oxygenations are demonstrated suggesting an OAT mechanism catalysed by a metal-based oxidant, e.g., the detectable $[Fe^{III}(OIPh)(tpena)]^{2+}$, $\{[Fe^{III}(OIPh)(tpena)]\}_2^{4+}$ or undetected iron(V)oxo species generated through heterolytic O-I bond cleavage. Halogen bonding and the different nature of the $Fe^{III}O$-X bond for PhIO compared to peroxides are believed to play central roles for the observations of the different reactivity patterns (OAT vs. HAT).

$[Fe(tpena)]^{2+}$ undergoes irreversible, light-promoted O_2-dependent *N*-deglycination to generate an iron(II) complex under ambient conditions. The transformation includes a mass loss equivalent to a glycyl group involving consecutive C-C and C-N cleavages documented by the quantitative measurement of the sequential production of CO_2 and formaldehyde, respectively. Time-resolved spectroscopy has allowed for the spectroscopic characterization of two iron-based transients along the reaction pathway.