Directing a Non-Heme Iron(III)-Hydroperoxide Species on a Trifurcated Reactivity Pathway

The reactivity of [Fe\textsuperscript{III}(tpena)]\textsuperscript{2+} (tpena=N,N,N'-tris(2-pyridylmethyl)ethylenediamine-N'-acetate) as a catalyst for oxidation reactions depends on its ratio to the terminal oxidant H\textsubscript{2}O\textsubscript{2} and presence or absence of sacrificial substrates. The outcome can be switched between: 1) catalysed H\textsubscript{2}O\textsubscript{2} disproportionation, 2) selective catalytic oxidation of methanol or benzyl alcohol to the corresponding aldehyde, or 3) oxidative decomposition of the tpena ligand. A common mechanism is proposed involving homolytic O-O cleavage in the detected transient purple low-spin (S=1/2) \{[tpenaH]Fe\textsuperscript{III}O-OH\}\textsuperscript{2+}. The resultant iron(IV) oxo and hydroxyl radical both participate in controllable hydrogen-atom transfer (HAT) reactions. Consistent with the presence of a weaker σ-donor carboxylate ligand, the most pronounced difference in the spectroscopic properties of [Fe(OOH)(tpenaH)]\textsuperscript{2+} and its conjugate base, [Fe(OO)(tpenaH)]\textsuperscript{+}, compared to non-heme iron(III) peroxide analogues supported by neutral multidentate N-only ligands, are slightly blue-shifted maxima of the visible absorption band assigned to ligand-to-metal charge-transfer (LMCT) transitions and, corroborating this, lower Fe\textsuperscript{III}/Fe\textsuperscript{II} redox potentials for the pro-catalysts.
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 5.46 SJR 2.902 SNIP 1.319
Web of Science (2011): Impact factor 5.925
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 2.791 SNIP 1.295
Web of Science (2010): Impact factor 5.476
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 2.753 SNIP 1.425
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 3.135 SNIP 1.473
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 3.449 SNIP 1.585
Scopus rating (2006): SJR 3.108 SNIP 1.553
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 2.78 SNIP 1.451
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 2.442 SNIP 1.483
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 3.265 SNIP 1.447
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 3.051 SNIP 1.446
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 2.872 SNIP 1.543
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 2.33 SNIP 1.551
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 2.904 SNIP 1.624
Original language: English
DOIs: 10.1002/chem.201704615
Source: FindIt
Source-ID: 2392639070
Research output: Research - peer-review › Journal article – Annual report year: 2018