The Design of Iron-TAML Activators: Effective Small Molecule Mimics of the Peroxidase Enzymes

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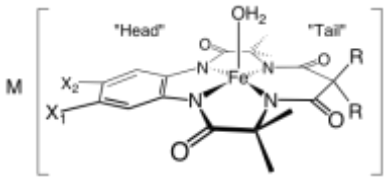
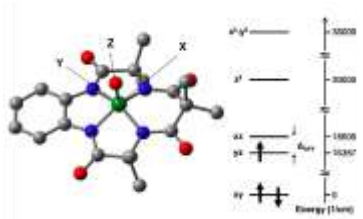
Research in Carnegie Mellon's Institute for Green Science is focused on the design, development, mechanism of action, and myriad uses of TAML activators. TAML activators with iron as the metal are the first miniaturized replicas of the peroxidase enzymes, which activate hydrogen peroxide throughout nature. The key to the TAML discovery and development has been the Collins iterative design protocol. This protocol is focused primarily on obtaining strongly electron-donating ligand systems where derivative complexes are able to resist both hydrolytic and oxidative degradation under the aggressive conditions of peroxidase-like processes. After being pursued for 15 years, the protocol yielded the prototype TAML activator. Further advancement via the protocol to higher generation catalysts has led to over 20 TAML activators that exhibit varying reactivities (with H_2O_2 and other peroxides), selectivities and lifetimes.



A TAML Activator: For the prototype, $X_1 = X_2 = H$, $R = CH_3$

Toxicity testing to date reinforces the idea that TAML activators and their processes are green. Designed to be environmentally benign, TAML activators are signature green oxidation catalysts that have the fundamental chemical properties to enable numerous new green chemical technologies. With peroxides TAML activators with iron produce extremely reactive intermediates, probably several, separately or jointly depending on the conditions. One is likely to be an iron(V)-oxo complex that has been trapped at low temperature (Figure). TAML activator catalysis is distinguished by low catalyst requirements (nM to low mM), efficacy under ambient conditions over a broad pH range (especially neutral to highly basic), rapidity, high efficiencies and turnover numbers, and flexibility for both selective and non-selective processes; the latter can be described as "fire-in-water". TAML activator/H_2O_2 can be used to purify water of numerous recalcitrant pollutants, including many endocrine disrupting chemicals (EDCs), as well as hardy pathogens.



An iron(V)-TAML-oxo Complex

REFERENCES

1. A. D. Ryabov, T. J. Collins, "Mechanistic Considerations on the Reactivity of Green Fe^{III}-TAML Activators of Peroxides", *Adv. Inorg. Chem.* **2009**, *61*, 471–521
2. T. J. Collins, S. K. Khetan and A. D. Ryabov, "Iron-TAML catalysts in green oxidation processes based on hydrogen peroxide", in "Handbook of Green Chemistry", Anastas, P. and Crabtree, R., Eds., pp. 39–77, **2009** WILEY-VCH Verlag GmbH & KgaA, Weinheim

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Terry will be speaking at Gordon College for our 8th Annual Green Chemistry Lecture.

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More on the lecture series can be found at:
http://tinyurl.com/GordonGCL2011