Catalysts for Green Oxidation Chemistry

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Oxidation chemistry plays a central role in many important industrial processes. Examples include the bleaching of wood pulp to make white paper, remediation of waste-water streams, dye bleaching in the textiles industry, and drinking water purification.[1,2] In most of these examples chlorine-based oxidants such as Cl_2, HOCl, or ClO_2 are used because these rapidly oxidise organic compounds under ambient conditions. However, a very undesirable by-product of reactions with these oxidants is the formation of organo-chlorines which are often highly toxic and prone to bio-accumulation when released into the environment.

Hydrogen peroxide (H_2O_2) is an attractive alternative oxidant because it does not display these inherent problems. Although hydrogen peroxide is a cost-effective and powerful oxidant, its uptake by industry has been limited because it suffers from the problem of being very slow to react with most organic compounds under ambient conditions due to high activation barriers. The development of efficient green catalysts that can lower these activation barriers would open the way for hydrogen peroxide to be used as an effective replacement for chlorine-based oxidants in industry. This in turn would completely eliminate the release of organo-chlorines to the environment from these sources.[3] Accordingly, the overall goal of this project is to develop new, efficient green catalysts for oxidations of organic compounds with hydrogen peroxide.

An excellent starting point for new catalyst development is the macrocyclic tetra-amido complex of iron, FeB*, (see Figure 1) that was recently prepared by Professor Collins' group at Carnegie Mellon University, Pittsburgh, PA.[4] This complex very effectively catalyses oxidation reactions of organic compounds with hydrogen peroxide at room temperature. It is moderately simple to prepare, is composed of non-toxic elements, is water soluble, and has high activities (< 1 μmol L^{-1}).[4] Weaknesses of this catalyst are its short lifetime in solution when no substrate is present, the high pH (ca. 11) required for optimal rates of oxidation and the sensitivity of the catalyst to acidic conditions. In a collaborative research programme with Prof. Collins we recently developed the related macrocyclic iron complex, FeB^J, (Fig. 1) that shows improved performance in each of these particular areas, although the rates of oxidation with this catalyst are lower. These results show that small changes to the tetra-amide macrocyclic ligand can result in significant changes to the performance of the catalyst.

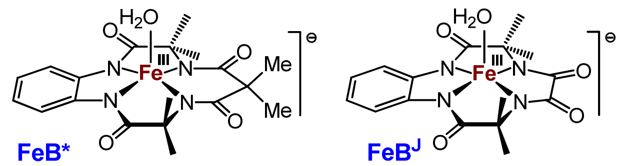

Figure 1

In this project it is proposed to develop new, superior oxidation catalysts by making further rational changes to the tetra-amide cores of the H_4B^* andH_4B^J ligands. Target macrocyclic complexes are illustrated schematically in Figure 2. Specific details of these structures are not presented because it is necessary to protect potential future patent applications. Syntheses of these tetra-amide macrocycles will be carried out using standard organic techniques. Once prepared, iron will be inserted into the macrocycles using $FeCl_3$ and base. The potential catalytic activities of the resulting complexes will be investigated initially using water soluble dyes such as orange(II) that become colourless upon oxidation. These dye-oxidation (bleaching) reactions will be conveniently followed by UV-vis spectroscopy and relevant kinetic data obtained. Complexes that are identified as promising new catalysts will then be tested for applicability in important industrial processes such as the bleaching of wood pulp and the remediation of waste water streams.

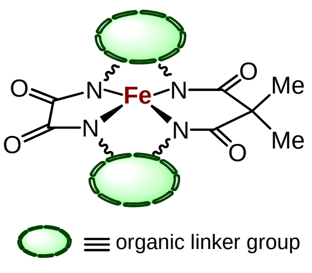

Figure 2

This proposed research is consistent with the Green Chemistry principles of replacing polluting industrial processes with feasible benign alternatives and the application of green catalytic processes where possible to reduce energy input and increase reaction efficiencies.

References:

1. C. P. Horwitz, T. J. Collins, J. Spatz, H. J. Smith, L. J. Wright, T. R. Stuthridge, K. G. Wingate, K. McGrouther, "Iron-TAML Catalysts in the pulp and paper industry," *ACS Symposium Series*, 2006, 921 (Feedstocks for the Future) Edited by J. J. Bozell and M. K. Patel, pp156-169.
2. J. L. Chen, S. Ravindran, S. Swift, L. J. Wright, N. Singhal "Catalytic oxidative degradation of 17α-ethinylestradiol by Fe(III)-TAML/H_2O_2: Estrogenicities of the products of partial, and extensive oxidation." *Water Research*, 2012, *46(19)*, 6309-18.
3. T. J. Collins, C. Walter, "Little Green Molecules," *Scientific American*, 2006 (March), 84-90.
4. A. Ryabov, T. J. Collins, "Mechanistic considerations on the reactivity of green FeIII-TAML activators of peroxides," *Advances in Inorganic Chemistry*, 2009, *61*, 417-521.