

Enhanced Organocatalyzed Redox Processes for Sustainable Chemical Synthesis

Report for 2008

Research team and Sites of Research:

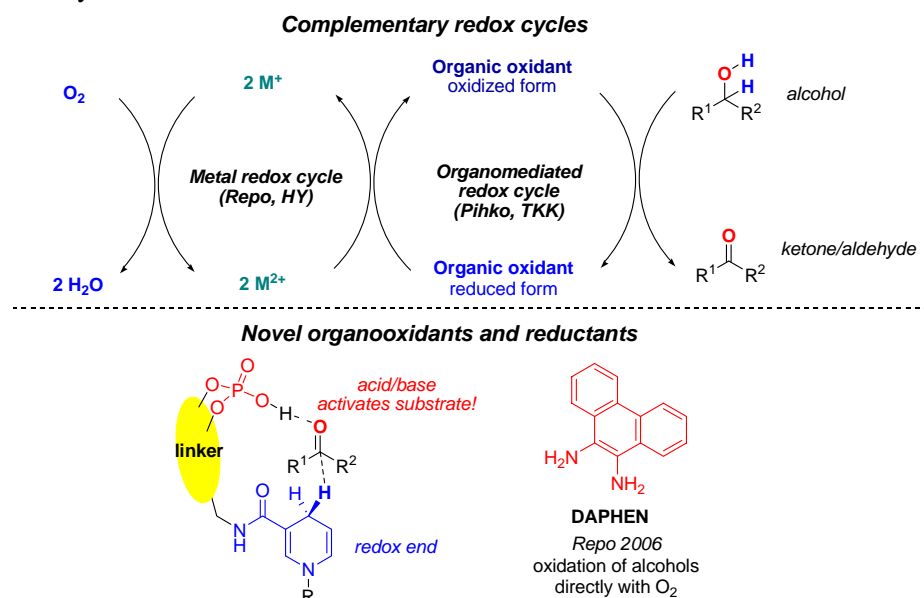
Prof. Petri Pihko and Inkeri Majander, TKK, Laboratory of Organic Chemistry (until March 2008) /Dr Syam Krishnan, University of Jyväskylä (October 2008-)

Prof. Timo Repo and Afnan Al-Hunaiti (full-time), University of Helsinki (HY), Department of Chemistry, Laboratory of Inorganic Chemistry

Description of the project and goals

The chemical and the materials industry is facing several challenges in the society's drive towards a sustainable economy. One of the key challenges for the future is the effective utilization of readily available biomass-derived materials as raw materials. The main difficulty lies in the lack of suitable and sustainable methods for converting these highly oxygenated carbohydrate and ligninous materials into smaller, less functionalized but more valuable building blocks. Another, very serious challenge is to improve the poor energy and atom efficiency of a majority of chemical processes, especially in the pharmaceutical industry.

One of the sectors where green, sustainable methods are especially lacking are selective oxidation and reduction processes. At present, nearly all *selective* oxidations and reductions of organic and biomass-derived materials are performed by highly wasteful protocols, using large amounts of oxidants or reductants and generating equally large quantities of waste. The aim of this project is to develop **highly selective and recyclable organocatalytic redox catalysts that can be coupled with metal-based recycling methods, allowing oxidations with oxygen and reductions with hydrogen or alcohols**. We believe that our biosynthetically inspired organo/metal-catalyzed redox couple systems would be much more environmentally friendly and easier to adapt to the needs of the chemical industry than currently available solutions.



The project will pool the expertise of two research groups, both of them needed to accomplish the project target. The *Laboratory of Organic Chemistry (TKK -> JY)* will focus on development of organocatalytic redox mediators and *Laboratory of Inorganic Chemistry/ (HY)* is responsible for preparation of organometallic and inorganic complexes capable to regenerate organocatalytic species with molecular oxygen or hydrogen.

Progress of Research

The project and the research activities of Prof. Pihko moved to the University of Jyväskylä during 2008. This move caused a short delay and the project will be continued with new people at JYU. The following gives a brief overview of the research progress in **2008**.

It was found previously that DAPHEN ligand possesses redox activity and is fully capable of aqueous oxidation catalysis even in the absence of a metal cofactor. Veratryl alcohol was selected as test substrate it turned out that it gave low conversion for benzyl alcohol due to substitution effect on the veratryl alcohol.

Now numerous different anthracenes were studied as organic catalyst for the oxidation of benzyl alcohol. It seems that the phenanthraquinones as catalysts don't have the same reaction mechanism as phenanthroline. Anyhow, the best yield 85% was achieved with 1,10-phenanth-5,6-dione followed by 82% and 75% anthraquinone-1-sulphonate and carboxylic anthraquinone, respectively. 9,10-phenanthraquinone and 1,8-dinitroanthraquinone gave lower yields due to solubility problems. The sulfonation and the carboxylation enhanced the solubility of the catalyst at the water phase.

The observed organocatalytic oxidation activity of 1,10-phenanthroline-5,6-dione is significant, as it provides a new and intriguing metal free concept for the oxidation of alcohols to aldehydes using O₂ as a terminal oxidant. Although, the reaction is enhanced by the addition of Cu, Fe salts, the fact that the polyaromatic diamine, and polyaromatic quinone alone are capable of direct O₂ activation is remarkable since usually a transition metal is needed for O₂ activation it enables the formation of iminoquinone which ultimately transfers hydrogen atoms from the substrate to O₂.

Apparently, the polyaromatic structure and the ability to accept and release hydrogen atoms reversibly are the main criteria for potential organocatalytic molecules of this type. Further studies on the redox properties of the new catalysts as well as the mechanism and development of novel organocatalysts with enhanced reactivity for O₂ oxidations are in progress.

➤ The study of benzyl alcohol oxidation using organocatalysis will be submitted during the year.

Impact of Research

Novel catalytic methods to activate molecular oxygen and also hydrogen have been developed. These are fundamental observations and further utilization of the catalysts during 2009 will show they potential towards various chemical transformations and their true impact towards sustainable redox-reactions.

Publications 2008

1. Pihko, P. M.*; Majander, I.; Erkkilä, A. 'Enamine Catalysis.' In: *Topics in Current Chemistry*, **2009**, 128, Chapter 21, in press. DOI:10.1007/128_2008_21

2. One poster abstract "Organocatalytic oxidation of benzylic alcohols" ADHOC 2008, Italy.

3. Manuscript under preparation: Conversion of benzylic alcohols to acids with in-situ generated catalysts using molecular oxygen as an oxidant"

In addition, the following publications were generated in collaboration with this project on the subject of hydrogen activation:

4. Victor Sumerin, Felix Schulz, Michiko Atsumi, Cong Wang, Martin Nieger, Markku Leskelä, Timo Repo, Pekka Pyykkö and Bernhard Rieger, 'Molecular Tweezers for Hydrogen: Synthesis, Characterization, and Reactivity' *J. Am. Chem. Soc.*, **2008**, 130, 14117–14119.

5. Sumerin, V., Schulz, F., Nieger, M., Leskelä, M., Repo, T., and Rieger, B. *Angew. Chem., Int. Ed.* **2008**, 47, 6001-6003. This article was also highlighted in the Cover of the *Angewandte Chemie*.