

## Enhanced Organocatalyzed Redox Processes for Sustainable Chemical Synthesis

Report for 2007

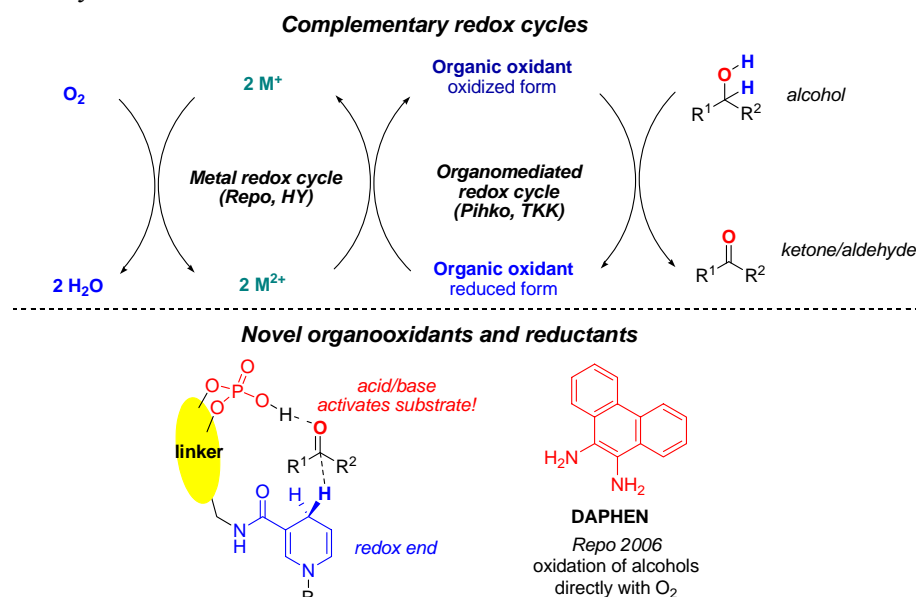
### Research team and Sites of Research:

Docent Petri Pihko and Inkeri Majander, TKK, Laboratory of Organic Chemistry  
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### 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)* 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. The key results expected from the research project include: 1) the development of efficient organocatalytic redox mediators for selective oxidations of alcohols to aldehydes, 2) the development of tunable and recyclable organocatalytic reducing agents for the reduction of aldehydes, ketones, imines and unsaturated carbonyls, including enantioselective versions of these catalysts, and 3) the coupling of these redox catalysts to highly effective catalytic systems with the aid of metal-based second redox cycles, with the potential of using oxygen or air as the environmentally benign end oxidants, and hydrogen or suitable alcohols as the end reductants.

### **Progress of Research**

The research on organocatalytic and redox chemistry has progressed relatively rapidly, as evidenced by the large number of publications from the research team (see below). In addition to the publications listed, significant progress has been made in several subtopics.

- In the one-pot reductive methylation of aldehydes (TKK, in collaboration with Prof. Ben List, MPI, Mülheim, Germany), we have now identified the good acid/catalyst combination and are currently expanding the scope of the reaction. The reaction has suffered from unexpected scale-up problems that we are currently addressing together with the List group.

- For the recycling of redox mediators, we are currently exploring ruthenium- and rhodium-based methods.

- Novel imido-amido based Cu(II) catalysts capable to aerobic oxidation of alcohols in alkaline aqueous solutions have been developed recently. As the catalytic system is water based and can use dioxygen as an oxidant, it can be considered as a cheap and environmentally benign concept. It is also worth to notice that with this system the use of pressurized air as the oxidant is safe as water as a reaction medium prevents formation of explosive gas mixtures that can take place with organic solvents. The manuscript is under preparation.

- In order to recycle organic hydrogenation reaction, attempts have been focused on hydrogenation of Hantzsch esters with literature known transition metal catalysts. However, those attempts led to a wrong isomer. Further efforts have been focused on transition metal free activation of hydrogen and as a result novel Lewis acid-base ion pairs have been identified. These ion pairs can be considered as candidates for various hydrogenation reactions as well as possible materials for hydrogen storage. Further studies are ongoing with Prof. Bernhard Rieger, TUM, Germany and the first manuscript is under preparation

### **Impact of Research**

Novel catalytic methods to activate molecular hydrogen and oxygen have been developed. These are fundamental observations and further utilization of the catalysts during 2008 will show their potential towards various chemical transformations and their true impact towards sustainable redox-reactions.

### **Publications 2007**

Erkkilä, A.; Majander, I.; Pihko, P. M.\* 'Iminium Catalysis.' *Chem. Rev.* **2007**, *107*, in press.

Erkkilä, A.; Pihko, P. M. 'Rapid Organocatalytic Aldehyde-Aldehyde Condensation Reactions.' *Eur. J. Org. Chem.* **2007**, 4205-4216.

Erkkilä, A.; Pihko, P. M.\*, Clarke, M.-R. 'Simple Primary Anilines as Organocatalysts for the Epoxidation of  $\alpha$ -Substituted Acroleins.' *Adv. Synth. Catal.* **2007**, *349*, 802-806.

Lahtinen, P.; Ahmad, J. U.; Lankinen, E. Pihko, P. M.; Leskelä, M.; Repo, T. 'Organocatalyzed Oxidation of Alcohols with Molecular Oxygen.' *J. Mol. Cat. A* **2007**, *275*, 228-232.

Korpi, Heikki; Figiel, Paweł J.; Lankinen, Elina; Ryan, Paul; Leskelä, Markku; Repo, Timo 'On *In Situ* Prepared Cu-Phenanthroline Complexes in Aqueous Alkaline Solutions and Their Use in Catalytic Oxidation of Veratryl Alcohol' *European Journal of Inorganic Chemistry*, **8**, (2007), 2465-2471.

Räisänen, Minna T.; Leskelä, Markku; Repo, Timo 'Oxidation of Gold in Alcohol Solutions' *Inorganic Chemistry*, 46, (2007), 3251-3256.

Figiel, Pawel; Leskelä, Markku; Repo, Timo 'TEMPO-copper(II) diimine catalyzed oxidation of benzylic alcohols in aqueous media' *Advanced Synthesis & Catalysis*, 349, (2007), 1173-1179.