

Ph.D. Thesis Summary

**EXAMINATION AND APPLICATION
OF GREEN CATALYTIC SYSTEMS**

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**PROGRAM OF SYNTHETIC CHEMISTRY, MATERIAL
SCIENCES, BIOMOLECULAR CHEMISTRY**

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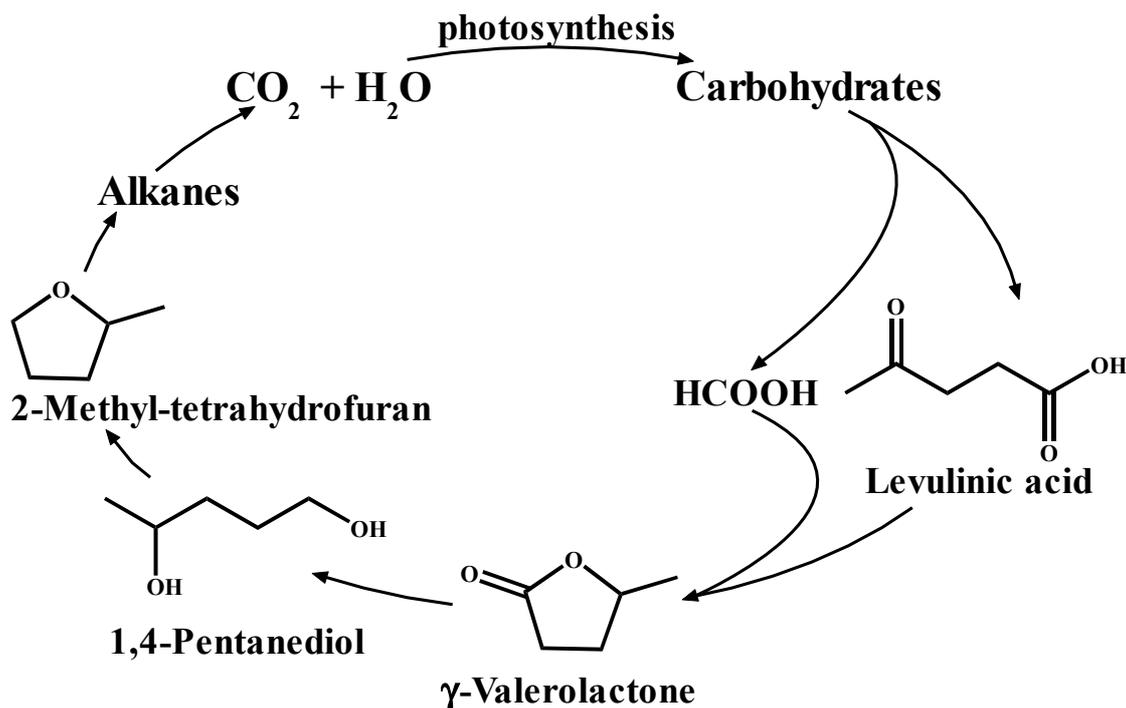
1. Introduction – Green Chemistry and Sustainable Chemistry

The development of chemistry during the 20th century led to the significant impact of the chemical industry both on the economical growth and on our daily life. The intensive energy consumption and industrial activity damage the environment. Green Chemistry principles say that products and chemical procedures have to be both environmentally friendly and economical. Nowadays the energy and the organic chemical industry use mainly fossil resources. The economical and political dependence on these resources, the increasing demand for energy and chemical products and the unavoidable depletion of fossil resources direct the attention of researchers to procedures that use renewable resources. The challenge now is how to sustain our society without compromising the long term health of our Planet. To sustain our society we need sustainable chemistry. The fundamentals of Sustainable Chemistry and Green Chemistry are similar, the difference is that Sustainable Chemistry emphasizes the use of renewables. Although, energy may become a more important issue in the future, resources for the production of organic substances have to be found as well. While the efficient conversion of carbon dioxide to chemicals is still not available, nature with the aid of sunlight produces a huge amount of carbohydrates.

2. Carbohydrates as Renewable Resources

The development of procedures that use carbohydrates as starting materials are essential to sustain mankind, our Planet and our standard of living. The aim of this work is to demonstrate that it is possible to convert carbohydrates to simple chemicals that can benefit the chemical industry and replace hydrocarbons, at least in some cases.

The reductive dehydration of carbohydrates resulted in the formation of γ -valerolactone, which was subsequently hydrogenated to 1,4-pentanediol or 2-methyltetrahydrofuran, depending on the reaction conditions. We have also shown that a mixture of alkanes can be obtained by further hydrogenation of 2-methyltetrahydrofuran. The overall scheme shows a possibility for the production of different chemicals obtained from renewable resources (Scheme 1.). Comparing these oxygenates with methanol, ethanol and methyl t-butyl ether, we realized that γ -valerolactone has very attractive properties. Its low melting point, high boiling and flash points make it a very safe liquid that can be transported all over the world with low risk. It does not form peroxides upon standing on air, it is non-corrosive and it has low toxicity.



Scheme 1. Reductive Dehydration of Carbohydrates.

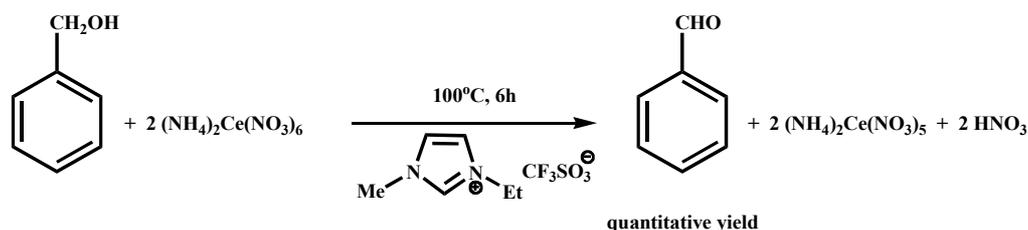
It is a good fuel additive, similarly to ethanol. γ -Valerolactone is not only a potential fuel substance but it is also a five-carbon building block for organic chemicals. The successful transfer hydrogenation of levulinic acid to γ -valerolactone using formic acid is a very important result towards sustainability. The dehydration of carbohydrates leads to levulinic acid with the simultaneous formation of formic acid. Thus formic acid is a renewable hydrogen source, making the production of γ -valerolactone really sustainable.

3. Cerium(IV)-Mediated Oxidation of Organic Compounds in Ionic Liquids

One of the twelve principles of Green Chemistry suggests that the use of additives (solvents, phase-transfer agents, ...) should be minimized or they have to be replaced by their green alternatives. **Ionic liquids** have received huge attention for the last two decades. They are compounds that purely consist of cations and anions having melting point below 100°C . Their attractive chemical and physical properties make them possible green alternatives for traditional solvents. One of the most important advantages of ionic liquids, besides their low melting point, is that they have low vapour pressure. The latter reduces the risk of air pollution, explosion and loss by evaporation. Solvent properties can be easily tuned by changing their structure giving a powerful tool for chemists and chemical engineers to

develop green ways for the production of chemicals. Our aim was to find a procedure that allows us using cerium(IV) salts for the oxidation of organic compounds in ionic liquids giving the possibility not to simply run the reaction in a homogeneous system but also to help the separation of the product from the cerium-containing ionic liquid phase and recycling the cerium salt.

Solubility tests of cerium(IV) salt in ionic liquids and preliminary studies on the oxidation of benzyl alcohol revealed that the use of cerium ammonium nitrate as oxidant and 1-ethyl-3-methylimidazolium triflate as solvent gives the best results. The yield of benzaldehyde was quantitative after 6 hours at 100°C (Scheme 2.).



Scheme 2. The cerium(IV)-mediated oxidation of benzyl alcohol in 1-ethyl-3-methylimidazolium triflate.

The formation of benzyl nitrate and benzoic acid in small amounts was observed by GC and GC-MS measurements. NMR experiments using ^{13}C -labelled $\text{Ph}^{13}\text{CH}_2\text{OH}$ confirmed the above mentioned results and allowed us to see line-broadening phenomena on the carbon signal of the $^{13}\text{CH}_2\text{OH}$ group suggesting a possible coordination / interaction of the benzyl alcohol to the cerium cation. The formation of nitric acid was proven by *in situ* IR investigations. Experiments run in the presence of Saltzman reagent showed that nitric acid slowly decomposed to nitrogen dioxide under the reaction conditions. We have shown that derivatives of benzyl alcohol can also be oxidized with good results by using this system, while anisol and naphthalene were nitrated on the aromatic ring. Cerium(IV) triflate gave good results too, but only when water was present in the reaction mixture. Under anhydrous conditions cerium(IV) triflate behaved as a Lewis acid leading to the formation of dibenzyl ether and benzylated derivatives of benzyl alcohol. The thermal and chemical stability of 1-ethyl-3-methylimidazolium triflate gave the possibility to run the reaction at temperatures higher than in the case of traditional solvents resulting in better selectivity and shorter reaction times.

4. Publications

Papers

”A zöld kémia tizenkét pontja”

Barta, K.; Csékei, M.; Csihony, S.; Mehdi, H.; Horváth, I. T.; Pusztai, Z.; Vlád, G.;
Magyar Kémikusok Lapja, **2000**, *55*, 173-181.

”Kinetic study of the metal triflate catalyzed benzylation of anisole in an ionic liquid”

Goodrich, P.; Hardacre, C.; Mehdi, H.; Nancarrow, P.; Rooney, D.W.; Thompson, J. M.;
Ind. Eng. Chem. Res., **2006**, *45*, 6640-6647.

”Lanthanide(III) nitrobenzenesulfonates and p-toluenesulfonate complexes of lanthanide(III), iron(III), and copper(II) as novel catalysts for the formation of calix[4]resorcinarene”

Deleersnyder, K.; Mehdi, H.; Horváth, I. T.; Binnemans, K.; Parac-Vogt, T. N.;
Tetrahedron, **2007**, *63*, 9063-9070.

”Imidazolium Ionic Liquids as Solvents for Cerium(IV)-Mediated Oxidation Reactions”

Mehdi, H.; Bodor, A.; Lantos, D.; Horváth, I.T.; De Vos, D.E.; Binnemans, K.;
J. Org. Chem., **2007**, *72*, 517-524.

” γ -Valerolactone - a sustainable liquid for energy and carbon-based chemicals.”

Horváth, I.T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T.;
Green Chemistry, **2008**, *10*, 238-242.

”Integration of Homogeneous and Heterogeneous Catalytic Processes for a Multi-step Conversion of Biomass: From Sucrose to Levulinic Acid, γ -Valerolactone, 1,4-Pentanediol, 2-Methyl-tetrahydrofuran, and Alkanes.”

Mehdi, H.; Fábos, V.; Tuba, R.; Bodor, A.; Mika, L. T.; Horváth, I. T.;
Topics in Catalysis, **2008**, *48*, 49-54.

”Bio-oxygenates and the Peroxide Number: A Safety Issue Alert”

Fábos, V.; Koczó, G.; Mehdi, H.; Boda, L.; Horváth, I. T.;
Energy Environ. Sci., **2009**, DOI: 10.1039/b900229b, www.rsc.org

Book Chapter

”Catalytic Conversion of Carbohydrates to Oxygenates” pp. 55-60.

Mehdi, H.; Tuba, R.; Mika, L.T.; Bodor, A.; Horváth, I.T.;

in ”Renewable Resources and Renewable Energy”, ed.: Graziani, M.; Fornasiero, P.; Taylor & Francis, (2006), Boca Raton

Presentations

Mehdi, H.; Bodor, A.; Steens, N.; Horváth, I.T.; Binnemans, K.;

”Oxidation of Organic Compounds with Cerium Salts in Ionic Liquids”, CERC3 Young Chemists Workshop, "Lanthanide-mediated organic reactions", Knokke, Belgium, 8-11 February 2006.

Mehdi, H.; Bodor, A.; Steens, N.; Horváth, I.T.; Binnemans, K.;

”Oxidation of Organic Compounds with Cerium Salts in Ionic Liquids”, Bilateral Collaboration in Molecular Design and Synthesis, Katholieke Universiteit Leuven, Leuven, Belgium, 10-12 May 2006.

Posters

Mehdi, H.; Tuba, R.; Bodor, A.; Mika, L.T.; Horváth, I.T.;

”Catalytic Conversion of Carbohydrates to Oxygenates”, 15th International Summer School on Coordination Chemistry, Szklarska Poreba, Poland, 6-12. June 2004.

Mehdi, H.; Tuba, R.; Bodor, A.; Mika, L.T.; Horváth, I.T.;

”Catalytic Conversion of Carbohydrates to Chemicals”, XVI. FECHEM Conference on Organometallic Chemistry, Budapest, Hungary, 3-8. September 2005.

Fábos, V.; Mehdi, H.; Kaposy, N; Horváth, I.T.;

”Efficient Catalytic Transfer Hydrogenation of Levulinic acid to γ -Valerolactone”, XVI. International Symposium on Homogeneous Catalysis, Florence, Italy, 6-11. July 2008.