Book of Abstracts

COST ACTION D30 Final Evaluation Meeting

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Welcome

Organisers

Prof. Gerard Demazeau
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Financial Support

COST

COST is one of the longest-running instruments supporting co-operation among scientists and researchers across Europe. COST now has 35 member countries and enables scientists to collaborate in a wide spectrum of activities in research and technology.

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Programme

Friday, 26 October

Opening remarks
Friday morning, 26 October, 9:00

Invited lecture
Friday morning, 26 October, 9:10

9:10 Invited

Integration of Homogeneous and Heterogeneous Catalytic Processes for Sustainable Biomass Conversion

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The sustainability of mankind depends whether we can supply the increasing population with enough energy, food, and chemicals, including carbon-based consumer products, simultaneously without compromising the long term health of our planet. While it is difficult to predict the exact date of the depletion of fossil fuels, the transition to renewable resources should be accelerated because of the frequently and unexpectedly changing political/economical environments resulting in limited access to and rising costs of fossil fuels. The development of sustainable liquids for energy and the chemical industry should be considered as a key research area in the next decades.

The conversion of biomass to chemicals represents a major challenge because of the complex nature of the substrates, e.g. the biomass, both chemically and physically. While large scale processes could take the advantages of heterogeneous catalysis, their use could be limited by the solid nature of biomass. The application of homogeneous catalysts, especially water soluble systems, could offer the possibility to deliver the catalytically species into the solid or swelled biomass. Integration of heterogeneous and homogeneous catalysts including enzymes could lead to the development of novel, commercially attractive multi-step processes.

We have proposed that g-valerolactone (GVL), a frequently used food additive, exhibits the most important characteristics of an ideal sustainable liquid. It is important to recognize that the use of a single chemical entity instead of a mixture of compounds could significantly simplify its worldwide monitoring and regulation. We have been investigating the selective conversion of carbohydrates to various C5-oxygenates including levulinic acid, GVL, 2-methyl-THF and alkanes using homogeneous and heterogeneous catalysts. The preliminary evaluation of GVL as a fuel additive, performed by adding 3, 6 and 9% to 95-octane gasoline, shows very attractive properties, comparable to ethanol.

Working Group Presentations
Friday morning, 26 October, 10:10

10:10 Invited

A summary of results obtained in Working Group 002 "Synthesis and Processing of Nanopowders"

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The area of research of the working group includes:

- **Methods of synthesis of nanopowders,**
- **Development of high pressure reactors for nanopowders synthesis**
- **Characterisation of nanopowders**
- **Their applications**

Nanopowders are powders with particle size below 100 nm. Nanopowders are produced in industrial scale since long time, e.g., carbon black, silica, titania etc. However, recently much interest is in nanopowders of high commercial value due to their specific optical and magnetic properties that result from nano-size.. Furthermore, from nanopowders, or using nanopowders, one can produce nanocrystalline materials or nanocomposites of radically improved strength. Nanopowders do already play an important role in many industrial fields, and the field of their application will continuously increase in future.

1. One of major barriers in the science and technology of nanopowders is that high value nanopowders need to be produced with well controlled and narrow grain size distribution, and these parameters are difficult to control and measure.

2. Wet chemistry methods for their production are usually cheap, but after such synthesis processes nanoparticles are frequently coated with a layer of untreated reaction precursors. Therefore a major issue is to obtain nanoparticles of high degree of crystallinity.

3. It is worth developing technology of nanopowders with engineered magnetic or optical properties. An efficient method to add to nanopowders controlled magnetic or optical properties is to dope them with ions of metals which have themselves magnetic or optical properties. These ions are then protected from the environment since they are embedded in a stable oxide lattice, and at the same time this particle is so small, that it can be embedded in various materials like polymers, textiles, other ceramics, dispersed in fluids, or used for imaging cells. Adding value to nanoparticles requites synthesis methods that permit to dope the nanoparticles to high level with such ions, without their segregation as clusters.

4. It is important to be able to coat the nanopowders with functional layers which enhance their sintering into usable mechanical parts or dispersion in fluids, or attaching to selected surfaces. . Such a process is impossible in high temperature production processes.

5. Therefore, there is a need for innovative synthesis methods that would permit to scale up production of nanopowders and at the same time meet all the above criteria, and for commonly agreed characterisation procedures to ensure delivery of quality nanopowders.

The above issues have been addressed by our working group and

solutions found will be reported bellow.

1. We have developed a method to **estimate the grain (or crystallite) size distribution of nanopowders based solely on an analysis of the shape of XRD peaks.** The peaks must be measured according to well defined procedures and can be analysed using an analytical formula.
2. **We introduced density measurements as an important tool for characterisation of nanopowders**. Density tells us about the thickness of the layers on the powders surface. We could optimise the synthesis process so that such layers thickness is the minimum possible under given thermodynamic conditions.
3. Competence we acquired in characterisation of nanopowders and nanoceramics nanostructure permitted us **to edit a first Nanometrology report focussed on Nanoparticles and nanomaterials, published as a prestigious Nanoforum report at the European nanotechnology web page www.nanoforum.org**
4. We have found that **solvothermal and hydrothermal synthesis,** i.e., a method where reagents in solution are heated above the boiling point at atmospheric pressure (and this is made possible because the fluids are in a high pressure vessel) **is a method that permits to incorporate in the lattice of ZnO a relatively large amount of metal ions:** Al^{3+}, Mn^{2+}, Ni^{2+},Co^{2+},Cr^{3+} without formation of measurable clusters or precipitates. It was found that addition of Al ions in the range 0f 0.4 mol %n is possible. And this leads to increase of luminescence by more than one order of magnitude. As far as magnetic ions, the material obtained was paramagnetic. Absence of ferromagnetism indicates that ZnO doped with Mn^{2+} is not a suitable material for spintronics, contrary to many claims. Probably the magnetic properties of material obtained by other methods is caused by segregation of Mn clusters.

   Also doping of Zirconia with rare earth ions was very successfully performed, and nanoparticles emitting under excitation by laser, UV or X-ray radiation emit a range of colours have been produced.
5. **We produced hydroxyapatite powders coated with collagen, which could be sintered into biocompatible material with very good mechanical properties**; combined strength and ductility. Such material can be sued in tissue engineering.
6. **Our studies show a range of advantages of the solvothermal method, and in particular when microwaves are used for heating:**

   - comparing to high temperature methods high levels of doping are possible, and non volatile ions can be doped.

   - comparing to precipitation/ calcination or sol-gel methods, no high temperature annealing is necessary for nanopowders production, and the powders can stay all the time in closed vessels.

   A drawback of solvothermal synthesises that high pressure vessels are slow to heat up and cool down due to high thermal inertia. Furthermore, contact with heating elements or steel parts of the vessel should be avoided **and highly pure products can be obtained.** This can be achieved by heating the reagents using microwaves, which act across a Teflon vessel where the reagents are enclosed. **In addition to that, if microwaves are used, the process of synthesis is shortened about 5 times or more, because the thermal inertia of the vessel is not limiting hating rates.** However, such Teflon lined reactors are not suitable for processes at temperatures above 300^{o}C.
7. We compared all the methods available in our group, and based on a SWOT analysis, w**e have developed two production processes:**

   St**opped – flow microwave – pressure reactor,** capable of producing about 1 kg of zinc oxide nanopowders per day, at pressure up to 4 MPa and temperature up to 250^{o}C. .

   Continuous synthesis of YAG nanopowders in supercrical water, at temperature about 450^{o}C and pressure about 40 MPa. The process includes also a thermal annealing of the powders at 600^{o}C to obtain a good density. Contrary to precipitation/calcination methods powders prepared in that way do not form aggregates. We have also shown several advantages of the present method over the claimed in the literature synthesis methods of YAG in continuous flow reactors.

   Both reactors are unique world wide, and give the opportunity of industrial production of nanopowders. There are some patents pending.

In summary, the results of our working group collaboration are as follows:

1. **Obtaining new information about synthesis of nanopowders with the use of microwave and pressure reactors.** It was found that these techniques are especially well suited to produce doped nanopowders of ZnO and ZrO2 as well as hydroxyapatite powders coated with organic material.
2. **Scaling up of the nanopowders production using high pressure and/or microwave reactors**. It was found that scaling up to industrial production is feasible. New concepts for such reactors have been developed.
3. **Developing procedures for characterisation of nanopowders.** We developed two new procedures, but still a lot has to be done in this field.
4. **First steps towards understanding basic phenomena which take place during synthesis and sintering.** This field of research is now a hot topic, since important data have been gathered and need to be explained.
5. **Ready for applications.** The powders produced can now be tested in various applications. Prototype devices need to be developed to convince industry about advantages of nanopowders based nanotechnology.

The general conclusion is that: **"High Pressure Technology for production and processing nanopowders is now a fact that needs to be taken into account by the scientific and industrial communities"**

WG D30/003 Papers

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Coffee break
Friday morning, 26 October, 11:10

Lectures
Friday morning, 26 October, 11:30

Lunch
Friday afternoon, 26 October, 12:30

Lectures
Friday afternoon, 26 October, 14:30

14:30 Invited

Final report of WG1

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1) Hydrogenation of unsaturated organic substrates

The attention on g-butyrolactones as structural elements in organic compounds is growing up in last years. This typical moiety is present in a large variety of natural and synthetic compounds involved in agrochemicals, food and pharmaceuticals industries. Furthermore some g-butyrolactones due to their smelly proprieties are added to many foodstuffs at concentration often comparable to those present naturally, in order to increase the flavour. The isotope dilution mass spectroscopy provides an accurate and convenient method for the quantification of these compounds if stable isotopomeric compounds are available. So far the possibility to settle a relatively simple method to realise the complete sequence of differently deuterated g□butyrolactones to be employed as internal standards seems desirable. Anyway despite of a plethora of methods regarding to the synthesis of g-butyrolactones present in the scientific literature only a few procedures have been devoted to the regioselective introduction of multiple deuterium atoms into the lactone ring.

So far we have developed a convenient general synthetic procedure to synthesise isotopomeric g□butyrolactones containing 2, 4 or 6 deuterium atoms. Three differently deuterated g□butyrolactones were synthesised in quantitative yield, starting from the saturated acid C_4 (succinic) and unsaturated acid C_4 (fumaric or maleic and acetylendicarboxylic) in the presence of $Ru_4H_4(CO)_8(PBu_3)_4$ using a deuterium pressure of 180 bar at 180 °C (Figure 1). This catalytic system is known to be active in the hydrogenation of carboxylic acids to the corresponding esters.

It was established, that depending on the pH, the hydrides formed from $[\{RuCl_2(m\text{tppms})_2\}_2]$ and excess *m*tppms (Na-salt of monosulfonated triphenylphosphine, 3□diphenylphosphinobenzensulfonate) catalyzed the selective hydrogenation of disubstituted alkynes either to the corresponding *cis*- or *trans*-alkenes. The selectivity decreased upon increasing the H_2 pressure to 10 bar or above – the reason of this change is presently unclear. The Joo group has described earlier that the selectivity of the hydrogenation of cinnamaldehyde catalyzed by the water-soluble complex $[\{RuCl_2(m\text{tppms})_2\}_2]$ (+ excess *m*tppms) was a sensitive function of the hydrogen pressure. During the D30 Action we made

detailed ^{1}H and ^{31}P NMR studies to establish the effects of the pH and the hydrogen pressure on the reaction of [{$RuCl_2$(*m*tppms)$_2$}$_2$] and excess *m*tppms with H_2, including the determination of the relevant T_1 and T_2 relaxation times. The results revealed the formation of the following complexes: a) in acidic solutions at 1 bar H_2: [RuHCl(*m*tppms)$_3$] and [{RuHCl(*m*tppms)$_2$}$_2$]; b) in acidic solutions at elevated H_2 pressure: *trans*-[RuH_2(*m*tppms)$_4$] c) in basic solution at 1 bar H_2: *cis*-[$RuH_2(H_2O)$(*m*tppms)$_3$]; d) in basic solution at elevated pressure: *cis*-[$RuH_2(H_2)$(*m*tppms)$_3$]. Of these complexes *cis*-[$RuH_2(H_2)$(*m*tppms)$_3$] is a dihydrogen complex with water-soluble phosphine ligands and *trans*-[RuH_2(*m*tppms)$_4$] is one of the rare trans-dihydrides. (Furthermore, *cis*-[$RuH_2(H_2O)$(*m*tppms)$_3$] was previously incorrectly described as *cis*-[RuH_2(*m*tppms)$_4$].)

2) Hydroformylation of olefins and amides

A series of platinum(II) methyl complexes bearing bis-phosphanyl monosulfides (P^PS) has been used in association with tin(II) chloride for the hydroformylation of 1-octene under 50 bar CO:H_2. The best catalyst performance was obtained using the monosulfide of 1,3-bis(diphenylphosphanyl)propane as chelating ligand. Combined conventional and high pressure multinuclear NMR studies established that: *i*) chelation of the P^PS ligand is retained during catalysis; *ii*) in this catalytic system, $SnCl_2$ plays three roles: it weakens the Pt–Cl bond in the chloro-Pt(II) precursors; it activates the insertion of CO into the Pt–alkyl bond; and it facilitates the hydrogenolysis of the Pt–acyl intermediate.

A collaboration between the groups of Liverpool and Tarragona has been initiated on the subject *"in situ* high pressure NMR studies of the hydroformylation of acrylamides". Preliminary catalytic studies were conducted in Tarragona to facilitate a collaborative high pressure NMR study in Liverpool into the factors determining catalyst performance in a new route to MMA via 3-hydroxy-2-methylpropionamide discovered in Tarragona. The effect of reaction temperature, pressure, and catalyst concentration, on selectivity and turnover were all investigated and the optimal ranges for the HPNMR study determined. It was found that changing the catalyst concentration had minimal effect on aldehyde regioselectivity, the catalytic system was relatively insensitive to changes in total and partial pressure and that the hydrogenation side reaction could be suppressed at low temperatures.

2) Hydrocarboxylation of terminal alkenes using Palladium catalysts

Regioselectivity control was studied in palladium catalysed hydroxycarbonylation of styrene in neat water with water-soluble phosphines, mostly trisulfonated triphenylphosphine, TPPTS, but also 4- (N, N, N', N' tetraethyl-diethylene methylenetriamine) phenyl diphenylphosphine, N3P. The factor giving the highest changes in regioselectivity in the TPPTS system, under similar reaction conditions, is the temperature. In the N3P case, only a minor variation in the *n/i* ratio as a function of temperature is observed. In-situ normal- and high-pressure NMR experiments were performed to obtain further information about the catalytic cycle and the reaction intermediates. Two palladium hydride intermediates, a palladium η^3-benzylic complex and both the branched and the linear palladium acyl complexes were identified in the HP NMR experiments. The hydroxycarbonylation in water using styrene as a substrate operates using a hydride mechanism for pathways leading to both linear and branched product. Insertion of styrene in the palladium-hydride bond gives an η^3-benzyl compound. A high CO pressure gives a kinetic preference for the *iso*-acyl in the next step. In the TPPTS system, at moderate temperatures, the hydrolysis of the *iso*-acyl is faster than its conversion to the thermodynamically more stable *n*-acyl. A low *n/i* therefore requires high pressures and reasonably low temperatures. The N3P ligand always favours the linear product since isomerisation of the *iso*-acyl to the *n*-acyl in this system is fast under all conditions investigated.

The kinetics and the mechanism of the catalytic hydrocarboxylation of linear alkenes to obtain carboxylic acids using supercritical carbon dioxide as a solvent was studied. High selectivities in acids have been obtained. The best results were achieved by adding a perfluorinated surfactant to the reaction mixture (93 % conversions and *ca* 90 % selectivity). Comparative multinuclear high pressure NMR studies in THF-d_8 and in supercritical CO_2 show the formation of Pd(0) species.

3) Cooperative Effect between Iridium and Platinum in the Carbonylation of Methanol into Acetic Acid

The iodocarbonyl monomer [$PtI_2(CO)_2$] promotes the iridium catalyzed carbonylation of methanol to acetic acid at low water contents. Studies based on low pressure or high pressure NMR and the use of labeled reactants were conducted close to the real conditions of catalysis in order to gain a deep insight into this system. Carbonylation of CH_3I at low water contents proceeds slowly and the migratory CO insertion step, leading from H[$IrI_3(CH_3)(CO)_2$] to H[$IrI_3(COCH_3)(CO)_2$] is rate limiting. The dimer [$PtI_2(CO)$]$_2$ reacts immediately with [PPN][$IrI_3(CH_3)(CO)_2$] (PPN is $Ph_3P{=}N^+{=}PPh_3$) under nitrogen to afford a mixture of species, among which the key heterobinuclear [Ir-Pt] intermediate [PPN][$IrI(CH_3)(CO)_2$(m-I)$_2$$PtI_2(CO)$] has been identified; [PPN][$IrI(CH_3)(CO)_2$(m-I)$_2$$PtI_2(CO)$] can in it's turn lead to the formation of [PPN][$PtI_3(CO)$], [$IrI_2(CH_3)(CO)_2$(solv)], [$Ir_2I_2(CH_3)_2$(m-I)$_2$$(CO)_4$] and [PPN][$Ir_2I_4(CH_3)_2$(m-I)$(CO)_4$]; all of these species have been characterized. Under CO pressure, [PPN][$IrI(CH_3)(CO)_2$(m-I)$_2$$PtI_2(CO)$] is a short-lived species that quickly leads to [$IrI_2(CH_3)(CO)_3$] and [PPN][$PtI_3(CO)$] showing that the main role of the platinum promoter is to abstract an I^- ligand from [PPN][$IrI_3(CH_3)(CO)_2$]. In the catalytic conditions, I^- is abstracted from H[$IrI_3(CH_3)(CO)_2$] by [$PtI_2(CO)_2$] and the rate determining step is accelerated; the relevant species H[$IrI_3(CH_3)(CO)_2$], H[$IrI_3(COCH_3)$ $(CO)_2$] and H[$PtI_3(CO)$] have been observed at 30 bar of CO. A catalytic cycle is proposed which depicts cooperative effect between iridium catalyst and platinum promoter.

4) Polymerization of olefins using single site catalysts

A calix[4]arene titanium catalyst has been employed for the synthesis of HDPE in the presence of MAO as co-catalyst. The 25,27-dipropyloxy-calix[4]arene titanium dichloride (Figure 2) has been synthesised and characterized through X-ray diffraction. This complex was employed as catalyst in the polymerization of ethylene under different polymerization conditions. The polymers were characterized through DSC and ^{13}C-NMR and the molecular weight evaluated through GPC and viscometric analyses. The activation step of the catalyst was followed through NMR experiments. A methyltitanium species was evidenced using ^{1}H- and ^{13}C NMR spectroscopy, probably involved in the activation of the titanium complex.

Also the stability of the starting titanium calix[4]arene and the

methyltitanium species were confirmed by NMR data, according to those reported in the literarure. Heating these species up to 373 K the NMR spectra were unaltered. Very high molecular weight were detected also when the reaction temperature was relatively high indicating a high stability of the catalytic system. The joint publication gave rise to the cover of the corresponding *Macromolecular* issue

5) Copolymerization of CO with olefins

The WG has continued to examine the preparation of Ni(II) and Pd(II) organometallic complexes containing P,O or P,N chelates capable to achieve the coupling of ethylene/CO/polar monomer, such as methylacrylate. The latter insertion represents a difficult step, the isolation of new complexes in which the coupling has been achieved are being currently characterized, including by X-ray diffraction.

During this period, attempts were made to monitor by IR and NMR techniques the course of reactions such as that described below. To this end, short-term visists to partner's institutions were performed. Reaction of [Pd(Me)(*P,O*)(NCMe)]PF6 **1** (*P,O* = $Ph_2PNHC(O)Me$) (Scheme below) was exposed to 1 atm. of CO, the acyl complex [Pd{C(O)Me}(*P,O*)(NCMe)]PF6 **2** was formed quantitatively. Insertion of ethene into the Pd-acyl bond of **2** occurred at ambient temperature, under atmospheric pressure. The reaction was completed after *ca.* 90 min. ($^{31}P\{^1H\}$ NMR monitoring) and afforded [Pd{$CH_2CH_2C(O)CH_3$}(*P,O*)] **3**. When complex **2** was reacted with methylacrylate, $^{31}P\{^1H\}$ NMR monitoring revealed its complete disappearance after *ca.* 4 h at ambient temperature and a new resonance appeared at d = 81.9, in the same region as that of **3**. The ^1H NMR spectrum of the new complex [Pd{CH[C(O)OMe]$CH_2C(O)CH_3$}(*P,O*)]PF_6 **4** in acetone-d_6 contains three methyl signals at d = 2.45 and 2.61 (Me-C(O)) and 2.91 (OMe), whereas the CH and CH_2 protons Ha, Hb and Hc resonate at d = 3.16, 3.22 and 3.44, respectively. Interestingly, the stability of the *(C,O)* chelate in **3** did not prevent facile CO insertion into the Pd-C bond to give the a-keto chelate [Pd{C(O)CH2CH2C(O)Me}(*P,O*)]PF_6 **5**, as evidenced by the occurrence of a new n(CO) vibration at 1708 cm^{-1} and a $^{31}P\{^1H\}$ NMR resonance (d = 63.0) (Figure 3). The six-membered metallacycle in **5** inserted ethene under ambient conditions to afford [Pd{$CH_2CH_2C(O)CH_2CH_2C(O)Me$}(*P,O*)]$PF_6$ **6**. Complex **5** was also treated with methylacrylate (under a CO atmosphere to avoid decarbonylation to **3**) and insertion into the Pd-C(O) bond was achieved after 16 h at ambient temperature ($^{31}P\{^1H\}$ NMR monitoring) and afforded [Pd{CH[C(O)OMe]$CH_2C(O)CH_2CH_2C(O)Me$}(*P,O*)] **7** as the sole product in 75% isolated yield. The use of a dissymmetric *P,O* ligand in this chemistry offers the advantage over symmetrical *P,P* or *N,N* ligands to orient the *trans* ligands in a more selective manner. The organic ligand in **7** was built-up in a stepwise manner from **1** by successive insertion into the Pd-methyl bond of CO, ethene, CO and methylacrylate. All the intermediates were isolated and characterized and this nicely mimic the desired sequences for terpolymerization reactions with these monomers. Progress were made in such studies but they were not complete enough to give rise to a joint publication.

In the course of this COST D-30 action, another fruitful collaboration developed in the field of cluster chemistry with the group of Bari, triggered by a research stay of Vito Gallo in our Laboratory, using a STSM. He studied in Strasbourg mixed-metal Pt-Co clusters with P,N,P short-bite ligands and discovered an unusual equilibrium between the chelate and bridged forms of such ligands as a functiuon of the steric properties of the N-substituent. A detailed study was undertaken which has given rise to a joint publication, although in a field initially not covered by our action. This work gave rise to the cover of the corresponding *Dalton* issue(Figure 4).

6) Carbonates via CO_2 –epoxide reactions

In this study the possibilities to react carbon dioxide with epoxides with structurally known transition or main group metal based catalysts are looked for. Coupling of carbon dioxide with epoxides is a desirable alternative route to carbonates especially because most of the industrial processes still use highly toxic phosgene route while manufacturing commodity carbonates. Although, the recent advances in this area have been impressive, sufficiently efficient process to succeed in an industrial setting has not been developed yet. There is also a challenge of competitive products.

The results obtained in the project show that aliphatic epoxides, eg. 1-hexene-epoxide and cyclohexene epoxide can be homo-and copolymerized by using heterogenous Zn-catalyst system. We have demonstrated that polycarbonates containing up to 98% polycarbonate linkages in the polymer backbone are formed. Also new catalyst candidates, iron(II) and cobalt(II) complexes bearing tetradentate ligands have been identified for the synthesis of cyclic carbonates. These complexes were found to be excellent catalysts for the reaction of epoxide and CO_2 when used in conjunction with Lewis base co-catalyst ($n\text{-}Bu_4NBr$).[2] This catalytic system gives propylene carbonate in high yield under soft reaction conditions (10 bars and 90 ºC) without need of reducing agent (Zn powder). Complex 2a had higher catalytic activity compared to its Fe and Mn analogues (Figure 5).

7) Pauson-Khand reaction catalysed by heterometallic cobalt based clusters

The Pauson-Khand reaction is the cycloaddition af an alkene, an alkyne and carbon monoxide. We have started a project aimed at studying the catalytic activity of heterometallic cobalt based clusters for the intramolecular cyclocarbonylation of diethyl allylpropargylmalonate. Tri- and tetranuclear clusters containing at least two Co atoms were found active as precatalysts of the Pauson Khand reaction under mild conditions. Among the tetranuclear clusters tested, $[RuCo_3(CO)_{12}]$(bmim) and $[RuCo_3(CO)_{12}](NEt_4)$ gave the best results in terms of productivity, and led to complete conversions of the substrate even at 2% load. Clusters $Co_4(CO)_{10}$(dppm) and $Co_4(CO)_8$(dppa)$_2$ containing a diphosphane were almost inactive, while (dppa)$PtCo_2(CO)_7$, containing a monodentate phosphane, exhibited a moderate activity. The effect of diphosphane ligands on catalytic activity was found dependent on the metal skeleton. With $PtCo_2$ clusters the productivity was higher when the species favors the chelating coordination mode on the Pt atom, confirming that the presence of P ligands onto Co atoms exerts a detrimental effect.

8) Mechanistic studies of Suzuki coupling by combined NMR and ESI-MS techniques

We have also carried out a detailed mechanistic study on the palladium catalysed cross-coupling reaction between aryldiazonium salts and aryltrifluoroborates. The precatalyst used in this study is bis(m-acetato)bis(4,4'-difluoroazobenzene-C^2,N)dipalladium(II) (6.

Figure 6). The reaction follows a Pd^0/Pd^{II} cycle after reduction of 6 to a molecular Pd^0 species (I). Based on the combined ESI-MS and ^{19}F NMR techniques the catalytically active Pd^0 species I is bearing the arylated azobenzene as a ligand. Oxidative addition by the diazonium salt generates an aryl-Pd^{II} intermediate (II) which was also detected in solution. The catalytic cycle is completed with the transmetallation between II and the organoborate, followed by fast reductive elimination of the cross-coupling product, restoring the molecular Pd^0 species I. A concurrent activation path was also observed. It consists of the formation of (4,4'-difluoroazobenzene-*C*^{2},*N*)dipalladium(II) tetrafluoroborate (7) by the reaction of 6 with the diazonium salt and subsequent reduction by aryltrifluoroborate to give I (Figure 7).

9) Dehalogenation of aromatics in ionic liquids

The catalytic hydrocarboxylation of linear alkenes to obtain carboxylic acids using supercritical carbon dioxide as a solvent was studied. High selectivities in acids have been obtained. The best results were achieved by adding a perfluorinated surfactant to the reaction mixture (93 % conversions and *ca* 90 % selectivity). Comparative multinuclear high pressure NMR studies in THF-d_8 and in supercritical CO_2 show the formation of Pd(0) species.

10) Supercritical fluid chromatography

In CO_2-based chromatography (supercritical fluid chromatography, SFC) both chiral and non-chiral SFC have been developed, especially cryogenic low-temperature chromatography for high-resolution SFC. The technique developed was applied for different types of chiral racemates (finrozole, guaifenesin and ferulic acid dimer dimethylester). A fast statistical screening method for assessing chiral resolution of racemates has been refined and published .

Coffee break
Friday afternoon, 26 October, 16:30

Lectures
Friday afternoon, 26 October, 16:50

16:50 Invited

High Pressure Tuning of Biochemical Processes: Protein dynamics and aggregation

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Since deposition of insoluble protein aggregates can be found in many serious diseases like Alzheimer's disease, familial amyloidosis, investigation of protein aggregation is a very important research topic. Pressure sensitivity of the protein aggregation makes high pressure a useful tool in these experiments.

The pressure – temperature phase diagram of the proteins was extended, to incorporate the intermediate and aggregated protein phases.

The physicochemical aspects of the polymorphism of amyloids, as well as the role of hydrational and volumetric factors in amyloidogenesis were also studied. As a result a physicochemical, solvational model explaining how preferential hydration or preferential binding of a cosolvent to an amyloidgenic protein may lead to different "strains" has been put forward.

The stability of amyloid fibrils towards high hydrostatic pressure was studied and found markedly different from the stability of the amorpous aggregates.

The volumetric aspects of protein interacitions were also investigated with number of spectroscopical and other methods from infrared and fluorescence spectroscopy, to pressure perturbation calorimetry.

Dinner
Friday evening, 26 October, 19:00

Saturday, 27 October

Lectures
Saturday morning, 27 October, 8:45

8:45 Invited

High Pressure Tuning of Biochemical Processes: Macromolecular Interactions and Cellular Physiology

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Scientific results

All major goals of the tasks have been achieved. In some areas unexpected additional results have been achieved, which highlight high pressure as a powerful tool in the investigation of macromolecular interaction.

Tasks 1 and 2

Characterization of HHP responses on the gene/genome/transcriptome and on the enzyme/proteome level

Bacterial systems: Proteomic and transcriptomic approaches and genetic analyses of high pressure mutants revealed that high pressure is a powerful tool to investigate cellular processes far beyond the mere inactivation of bacteria. Two approaches can be separated for which different responses to high pressure are apparent. Organisms can be shocked by short (nearly) lethal pressure puls(es) (e.g.150-400 MPa) and their response is characterized upon recovery. Alternatively,

bacteria can be grown under sublethal (comparably low) pressures (e.g. 20-150 MPa) for a prolonged time possibly resulting in adaptation and (another type of) mutation. Two major effectors of the pressure response were identified in the different approaches. Overexpression of ssrA enables growth under high pressure by helping to maintain ribosomal function in Gram-positive bacteria (Lactobacillus sanfranciscensis). The restriction endonuclease mrr, specifically cleaving methylated DNA was identified as a major mediator of the high pressure response in Gram-negatives (*E. coli*).

Primary thermodynamic targets present in the cell were identified to be the cellular membrane and the ribosome. It appears that translation is stalled in vivo at pressures above 40 MPa. Ribosomes can be returned to functionality by trans-translation and peptide tagging mediated by tmRNA and the ClpX protease/chaperon system. Both systems are turned on as a specific reaction of high pressure stress. Many other stress responses observed appear to be secondary effects, which are the result of the typical response pathways present in a respective cell. As the approaches in E. coli and L. sanfranciscensis are highly complementary, the respective systems were studied in the respective other system in close collaboration of the groups in Munich, Germany and Leuven, Belgium. Furthermore, it was shown that the expression of virulence factors and changes in antibiotic resistance can be triggered by high pressure treatments. This was studied in collaboration of the groups in Munich, Germany and Monells, Spain.

Eukaryotic systems: Systems involving muscle cells and chondrocytes are investigated in this WG. It was demonstrated that these systems also as a result of their larger size as compared to bacteria, are valuable models in using pressure as a tool in cell biology. High pressure microscopy facilities at the Technische Universität München have already been used to study muscle cells and their ion channels under pressure in situ in an STSM (self funded within Germany). These investigations were continued in an STSM between the Heidelberg group (Germany) and the JAMSTEC (Japan). For the first time resting membrane potentials recorded on-site in intact skeletal muscles from deep sea fish (gonostoma gracilis sp.) salvaged from depths up to 1.000 m were recorded. In 'in situ' high pressure microscopy it was shown that intracellular Ca2+ homeostasis is pressure-dependently altered in single muscle cells. Ca2+ leaks from intracellular stores upon compression and is first taken up and buffered by mitochondria. Then, at about 30 MPa, mitochondria buffer capacity breaks down and Ca2+ ions are poured back into the cytosol resulting in irreversible contracture of the cells. For these experiments, a high pressure optical vessel was combined with a confocal laser scanning microscope. The results are interpreted in terms of a model for high pressure limits in mammalian muscle for prolonged high pressure applications. There is a rather sharp limit for functional breakdown at ~25 MPa that coincides with the deepest dive depths recorded for mammals (sperm whales). Therefore, deep sea fish must have evolved some protective mechanisms of the membrane level to keep up their excitability. In these fish depth and temperature both alter passive membrane parameters with a tendency towards larger relative Na+ permeabilities and intracellular K+ concentrations in samples from deeper depths (e.g. 700-800 m vs. 200-400 m).

Task 3

Functional analysis of cellular membranes and membrane proteins

In a joint project of the German research foundation members of WG007 (TUM, Germany) collaborated with a member of WG006 (Universität Dortmund, Germany) on the piezophysiology of bacterial membranes. Systems were developed to study membrane protein interaction in vivo and in membrane vesicles. It was shown, that high pressure can mediate signaling processes by interfering with protein dimerization in a cellular membrane system. Also, membrane transporters are affected via their changes ATPase activity. The systems involved the multi-drug-transporter LmrA of Lactococcus lactis and the ToxRS systems of Vibrio cholerae and the deep sea bacterium Photobacterium profundum. An STSM is ongoing until the end of the action between Reading and Munich to study protein secretion as a function of high pressure. All of the proteins released from pressure-treated cells had a molecular weight below 80 kDa. This cut-off point is consistent with the suggestion that the peptidoglycan of the cell wall acts as a molecular sieve for proteins leaking from bacterial cells.

Tasks 4 and 5

Characterization of HHP responses on the population level

Interaction of HHP effects on microorganisms with environmental factors

The characterisation of responses to high pressure of microorganisms in food systems has been elucidated with respect to population level and interaction of high pressure with environmental parameters in the groups situated in Belfast, UK, Reading UK and Monells, Spain. Mathematical models were established to describe the inactivation of bacteria in these systems. A new primary model for inactivation of microbes under pressure was constructed to describe non-log-linear inactivation kinetics of pressure-treated bacteria. The model assumes a first-order process in which the specific inactivation rate changes inversely with the square root of time. The model gave reasonable fits to experimental data over six to seven orders of magnitude. It was also tested on 138 published data sets and provided good fits in about 70% of cases in which the shape of the curve followed the typical convex upward form. In the remainder of published examples, The model parameters varied regularly with pressure which may reflect a genuine mechanistic basis for the model. This property also allowed the calculation of (a) parameters analogous to D and z in thermal processing, and (b) the apparent thermodynamic volumes of activation associated with the lethal events. Further, application of fuzzy logic and neuronal networks provided by the Munich group was successfully applied to describe metabolic and cellular functions under high pressure. With these it was possible to include into the models intermediate states of inactivation and interaction with the matrix. Synergisms with antimicrobial compounds and high pressure were studied in Monells, Spain and Leuven. Belgium.

WG activities

The WG has held 3 meetings, 2004 in Munich, Germany, 2005 in Reading, UK and along the EHPRG symposium 4-6th September 2006 in Prague, CZ as a joint meeting of WGs 6 and 7.

Three STSMs Spain => Germany, Germany => Japan, and UK => Germany were successfully performed in 2006 and 2007 on the expression of virulence factors in Enterococcus faecalis, the investigation on muscle cells of deep sea eels, and the high pressure induced protein release in E. coli, respectively. The STSM Germany => Japan involved our Non-EU member offering the unique opportunity of a deep sea cruise and experiments with cells of deeps sea eels.

Interactions with other WGs:

In a joint project of the German research foundation members of WG007 (TUM, Germany) collaborated with a member of WG006

(Universität Dortmund, Germany) on the piezophysiology of bacterial membranes. Another highlight was the joined WG meeting in Prague. Some of the scientists in WG007 will participate in the final meeting in Bordeaux in October 2007 to share their results and finish joint publications from ongoing collaborations.

Other

The first book on "High pressure microbiology" with several members of the WG being authors, will be printed in 2008 by ASM press. This is considered a major achieved in jointly publishing the results of the WG007 during COST and beyond.

9:45 Invited

Enzymic catalysis in supercritical carbon dioxide

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We outlined three main tasks: each one of them included one or more subprojects and was aligned with one of the participating research groups, a condition which proved to be critical for the achievement of the goals envisaged.

(i) Testing the enzyme activity and stability in supercritical carbon dioxide.

Two types of enzymes (lipase and glucose 2-oxidase from *Coriolus versicolor*) were tested under SC-CO_2 from the point of view of enzyme stability and enzyme specificity.

(ii) Investigating the enzyme reaction in continuous-flow reactor, conversion of the reactions and specificity of enzymes

Two model reactions were tested: 1) hydrolysis of blackcurrant oil by lipase from *Mucor miehei* immobilized on macroporous anionic resin (Lipozyme®) and lipase from *Geotrichum candidum*, 2) the oxidation of D-.glucose at carbon 2 in the presence of molecular oxygen producing D-glucosone (2-keto-glucose and D-arabino-2-hexosulose) and hydrogen peroxide catalysed by glucose 2-oxidase. The processes in respect of the products of the reaction were optimised.

(iii) Understanding thekinetic, thermodynamic, and transportphenomena whichinfluencetheenzyme-catalyzed reactions

Particular attention was given to studying and modeling the kinetics of the enzyme-catalysed reactions, and to modeling the simultaneous phase and chemical equilibrium.

Acknowledgement: The authors appreciate financial support from the Ministry of Education of the CR through the COST project D30/0008/06 (COST D30.001).

Poster session

Saturday morning, 27 October, 10:45

10:45 Poster 1

High Pressure Tuning of skeletal muscle function on the cellular level in mammalian and fish muscle: How pressure specifically interacts with excitation-contraction coupling

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Skeletal muscle is the bodie's largest organ and the source of locomotion. Muscle contraction is the result of a cascade of events that transfer electrical signals involving surface ion channels to intracellular chemical signals that involve release of Ca^{2+} ions from intracellular stores. Finally, increases in cytosolic Ca^{2+} concentrations are transferred to mechanical signals that involve the activation of the motorproteins, actin and myosin, that ultimately result in force production by power strokes of the myosin molecule along the actin filament.

High hydrostatic pressure (HP) acts very distinct on elements in the different steps of this cascade. We have focussed on prolonged high pressure treatments that may irreversibly change the conformational states of the proteins involved such as their function will be permanently compromised even in the decompression phase. Using mouse skeletal muscles that were pressurised for 3 h at 4°C, 'ex situ' experiments showed that isometric force production markedly declined for pressures larger than 20 MPa as muscle became tremendously stiff [1]. For larger pressures, cells were usually irreversibly contracted.

During the COST D30 funding period, we found that Na^+ and Ca^{2+} channels which represent the switch for membrane excitability and excitation-contraction coupling were functionally *'knocked out'* as the surface density of functional channels decreased significantly from 20 MPa as judged by the reduction of peak current amplitudes with unaltered steady-state inactivation [2,3]. Interestingly, intracellular RYR1 release channels were much less affected by HP up to 30 MPa probably due to a more protected environment within intracellular membranes [5]. Using a novel 'in situ' high pressure epifluorescence/confocal microscopy technique, we could clarify the underlying process of the irreversible contracture induced by HP >20 MPa. A general breakdown of membrane integrity could be excluded. However, we found that HP seemed to induce a sustained leakage of Ca^{2+} ions from intracellular stores that could partially be buffered by mitochondria. As mitochondria function became more impaired, Ca^{2+} concentrations began to rise and irreversibly activated the contractile apparatus [4]. For these results, we collaborated with TU Munich within the D30 working group.

As skeletal muscle function and proteins are highly conserved in vertebrates, we wondered whether some adaptive mechanisms must have evolved in deep sea fish to counteract high ambient pressures. During the funding period, a STSM was performed with JAMSTEC, Japan, to conduct electrophysiology experiments in deep sea fish that were salvaged from depths up to 1.000 m. So far, we found that HP seems to change the K^+ selectivity of resting membranes, i.e. a decrease with depth, and that deeper fish seem to have higher internal K^+ levels [6].

In a final conclusion, our HP limits found in mammalian muscle closely resemble the depth limits of diving whales. Therefore, muscle from terrestrian mammals studied under HP may serve as a model for muscle function in diving mammals. Further studies in fish species will show whether there is a profound difference between mammalian and fish muscle under HP.

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10:45 Poster 2

Lipases from fungus Geotrichum candidum 4013 - biocatalysts in SC-CO_2

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*Geotrichum candidu*m 4013 produces extracelular and cell bound lipases. Extracelular lipase displays specificity to natural unsaturated compounds (such as polyunsaturated fatty acids and their derivatives from natural plant oils). Cell bound lipase displays specificity to saturated compounds. The lipases were used as biocatalysts of the blackcurrant oil hydrolysis performed in water (101.3 kPa, 25°C, stirring, 72 hours) and in SC-CO_2 (15 MPa, 40°C, streaming CO_2 0.43-0.48 $g.min^{-1}$). Cell bound lipase was used in the form of acetone powder and extracelular lipase was immobilized on IDA-Agarose support. The chemical yields of both reactions were satisfactory (ch.y. = 34 - 59%).

SC-CO_2 exhibits properties similar to organic solvents, but with additional capacity of encouraging transport phenomena (due to their high diffusivities) and facilitating reaction product separation by tuning solvent power, which makes it more atractive for using as green solvent.

Acknowledgement: The authors appreciate financial support from the Ministry of Education of the CR through the COST project D30/0008/06 (COST D30.001).

10:45 Poster 3

New classical and non-classical hydrides of Ru(II) in aqueous solution

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We have described earlier that the selectivity of the hydrogenation of cinnamaldehyde catalyzed by the water soluble complex $[\{RuCl_2(m\text{tppms})_2\}_2]$ (+ *m*tppms) was a sensitive function of the hydrogen pressure (*m*tppms = *meta*-monosulfonated triphenylphosphine). This effect was attributed to the shift of the equlibrium between the known Ru(II)- monohydride: $[RuHCl(m\text{tppms})_3]$ and a dihydride, supposedly $[RuH_2(m\text{tppms})_4]$, although it was also noted that a new hydride species was formed at slightly elevated pressure of H_2 (5-10 bar). The situation is even more complicated since the formation of the various hydride species is also strongly influenced by the pH of the aqueous solutions.

Recently we made detailed ^1H and ^{31}P NMR studies in order to establish the effects of the pH and the hydrogen pressure on the reaction of $[\{RuCl_2(m\text{tppms})_2\}_2]$ (+ *m*tppms) and H_2, including the determination of T_1 and T_2 relaxation times. The results revealed the formation of the following complexes:

a) in acidic solutions at 1 bar H_2: $[RuHCl(m\text{tppms})_3]$ and $[\{RuHCl(m\text{tppms})_2\}_2]$

b) in acidic solutions at elevated H_2 pressures: *trans*-$[RuH_2(m\text{tppms})_4]$

c) in basic solutions at 1 bar H_2: *cis*-$[RuH_2(H_2O)(m\text{tppms})_3]$

d) in basic solutions at elevated H_2 pressure: *cis*-$[RuH_2(H_2)(m\text{tppms})_3]$

Of these complexes, *cis*-$[RuH_2(H_2)(m\text{tppms})_3]$ is a dihydrogen complex with water soluble phosphine ligands and *trans*-$[RuH_2(m\text{tppms})_4]$ is one of the rare *trans*-dihydrides. (Furthermore, *cis*-$[RuH_2(H_2O)(m\text{tppms})_3]$ was previously incorrectly described as *cis*-$[RuH_2(m\text{tppms})_4]$.)

10:45 Poster 4

Effect of physico-chemical parameters on biocatalysis of glucose 2-oxidase from Coriolus versicolor at high pressure

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Glucose 2-oxidase (pyranose oxidase, pyranose:oxygen-2-oxidoreductase, EC 1.1.3.10) catalyses the oxid-

ation of D-.glucose at carbon 2 in the presence of molecular oxygen producing D-glucosone (2-keto-glucose; D-arabino-2-hexosulose) and hydrogen peroxide(1). This enzyme is of great importance since the reaction product (D-glucosone) is an important precursor for biosynthesis of the antibiotic cortalcerone (2). On the other hand, D-glucosone has been shown to exhibit anti-cancer activity *in vitro* against some cancer cell lines. The present work involves the conversion of D- glucose into D-glucosone in the presence of glucose 2-oxidase from *Coriolus versicolor* at high pressures with compressed air in a modified commercial reactor. The apparatus consists basically of one batch reactor (Micro Reactor Parr Instruments CO, 4843) with 25 ml of capacity equipped with agitation, temperature and pressure reading devices (3). Several parameters affecting biocatalysis at high pressures, up to 20 MPa, were investigated as follows: pressure, temperature, pH, enzyme concentration, enzyme immobilization and the presence of catalase. The conversion of D-glucose into D-glucosone in the presence of glucose 2-oxidase activity was investigated by using an HPLC system. The data presented in this work revealed an increase in the rate of reaction as a function of pH in the following order: pH 8.0> pH 5.0> pH 6.5 in the presence of catalase. The presence of catalase was found to increase the rate of conversion of D-glucose both at high pressures as well as at NTP with or without bubbling with pure O2. The immobilized form of enzyme in a dialysis membrane exhibited about 50% of activity compared with the free enzyme and it could be re-used several times without a significant loss of enzyme activity.

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10:45 Poster 5

Synthesis of nanopowders in supercritical water in a continuous flow reactor

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The synthesis of yttrium aluminium garnet (YAG or $Y_3Al_5O_{12}$) has received much attention on account of its use in structural and functional materials. Polycrystalline YAG also has considerable potential as a refractory fibre material. Furthermore YAG displays a cubic crystal structure, which imparts optical isotropy (unlike sapphire). Doping YAG with different trivalent ions changes the optical properties of the doped materials. YAG has also been used in phosphors for scanners and contrast-enhanced display applications. Whether manufacturing YAG for phosphor applications or ceramic fabrication, fine-sized particles with no agglomeration are desirable.

The poster presents the collaborative efforts that have been ongoing between UNIPRESS and The University of Nottingham in the production of doped and non doped Zirconia and YAG nanoparticles.

The paper will describe the various production techniques, the relationship between operating conditions and particle quality, the similarities and differences between the two synthesis techniques, as well as the effect of the raw powders.

10:45 Poster 6

High pressure crystal structure of ribonuclease A

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Two different factors, high pressure and mutation, can act as perturbants very useful to study several biological aspects of protein, including folding/unfolding processes, stability, oligomerization and aggregation. Detailed analysis of inter and intramolecular interactions and factors that affects them is important for understanding mechanism of structural changes being the origin of molecular diseases.

To determine the influence of high pressure and mutations on protein structure for crystallographic experiments we selected RNase A, protein that is small, easy to crystallize and can form oligomers[1]. Trigonal crystals of wild-type ribonuclease A (WT RNase A) and its mutated variant I106A were loaded into the Diamond Anvil Cell and pressurized in the presence of crystallization solution. The pressure was monitored using a ruby chip[2]. Diffraction data were collected on Nonius KappaCCD diffractometer with standard Mo sealed tube (55 kV, 30 mA) for one crystal of WT RNase A at 0.5 and 0.7 GPa, and for two crystals of I106A RNase A at 0.35 and 0.48 GPa. All four high pressure (HP) structures were solved and refined with resolution between 2.4–2.8 Å. To find out structural changes being result of high pressure, the structures were compared with the ambient pressure (AP) structures determined by us using the same diffractometer and radiation.

The most important differences introduced to the structure by the high pressure were observed for the main hydrophobic cavity volume. Cavities observed in WT HP structures are visibly smaller ($V_{HP\ WT\ I}$ = 20.8 Å^3) from that one observed in AP structure ($V_{AP\ WT}$ = 30.8 Å^3). Cavity formed in HP I106A structures ($V_{HP\ I106A\ I}$ = 109.6 Å^3, $V_{HP\ I106A\ II}$ = 68.6 Å^3) also differ from the cavity found in AP I106A ($V_{AP\ I106A}$ = 80.9 Å^3).

In all cases the overall HP structures of WT and I106A RNase A were indistinguishable from AP structures. Nevertheless, calculation of difference distance matrices has revealed subtle rearrangements of some regions of ribonuclease molecule present in all HP struc-

tures. Magnitude of rearrangements suggests that changes observed for HP WT structures are enhanced by introduced mutation. The HP structures allowed to identify five flexible regions of RNase A molecule that can move against each other. Moreover, some of those regions were previously reported as a fragments that play curial role in high pressure unfolding of RNase A in solution[3,4].

This work was undertaken within the frame of COST Action D30. It was partially funded by grants T09A 108 30 from Ministry of Science and Higher Education (Poland) and WRBW/6/2007 from Jagiellonian University, Faculty of Chemistry (Poland).

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10:45 Poster 7

Cell concentration effects on survival of Escherichia coli during high pressure processing

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The inactivation kinetics of *Escherichia coli* NCTC 8164 during pressure treatment at 400 MPa in phosphate buffered saline were influenced by the initial cell concentration such that the rate of inactivation increased as cell concentration decreased. Cells in sparse populations (3 x 10^6 /ml), were protected by cell-free supernatants from dense (3 x 10^9 /ml) pressure-treated suspensions suggesting that material leaking from cells was responsible for the protective effect. Pressure-treated cells lost about 14% of their cellular protein but the resultant concentration of protein in the supernatant (80 micrograms/ml) was considered unlikely to be sufficient to afford significant non-specific protection. The protective factor was stable to heating at 78°C for 15 min, and was lost by dialysis indicating a molecular mass of less than 2 kDa. Both calcium and magnesium are known to have a protective effect and both leaked from cells during pressurisation. However the concentrations found in the supernatant (*ca*. 0.2 and 0.05 microgram atoms/L respectively) were too low to be protective. Complex growth media are more similar to foods than buffer solutions and a cell density affect was seen in Luria Bertani broth but not Tryptone Soya broth. These results show that inactivation can be highly dependent cell concentration and on small differences in the composition of the suspending medium and identification of the mechanisms of protection would help clarify the critical factors leading to cell death.

10:45 Poster 8

Pressure effects on amyloid fibrils: a review

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A number of medical disorders, including Alzheimer's disease and type II diabetes, is characterised by the deposition of amyloid fibrils in tissue. The insolubility and size of the fibrils has largely precluded the determination of their structures at high resolution. Studies probing the stability of amyloid fibrils can reveal which non-covalent interactions are important in the formation and maintenance of the fibril structure. In particular, we review here the use of high hydrostatic pressure and high temperature as perturbation techniques. In general, small aggregates formed early in the assembly process can be dissociated by high pressure, but mature amyloid fibrils are highly pressure stable. This finding suggests that a temporal transition occurs during which side chain packing and hydrogen bond formation are optimised, whereas the hydrophobic effect and electrostatic interactions play a dominant role in the early stages of the aggregation. High temperatures, however, can disrupt most aggregates. Though the observed stability of amyloid fibrils is not unique to these structures, the notion that amyloid fibrils can represent the global minimum in free energy is supported by this type of investigations. Some implications regarding the nature of toxic species, associated with at least many of the amyloid disorders, and recently proposed structural models are discussed.

10:45 Poster 9

Characterization of nanopowders

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Characterisation of the nanostructure of powders is a challenge frequently not properly met by researchers in this field. The properties measured strongly depend on:

- size of crystallites,
- size distribution, and
- thickness of the surface layers, which may consist of hydroxides or not fully reacted reagents.

As far as crystallite size distribution, we developed an analytical equation that permits to determine two parameters: crystallite size and their dispersion at the same time (d and sigma, where d is particle diameter and sigma is its disorpsion). Broadening of the XRD peaks will lead to a considerable error when used to estimate crystallite sizes and their distribution is not taken not account. Fitting of an analytical expression to the XRD data is a relatively easy procedure that can be followed in any laboratory, providing the XRD data are of sufficient quality. We defined also criteria of quality of XRD patterns for crystallite size and their distribution determination.

As far as the degree of crystallinity of the powders is concerned, we have shown that pycnometric density is an excellent tool to discriminate between 'good powders" with little non crystalline phases, and poor powders, with a lot of hydroxides on surface or other phases. We postulate that the pair of data (specific surface area, density) should be always requested for characterization of nanopowders.

10:45 Poster 10

Synthesis of doped ZnO nanopowders in microwave hydrothermal reactors

Agnieszka Opalińska[1,2], Witold Lojkowski[1], Tadeusz Chudoba[1], Ewa Grzanka[1], Tomasz Strachowski[1,2], Aharon Gedanken[3], Robert R. Piticescu[4], Marek Godlewski[5,6], Sergiy A. Yatsunenko[5], Edward Reszke[7,8]

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ZnO nanopowders and ZnO doped with Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+} and Al^{3+} ions have been produced in hydro and solvothermal reactions. The reactors were lined with Teflon, to ensure high purity of the powders, and preventing corrosion products to be mixed with the powders.

The main result of the studies of synthesis process was that during solvo or hydrothermal synthesis high level of doping is possible, comparing to high temperature processes.

In the case of ZnO:Mn it was shown that even for 8 mol % doping the material is paramagnetic. Therefore It seems that this is not a prospective spintronics materials.

In the case of Al doped nanopowders it was found that addition of aluminum strongly increases luminescence of the powders.

Use of microwaves for heating of the reagents we could considerably (about 5 times) shorten the reaction time. This is so because thermal inertia of the pressure vessel was not a time limiting factor: energy was delivered directly to the reagents.

10:45 Poster 11

"Investigating Catalytic Intermediates in the Rh/PPh_3 Catalysed Hydroformylation of Acrylamide by in situ High Pressure NMR"

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Preliminary catalytic studies were conducted in Tarragona to facilitate a collaborative high pressure NMR study in Liverpool into the factors determining catalyst performance in a new route to methyl methacrylate via the Rh/PPh_3 catalysed hydroformylation of acrylamide discovered in Tarragona.[1] The effect of reaction temperature, pressure, and catalyst concentration, on selectivity and turnover were investigated and the optimal ranges for an HP NMR study determined. It was found that changing the catalyst concentration had minimal effect on aldehyde regioselectivity, the catalytic system was relatively insensitive to changes in total and partial pressure and that the hydrogenation side reaction could be suppressed at low temperatures. A preliminary HP NMR study has been carried out on the catalyst system under the optimised reaction conditions, to identify the species present without the addition of the substrate. A HP NMR study was then attempted on the full Rh/PPh_3 acrylamide system.

Reference

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10:45 Poster 12

Synthesis of Al doped ZnO nanopowders and their enhanced luminescence

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Nanocrystalline ZnO doped with different ions shows improved electronic, optical, catalytic or antiseptic properties with high poten-

tial for high tech applications. These properties are strongly dependant on the microstructure and surface characteristics. New processes for the synthesis and processing are required to control and optimize the chemical composition, crystalline sizes and grain morphology. We present original results on the synthesis of zinc oxide powders with different Al content by two different procedures: hydrothermal route starting from soluble aqueous precursors and evaporation-condensation in a solar furnace of the hydrothermal synthesised powders.

The influence of the synthesis parameters on the chemical and microstructural characteristics of nanophases synthesized in the two methods has been studied using chemical analytical methods, XRD, BET, picnometric density, SEM and TEM. Some results on the luminescence properties of Al-doped ZnO nanopowders are finally presented.

Acknowledgement: Research supported by contract CEEX 69/2006 SINAPS financed by Romanian Agency for Research and Innovation , ECO-NET "Fun Nanos" financed by EGIDE-France and COST Action D 30.

10:45 Poster 13

New inorganic-organic hybrid materials with strong chemical bonding

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Pressure is always involved in Solvothermal and Hydrothermal Processes(autogeneous our imposed pressure). Consequently it is necessary to take into account different factors induced by such a parameter: the weak energy involved by pressure, the negative DV volume difference between the final state and the starting state value leading to the denser phases, the improvement of reactivity. *Due to the small energy conveyed by pressure such a parameter can be used in developing nano-bio-materials with low thermal stability.* It is therefore possible the development of research at the interface between different domains, such as**:** Hybrid Materials (inorganic chemistry/Organic chemistry); Hybrid Systems (nano-chemistry/Biosciences). Optimisation is required for: physical-chemical properties of the precursors and solvent as well as the thermodynamic parameters P, T.

Original results on the synthesis of complex hybrid inorganic-organic systems with applications in nanomedicine are presented.

Acknowledgment: Romanian Agency for Scientific Research for financial support in the frame of Research for Excellence contracts 46-ReteBdent, 16-TECOREMED and COST D30 – High pressure Tuning of Materials.

10:45 Poster 14

Ankyrin, a good model protein for folding/unfolding studies

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The understanding of the protein folding mechanisms is still incomplete despite a long time of study. Although the importance of the amino acid chain topology and the contribution of the hydrophobic interactions are clear, the role of the solvent remains to be defined in this folding pathway. The application of high pressures on proteins is an experimental approach which allows us to observe the changes of hydration arising during the conformational changes of the proteins, as these changes are accompanied by variations in volume. The application of the pressure stabilizes the states of the protein-solvent systems occupying the smallest specific volume. At ambient temperature, the smallest volume corresponds to the unfolded state because the high volume hydrophobic cavities of the protein disappear upon being filled with solvent. The unfolded state is more hydrated than the folded one. We neither know today when nor how these hydration variations occur in the folding reaction. High-pressure fluorescence permits us to study the volume changes during the folding / unfolding of proteins and to study the Transition State Ensemble (TSE) by a kinetic approach. We use the Notch Ankyrin domain, which seems to be a good model protein, to study the volume changes and the thermodynamics variables of it's folding, and to better understand the relationship between volume changes, the TSE and the folding pathway.

10:45 Poster 15

Changes at the intersubunit interface of human Hemoglobin A upon effector binding does not result in a compressibility change at the heme pocket.

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The mechanism of allostery in Hemoglobin is still not completely understood. Various models have been published in the literature, however the details of the communication pathway are still not completely clear. Recently a new model has been proposed (Yonetani et al, 2002 *J. Biol. Chem*. **277**, 34508-34520) which relates global tertiary conformational changes to allostery. In this framework, in every subunit tertiary conformational changes occur upon the binding of allosteric effectors, that lead to the observed changes in oxy-

gen binding affinity. We have shown (Fidy et al, 2006 *BBA Proteins and Proteomics* 1764(3):516-21 ; and Fidy et al, 2006. submitted to *J. Biol. Chem.*) , that substantial conformational changes occur at the interdimeric interface region of every subunit upon the binding of allosteric effectors. We have extended this study, to assess possible changes at other parts of the protein matrix, and thus gain additional knowledge about the communication pathway. In this study we used a zinc hybrid, and fluorescence line narrowing to assess the compressibility of the matrix around the heme. We have shown, that the high-pressure compressibility of the heme pockets - measured by using high pressure - does not change significantly upon the binding of allosteric effectors. This suggests that changes in oxygen binding are related to the fine tuning of the structural conditions in the heme pocket, which can not be observed when the protein is compressed by pressures higher than 1 kbar.

Lectures
Saturday morning, 27 October, 11:45

11:45 Invited

Structural transformations under high pressure: an interesting class of oxides – the oxoborates

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At the moment, over 1100 borate crystal structures are listed in the Inorganic Crystal Structure Database ICSD. High-pressure investigations are rare and were mainly performed from the geological point of view. Starting in the year 1999, systematic high-pressure experiments up to maximum pressures of 16 GPa have been carried out in our group. The talk will give an overview about recent results in this field.

Lunch
Saturday afternoon, 27 October, 12:45

6th Management Committee Meeting
Saturday afternoon, 27 October, 14:30

Unscheduled abstracts
Author alphabetical order

Poster

High Pressure Hydrogen Generation from Formic Acid

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The generalisation of the use of hydrogen as a fuel, although very promising, is currently limited mainly because of storage [1] We have developed a continuous hydrogen generation process under pressure using formic acid as hydrogen storage material.[2] The formic acid is decomposed into H_2 and CO_2 in aqueous solution using a homogeneous transition metal catalyst.

$$HCOOH \rightarrow H_2 + CO_2$$

The hydrogen production exhibits very good robustness and efficient hydrogen generation from formic acid. Formic acid has previously been proposed as hydrogen storage material, although up to now applications were limited by rather extreme reaction conditions, catalyst regeneration requirements, and lack of selectivity. These limitations have been overcome by the proposed process.

We are grateful to Swiss National Science Foundation and COST D30 (WG001) for financial support.

1. L. Schlapbach, A. Züttel, *Nature*, **414**, 353 (2001).

2. C. Fellay, P. J. Dyson, G. Laurenczy, European patent application filed (2006).

Poster

Synthesis and catalytic properties in the hydrogenation reaction of new iridium(I) NHC complexes

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N-Heterocyclic carbenes are universal ligands in organometallic and inorganic coordination chemistry. In addition to transition metals in low or high oxidation states, N-heterocyclic carbenes form complexes also with main group metals. The large number of NHC compounds allowed improved catalytic applications [1]. From the [IrCl(bmim)(cod)] (bmim = 1-butyl-3-methylimidazol-2-yliden; cod = 1,5-cyclooctadiene) neutral compound we have synthesized new water soluble complexes: [Ir(bmim)(cod)(P)], [Ir(bmim)(cod)(S)]CF_3SO_3 and [IrH_2(bmim)$(NCMe)_2$(*m*tppts)]Cl, (P= *m*tppms, *m*tppds, *m*tppts; *m*tppts = 3,3',3''- trisulfonated triphenylphosphine, *m*tppds = 3,3''- disulfonated triphenylphosphine *m*tppms = 3-diphenylphosphinobenzenesulfonic acid, S = solvent). All these compounds were characterised by NMR, ESI, and IR, and for [IrCl(bmim)(cod)] and [Ir(bmim)(cod)(H_2O)]CF_3SO_3 the crystal structures have been determined by X-ray diffraction. These complexes were used as catalyst precursors in hydrogenation reactions in organic solvents and in water. Generally these compounds showed good catalytic activity.

References:

[1] W.A. Herrmann, Angew. Chem. Int. Ed. 2002, 41, 1290;

Poster

Utilization of CO_2

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Research under the theme "green chemistry" is challenged by the development of environmentally and economically sustainable processes for industrial applications. While looking for new and renewable raw material resources carbon dioxide is an attempting alternative, because it is cheap, abundant and non-toxic. By being a stable molecule, a high amount of energy or a suitable catalyst is however required to transform carbon dioxide into chemical products. In COST D30 activity the main emphasis has been on chemical activation of CO_2, especially on the synthesis of carbonates via epoxide reactions/**1, 2**/. In addition the reduction of CO_2 to produce formic acid was studied/**3**/

1.Carbonates via CO_2 –epoxide reactions

Coupling of carbon dioxide with epoxides is a desirable alternative route to carbonates especially because most of the industrial processes still use highly toxic phosgene route while manufacturing commodity carbonates.

The results obtained in the project show that aliphatic epoxides, eg. 1-hexene-epoxide and cyclohexene epoxide can be homo-and co-polymerized by using heterogenous Zn-catalyst system/**1/.** Also new catalyst candidates, especially cobalt(II) complexes bearing tetradentate ligands have been identified for the synthesis of cyclic carbonates. These complexes were found to be excellent catalysts under mild conditions for the reaction of epoxide and CO_2 when used in conjunction with Lewis base co-catalyst ($n\text{-}Bu_4NBr$) /**2**/.

2.Reduction of CO_2 to formic acid

Highly water soluble cationic catalyst precursors, **[RuCl2PR3(h6arene)]+** where arene= 1-(2-benzylethyl)-3-methylimidazolium or 1-(2-benzylethyl)-2,3-dimethylimidazolium and PR3 = PPh3, PCy3, were also prepared and used for CO2 hydrogenation to formic acid /**3**/.

The reduction of CO2, bicarbonate and carbonate ions to formic acid/ formate ion in aqueous solution under mild conditions, though with moderate activity. In case of cationic ruthenium(II)-arene

complexes with tethered imidazolium moieties, hydrido-carbonate. The reduction of CO2 takes place via bicarbonate species, with the rate-determining step to be the intramolecular hydride transfer from the metal to the complexed bicarbonate.

Referencies:

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Poster

Hydroxycarbonylation of 1-octene in supercritical carbon dioxide

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Hydroxycarbonylation of 1-octene in supercritical carbon dioxide

Clara Tortosa Estorach[a], Arantxa Orejón,[a] Núria Ruiz,[a] Anna M. Masdeu-Bultó[a,*] and Gábor Laurenczy[b]

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Catalytic hydroxycarbonylation of terminal long chain alkenes is an interesting reaction to transform alkenes into carboxylic acids with CO using a palladium complex as catalyst (1).

(1)

The interest of supercritical carbon dioxide ($scCO_2$), as a substitute solvent for catalytic reactions has quickly increased in the last years because of the advantages it presents compared with organic solvents.??? Unfortunately, ionic and polar reagents generally exhibit low solubility in $scCO_2$, and it has limited application of $scCO_2$ in this catalytic processes.??? To overcome this limitation modified ligands such as perfluorinated phosphines or/and soluble surfactants, which induces the formation of micelles with high-density fluid phase, have been employed. ???

In the present work, the hydroxycarbonylation of 1-octene in $scCO_2$ has been studied using palladium catalytic precursors with fluorinated phoshines. Particular attention has been paid in the effect of perfluorinated surfactants (2) in order to generate microemulsions of water.

(2)

Although this reaction in organic solvent affords high conversions and selectivities, the chemioselectivity in acids is shown to improve in $scCO_2$. The use of perfluorinated surfactant also enhances the activity and the regioselectivity to the linear acid.

High pressure NMR experiments in toluene-d_6 and $scCO_2$ showed the formation of Pd(0) species.

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Poster

Cellular impact of sublethal pressures on Escherichia coli

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In surface adapted bacteria, such as *Escherichia coli*, high pressure (HP) shock greatly perturbs cellular homeostasis. Nevertheless, the cellular impact of HP stress and the actual damage it provokes remain poorly characterized. Using the Differential Fluorescence Induction (DFI) technique coupled to fluorescence activated cell sorting, we have studied the response of *E. coli* to sublethal HP shock (< 150 MPa). It was found that HP shock induces several genes belonging to the heat shock regulon, and also genes belonging to the SOS regulon. Since the SOS response is a response to DNA damage, and HP is not known to cause direct DNA damage, the mechanism of SOS induction was further analysed in more detail. It was shown that SOS induction stems from the HP mediated activation of the restriction endonuclease Mrr and the subsequent formation of double stranded DNA breaks, which trigger a genuine RecA and LexA dependent SOS response. Several phenotypes linked to SOS induction were observed, including the induction of prophage and cell filamentation. The SOS response is also anticipated to cause an increased mutation rate, and this is indeed supported by some experimental observations.

Poster

Hydrogenation of dicarboxylic acids to diols using Ruthenium catalyst

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Hydrogenation of dicarboxylic acids to diols using Ruthenium catalyst

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$RuH_4(CO)_8(PBu_3)_4$ catalyzes selectively the reduction of disubstituited dicarboxylic acids to esters but is not able to reduce the esters to the corresponding alcohols.

On these bases, recently 1, we have settled a convenient procedure for the reduction of 1,4-dicarboxylic acid to isotopomeric g-butyrolactones containing 2, 4 or 6 deuterium atoms using $Ru_4H_4(CO)_8(PBu_3)_4$ as homogeneus catalyst under a D_2 pressure.

Tetradeuterated gamma-butyrolactone-[3,4,5,5-D_4] from maleic or fumaric acids, dideuterated gamma-butyrolactone-[5,5-D_2] from succinic acid and hexadeuterated gamma-butyrolactone-[3,3,4,4,5,5-D_6] from acetylenedicarboxylic acid.

Now our interest is focused on the syntheses of differently deuterated 1,4-butandiols starting from the appropiate dicarboxylic acids. Aware of the ability of the [$Ru(acac)_3$]/$MeC(CH_2PPh_2)_3$ system to catalyze, in the homogeneous, the hydrogenation of dimetyl oxalate to ethylenglycol, we have explored to employ such system in the one-pot syntheses of 1,4-butanediol (1,4-BD) from gamma-butyrolactone (GBL) or fumaric acid . The catalyst tested gives up to 49.6 yiled of 1,4-BTD from fumaric acid using methanol as solvent.

Reaction conditions and preliminary results are collected in the table below:

Entry	Substrate	Solvent	T	Time	Reaction	Products	Composition	(%)
			°C	h	GBL	1,4-BTD	DMS	MHS
1	Fumaric acid	MeOH	120	16	12.8	0.7	74.1	12.4
2	Fumaric acid	MeOH	120	48	7.8	49.6	19.2	23.4
3	Fumaric	THF	120	48	69.2	8.3	22.5	0.0
5	GBL	MeOH	120	48	11.8	48.8	0.0	39.4
6	GBL	THF	120	48	77.7	13.8	0.0	0.0

Substrate 1.77 mmol, Ligand/Ru 1.37, $Ru(acac)_3$ 0.021 mmol, Solvent 12 ml, p(H_2) 80 bar, Substrate/Zn 1/0.26. DMS: Dimethyl succinate, MHS: Methyl 4-hydroxysuccinate.

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