

43rd Heyrovský Discussion

Electrochemistry of Organic Molecules
and
Coordination Compounds

Book of Abstracts



30. May – 3. June 2010

The 43rd Heyrovsky Discussion 2010 was held at the Conference centre in chateau Třešť in town Třešť in the Czech Republic, from 30 May to 3 June 2010.

Sponsors



43rd Heyrovsky Discussion

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Edited by Věra Hudská, Jiří Ludvík

80 pages – Number of copies: 70

ISBN 978-80-87351-06-2

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Třešť (town)	
Žďár nad Sázavou - Zelená Hora (monastery)	
Jaroslav Heyrovský - 120th Anniversary	

PROGRAMME

Sunday, May 30 th				
10:00	Refreshment, registration in the entrance hall of the J. Heyrovský Institute, possibility to leave the luggage and walk in the town			
15:00	Departure of a special bus from the J. Heyrovský Institute (Dolejškova 3, Prague 8 – Kobylisy)			
18:00	Arrival, registration at the Castle Třešť			
19:30	Welcome apéritif			
20:00	Dinner			
Monday, May 31 th				
from				
7:00	Breakfast			
8:30	Opening of the Discussion			
	Proton and electron transfers			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:45	W. Kaim	Jean-Michel Savéant	FR	Concerted Proton Electron Transfers. Electrochemical and Related Approaches (introductory lecture)
9:40		C. Tard	FR	Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers
		R. Sokolová	FR	The Importance of a Proton Donor in Reduction of Halogenated Benzonitriles
10:30	Coffee break			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
11:00	W. Kaim	Anxolabéhère-Mallart E.	FR	Cobalt Clathrochelate Complexes as Hydrogen-Producing Catalysts
		M.-N. Collomb	FR	Electron transfer processes in heterobimetallic ruthenium- manganese terpyridyl complexes for modeling photosystem II
		V.A.Kurmaz	RU	Metastable Complex of a Radical with a Proton Donor/Acceptor as a New Key Intermediate in Organic Electrochemistry
		M. Heyrovský	CZ	Wide Prospects for Electrochemical Studies of Organic Molecules and Coordination Compounds (Review)
12:30	Lunch			

Monday, May 31 th				
Afternoon session:				
Electrochemistry of coordination compounds				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30	R. Holze	A. J. L. Pombeiro	P	Electrochemical Characterization of Coordination Compounds and Selected ET-Induced Reactions (Introductory lecture)
15:20 Coffee break				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
15:50	R. Holze	I. Hoskovcová	CZ	Variable π -acidity of η^2 -bonded allyl and of carbene ligands with respect to the central metal atom
		P.R. Mussini	IT	Electrochemistry of dinuclear Re(I) complexes with bridging 1,2-heteroaromatic chromophore ligands
		J. Fiedler	CZ	Electrochemical and Spectro-electrochemical Investigation of Iridium-(1,4-diazabutadiene) redox system: Two-electron reduction of [IrCl(Cp*)(DAB)] ⁺ versus two successive one-electron oxidations of [IrCp*(DAB)]
		W. Kaim	GE	Reversible Intramolecular One-Electron Oxidative Addition: Structure, Spectroelectrochemistry and Theory
		S. Zálíš	CZ	Quantum Chemical Interpretation of Spectroelectrochemical Properties of Ruthenium Complexes with Redox Active Ligands
18:00 Concert of chamber music				
19:00 Dinner				

Tuesday, June 1 st				
from 7:00 Breakfast				
Mechanisms and radicals (and also elements of symmetry)				
Morning session I :				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30	L. Dunsch	A. Jutand	FR	Electrochemistry: a way to solve mechanistic problems in organometallic catalysis (Introductory lecture)
9:20		V. A. Grinberg	RU	The electrochemically generated radicals and ion-radicals in the synthesis of organofluorine compounds
		A. Liška	CZ	Electrochemical reduction of molecules with more redox centers: Mono-, Di-, Tri and Tetranitrocalix-[4]-arenes and Their Models
		T. Mikysek	CZ	Electrochemistry of the "push-pull" type molecules with a systematically extended π -conjugated system
		L. Šimková	CZ	Decomposition mechanism of 1,1-diamine-2,2-dinitroethene - a spectrometric study
10:30 Coffee break				
Morning session II :				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:50	W. Kutner	E. Dunach	FR	Electrochemical Boration of Organic Halides (Introductory lecture)
11:40		G. Somer	TR	Intermetallic compound formation on mercury electrode during polarographic studies in the presence of selenite
		A. Wahab	IN	Electrochemistry of 1-X-12-Y-CB ₁₁ Me ₁₀ ⁻ Carborane anions in Liquid SO ₂
		L. Dunsch	GE	In-situ ESR/UV-Vis-NIR Spectroelectrochemistry of Endohedral Fullerenes: The Story of Sc ₃ N@C ₆₈
		J. Fábry	CZ	Elements of the Quasiperiodic Symmetry Found in the Baroque Pilgrimage Church of St. John Nepomucen and the Surrounding Cloister close to Žďár nad Sázavou, CZ
13:00 Lunch				

14:00	Excursion by bus – UNESCO World Heritage - Barock monuments by Santini at Žďár nad Sázavou			
19:00	Dinner			
21:00	Open air sausage party, beer, soft drinks			
Wednesday, June 2 nd				
from 7:00	Breakfast			
Morning session:				
Molecular electrochemistry applications				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30	V.A. Grinberg	A. Deronzier	FR	The electrocatalytic reduction: A convenient process to use CO₂ as renewable carbon source (Introductory lecture)
9:20		R. Holze	GE	A Comparative Spectroelectrochemical Study of the Redox Electrochemistry of N-(polyvinylamine)-substituted-o-Nitroaniline
		V. Bonometti	IT	Electrochemistry of 3-D, inherently chiral thiophene-based monomers
10:00	Coffee break			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30	V.A. Grinberg	K. Haubner	GE	In situ spectroelectrochemistry of α,ω -endcapped oligothiophenes
		W. Kutner	PL	Supramolecular complexation of biogenic amines by functional electroactive monomers of thiophene derivatives for formation of molecularly imprinted polymer (MIP) films for biosensor development
		H. Randriamahazaka	FR	Electrochemical properties of an electroactive ionic liquid: From the heterogeneous electron transfer to the formation of intermetallic compounds
		D. Walton	UK	Recent Developments in Organic Sonoelectrochemistry and Other Multiperturbation Electrochemical Systems
		J. Klíma	CZ	Sonoelectrochemistry - Desired Effects, Possible Mechanisms and Design of Experimental Arrangement
12:30	Lunch			

Afternoon session:				
Electrochemistry of biologically active molecules				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30	P. Mussini	C. Frontana	MX	Using Molecular Electrochemistry approaches to evaluate properties of reactive radical anions: Towards a molecular level understanding of pharmacological and biological effects (Introductory lecture)
15:20 Coffee break				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
15:50	P. Mussini	J.P. Correia	P	Modified electrodes incorporating Vitamin B 12 – Preparation and electrocatalytic activity
		I. Šestáková	CZ	Electrochemical Methods in Research on Metallothioneins and Phytochelatins
		L. Havran	CZ	Application of organometallic compounds in electrochemical analysis of DNA
		E. Paleček	CZ	Electrochemistry of biomacromolecule adducts with osmium complexes
		E. Wierzbinski	US	Charge transfer through Peptide Nucleic Acid oligonucleotides
		O. Buriez	FR	Molecular Electrochemistry: A Powerful Tool for Mechanistic Investigations and Selective Preparation of Therapeutic Molecules
18:00 Closing Remarks				
18:15 Walk around Třešť				
20:00 Farewell dinner				

Thursday, June 3 rd	
from	
7:00	Breakfast
8:45	Departure to Prague
12:00	Expected arrival to the Institute
12:45	Expected arrival to the Prague Airport
note:	POSTERS SHOULD BE ON DURING THE WHOLE MEETING IN THE FOYER OF THE CONFERENCE HALL (No special poster session will be organized, discussion may proceed during coffee-breaks)

ORALLY PRESENTATIONS

Cobalt Clathrochelate Complexes as Hydrogen-Producing Catalysts

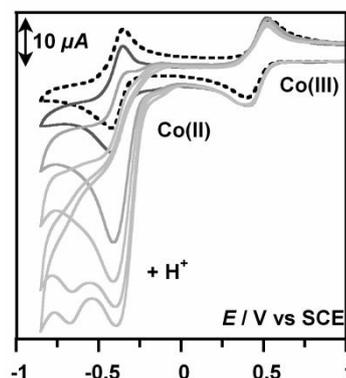
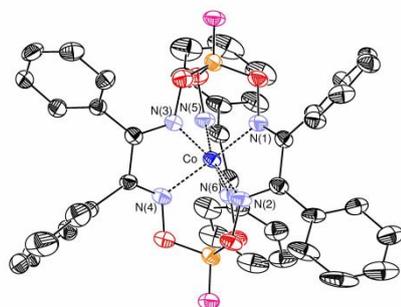
ÉLODIE ANXOLABÉHÈRE-MALLART^{a,*}, A. AUKAULO^b, C. COSTENTIN^a,
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Developing a hydrogen-based economy is one possible scenario to reach a sustainable energy development and also to put ourselves on a path to cut the carbon emissions for obvious climate issues. For domestic application the proton exchange membrane (PEM) process provides a safe and efficient way to split water into molecular hydrogen and oxygen. The challenge is to replace the expensive and limited platinum metal used as catalyst in this technology, by non-noble metal complexes. Several Gross [1, 2, 3, 4], including our [5, 6] have already proposed coordination metal complexes for the electrocatalysis of hydrogen production. We present here the synthesis and characterization of cobalt complexes together with their unexpected electroactivity towards H₂ production. X-Ray diffraction of Co(III) and Co(II) complexes have been obtained. Complete electrochemical characterisation involving spectroelectrochemistry of the complexes in various red-ox states (Figure 1) is reported as well as DFT calculations allowing a better description of the electronic structure of the complexes. Their ability to catalytically reduce protons into molecular hydrogen is discussed and insight into the catalytic mechanism is investigated. Finally, their catalytic activity when immobilized at the surface of a solid electrode using recast nafion film in view of PEM application is presented.



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- [1] Razavet M., Artero V., Fontecave M., *Inorg. Chem.*, **2005**, *44*, 4786-4795.
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- [3] Bigi J.P., Hanna T.E., Harman W.H., Chang A., Chang, C.J., *Chem. Commun.*, **2010**, 958-960.
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- [5] Pantani O., Anxolabéhère-Mallart E., Aukaaloo A., Millet P., *Electrochem Com.*, **2006**, *9*, 54-58.
- [6] Pantani O., Naskar S., Guillot R., Millet P., Anxolabéhère-Mallart E., Aukaaloo A., *Angew. Chem. Int. Ed.* **2008**, *47*, 9948–9950.

Electrochemistry of 3-D, Inherently Chiral Thiophene-Based Monomers

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The availability of materials which could couple electroactivity and enantioselective recognition capability is an ambitious objective of the modern chemical research. So far chirality in organic semiconductors has mostly been introduced by attaching chiral pendants to the electroactive conjugated backbone through suitable linkers; however, this approach usually results in modest chirality manifestations. We have planned to make a revolution to this strategy by preparing polymerizable chiral oligothiophene monomers in which chirality results from a tailored torsion internally produced in the oligothiophene backbone (inherently chiral monomers) so that the whole monomer, and the resulting polymer films, are chiral. To achieve this goal we are introducing into the monomer structure different typologies of stereogenic elements which do not interrupt the conjugated sequence. The structural design of the monomers also requires that the polymerization sites of the monomers be homotopic, thus granting the perfect constitutional regularity of the polymers. Moreover, all the substrates are conceived so as to envisage the possibility of a large scale production, starting from inexpensive, commercially available reagents. We will present and discuss in detail the electrochemical properties and polymerization ability of the first three inherently chiral monomers developed within this project, both as racemates and as separated enantiomers. The first one has recently performed outstandingly, even as a racemate, as a 3D promoter building block in copolymerizations with co-monomers endowed with key functional properties but scarce attitude to polymerization, affording the development of an outstandingly performing melamine sensor [1]; the corresponding separated enantiopure monomers fully retain the high attitude to fast and regular polymerization; moreover, the resulting polymer films fully retain the dissymmetry of enantiopure monomers, well evidenced by solid-state dichroism measurements.

Reference

- [1] A. Pietrzyk, W. Kutner, R. Chitta, M. E. Zandler, F. D'Souza, F. Sannicolò, P.R. Mussini, *Anal. Chem.* 81 (2009) 10061.

Molecular Electrochemistry: A Powerful Tool for Mechanistic Investigations and Selective Preparation of Therapeutic Molecules

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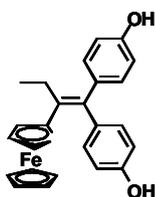
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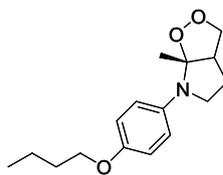
Through two recent examples it will be shown that electrochemical methods provide reliable tools for both mechanistic investigations and selective preparations of organometallic and organic therapeutic compounds.

The first example will deal with ferrocenyl-tamoxifen adducts (A), a new and promising class of breast cancer drug candidates [1]. These compounds which are obtained by grafting a ferrocenyl group to the tamoxifen skeleton exhibit both endocrine-modulating properties and a cytotoxic activity. This duality presents the advantage to target and kill both hormone-dependent and independent breast cancer cell lines. In this context, we have been using electrochemistry as a tool to probe the reactivity of these potent molecules. It was notably showed that the production of a quinone methide through a ferrocene-mediated proton-coupled electron transfer mechanism would be at the origin of the cytotoxic activity of these compounds [2].

The second example will be devoted to the electrochemical aerobic oxidation of aminocyclopropanes to endoperoxides exhibiting antiplasmodial activities (B). This original electrochemical method allows the facile preparation of peroxides efficiently, selectively, and rapidly. The use of a transient electrochemical method such as cyclic voltammetry shows that this original reaction occurs through an electron catalytic process [3].



(A)



(B)

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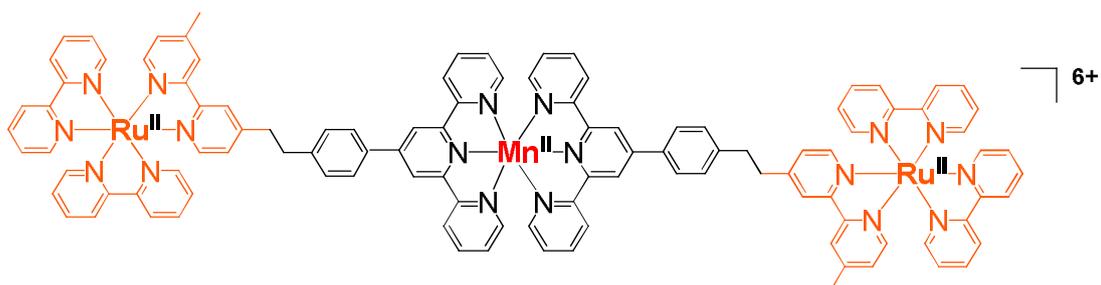
Electron Transfer Processes in Heterobimetallic Ruthenium-Manganese Terpyridyl Complexes for Modeling Photosystem II

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The active site of photosystem II, which catalyzes the oxidation of water into dioxygen during photosynthesis, is a μ -oxo bridged cluster containing four manganese and one calcium ions [1]. During the catalytic cycle, the cluster is four-electrons oxidized following the successive absorption of four photons by a photoactive P₆₈₀ chlorophylls, the electrons are then transferred to a series of electron acceptor. With the aim of modeling these photoinduced electron transfer reactions, several ruthenium-manganese heterobimetallic complexes have been synthesized [2-6]. The main strategy used involves the covalent coupling of a photoactive Ru(II) *tris*-bipyridyl like unit, which mimics the function of the P₆₈₀, to some manganese complexes. We will present our recent results in this area based on the synthesis of a trinuclear complex in which a central mononuclear Mn(II) bis-tolyl-terpyridyl unit is covalently linked to two Ru(II) *tris*-bipyridyl units. The electrochemical and photochemical properties of this new complex in organic and hydro/organic media will be reported [7, 8].



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Modified Electrodes Incorporating Vitamin B₁₂ – Preparation and Electrocatalytic Activity

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The modification of electrode surfaces by macrocyclic Co complexes has been receiving increased attention from the fields of sensors and electrocatalysis. Special attention has been paid to the immobilization of Vitamin B₁₂ and its derivatives due to their catalytic ability to conduct unique electroorganic reactions [1] as well as for waste water treatment [2] and in sensing applications [3]. The catalyst have been immobilised on pyrolytic graphite just by adsorption [4], but the required long-term stability was not observed. Also, the immobilization through self assembly of Vitamin B₁₂ disulphide derivatives was proven [5]; however the reduction of the dicyano form of Co(III) to Co(I) takes place very near to the potential domain where the monolayer is reductively desorbed. A more reliable way to prepare stable VB₁₂ incorporating modified electrodes was reported by the authors and consists in the electropolymerization of a VB₁₂-Pyrrole monomer [6]. Although the catalytic activity revealed by such polymers is undoubtedly assigned to the presence of VB₁₂, the obtained films appears to be formed by short chains and display poor conducting character.

In the present work, the immobilization of a specially synthesised Vitamin B₁₂ derivative, the hexamethyl cob(III)yrinic acid *c*-tyramide 2 (B₁₂-Ty), containing an electropolymerizable head group, the tyramine, is considered. Its electrochemical properties and potential for fixation at the surface of bare platinum and glassy carbon electrodes by electropolymerization are analysed using cyclic voltammetry and ellipsometry.

The electrochemical characterization of the modified electrodes reveals the presence of conducting phases where the redox activity of the metallic centre is preserved. Both modified electrodes display interesting catalytic activity for relevant electrochemical processes, as evidenced by the exploratory experiments for reduction as well as for oxidation reactions.

A new approach to achieve the immobilization of this novel VB₁₂ derivative on polytyramine modified electrodes is also addressed.

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The Electrocatalytic Reduction: A Convenient Process to Use CO₂ as Renewable Carbon Source

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Depletion and increasing costs of fossil resources have led to search for new alternative carbon raw materials for chemical synthesis. Utilizing renewable resources is a prerequisite for sustainable organic chemistry. One easily available green renewable carbon source is carbon dioxide (CO₂) which is naturally abundant, inexpensive, non-flammable and non toxic. The biggest obstacle in CO₂ utilization is its low energy level since CO₂ is the most oxidized form of carbon. Therefore the conversion of CO₂ requires the use of catalysts to overcome high kinetic barriers stabilizing CO₂. The catalytic electroreduction using molecular catalysts appears as a convenient method to achieve the transformation of CO₂ into more reactive forms such as HCOOH or CO.

In this context, we have developed a method to synthesize original electrocatalytic molecular redox systems, based on linear polymetallic chains involving non-bridged metal–metal bonds. An example of such molecular wire is [Ru(bpy)(CO)₂]_n (bpy = 2,2'-bipyridine).

The metal–metal chain formation is easily achieved by electrochemical reduction of a mononuclear precursor complex like [Ru(bpy)(CO)₂Cl₂] for instance, the resulting molecular wires being obtained as strongly adherent films on conducting surfaces. Those molecular cathodes operate at a low overpotential in pure aqueous solution for the efficient electrocatalytic reduction of CO₂. The product selectivity toward CO/HCOOH can be tuned by varying substituents at the bpy ligands.

To facilitate the handling of this type of material in air and to avoid its disintegration, more practical materials have been developed based on thin films of preformed polypyrrole (ppy) N-functionalized by the precursor of those polymetallic chains.

Moreover in order to test the capabilities to this kind of material to reduce CO₂ into highly valuable compounds like fuels (hydrocarbons or alcohols) we have designed some new materials. We combined in a same polymeric matrix a metallic centre able to electroreduce CO₂ into CO with a catalytic one able to hydrogenate CO in-situ. Two strategies have been used, the first one involved a metallic complex known as an hydride producer, the second one noble metal nanoparticles

We will present here an account on the elaboration and characterizations of the whole kind of polymetallic materials that we have developed and on their application as catalysts for electroreduction of CO₂.

Electrochemical Boration of Organic Halides

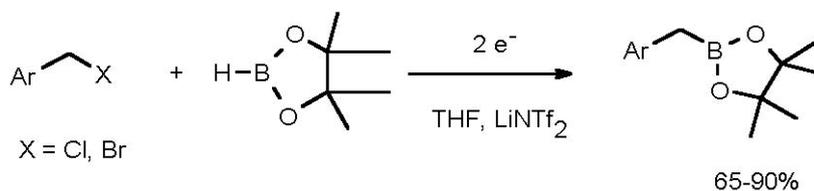
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A high interest is devoted since the last decade to organoboronic acid derivatives, assynthetic intermediates of wide application, particularly in the fields of pharmaceuticals, natural products, new materials, fine chemicals [1]. Their wide applicability is mainly due to their efficient use as coupling agents in the Suzuki reaction [2], as well as their general stability and non-toxicity. Numerous applications of arylboronic acids have been developed; however, the access to organoboronic acids or esters and the synthetic applications of other organoboron derivatives still lack of generality. We examined a novel electrochemical synthetic approach to arylboronic derivatives, as well as to benzylboronic and allylboronic esters. The electrochemical method is based on the reductive coupling of organic halides with pinacolborane, as shown in the example.

Synthetic and mechanistic aspects of these reductive coupling reactions will be presented and discussed. As a result of mechanistic studies, a novel and efficient



processes for the one-step selective synthesis of benzylboronic esters from benzylic halides has been found, involving a catalytic process.

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***In-situ* ESR/UV-Vis-NIR Spectroelectrochemistry of Endohedral Fullerenes: The Story of Sc₃N@C₆₈**

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The electrochemistry and spectroelectrochemistry of nitride clusterfullerenes is of great interest due to the surprising behaviour of these fullerenes upon charging. We focus on the electrochemistry and *in-situ* ESR/UV-Vis-NIR spectroelectrochemistry of both the anionic and the cationic structures of the non-IPR (IPR=isolated pentagon rule) fullerene Sc₃N@C₆₈ to demonstrate that even a non-IPR fullerene can result in radical ions of sufficient stability. As the cyclic voltammogram of Sc₃N@C₆₈ exhibits two electrochemically irreversible but chemically reversible reduction steps a more complex situation is expected for the anionic structures. Upon reduction of the diamagnetic Sc₃N@C₆₈, an ESR signal of the monoanion is detected. It undergoes a follow-up reaction to result in a diamagnetic dimer. The two oxidation steps of Sc₃N@C₆₈ are found to be electrochemically reversible and the charged states of Sc₃N@C₆₈ formed upon oxidation can be easily followed by the *in-situ* ESR/UV-vis-NIR spectroelectrochemistry. The generation of the stable radical monocation ([Sc₃N@C₆₈]⁺) is proved by *in-situ* ESR spectroscopy, indicating three equivalent Sc hyperfine splittings of 1.289 G. A DFT analysis reveals the differences in the spin distribution of [Sc₃N@C₆₈] ions dependent on the charge at the C₆₈ cage.

Elements of the Quasiperiodic Symmetry Found in the Baroque Pilgrimage Church of St. John Nepomucen and the Surrounding Cloister close to Žďár nad Sázavou, Czech Republic

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The church been constructed between 1719-1722 by the famous architect Johann Blasius Santini. The church and the cloister have been recognized as a part of the World Heritage by UNESCO in 1994. The church's plan shows a close similarity to Fig. Aa of the XIX part of Johannes Kepler's Second Book of Harmonices Mundi which was first published in Linz in 1619. The central part of the church can be imagined as if it were built of three stacked five-fold groupings of the prolate golden rhombohedra. This type of rhombohedron is one of two building elements of the three-dimensional Penrose tiling with local pentagonal symmetry that is used in modelling of quasicrystals. This grouping of five rhombohedra has also been described by J. Kepler in the same book when mentioning construction of the triakontahedron. Moreover, it can be shown that the church is geometrically related to the surrounding cloister by the patterns of the packed regular pentagons while maintaining the five-fold symmetry. The same pattern has been partly preserved in the original pavement of the church. The reasons for this prominent five-fold symmetry of the church and the cloister and other architectural details are derived from the iconography of Saint John of Nepomuk and the hierarchically higher Holy Trinity. These symbols are expressed, respectively, by the architectural elements of pentagonal and trigonal symmetry. The architecture of the church is probably the first example of the application of elements of pentagonal quasiperiodic symmetry in Christian Art. Moreover, with regard to other Santini's works, the church can be envisaged as inspired by Christian Platonism.

Electrochemical and Spectroelectrochemical Investigation of Iridium-(1,4-diazabutadiene) Redox System: Two-electron Reduction of $[\text{IrCl}(\text{Cp}^*)(\text{DAB})]^+$ versus Two Successive one-Electron Oxidations of $[\text{IrCp}^*(\text{DAB})]$

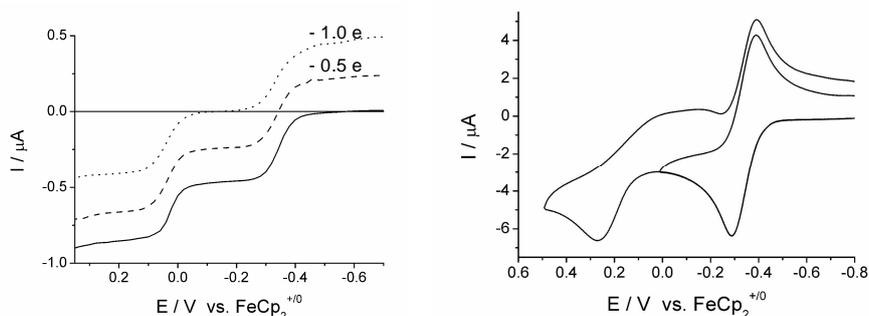
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Compounds $[\text{IrCl}(\text{Cp}^*)(\text{DAB})] \text{PF}_6$ (**1**), DAB = 1,4-bis(2,6-dimethylphenyl)-1,4-diazabutadiene, and $[\text{IrCp}^*(\text{DAB})]$ (**2**) were investigated with the aim to detect and characterize coordinatively unsaturated species. Reduction of (**1**) proceeds in a two-electron chloride dissociative step to yield (**2**). Reoxidation in a voltammetric peak shifted positively by 0.43 V (vs. the cathodic peak) involves a back association of chloride and regeneration of the starting complex (**1**). The electron uptakes proceed on the DAB ligand, in contrast to metal-based processes ($\text{Ir}^{\text{III}}/\text{Ir}^{\text{I}}$) detected for analogous complexes with less “noninnocently” behaving ligands, like derivatives of 2,2'-bipyridine or 1,10-phenanthroline. The (synthesized) complex (**2**) undergoes two-electron oxidation in presence of halide or in strongly coordinating solvents. However, in dichloromethane or propylene carbonate solutions of (**2**) a different oxidation pattern has been revealed. Two successive one-electron uptakes proceed in two well potentially separated oxidation waves, reversible first one followed by an apparently irreversible second step.



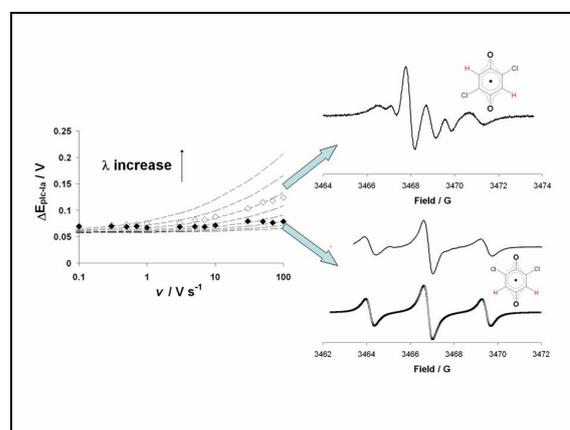
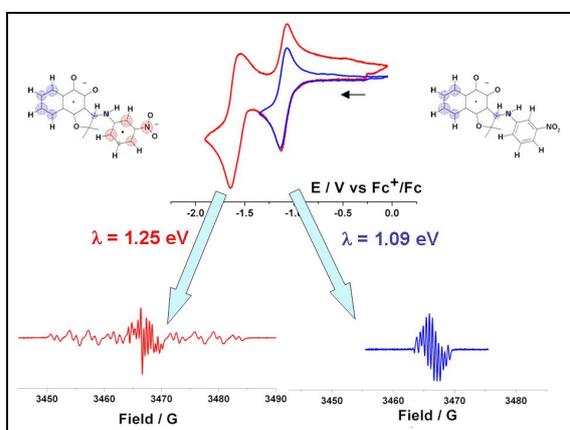
The radical intermediate $[\text{Ir}^{\text{III}}\text{Cp}^*(\text{DAB})]^+$ could be characterized spectroelectrochemically, by UV-Vis spectra and EPR. Addition of chloride leads to an immediate conversion to (**1**) and (**2**), which demonstrates the coordinative unsaturation of $[\text{IrCp}^*(\text{DAB})]^+$ and a redox instability (disproportionation) of $[\text{IrClCp}^*(\text{DAB})]$, in agreement with the observed two-electron character of the electrochemical reduction of $[\text{IrClCp}^*(\text{DAB})]^+$. The results were supported by DFT calculations.

Using Molecular Electrochemistry Approaches to Evaluate Properties of Reactive Radical Anions: Towards a Molecular Level Understanding of Pharmacological and Biological Effects

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Several natural occurring compounds have in their structure redox active groups such as quinones bearing an α -hydroxy group [1-4] and nitro groups. As Michael acceptors, quinones can induce cellular damage through alkylation of crucial cellular proteins and/or DNA. Alternatively, they are highly redox active molecules which can, by intermediacy of their semiquinone radicals, lead to formation of reactive oxygen species (ROS) [5, 6]. Concerning nitrocompounds, their assumed biological activity is also related to their facile reduction to RNO_2^\bullet species promoted *in vivo* by nitroreductases [7-9]. As the reduction of both type of compounds leads to the formation of reactive radical species, the main goal of research relating electrochemical and biological activity should be devoted to evaluate the way in which specific reactions determine the stability and lability of these radicals. In this context, the use of Electron spin resonance (ESR) is critical for addressing the molecular and electronic structures of radical compounds. A combination of using classical electrochemical approaches (based on voltammetric and chronoamperometric analysis), with the use of spectroelectrochemical-ESR experiments and electronic structure calculations has provided a good insight on the way that the reactivity of the electrogenerated radical species can be related to their structural properties. Several experimental cases discussing this relationship fact will be presented in this lecture [10-18]



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The Electrochemically Generated Radicals and Ion-Radicals in the Synthesis of Organofluorine Compounds

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Radicals and ion-radicals generated in electrochemical processes exhibit considerable reactivity and can participate in various organic reactions. The electrochemical methods of preparing organofluorine compounds with participation of fluoroaliphatic radicals and cation-radicals are considered, including Kolbe electrosynthesis in the presence of unsaturated hydrocarbon compounds, fluoro-olefines, aromatics and halogens, along with the direct and indirect fluorosulfation of fluoro-olefines in fluorosulfuric acid.

Electrooxidation of perfluoro- and oxoperfluorocarboxylic acids at the electrodes with different adsorbability in the solvents of various types is examined. It is demonstrated that depending on the solubility of generated radicals in the solvent used the processes with participation of these radicals can occur both at the electrode surface and in electrolyte bulk.

The formation of radicals, generated under the conditions of Kolbe electrosynthesis and related reactions was confirmed by the EPR technique in the presence of the radicals' traps. The dependence of concentration of the spin-adducts formed on the radical and electrode-catalyst nature was ascertained.

***In situ* Spectroelectrochemistry of α,ω -Endcapped Oligothiophenes**

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Novel α,ω -dicyano substituted β,β' -dibutylquaterthiophene (DCNDBQT) was synthesized for detailed studies of the influence of the molecular structure on the stabilisation of charged states. As the oligomer is well dissolved in solution any interaction of the molecules like in the solid state can be neglected.

For the first time the electrochemically generated cation and anion radical ions of the specially synthesized oligomer have been characterized by voltammetry and *in situ* ESR/Vis-NIR. A combination of *in situ* ESR/Vis-NIR spectroelectrochemistry and *in situ* NMR spectroelectrochemistry was used to get a more detailed insight into structural changes even of diamagnetic molecules and to study the reaction mechanism of both the cathodic and anodic reaction.

The voltammetry of DCNDBQT results in two separate oxidation steps the first of which is reversible. The vis-NIR absorption maxima at 646 and 1052 nm and an ESR signal at the first anodic step prove the presence of a radical cation. *In situ* NMR spectroelectrochemistry show the irreversible formation of a dimer from the dication of the second oxidation step.

In general substitution by cyano groups opens the route to cathodic reductions of the structure. DCNDBQT shows a single reduction step which turns out to be quasi-reversible. Here *in situ* ESR/Vis-NIR spectroelectrochemical experiment let us confirm the electrochemical generation of anion radical. As we found a low intensity of the ESR signal and an appearance of the additional bands in the absorption spectra the formation of follow-up reaction products must be considered. Surprisingly, no dimer structure was not detectable by *in situ* NMR measurements. The structure formed in the reduction step was analysed by MALDI-TOF mass spectrometry and shows formation of a trimer due to the polymerisation initiated by electrochemical reduction.

For conclusions the role of the dimerisation reaction and the reaction mechanism of the charge transfer reaction in general are discussed.

Application of Organometallic Compounds in Electrochemical Analysis of DNA

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Electrochemical analysis of DNA has been one of the most dynamically developing fields in bioelectrochemistry in last two decades [1]. This progress starts mainly due to try to develop electrochemical sensors for detection of DNA hybridization. Application of reporter (signaling) DNA probes (short oligonucleotide molecules, RP) modified by some electroactive tags belong to techniques frequently used in this area. Organometallic compounds are one from electroactive tags commonly used for this purpose. A typical approach to the preparation of modified nucleic acids is the solid-phase oligonucleotide synthesis using functionalized nucleoside phosphoramidites or post-synthetic oligonucleotide modification. Another possibility is based on incorporation of electroactive tags-modified nucleotides into the oligonucleotide chain by using enzymes – DNA polymerases and deoxynucleoside phosphate (dNTP) conjugates with the given tags. Modified dNTPs can be synthesized by simple cross-coupling reaction in aqueous media [2]. In this contribution we demonstrate utilization of two different approaches for preparation of electroactive labeled RPs: direct modification of DNA by osmium tetroxide complexes [3] and incorporation of dNTPs labeled by ferrocene [4] or Ru(II) and Os(II) complexes [5]. Prepared RPs were used in the development of electrochemical sensors for the analysis of nucleotide sequences.

Acknowledgments

This work was supported by the GA ASCR (IAA 400040903, IAA400040901), by MEYS CR (LC06035) and institutional research plans Nos. AV0Z50040507 and AV0Z50040702.

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Wide Prospects for Electrochemical Studies of Organic Molecules and Coordination Compounds (Review)

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Apart from electroreduction or electrooxidation, the electrochemical reaction which can give variety of valuable information to a researcher is the catalytic evolution of hydrogen. Catalytic evolution of hydrogen can be best followed on metals with high hydrogen overvoltage - i.e., on mercury or on amalgam electrodes. It is a complex phenomenon determined by the type of interaction of the given species with electrode surface and by the kinetics of proton transfer from solution to the electrode. Both these processes depend on many variable factors: on the size, structure, solvation, charge distribution/protonation, redox state and concentration of the species, in the case of biomacromolecules whether they are in native or denatured state, on the solvent, on the composition, pH and concentration of the electrolyte, on the electrode potential and on the rate of its time change.

Catalytic evolution of hydrogen has been known in polarography for several decades to yield the "presodium wave"¹, and the Brdička reaction². However, in the recent years the best method of its study proved to be direct current derivative chronopotentiometry with hanging mercury drop electrode³. In that method hydrogen catalysis produces a highly sensitive signal known as peak H - its height and the potential of its occurrence are affected by all the above mentioned experimental factors. In current-controlled electrolysis the rate of potential change of the electrode is much higher than in voltammetry, of the order of the rates of some kinetic steps of the catalytic process. This gives the possibility to affect the electrochemical process also by changes of the applied current. Before the current is applied it is possible to accumulate the studied substance at the electrode surface for some time at a definite constant potential - in this way the sensitivity of the "stripping" technique⁴⁻⁷ can be increased to nanomolar concentration per litre and further.

As catalytically active have been known substances containing sulphur or nitrogen atoms with free electron pair enabling transfer of proton from solution to the electrode surface; recently some catalysts were described where the catalytically active atom is oxygen with free electron pair⁸. The tendency of the species to adsorb at the electrode increases its catalytic activity. From these conditions it follows that catalytically active can be many organic compounds, particularly the various biopolymers, but also inorganic complexes containing ligands with nitrogen, oxygen or sulphur atoms⁹. The experimental experience with peak H shows that it is the matter of chemical practice to prepare a specific and highly sensitive electroanalytical reaction for a given substance which would allow its study and determination.

Acknowledgement

Author's thanks for financial support are due to the Czech GAAV, grant No IAA 400-400-806.

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A Comparative Spectroelectrochemical Study of the Redox Electrochemistry of N-(polyvinylamine)-Substituted-*o*-Nitroaniline

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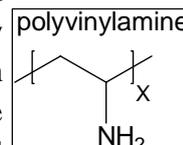
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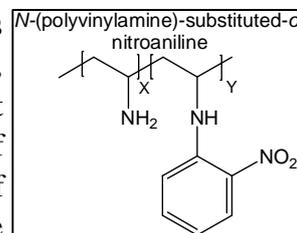
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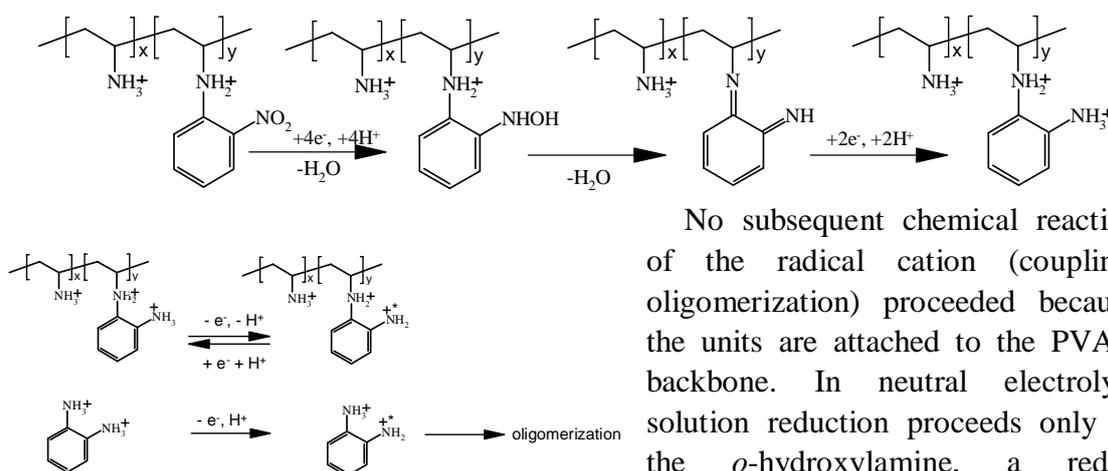
Polyvinylamine (PVAm) is a cationic polyelectrolyte (macromolecule with ionizable groups of cationic character). It has received considerable attention in recent years due to the high reactivity of the primary amino group in derivatization and crosslinking as well as the high cationic density of this polymer at low pH-values. In addition, an improved control of the ionic properties, such as charge density and acid-base strength, is possible by simple protonation. The acid-base behavior of PVAm has been studied



extensively by means of potentiometric titration. PVAm is frequently used in catalysis, chelation, biomedical research, liquid chromatography, and paper-making. Aromatic pendant groups can be used to modify the electronic properties of PVAm. N-(polyvinylamine)-substituted-*o*-nitroaniline is of interest among other properties because of solvatochromism. We have studied the redox and adsorption behavior of PVAm with different molecular weights and numbers of nitroaniline units in the polymer with cyclic voltammetry and surface enhanced Raman spectroscopy.



CVs revealed establishment of a redox couple after reduction of the nitro group in acidic electrolyte solution indicative of transformation of the *o*-nitroaniline into the respective phenylenediamine according to:



No subsequent chemical reaction of the radical cation (coupling, oligomerization) proceeded because the units are attached to the PVAm backbone. In neutral electrolyte solution reduction proceeds only to the *o*-hydroxylamine, a redox behavior typical of a moiety

corresponding to formation of a phenylenediamine could not be observed.

SER spectra recorded with PVAm containing various amounts of nitroaniline groups and having different molecular weight at different electrode potentials and in solution of various pH-values showed new bands indicative of interactions between nitro-functions, amino-groups and perchlorate anions and the electrode surface. Models of the interphases between the metal and the bulk electrolyte solution are proposed taking into account these observations.

Variable π -acidity of η^2 -bonded Allyl and of Carbene Ligands with Respect to the Central Metal Atom

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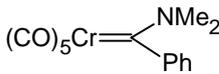
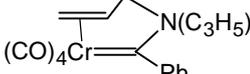
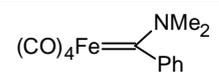
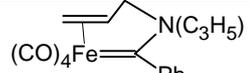
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In coordination chemistry, various molecular properties are compared and evaluated with respect to the bonding character of ligands. Nature of ligands with respect to their σ -donor and π -donor or π -acceptor ability was used to the successful explanation of the ligand sequence in the spectrochemical series of ligands.

Electronic spectra and oxidation potential of a molecule are both connected with HOMO energies and obey similar rules, thus, inspired by the spectrochemical series, several theories correlating E_{ox} and E_{red} potentials with ligand properties have been published (for a recent review see[1]). These theories assign to each ligand certain value of an additive constant and with help of it they are able to predict, among other data, E_{ox} of an unknown molecule.

In all the theories cited above, bonding ability of the ligand is taken as a given, constant characteristic. We would like to show that this premise must be taken with with some precaution.

In course of our recent measurement of Cr and Fe aminocarbenes [2], we have found out following E_{ox} (vs. SCE):

compound	$Cr(CO)_6$	$(CO)_5Cr=$ 	$(CO)_4Cr=$ 
E_{ox} [V vs. SCE]	+1,53*	+0,85	+0,52
compound	$Fe(CO)_5$	$(CO)_4Fe=$ 	$(CO)_4Fe=$ 
E_{ox} [V vs. SCE]	+1,51*	+0,42	+0,47

*data taken from C. J. Pickett, D. Pletcher, *J.C.S.Dalton* **1975**, 879

Parallel evaluation of E_{ox} , E_{red} , IR spectra and [1] H NMR data leads to the most plausible explanation: π -acceptor ability of both η^2 -bonded allyl and carbene ligands is not constant and depends on the central metal atom, the key property could be its electron configuration and corresponding geometry.

Acknowledgement

This work was supported by the GA AV CR (grant No. IAA 00400813).

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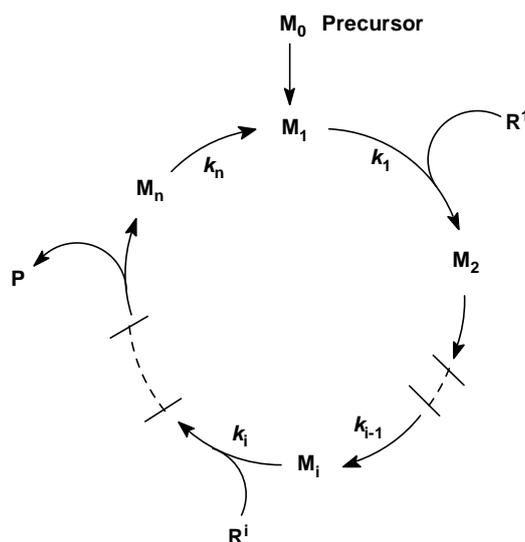
Electrochemistry: A Way to Solve Mechanistic Problems in Organometallic Catalysis

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Many reactions are nowadays catalyzed by transition metals which not only accelerate the reactions but allow, via their ligands, a fine control of their selectivities. Transition metal-catalyzed reactions proceed via catalytic cycles involving organometallic catalytic species with different oxidation states.



Most organometallic complexes may be oxidized or reduced. Consequently they can be detected, generated and characterized by electrochemical techniques. Moreover, their reactivity can be followed by the same techniques, taking advantages that currents are proportional to the concentrations of electroactive species. It thus becomes possible to investigate the rate and mechanism of all steps of a catalytic cycle (involving or not electron transfers), to determine factors that control the efficiency of a catalytic reaction, to understand how and why a catalytic reaction works, so that to increase its efficiency in terms of turn-over and selectivity.

It will be shown how the first step of a catalytic cycle can be fully investigated using electrochemical techniques (cyclic voltammetry, chronoamperometry, conductivity measurements). The full mechanism of palladium-catalyzed reactions involving organoboranes (cross-coupling and heterocoupling) will be presented.

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Reversible Intramolecular One-Electron Oxidative Addition: Structure, Spectroelectrochemistry and Theory

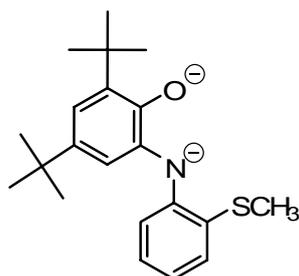
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Redox-switched catalytic oxidation of dihydrogen has been described recently^{1,2} by the group of Rauchfuss, using organoiridium complexes of o-aminophenolate/o-iminoquinone non-innocent ligands. Using a combined structural/theoretical/spectroelectrochemical approach as described by us for 1,4-diazabutadiene compounds³ we have now employed the o-aminophenolate/o-iminoquinone redox system Qn in the form with an additional hemilabile thioether sulfur function.⁴ Similarly as postulated for copper(II) compounds⁴ we have observed that the Qn ligand can act as tridentate (O,N,S) or as bidentate (O,N) ligand with coordinatively unsaturated [Ir(C5Me5)]²⁺, depending on the charge n. Both forms were isolated and structurally characterized and calculated by DFT in the ground state, the alternative structures were also assessed by DFT. Following cyclic voltammetry with two successive steps and a typical slow rearrangement behavior between forms with five- and six-coordinate metal, the spectroelectrochemical and EPR data helped to establish that the intramolecular process involves electron transfer at the ligands, thus leading only indirectly to an oxidative addition at the metal which remains invariant with respect to its oxidation state.



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Sonoelectrochemistry – Desired Effects, Possible Mechanisms and Design of Experimental Arrangement

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Sonication of working electrode in sonoelectrochemical cell may result in very intense mass transfer enhancement and/or electrode activation, i.e. in facilitation of electrochemical process. Though this effect was described as early as in 1934 [1] and 1937 [2], the exact mechanism by which ultrasound influences the process is still under discussion.

An overview of advantages resulting from application of ultrasound in electrochemistry based on understanding of possible mechanisms by which sonication can influence electrochemical processes will be given.

Four mechanisms will be discussed:

- acoustic streaming;
- microstreaming and turbulence due to cavitation;
- formation of microjets in the course of collapse of cavitation bubble;
- shock waves.

From the point of electrochemistry, the most effective process is formation of microjets, which can not only decrease diffusion layer under 1 μm , but especially activate (depassivate) electrode surface.

The most important parameter, deciding which mechanism predominates, is distribution of ultrasonic field within the cell. For microjetting and microstreaming, the intensity of cavitation in the closest vicinity of the working electrode is crucial. That means that only local value of ultrasonic pressure amplitude (which is definitive for cavitation) is deciding about these processes. On the contrary, for acoustic streaming the shape of the cell and an integral amount of energy delivered to the system is decisive factor - it is possible, that a large increase of current due to acoustic streaming can be observed even when the local value of ultrasonic intensity around the working electrode is low. That is why; the estimation of distribution of ultrasonic field is dominant problem in development of new sonoelectrochemical cell. The best approach for such estimation is numeric simulation of ultrasonic field with the help of solution of wave equation (the shape of the cell is introduced to the simulation in the form of boundary conditions) [3,4].

The design of experimental arrangement with maximum participation of microjets will be discussed.

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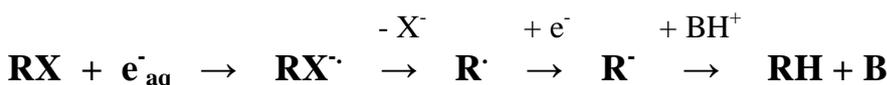
Metastable Complex of a Radical with a Proton Donor/Acceptor as a New Key Intermediate in Organic Electrochemistry

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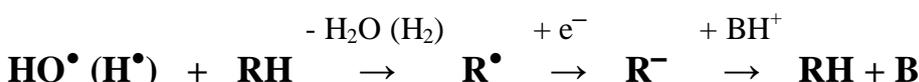
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It was comparatively studied by laser photoemission [1] the electrochemical behaviour of various categories of organic radicals adsorbed on a mercury electrode (R_{ads}) over wide range of electrode potentials, concentrations of proton donors (H_3O^+ , NH_4^+), and temperatures. The radicals were formed via the capture of hydrated electron by an acceptor RX (X is a halogen or other leaving group):



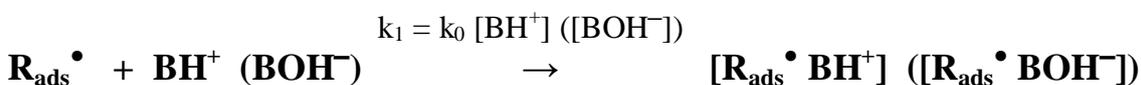
or by the reaction of RH acceptor with photoemission generated OH- or H-radical:



A general scheme of electrode reactions of organic intermediates is discussed. The suggested kinetic model considered two parallel pathways of electron transfer. The first one is the irreversible electron transfer to an adsorbed radical (ion radical) R_{ads} to form a carbanion (dianion) $R^- (R^{2-})$:



and the second one is the electron transfer to a metastable complex of an adsorbed radical with a proton donor BH^+ /acceptor BOH^- , i.e., $[R_{ads} \cdot BH^+ BH]/[R_{ads} \cdot BOH^-]$:



The studied intermediates were alkyl, aryl radicals, α -, β - and dihydroxy alkyl, carboxyl, formyl, carboxy- and halogenocarboxyalkyl radicals and ion radicals, radicals of linear and cyclic ethers, oxa- and 1,3-dioxacycloalkanes; their halogen (Cl or Br) derivatives. The experimental dependencies of rate constants of reduction (V_e , V_e') and oxidation of intermediates on electrode potential, and on donors/acceptors concentration were demonstrated to describe quantitatively within frameworks of the proposed model. The formation of metastable complexes was shown to facilitate for radicals having one or more functional groups whereas simple hydrocarbon or hydrohalogenated carbon radicals did not form usually [2] such complexes. The particular reduction pathway is determined predominantly by the difference between overvoltages of electron transfer to R_{ads} and on its metastable complex with BH^+/BOH^- under other the same constant conditions (i.e., nature and concentration of a proton donor, electrode potential).

Acknowledgement

Financial support from the Russian Foundation for Basic Research (grant No. 09-03-00598) is gratefully acknowledged.

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Supramolecular Complexation of Biogenic Amines by Functional Electroactive Monomers of Thiophene Derivatives for Formation of Molecularly Imprinted Polymer (MIP) Films for Biosensor Development

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We synthesized electronically conducting polymers for devising selective chemical sensors. Toward that, electroactive functional monomers were derivatized to bear recognition sites capable of formation of complexes in solution with target analytes. These monomers included derivatives of bis(2,2'-bithienyl)methane substituted with either the 18-crown-6, 3,4-dihydroxyphenyl, or dioxaborinane moiety. The analytes were selected from biogenic amines. These included adenine, dopamine, histamine, and melamine. By DFT quantum chemistry calculations at the B3LYP/3-21G(*) level, we modeled geometries of these complexes. Initially, the analytes played a role of templates. Then, the complexes were electropolymerized in the presence of suitably selected cross-linking monomers and porogenic solvents. A derivative of 3,3-bithianaphthene and an ionic liquid suited that purpose very well. Next, the resulting molecularly imprinted polymer (MIP) films were washed with abundance of a base solution to extract the templates. That way, molecularly imprinted cavities were left in the MIP film. Size and shape of these cavities were compatible to those of the analyte molecules. In this form, the film was suitable for use as a recognition material in a chemosensor. A 10-MHz thickness-shear-mode bulk-acoustic-wave resonator of a quartz crystal microbalance was used as the piezoelectric transducer of the detection signal into the mass change signal. The MIP-template interactions of the covalent bond, hydrogen bond, and inclusion complex nature appeared to be reversible allowing for extensive and reversible accumulation of the analyte in the film and its subsequent removal for the analytical reuse. Due to this accumulation, detection limits reached the nanomole concentration level. Imprinting of the adenine, dopamine, and histamine electroactive analytes required preliminary coating of the electrode with a barrier underlayer film. This film served to prevent electrode processes of the analytes on the one hand and to afford efficient charge exchange with the MIP film deposited by electrochemical polymerization on top of the barrier film on the other. The electrode processes of the analytes were highly undesired because adsorption of products of these processes would be imprinted instead of the analytes themselves. Moreover, products of these processes would adsorb on the electrode surface blocking it and obstructing adhesion of the MIP film. Selectivity of the imprinting was tested by using typical interfering compounds structurally or functionally analogous to the analytes. This selectivity was high being mainly governed by complementarity of the stereo geometry of the analytes and imprinted molecular cavities of MIPs as well as affinity of the MIP binding sites located in these cavities to the binding sites of the analytes.

Electrochemical reduction of molecules with more redox centers: Mono-, Di-, Tri and Tetranitrocalix-[4]-arenes and Their Models

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Calixarene is a stable supramolecular frame able to bear various substituents – redox centers or ligands, capable to exhibit unusual redox properties including host-guest interaction. For these reasons a suitable substitution is necessary, namely on the upper rim. The title nitro derivatives are precursors enabling electrochemical introduction of other functional groups and prolongation of the pendant carbon chains.

These poly-nitro compounds are also an example of molecules with more redox centers. The presence of one, two, three or four nitro groups in one molecule provokes many principal questions: What is the intramolecular electronic interaction between them? Are they reduced simultaneously or stepwisely? Which part of the molecule is reduced first? What is the role of the lower rim substitution in the reduction of the nitro groups? What is the influence of the conformation of the calix arene (CONE, PACO, 1,2-ALT, 1,3-ALT) on its reducibility? What is the influence of the reduction on the molecular geometry?

At first, the reduction mechanisms of *p*-substituted nitrobenzenes in aprotic DMF had to be clear. Besides the classical nitro group reduction (1rev. + 3 electrons), several other mechanisms (dianion formation, 6-electron reduction, dimerization, autoprotonation mechanism, etc.) depending on *p*-substitution were observed and described.

Electrochemical reduction of the tetranitrocalix-[4]-arenes starts with two 2-electron reversible waves corresponding to the presence of two different couples of equivalent non-communicating nitro groups. This result reflects well the finding of the x-ray structural analysis, that the "calix" has in fact a pinched shape with a strong " π -stacking" of the opposite benzene rings. The first two waves are followed by a single 12-electron wave.

The quantum chemical calculations (electrostatic potential maps of the neutral molecule as well as of the mono-, di-, tri- and tetraanion and localization of HOMO and LUMO of the dianion) confirmed the above mentioned interpretation of experimental data and revealed, that the first electron transfers attacks the "distant" nitro groups, whereas the pinched position is reduced at more negative potential.

The electrochemical results of a series of mono-, di-, tri- and tetranitrocalixarenes are fully consistent with previously described type of redox behaviour.

In addition to this, the role of the lower ring substitution and conformation type of the calixarenes are discussed.

Acknowledgement

The authors thank to prof. Pavel Vojtisek (Charles Univ., Prague) and to prof. Pavel Lhotak (Prague Inst. of Chem. Technol.) for granting the compounds. The financial support of the project KONTAKT No. ME 00209 (Ministry of Education, Youth and Sports of the Czech Republic) is highly appreciated.

Electrochemistry of the "Push-Pull" Type Molecules with a Systematically Extended π -Conjugated System

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Push-pull molecules with large delocalized π – electron systems are in centre of focus of material chemistry due to their promising optoelectronic properties [1]. Recently, some new series of imidazole derivatives were synthesized and basic characterisation has been performed [2,3]. The first serie was based on 4,5-dicyanoimidazole whereas the second one contained 4,5-bis(dimethylanilino) imidazole unit. Both series of structures featured systematically enlarged π -conjugated spacer in position 2 of imidazole ring. In both cases the linker was end-capped with dimethylamino group (serie 1) playing the role of donor and with CN or NO₂ group (serie 2) as an acceptor. These derivatives of various structure were selected in order to characterise them electrochemically using polarography, cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile, N,N-dimethylformamide). From the CV measurements resulted that there are several redox processes. The attention has been paid to the first oxidation and reduction. In both series the first oxidation process as well as the first reduction seems to be one electron and diffusion controlled. The influence of different linker has been also studied and from CV has been pointed out that length of π -conjugated spacer plays an important role in electrochemical behavior. While in serie 1 the linker influenced both oxidation and reduction, in case of serie 2 only potentials of first reduction were shifted whereas potential of first oxidation was fixed. Next step in evaluation of the CV data was determination of HOMO-LUMO gap which helps with selection of some derivatives for further experiments. Based on this preliminary characterizations it will be possible to tune the structure for use of the derivatives in electronic applications.

Acknowledgement

Financial support from the Ministry of Education, Youth, and Sports of the Czech Republic (No. MSM0021627502 and Project No. LC 510) is gratefully acknowledged. The authors thank Assoc. Prof. Filip Bureš for synthesis of examined organic compounds.

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Electrochemistry of Dinuclear Re(I) Complexes with Bridging 1,2 Heteroaromatic Chromophore Ligands

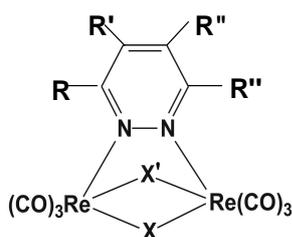
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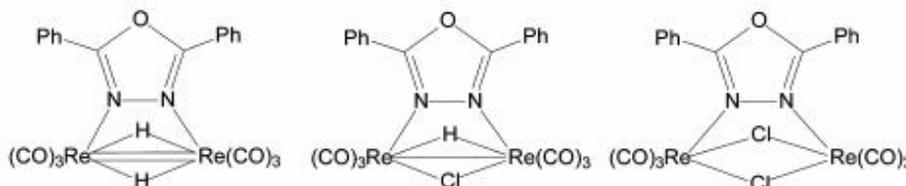
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In the last years we have been developing [1-3] a new class of photoluminescent complexes with high quantum yields, having a dinuclear $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6$ scaffold with: (a) a bridging 1,2 heteroaromatic ligand, either a pyridazine (with many combinations of electron donating or electron attractor substituents R, R'; R'', R''' on the aromatic ring) or an oxadiazole; (b) two ancillary bridging ligands X and X' (either halides Cl, Br, or I; and/or H; or OH, OCH₃, OC₆H₅, OC₆F₅, SC₆H₅).



The nature of the ligands greatly influences (a) the electrochemical properties of the molecule, in terms of energies of the HOMO (localized on the dinuclear $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6$ core) and LUMO (localized on the heteroaromatic ring), and (b) the electrochemical and chemical reversibility of the electron transfers. These features will be discussed in detail also in comparison with the electrochemical reactivity of the free heteroaromatic ligands, and with the functional properties of these molecules. The electrochemical study, combined with other techniques, is important for interpretation and prediction purposes, in order to develop electroluminescent devices based on these new classes of Re(I) complexes. Nevertheless, it also looks attracting (in some cases intriguing) in itself, since the wide, systematic compound family now available provides an unusually complete and neat model case of multivariate electrochemical reactivity in a complex system.

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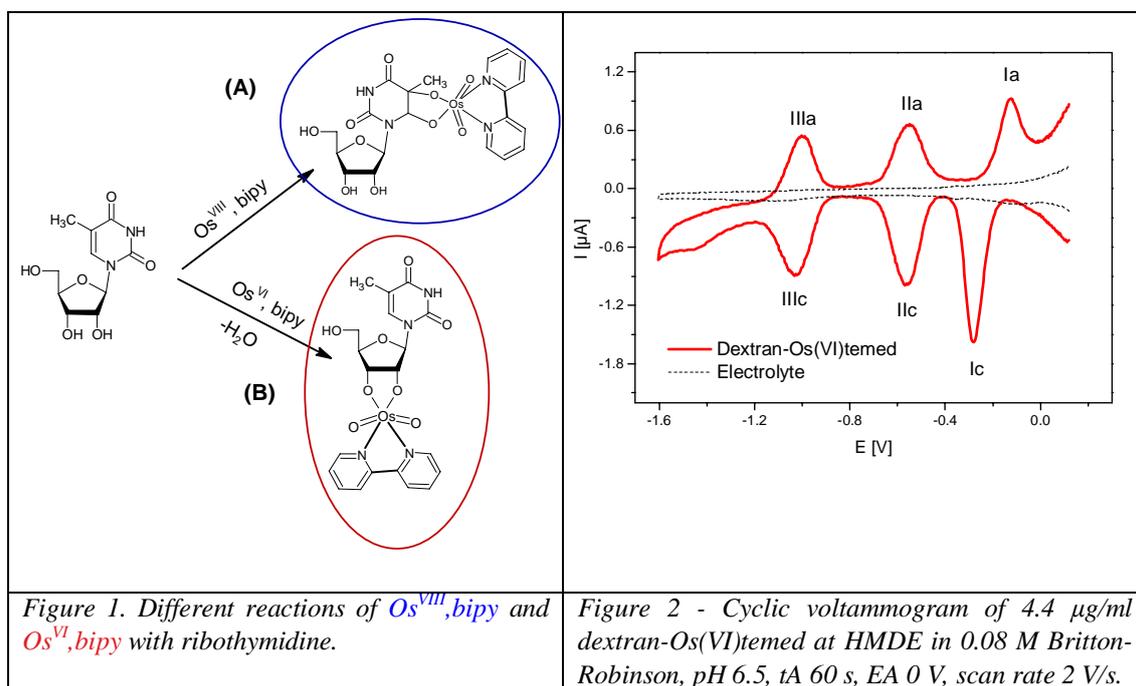
Electrochemistry of Biomacromolecule Adducts with Osmium Complexes

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Almost 30 years ago we showed that covalently bound electroactive labels can be introduced in nucleic acids using osmium tetroxide complexes with nitrogenous ligands (L) reacting with pyrimidine bases in DNA and RNA (Fig. 1A) [1, 2]. These complexes turned out to be important probes of the DNA structure in vitro [2] and in vivo [3, 4] at single nucleotide resolution. Moreover, Os(VIII)L complexes have been recently utilized to end-label DNA in electrochemical DNA hybridization sensors [5, 6]. Recently we have shown that a similar strategy can be applied for end-labeling of peptide nucleic acid (PNA) [7] and modification of tryptophan residues in proteins [8].



Recent progress in elucidation of biological functions of oligosaccharides (OSs), and polysaccharides (PSs), including their roles in cancer and some neurodegenerative diseases, supported improvement of analytical methods. Due the alleged electroinactivity of PSs, electrochemical methods lagged behind. Recently we have shown that electroactive labels can be introduced in PSs and OSs using complexes of six-valent osmium with different ligands [$\text{Os}^{\text{VI}}\text{L}$] (Fig. 1B) [9, 10]. The PS- $\text{Os}^{\text{VI}}\text{L}$ adducts produce three redox couples at carbon and Hg electrodes (Fig. 2) and an electrocatalytic peak (only at Hg electrodes) enabling determination of PSs and OSs at picomolar level (not shown). Using this approach, carbohydrate components of glycoproteins can be analyzed. It is interesting that some types of unmodified PS, such as sulfated carrageenans (occurring in seawater) catalyze hydrogen evolution at mercury electrodes and produce well-developed chronopotentiometric stripping peaks [11], similar to peak H of proteins [12-14].

Acknowledgment

This work was supported by the AS CR grant KAN400310651.

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Electrochemical Characterization of Coordination Compounds and Selected ET-Induced Reactions

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Redox potentials of coordination compounds have been correlated to many other properties, e.g., the HOMO energy, gas-phase ionization potential, ligand field stabilization energy, Hammett's and related constants, energy of CT bands, IR and NMR parameters, etc., which are often dependant on the electronic/structural properties of the ligands and their coordination metal centres, suggesting that one could define suitable electrochemical parameters, based on the redox potential, for measuring such ligand and metal site properties.

The research has often been oriented towards the establishment of additive ligand effects on the redox potential and the relevant models of Pickett and Lever (on a partial or a full additivity basis, respectively), as well as extensions and developments thereof namely proposed by the current author, will be presented. They comprise a ligand parameter (P_L or E_L , respectively) that relates linearly with the redox potential and constitutes a measure of the electron donor character of a ligand.

Such approaches will be illustrated for representative coordination compounds with various types of N-, O- and C-ligands that have been investigated in the author's laboratory, namely involving Ru-scorpionates and Ru-azoles with antitumor activity (a redox potential – activity relationship will be shown), Re-N,O and Rh-P complexes.

When the electron-transfer induces a chemical reaction, direct redox potential-structure relationships may fail but nevertheless the redox potential can determine the reaction pathways and the mechanisms of the redox process. Examples studied by the author's Group include anodically-induced geometrical isomerisations and metal-hydrogen bond cleavages, cathodically-induced metal-halogen bond ruptures and protonations, in a few cases occurring via electrocatalytic processes.

Acknowledgements

The co-authors and the Foundation for Science and Technology (FCT), Portugal, are greatly acknowledged.

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Electrochemical Properties of an Electroactive Ionic Liquid: From the Heterogeneous Electron Transfer to the Formation of Intermetallic Compounds

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Room temperature ionic liquids (RTILs) represent an attractive alternative to traditional organic solvents due to their properties such as a negligible vapor pressure, high thermal, electrochemical stability, and good ionic conductivity. Furthermore RTILs are tunable, multipurpose materials for a variety of applications rather than as just solvents. Then, RTILs provide a unique environment for studying electrochemical phenomena and their prospective applications are increasing enormously. In this work, we investigate the electrochemical properties of an electroactive ionic liquid, 1-(ferrocenylmethyl)-3-methylimidazolium bis(trifluoro-methanesulfonyl)amide referred as FcEmiTFSI.

The heterogeneous rate constants are determined for the pure compound and for solutions in acetonitrile (ACN) and in a room-temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmiTFSI). Cyclic voltammetry data are compared with those obtained for the ferrocene (Fc) in EmiTFSI and ACN. The half-potential of FcEmiTFSI/Fc⁺EmiTFSI is higher than that of Fc/Fc⁺ in both media. The apparent heterogeneous rate constants k_{app} of FcEmiTFSI and Fc are determined in both solvents by means of the high scan rate cyclic voltammetry and electrochemical impedance spectroscopy. We show that the values of k_{app} for these two redox probes in the same solvent are of the same order of magnitude. However, k_{app} is lower in EmiTFSI than in ACN. Comparison of k_{app} in these solvents indicates that the decrease in k_{app} cannot be explained in terms of Marcus–Hush theory [1].

We have also investigated the electrochemical formation of intermetallic compounds from the uptake of guest ions by host lattices. Here, the electrochemical reduction of noble metal electrodes in the presence of redox ionic liquid, FcEmiTFSI, was studied by cyclic voltammetry. Our results suggest the formation of metal with negative oxidation states for both the platinum and gold electrodes [2]. By analogy with the previous work [3], the formation of these phases is concomitant with the insertion of the supporting electrolyte; which correspond in our experimental condition to the redox cation of the ionic liquid [M_n⁻, FcEmi⁺]. As an exciting result, the electrochemical investigations of the reduced electrode in electrolytic solution, containing only solvent and supporting electrolyte, evidence the presence of the ferrocene groups at the electrode surface. Moreover, the reduced electrode exhibits the presence of the ferrocene even after, contact with air, after ultrasound, and after physical polishing, highlighting the large stability of this organo-metallic phases formed in this media. The AFM investigations demonstrate the morphological change of the platinum surface after the reduction process. X-ray photoelectron spectroscopy (XPS) techniques bring a direct spectroscopic evidence of the formation of a reduced platinum state. Finally, our works gives a formal electrochemical proof of the presence of the ionic liquid cation inside the electrode material after the cathodic treatment in this media. This kind of modified electrode will be of interest for electrocatalysis applications.

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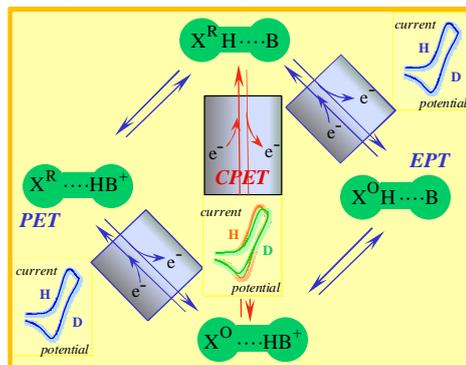
Concerted Proton Electron Transfers. Electrochemical and Related Approaches

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Proton-coupled electron transfers (PCET) are omnipresent in natural and artificial chemical processes. Understanding mechanisms and activation-driving force relationships, which underlie their practical efficiency, is a timely task in front of contemporary challenges concerning energy conversion, depollution and development of high-performance sensing. Focusing on PCET reactions in which, in contrast with hydrogen-atom transfers, proton and electron transfers involve different centers, the reaction may go through an electron or proton transfer intermediate, giving rise to an EPT and a PET pathway, respectively. "CPET" reactions, in which proton and electron transfers are concerted, have the advantage of by-passing the high-energy intermediates of the stepwise pathways, even though this thermodynamic benefit may have a kinetic cost. The main task of the kinetics-based mechanism analysis is therefore to distinguish the three pathways and to uncover the factors governing the competition between them, which implies the modeling of CPET reactions. More or less sophisticated models have appeared but the large number of parameters involved and the uncertainty of quantum chemical calculations they may have to resort to make inspiration from and confrontation with experiment compulsory.



Electrochemical PCETs are worth particular attention if only because most applications in which PCET intervenes, involve collection or injection of electricity through electrodes. On a more fundamental side, changing the electrode potential is an easy and continuous way of varying the driving force of the reaction, whereas the current flowing through the electrode is a straightforward measure of its rate, making the current-potential response in non-destructive techniques like cyclic voltammetry readable as an activation-driving force relationship provided the contribution of diffusion has been taken into account. Intrinsic properties (properties at zero driving force) are consequently a natural outcome of the electrochemical approach.

The choice of the illustrating experimental examples was inspired by two biological systems, photosystem II and superoxide dismutase. A first series of studies accordingly concerned the oxidation of phenols, with, as proton acceptor, either an attached nitrogen base or water (in water as solvent). The second example addressed interconversion of aquo-hydroxo-oxo couples of transition metal complexes with the example of osmium complexes. Lastly the reduction of superoxide ion, closely related to its dismutation, gave the occasion of observing and rationalizing the remarkable properties of water as proton donor. Water is also a remarkable proton acceptor in the oxidation of phenols, endowed with very small reorganization energies both in the electrochemical and homogeneous cases. Coming from all different corners of chemistry, these examples reveal general features of PCET reactions that may serve as guidelines for future studies, among which emphasis should be put on new biological systems on the one

hand and on the role H-bonding and H-bonded environments (water, proteins) on the other.

Acknowledgment

Julien Bonin, Cyrille Costentin, Cyril Louault, Marc Robert, Mathilde Routier and Anne-Lucie Teillout are thanked for their participation to the work described in this lecture

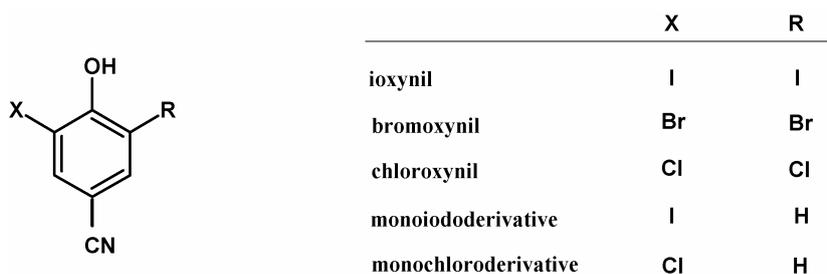
The Importance of a Proton Donor in Reduction of Halogenated Benzonitriles

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The mechanism of the overall one electron reduction of hydroxybenzonitriles substituted by one or two halogen atoms was explained by the autoprotonation. An anion radical is formed in the first one electron reduction step of 3,5-dihalogeno-4-hydroxybenzonitriles (Scheme 1) and the cleavage of carbon-halogen bond follows. This was based on the interpretation of cyclic voltammograms and DC polarograms, on the electrochemical detection of halide anions formed in the process and on the detection of dehalogenated products by GC-MS analysis [1]. The uptake of one electron per molecule in the first reduction wave was confirmed by controlled potential coulometry with potential set at the limiting current of the first reduction wave. At higher potentials monohalogenated intermediates are further reduced to their anion radicals. The protonation of the anion formed in ECE process is involved in the reduction mechanism of benzonitrile pesticides.



Scheme 1. The chemical structure of investigated substituted benzonitriles.

The reductive cleavage of carbon-heteroatom bond was intensively studied by the group of J.-M. Savéant [2-5]. The mechanism of the overall one electron reduction of ioxynil was explained by the autoprotonation in our recent paper [6]. Aryl radical formed by the cleavage of halogenide undergoes immediately electron transfer in ECE type reaction and an anion is formed. In the absence of proton donor in solution, the hydroxyl group of ioxynil provides a proton for the protonation of the formed anion. The number of electrons is two per two starting molecules, which explains the overall one electron process.

The first polarographic wave of ioxynil changes from a one electron wave (see curve a in Fig. 1) to a two electron wave in the presence of strong proton donor (see curve e in Fig. 1). The suitable proton donor should be a stronger acid than the starting molecule and should not be electroactive at the same reduction potential.

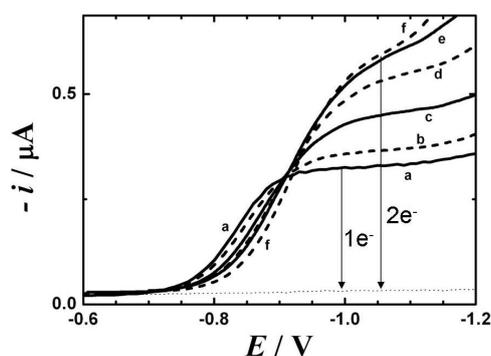


Fig. 1. DC polarogram of 2.5×10^{-4} M ioxynil in 0.1 M TBAPF₆ and DMSO at different concentrations of potassium tetraoxalate: (a) 0, (b) 4.3×10^{-5} M, (c) 1.4×10^{-4} M, (d) 2.9×10^{-4} M, (e) 4.3×10^{-4} M and (f) 7.0×10^{-4} M. Drop time was 1.5 s. Dotted line represents the DC polarogram of the supporting electrolyte.

The ability to provide protons increases in order p-hydroxybenzotrile < 3-iodo-4-hydroxybenzotrile < ioxynil < bromoxynil ~ 3-chloro-4-hydroxybenzotrile < chloroxynil

Acknowledgement

This work is supported by the Grant Agency of the Czech Republic (203/09/1607) and Ministry of Education (COST OC140).

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Intermetallic Compound Formation on Mercury Electrode during Polarographic Studies in the Presence of Selenite

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In our former polarographic and voltammetric ASV studies [1,2] in acidic solutions we observed that selenite and some ions, such as cadmium, arsenic III, lead, copper, tin and zinc diminished the peak of each other, and new peak formations at more positive potentials for the corresponding ions appeared.

This observation was attributed to the formation of an intermetallic compound (Somer mechanism) [3] between selenium and the ions present. We observed that when selenium and one of the interfering ion were present together and when selenite concentration was higher than the other ion, two peaks were observed in acidic media. One corresponded to free selenite and the second to an intermetallic compound. The other ion concentration can be determined from the peak of intermetallic compound by standard additions. The selenite concentration on the other hand can be determined by the addition of the other ion in excess. It should be remembered here that one of the ions in the solution has to be at a higher concentration than the other to complete the reaction between them. Se and Pb in blood samples could be determined [4] using this intermetallic compound formation peak.

As can be seen selenite may interfere with the determination of many cations and anions and thus will create problems when using polarography. Since it may be present in many biological materials its elimination will be very important.

The pH dependence of the interference between selenite and some ions and the optimum conditions for the elimination of interference was investigated [5] and it was shown that this interference could be eliminated at pH 8.5 (0.1 M NaAc). Under these conditions it was possible to determine copper, cadmium, lead and zinc (each 10^{-5} M) in the presence of 50–100 times of selenite with great accuracy. Only the interference between Cr(VI) and selenite could not be eliminated at this pH. However, in the presence of B-R (Britton-Robbinson) buffer at pH 8.5 there was no intermetallic compound formation. Thus, the effect of components present in B-R buffer is investigated and this method was applied to Gerede river water.

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Electrochemical Methods in Research on Metallothioneins and Phytochelatins

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Metallothioneins (MT) is a collective name for a superfamily of ubiquitous low molecular weight (6-7 kDa) metal-binding proteins or polypeptides, characterised by high thiolate sulphur and metal content, both of the order of 10% (w/w). In plants, more simple polypeptides (phytochelatins) belonging to MT group are synthesised, of general formula $(\gamma\text{-Glu-Cys})_n \text{R}$, where R = Gly, scarcely Glu, Ser or Ala, $n = 2-11$. The formation and behaviour of metal-thiolate complexes can be advantageously studied by electrochemical methods – voltammetry and constant current chronopotentiometry. Three types of mammalian metallothioneins were studied, namely Cadmium Rabbit Liver Metallothionein - Cd₇MT and its Zn containing analogues - Zn₇MT and Cd₅Zn₂MT. As model of phytochelatins, synthetically prepared peptide $(\gamma\text{-Glu-Cys})_2 \text{Gly}$ was used. Voltammetric methods employing hanging mercury drop electrode can distinguish cadmium(II) coordinated by one, two or four sulphur atoms, having its reduction peak at different potentials. This was demonstrated on complexation of peptide $(\gamma\text{-Glu-Cys})_2 \text{Gly}$ with cadmium ions, where stoichiometric ratio could be determined, using method of multivariate curve resolution. Reduction peak corresponding to tetraordinated Cd(II) in Cd-peptide complex exhibited similar behaviour in cyclic voltammetry as Cd(II) - reduction peak of CdMT, whereas for higher cadmium content, labile behaviour was observed. Analogous voltammograms were obtained for CdMT and Cd-complex of peptide $(\gamma\text{-Glu-Cys})_2 \text{Gly}$ also on carbon paste electrode (10% w/w of silica gel). Similar behaviour as for CdMT has been observed also for Zn-containing MT on HMDE, namely in the presence of excessive zinc or cadmium ions, when slow scan rates were used. Using constant current chronopotentiometry with adsorptive accumulation, the different values of applied constant current showed possibility of formation on the electrode of reorganized MT structure, which is responsible for labile behaviour.

Acknowledgements

The support by the grant N° IAA 400400806 from GA AV CR and grant COST D21.002 from MSMT is gratefully acknowledged.

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Decomposition Mechanism of 1,1-diamine-2,2-dinitroethene - a Spectrometric Study

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Recently synthesized compound 1,1-diamine-2,2-dinitroethene[1] (FOX-7), is an energetic material with low sensitivity and high performance. Due to two nitrogroups and a double bond, the molecule is easily reducible. In addition to this, the presence of two geminal aminogroups creates a so called push-pull effect of electrons. In other words, one part of the molecule is strong oxidation center and the opposite part is an electron donor. Therefore the electron structure of this species is unbalanced enabling intramolecular electron transfer reactions. The main goal of this project is to understand the reaction abilities of this complicated system with multiple redox centers.

Whereas under analytical conditions (small electrode, large volume and low concentration) the reduction process involves expected 18 electrons, the exhaustive electrolysis even in acidic media shows the consumption of only 4–6 electrons per a molecule. Moreover, after the electrolysis no expected organic product (1,2-diaminoethan) was detected, only gases were found and identified. This finding suggests the analogy of the observed reduction-initiated degradation reaction with the chemical process during explosion. For understanding the mechanism the interception of intermediates is necessary. For this purpose we used the following spectrometric techniques.

At first, CID (collision-induced dissociation) technique in mass spectrometry was utilized. This approach can simulate degradation of FOX-7 by electrical impulse which results in bond breakage and the fragmentation of the molecular ion into smaller fragments analyzed by a mass spectrometer. Other methods are LIBS and SIFT-MS. In addition to this, during electrolytic reduction of FOX-7 (namely in aprotic media) changes of color are observed. For this purpose an UV/Vis spectrometric study was performed. Since the parent molecule can exhibit tautomeric changes depending on the media, the first part of experiments involves a concentration and pH-dependence of spectra together with measurements in various organic solvents. There are two pH values in which the pattern (number of reduction waves and their potential) is changed. The changes of spectra at various pH is reversible. This finding is consistent with results from DC-polarography. UV/Vis spectra of FOX-7 are different in aqueous solvent and in aprotic solvent.

Acknowledgement

The support of the grant IAA400400813 (GAAVČR) is appreciated.

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Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers

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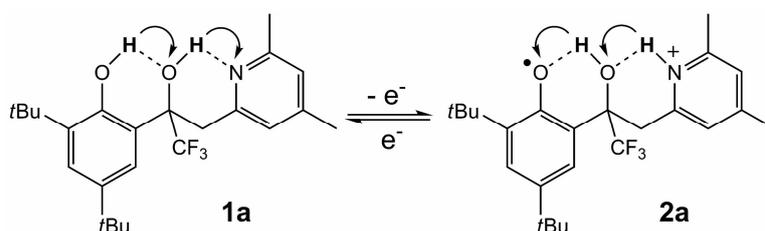
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Long-distance electron and proton transfers are found to be key processes in numerous biological reactions [1]. Due to its mass, proton transfer is limited to short distances, whereas the electron may transfer over much longer distances. For this reason proton transfer distances are confined to the hydrogen-bond length scale. However the efficient proton transfer to water opens the possibility of transferring efficiently proton over long distance through water chain molecules within proteins.

Two types of mechanisms may occur, a mechanism in which the two reactions are taking place in a stepwise manner (electron proton transfer, EPT, or proton electron transfer, PET), and a mechanism in which proton and electron transfers occur in a concerted manner (concerted proton electron transfer, CPET). In the case of CPET mechanism coupling proton transfer to the electron transfer would provide additional driving force but with a kinetic price to pay [2].

Herein we will explore the idea that distance between the group being oxidized and a proton acceptor might be substantially increased by inserting a hydrogen bond relay [3]. The relay is a group bearing an hydrogen atom, able to accept a hydrogen bond from the moiety being oxidized and to form an hydrogen bond with the proton accepting group without going through a protonated state to avoid a high-energy intermediate (see scheme below).



Molecule 1a does not retain the properties of water chains engaged in a Grotthuss type transport of proton, but the relay alcohol group possesses the basic property of water molecules of being hydrogen bond accepting and hydrogen bond donating at the same time.

To investigate the mechanism involved in this process, we chose to use electrochemical approach rather than homogeneous approach, because non-destructive technique such as cyclic voltammetry allows a quick investigation of a continuous range of driving forces, leading to the determination of standard rate constants.

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Electrochemistry of 1-X-12-Y-CB₁₁Me₁₀⁻ Carborane Anions in Liquid SO₂

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Icosahedral closo-carborane anions CB₁₁H₁₂⁻ and their derivatives are regarded as 3D σ -aromatic systems [1]. They have received diverse applications, mainly because of their great stability, low nucleophilicity and high redox potentials. Preliminary electrochemical studies of some polymethylated anions are intriguing [2, 3]. Here, a systematic investigation of electrochemical oxidation of 29 1- and 12-substituted 1,12-CB₁₁H₂Me₁₀⁻ anions has been made in order to understand the substituent effects on electrooxidation behavior of the icosahedral anions. Several series of carboranes with different substituents in vertex 1 and 12 (Chart 1) were synthesized using modified or known procedures. The electrochemical measurements like cyclic voltammetry and exhaustive electrolysis were carried out in dried liquid SO₂. All the carborane anions examined exhibit a completely reversible one-electron oxidation over the studied scan rates except for those containing iodine in vertex 12, which show two oxidation peaks. The measured reversible redox potentials (E^0) are linearly proportional to the substituent Hammett constants, σ_p . The slopes (called reaction constants) indicate much higher susceptibility of vertex 12 compared to vertex 1 for electrochemical oxidation and are in agreement with preferential site of chemical reactivity of the permethylated radical [4].

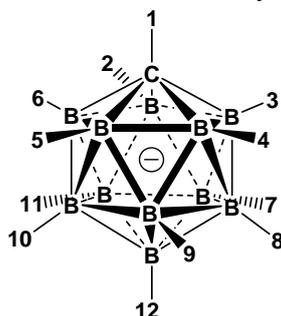


Chart 1: Vertex numbering in CB₁₁ icosahedral cage

The first oxidation process of the carborane anions with iodine in position 12 is always irreversible while the second oxidation process appears to be reversible. An analysis of the electrolyzed products of this series of carboranes by Mass and UV/Vis spectroscopy suggests that the first one-electron oxidation of the anions causes dissociation of B–I bond leading to the formation of highly reactive 12-boronium ylide and iodine atom. The ylide reacts immediately with a starting carborane anion to form iodine-bridged carborane dimer anion which oxidizes reversibly imparting the second peak. In acetonitrile with trace amount of water, the ylides react instantaneously with water forming different monomers and dimers, and weakly with acetonitrile forming dimers.

Acknowledgements

Project No. LC-510 (Ministry of the Education, Youth and Sports of the Czech Republic), GA AVCR grant No. IAA400550708 and GACR AV0Z40550506. Authors are thankful to Michal Valasek, Jan Stursa and Miroslav Polasek for their help in synthesis and measurements.

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Recent Developments in Organic Sonoelectrochemistry and Other Multiperturbation Electrochemical Systems

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The combination of ultrasound with electrochemistry ('sonochemistry') has been a fruitful recent topic for research, with international interest in the field.

The use of ultrasonic irradiation in an electrochemical system provides a number of useful benefits (see below), either directly by simultaneous combination of the technologies, or by separate sonochemical step(s) upstream or downstream of an electrochemical one. Such a combined approach is an example of 'multiperturbation' systems in electrochemistry, and was one of the key themes of the EU COST Action D32 'Chemistry in High-Energy Microenvironments', having been also a key topic in the earlier COST Actions D10 'Innovative Methods and Techniques for Chemical Transformation' and D6 'Chemical Processes and Reactions Under Extreme and Non-Classic Conditions'. COST D32 finished in 2009, but interest in sonochemistry continues, as does interest in another D32 theme, the use of microwave irradiation in chemical systems, including electrochemical ones.

The speaker held the position of Chairman of the Management Committee of COST D32, and also represented a participating laboratory dedicated to sonochemistry in Working Groups in D32 and D10. He will review recent developments in this and related fields. Other interesting multiperturbation techniques that have found recent revitalised interest, usually in view of improved modern technology, are 'magnetochemistry' the combination of magnetic fields with electrochemical systems, and also the use of centrifugal fields in electrochemistry. These are very interesting variants of electrochemistry, and recent published work in these areas will be mentioned.

The presentation addresses a range of different electrochemical systems, showing how ultrasound can produce benefits, depending upon the electrochemical system under investigation, and its precise mechanistic requirements. Improvements that have been noted by various workers in sonochemical systems are as follows:

- Improved mass transport and motion of species
- Increased redox currents, improved analytical sensitivity
- Cleaning of electrodesurfaces, diminution of fouling
- Greater reproducibility in electroanalysis and voltammetry
- Increased light emission in electrochemiluminescence
- Altered kinetic regimes in local microenvironments
- Altered product distributions in synthesis
- New/Unusual Products, possible new reaction mechanisms
- Emulsion formation, replacement of toxic or expensive solvents by water-based systems
- Effects on electrodeposited species
- Lessened electrolysis power requirements
- Effects on particle sizes and distributions, including routes to nanoparticles
- Effects on crystallisation and related phenomena

Charge Transfer Through Peptide Nucleic Acid Oligonucleotides

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Peptide Nucleic Acid (PNA) is a synthetic analog of DNA that forms duplexes with itself and with DNA by Watson-Crick base pairing. In contrast to negatively-charged DNA, the backbone of PNA based on aminoethylglycine is neutral. Therefore PNA duplexes are more stable than their DNA analogs, and are potentially better candidates than DNA for self-assembly on surfaces; correspondingly they are desirable candidates for biosensor technologies and molecular electronics. Moreover, PNA is not affected by enzymatic cleavage, so that they are good candidates for use in durable medically oriented biodevices working under physiological conditions.

Here we report on the influence of the PNA length and sequence on their charge transfer capability. Our studies measure charge transfer properties of single and double stranded ferrocene-terminated PNAs, as well as conductivity of single PNA oligonucleotide molecules trapped within a break junction controlled by scanning tunneling microscope. Cysteine moieties are used to anchor the PNA oligonucleotides to gold contacts and electrodes; the PNA molecules have cysteine moieties on both ends for the conductivity measurements and on one end for the electrochemical measurements. Despite major differences between these two experimental approaches, the single molecule conductivity study and the electrochemical investigation of the kinetics of the charge transfer between ferrocene and a metallic electrode through the PNA, the two measurements have a similar correlation between structure of the studied molecules and their ability for charge transfer. Our experiments contribute to the understanding of charge transfer in nucleic acids, and may be useful for designing future technologies based on oligonucleotides.

Quantum Chemical Interpretation of Spectroelectrochemical Properties of Ruthenium Complexes with Redox Active Ligands

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Redox series corresponding to the oxidation or reduction of organometallic species can be characterized spectroscopically by UV/Vis/NIR, IR and ESR spectroelectrochemistry which can indicate if the redox processes are centered at metal centers or the organic ligand. Quantum chemical calculations on complexes in different oxidation states can predict the electron density redistribution during the redox process and indicate the variations of various physical properties. In principle the correct description of the redox sequence requires the multideterminantal approach. Due the size of systems, this approach is hardly applicable for transition metal complexes with multiple redox centers. A compromise which is frequently used is DFT method.

We will illustrate the use of DFT method on mono-, di- and tetraruthenium complexes containing different types of organic ligands. Metal contribution to the redox orbitals can be monitored by a shift of the CO stretching bands to notably different energies upon stepwise redox change. The vibrational analysis based on DFT optimized structures was used for interpretation of shifts of CO stretching frequencies. The observed electronic transitions were assigned by TD DFT. The investigations on bridged diruthenium complexes [1] established how the electronic balance of bridge and metal contribution to the occupied frontier levels can be controlled by the appropriate choice of the co-ligands. DFT calculations in line with IR- UV/Vis/NIR and ESR spectroscopy show that oxidation of these systems is largely centered on the organic bridge.

Acknowledgements

This work was supported COST D35 action and by the Ministry of Education of the Czech Republic (1P05OC68).

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POSTER PRESENTATIONS

Lithium Insertion Electrochemistry in Polycrystalline TiO₂ Anatase with a Large Percentage of (001) Faces

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Nanocrystalline TiO₂ belongs to widely studied semiconducting metal oxides. TiO₂ anatase is an attractive material for applications in photoelectrochemical solar cells and Li-ion batteries. The usual TiO₂ anatase crystal is dominated with (101) face, due to its thermodynamic stability, but presently the (001) face is the other point of interest, because it is supposed to be more active for Li-insertion than (101) face. The fluorine terminated TiO₂ anatase with a large proportion of (001) faces was thermally treated to be F-free and characterized by common methods. There are improved electrochemical properties after calcination. The electrochemical measurements of TiO₂ anatase with (001) faces indicate the better Li-ion insertion/extraction behaviour than the ordinary anatase crystals with dominating (101) faces.

Acknowledgements

This work was supported by the Academy of Sciences of the Czech Republic (contract KAN200100801). We are grateful to Lightanate Pty Ltd for providing us with the titania samples.

Mixed Self-assembled Monolayers of Co-Porphyrin and Alkane Phosponates on Gold

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Phosphonic acid monolayers mainly deposited onto metal oxides, exhibit structural and chemical properties that resemble organothiol/Au SAMs, and have been used in distinct areas [1,2]. Specially designed phosphonic acid derivatives containing metalloporphyrins could provide a range of novel electrocatalytic surfaces, which performance can be compared to the widely reported studies of sulphur derivatives on gold [3,4].

The present work focuses on the surface immobilisation by self-assembly of pure and mixed Co-porphyrin (Co-Porph-PO₃) and alkane phosphonic acids (C_nPO₃; n = 4, 5 and 10) from butanol solutions on gold substrates. The stability, amount, and packing of the phosphonic molecules attached to the Au (111) surface have been investigated by electrochemical reductive desorption studies, and the monolayers thickness estimated by ellipsometry. The redox behaviour of Co-Porph-PO₃ SAMs was accessed in organic medium and compared that of Co-Porph-CO₂CH₃ precursor in solution, confirming the self-assembly of the metalloporphyrin molecules. C₅PO₃ and C₁₀PO₃ were used to form mixed monolayers with Co-Porph-PO₃ on gold, with the purpose of reducing the electrostatic interactions between these bulky terminal groups in the SAM. Intermediate electrochemical desorption potentials regarding those of pure monolayers, as well as an increase of phosphonate surface density compared to that of Co-Porph-PO₃ SAM, confirms the presence of two-component SAMs, indicating that porphyrin moieties are diluted in the monolayer. The electrocatalytic activity of the immobilised molecules was demonstrated towards the reduction of molecular oxygen, in acidic medium.

Acknowledgments

J. F. Cabrita acknowledges the PhD scholarship SFRH/BD/47703/2008 (Fundação para a Ciência e Tecnologia).

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Electrochemical Properties of 1, 3-disubstituted (CH₃, OCH₃) Phenyl-5-phenylformazans and Comparison with Spectral Properties

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In this study electrochemical behaviors of formazans were investigated. The compounds contained CH₃, OCH₃ groups at the *o*-, *m*-, *p*-positions of the 1-phenyl ring and OCH₃ group at the *p*-position of the 3-phenyl ring. Their electrochemical behaviors such as the number of electrons transferred, diffusion coefficients and heterogeneous rate constants were studied by cyclic voltammetry, ultramicrodisc electrode and chronoamperometry. Possible mechanisms were proposed based upon the data obtained. There was a correlation between the absorption and electrochemical properties. A linear correlation was obtained between λ_{\max} , with E_{red2} and Hammett substituent coefficients with E_{red2} and k_s values.

Keywords:

Formazans, Substituent effect; Cyclic voltammetry; Ultramicrodisc electrode, Chronoamperometry

The Electronic Effect of Substituents in Zirconocene Complexes

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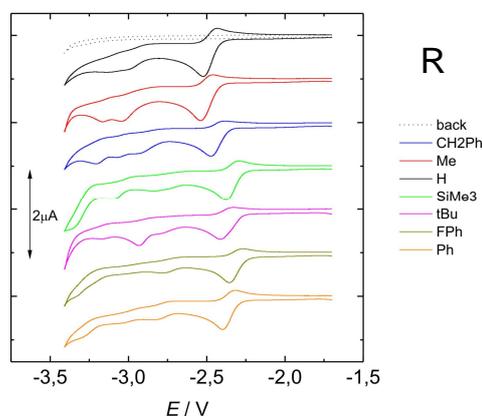
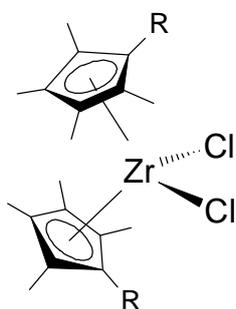
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Any investigations of stability of the zirconocene fragment have to deal with the effect of substituents on the cyclopentadienyl ligand. It has been well established that the presence of methyl substituents at the cyclopentadienyl ring increases the electron density at the metallic centre, this effect being more pronounced with the increasing number of methyl groups. The chemical properties rapidly change in the range of methyl-substituted zirconocene complexes starting from the non-substituted up to the permethylated derivative [1]. The properties of permethylated metallocene compounds can be further finely tuned by substituting one methyl group on both cyclopentadienyl rings for a different substituent [2].

This contribution discussed the effect of substituents on the cyclopentadienyl ligand in zirconocene complexes which have an important influence on the electronic properties of the metal centre that is active in catalytic dimerization of terminal acetylenes.

The electronic effects of the auxiliary ligands are reflected in first reduction potentials of the zirconocene dichlorides. These were measured by cyclic voltametry for the whole series of substituted zirconocene dichlorides.

The present state of art in investigations of zirconocene complexes with SiMe₃, t-Bu, benzyl, *p*-FPh or Ph groups will be presented and discussed.



Acknowledgements

This investigation was supported by Ministry of Education, Youth and Sports (project No. LC06070).

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Liquid Film Embedded Electrode for Electrochemical Investigation of Redox Systems Soluble in Nonaqueous Solvents

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Presented cell arrangement was developed to perform electrochemistry of newly synthesized water-insoluble compounds, available usually in mg-amounts.

The principle is in utilization of a thin layer of nonaqueous water immiscible phase where the studied compound is dissolved. The film of nonaqueous phase embedded to the solid supporting electrode is overlaid by aqueous electrolyte solution where both the reference and counter microelectrodes are situated. The volume of nonaqueous phase can be typically less than 100 μl . Low amounts of studied compounds allow also performing stability measurements and detection of intermediate products respectively, which task usually requires notably longer time scales in a traditional (bulky) arrangement of the cell.

To compare the electrochemical response of both arrangements we have employed decamethylferrocene (DMFc) as a model compound dissolved in *o*-DCB with tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. The corresponding cyclic voltammograms of DMFc/DMFc⁺ couple are shown in Fig. 1. The curve 1 was acquired in traditional (bulk) arrangement and the curve 2 represents the nonaqueous phase (*o*-DCB/TBAP) embedded to HOPG electrode overlaid by aqueous solution of lithium perchlorate (LiClO₄).

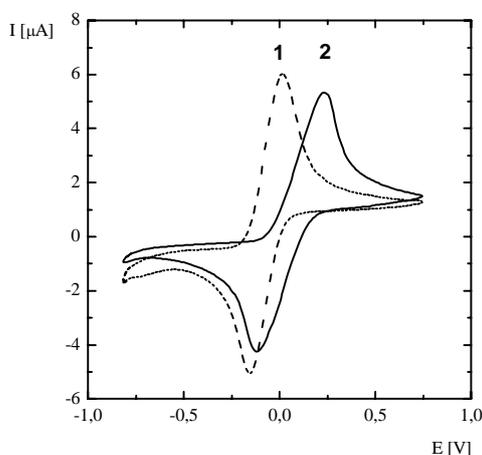


Fig 1. Cyclic voltammograms of DMFc in bulk *o*-DCB/TBAP (1) and in HOPG-embedded thin-layer *o*-DCB/TBAP overlaid by aqueous LiClO₄ (2). Potentials vs. Ag-quasi-reference (1) and SCE (in water phase) (2). Scan rate 10 mV s^{-1} in both cases.

Acknowledgement, grant citation.

We are grateful to N. Kobayashi, Tohoku University, Japan for supplying phthalocyanines used in this work. This work was supported by the research project MSM0021620857 and the development project RP 14/63 of the Ministry of Education Youth and Sports of the Czech Republic.

DFT Calculations of Electrochemical and Spectral Properties of Aminocarbene Complexes of Cr and Fe

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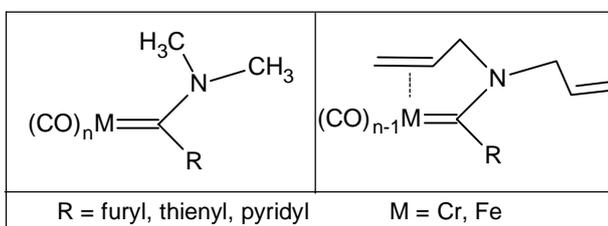
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In previous work series of transition metal Fischer-type aminocarbene complexes with a substituted phenyl ring on the carbene carbon have been studied [1]. It has been shown that the molecules have two electrochemically active centers: oxidation centre on the central metal and reduction centre on the carbene carbon and the phenyl ring. Nature of the phenyl substituent has significant impact on E_{red} , while E_{ox} remains untouched. This has been explained as a result of π -electron conjugation throughout the carbene moiety of the molecule.

The aim of this work is to survey influence of another type of substituents capable of π -electron conjugation, heterocycles, on electronic behaviour of the molecules. Results of theoretical calculations are to be compared to experimental data and used as support for derived conclusions. In order to study impact of both the type of heteroatom and the binding site of the cycle, Cr and Fe aminocarbene complexes with 2-furyl, 2-thienyl, 3-furyl, 3-thienyl, 2-pyridyl and 3-pyridyl substituents have been studied.



Calculations have been done by density functional theory method (DFT) using Gaussian 09 program package. B3LYP hybrid functional was used with 6-31g* basis set. The solvent was described by the polarizable conductor calculation model (PCM). Vibrational analysis and analysis of molecular orbitals were carried out at optimized structures both in vacuum and in *N,N*-dimethylformamide. UV-Vis spectra were calculated using TD-DFT method with same functional and basis set and with acetonitrile as solvent.

Observations made on these systems so far are in agreement with the previous results. Reduction centre is located mainly on the carbene carbon-heterocycle part of molecule, oxidation centre spreads across the central metal and carbonyl ligands. Contribution of the heterocycle to LUMO is about the same in case of 2-thienyl and 2-furyl as well as for 3-thienyl and 3-furyl derivatives while 2- and 3-bound substituents' contribution to LUMO differs by approximately 15%, the later being lower. This indicates that resonance effect predominates over inductive effect of the heteroatom.

Acknowledgement

This work was supported by the GA AV CR (grant No. IAA 00400813) and the Ministry of Education of the Czech Republic (1P05OC68).

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Phthalaldehyde and Other Two Isomeric Benzenedicarboxaldehydes

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Presence of a second formyl group on a benzene ring, located in position 2-, 3-, or 4- affects both the chemical and electrochemical reactivity. The interaction between the two aldehydic groups results in inductive and resonance effects.

In the 1,3-dialdehyde the reduction of the first CHO group occurs at more positive potential than that of benzaldehyde. Reduction of the second CHO group occurs at a potential identical to that of 3-methylbenzaldehyde. Hydration is negligible.

The first reduction in the 1,4-dialdehyde occurs at a potential even more positive than that in 1,3-dialdehyde due to both, inductive and a strong resonance effect. The strong resonance interaction between the two CHO groups results in an increased reactivity towards nucleophilic additions, such as reactions with water molecules and primary amines. In equilibrium about 15% of 1,4-dialdehyde molecules are hydrated.

The reduction of the 1,2-dialdehyde in aqueous solutions is even more affected by the mutual influence of the two carbonyls than that of the 1,4-isomer. These strong inductive and resonance interactions accompanied by steric effects, can result in strong hydration followed by five-member ring formation. As a result, 1,2-dialdehyde exists in aqueous solutions in equilibria between 3 forms. About 20% of the dialdehyde remains unhydrated (reactive and easily reducible form), some 8% is present in the acyclic monohydrated form and about 72% in the cyclic hemiacetal form.

The ring formation plays an important role also in reactions of 1,2-dialdehyde (phthalaldehyde, OPA) with primary amines. The imine formed in a first, fast step undergoes in a slower process a cyclization. Establishment of this equilibrium is followed by a still slower conversion into an electrochemically reducible heterocyclic species. The whole sequence involves at least 4 equilibria. With exception of the last one, their establishments are too fast to be followed when primary amines were used as the nucleophiles.

More detailed information was obtained for the reaction of OPA with NH₃. In the initial step of this reaction a carbinolamine is rapidly formed. Its dehydration yields a reducible imine. In the sequence of following reactions, the imine is first rehydrated to carbinolamine, which undergoes cyclization. This equilibrium is established slower, but the driving force is the shift of the equilibrium in favor of the benzimidazole derivative.

The combination of reducibility, hydration/dehydration equilibrium and reactivity with nucleophiles is crucial for the use of phthalaldehyde as disinfection agent or as a pre-column derivatization reactant in the analysis of aminoacids. DC polarography with UV-vis spectrophotometry proved to be useful in elucidation of this complex system.

Acknowledgement

The work is supported by the grant KONTAKT ME 09002.

Reduction of Chromium(0) and Iron(0) Aminocarbene Complexes with Heterocyclic Substituents on the Carbene Carbon

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Carbene complexes have general formula $[L_nM=CR_2]$ and they are divided into two groups: Schrock-type carbenes with a nucleophilic carbene carbon, the double bond polarization $M^{\delta+}=C^{\delta-}$; and Fischer-type carbenes with an electrophilic carbene carbon and opposite polarization $M^{\delta-}=C^{\delta+}$. The polarity of the double bond arise from mutual influence of the central metal, ligands L and substituents of the carbene carbon. Fischer carbenes are stabilized by π -accepting ligands L and by a heteroatom, O or N, which is bonded directly to the carbene atom and conjugates its free electron pairs with the vacant p orbital of the carbene carbon.

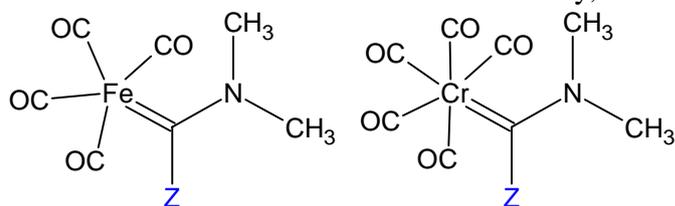
In our previous work, we measured E_{red} and E_{ox} of chromium and iron aminocarbenes with the following structure ($n = 5$ for $M = Cr$;

$n = 4$ for $M = Fe$).

The results for six different substituents R were treated by LFER method. The dependence of E on the Hammett constant of R was

linear except of the complexes with $R = -COOCH_3$. A plausible explanation was based on formation of a conjugated π -electron system involving the substituted phenyl ring, carbene carbon and nitrogen atoms.

In order to measure the importance of mesomeric and inductive contribution to electron distribution on the carbene moiety, we have synthesized several complexes



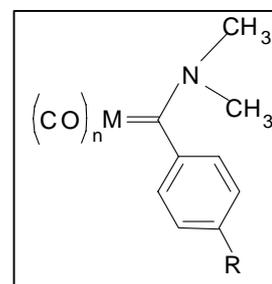
with carbene carbon substituted by a heterocycle. In order to study influence of both the nature of heteroatom and the binding site of the heterocycle, molecules bearing 2-furyl, 3-furyl, 2-thienyl, 3-

thienyl, 2-pyridyl and 3-pyridyl substituents have been studied, although not all possible molecules were found to be stable.

Experimental results have shown that the importance of inductive effect is several times higher than of mesomeric effect. Variation of E_{red} which we have found between molecules substituted by 2-furyl and 2-thienyl (3-furyl and 3-thienyl) is rather small - tens of mV, while E_{red} of the pair of molecules with the same substituent and different binding site rise up to 150 - 200 mV.

Acknowledgement

This work was supported by the GA AV CR (grant No. IAA 00400813).



Electrochemical monitoring DNA modification by platinum complexes

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Electroanalytical methods are powerful tools for monitoring structure, interactions and damage of natural as well as chemically modified nucleic acids. In cyclic voltammetry at mercury electrodes adenine and cytosine produce a cathodic peak CA, guanine produce an anodic peak G (due to oxidation of reduction product of guanine that is reduced at very negative potentials) [1]. When the DNA is chemically modified, electrochemical signals in voltammograms can be changed. In some case, attachment of a new electrochemically active group to DNA can give rise to a new signal. This presence can be used for monitoring of DNA modification.

Cisplatin [*cis*-diamminedichloroplatinum(II)], oxaliplatin [(1*R*,2*R*)-cyclohexane-1,2-diamine](ethanedioato-*O*,*O'*)platinum(II) and carboplatin [*cis*-diammine(cyclobutane-1,1-dicarboxylate-*O*,*O'*)platinum(II)] are some representatives of cytotoxic and antineoplastic metallodrugs used for the treatment of various malignancies [2]. The drugs binds covalently to DNA, forming several kinds of adducts. The most frequent of them being intrastrand cross-links in sequence motifs GG, AG and GNG (where N stands for any nucleotide). Guanine is the primary site of DNA modification by platinum complexes.

Using CV at mercury electrodes we observed remarkable enhancement of cathodic currents in the presence of DNA modified by platinum complexes. Based on characteristic dependence on scan rate, these effects have been ascribed to catalytic hydrogen evolution accompanying electrochemical reduction of the platinated DNA adducts. In square-wave voltammetry the catalytic currents gave rise to well developed and analytically useful peak (peak P). Intensity of the peak P responded to the extent of DNA modification at levels relevant for biochemical studies ($rb=0.01 - 0.10$, where rb is the number of platinum atoms bound per DNA nucleotide). We introduce a new method for monitoring of DNA modification by platinum complexes based on using of mercury electrode and catalytic peak P.

Acknowledgements

This work was supported by grants of the GA ASCR (IAA400040903, IAA500040701), MEYS CR (LC06035), Czech Science Foundation (203/07/1195) and institutional research plans Nos. AV0Z50040507 and AV0Z50040702.

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TŘEŠŤ

In the heart of Czech-Moravian Highland, nearly at the halfway between Prague and Vienna, in the hill pass, the town of Třešť is situated. The parish village Třešť was founded during the colonization of the Czech-Moravian deep forest in the course of the 13th century at the crossroads of two historical trade routes. The first written record about Třešť comes from 1349, when the parish church is reminded. Jewish community appeared quite early in Třešť; there are some references about a rabbi Jakub from Třešť even from the second half of 13th century. The Jewish population in Třešť was 621 people in 1845 but the number was falling and, in 1930, only 64 Jewish citizens remained in Třešť. They became the victims of holocaust.

In the town, many handicrafts were developing and guilds were flourishing. In 19th century, the cloth making factories, furniture plants (producing especially carved clock cabinets exported all around Europe) and matches industry was gradually emerging.



The former aristocrat mansion,

nowadays a castle hotel went through a difficult development. It stands on the place of the medieval citadel from 1513 which dissolved by the rebuilds. In the 16th century a four-wing building with corner towers and arcades was built. It was rebuilt in 1960 for residential purposes: there was a town museum and a gallery inside. Nowadays the chateau as well as the park belongs to the Academy of Science of the Czech Republic.



The parish church of St. Martin

It is the oldest monument in the town. It was founded in the 13th century, completed in the second half of the 15th century and later baroquized. We can notice a Gothic tombstone, a stone late Gothic pulpit and a Renaissance Kryštof Vencelík's tombstone.

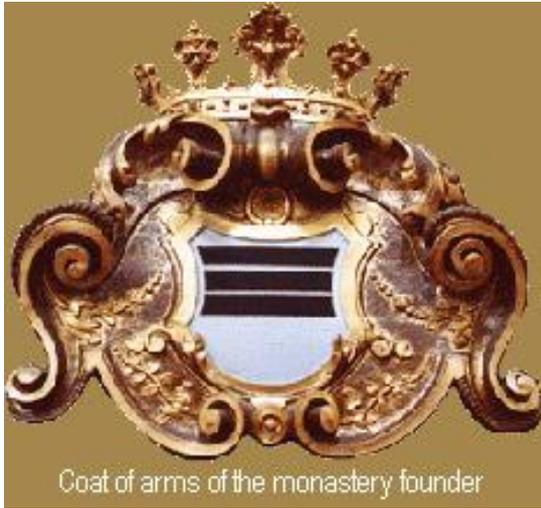
The church of St. Catherine Siens

is also a remarkable point of interest. It was founded as a German Lutheran church in the 16th century, in times when Třešť belonged to the Vencelík family. The presbytery was rebuilt in the 18th century, the inside furnishing of the church is from the 19th century (the restoration after the fire in 1824). There are two late Renaissance tombstones: of J. V. Vencelík from Vrchoviště on the outside plaster from 1616 and an unknown knight with the coat of arms where a half-lion is pictured.

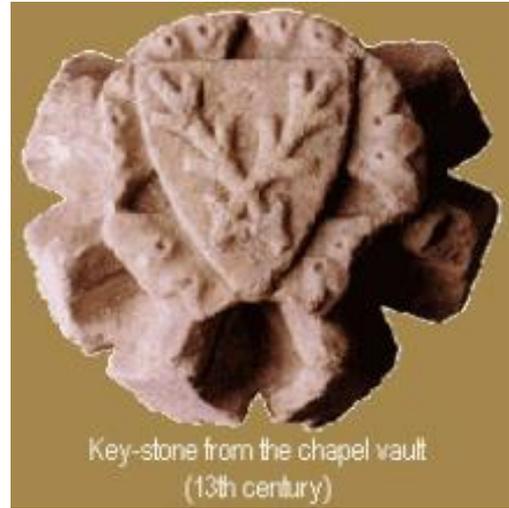


Former Jewish Synagogue

An Empire synagogue was constructed after a great fire (2nd October 1824) which destroyed all the Jewish ghetto. It was restored and consecrated on 22nd September 1825. On the ground floor facing the street an arcade is its typical feature. Nowadays the synagogue serves as a church of Czechoslovak Hussite Church. You can visit there an exhibition with many documents describing the history of Třešť Jewish community.



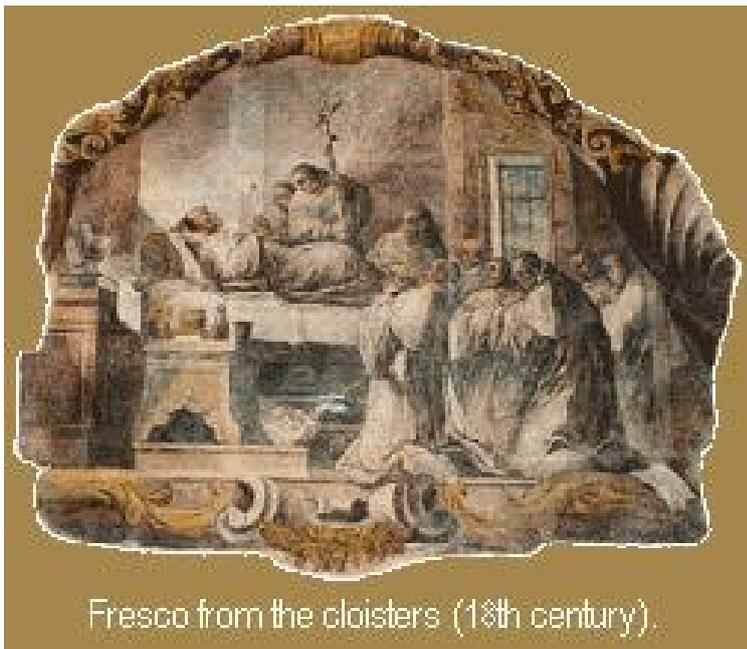
Coat of arms of the monastery founder



Key-stone from the chapel vault
(13th century)

Ždár nad Sázavou - History of the Monastery

History of the today's town Zdar nad Sazavou is closely associated with the local Cistercian monastery establishment and development. Foundation was initiated by St Zdislava's father, Pribyslav from Krizanov. Nevertheless, his intention was only implemented by his sons-in-law, Bocek from Obrany and Smil from Lichtenburk. For that purpose they invited a group of Cistercian monks to Nepomuk in 1252 and presented them the lots for monastery building and left a part of their property. Hard starts when the monasterial community lived in a log house and began to build the stone church were described by one of the participants, the monk Jindrich Rezbar, in the Latin-versed book *CRONICA DOMUS SARENSIS*. Naturally, the monastery was affected by all historical and social changes in the Czech lands. It was plundered and burned out during the Hussite wars and was not re-established until the rule of the King George of Podebrady who was the akin to the monastery founder. The new appearance of the monastery premises was achieved by the enlightened and virtuous Vaclav Vejmluva who was elected the abbot of the convention in 1705.



Fresco from the cloisters (13th century).

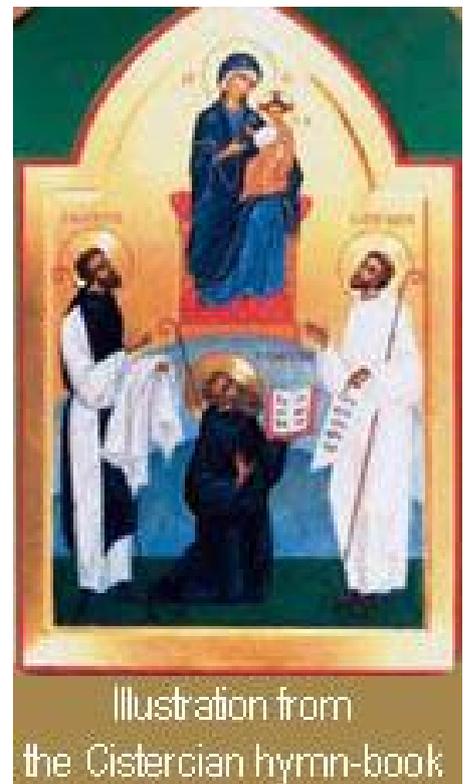


Illustration from
the Cistercian hymn-book

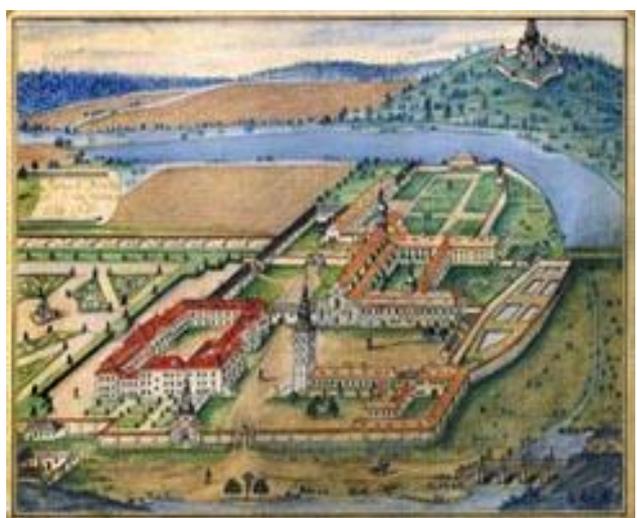
He invited to Zdar a remarkable architect Jan Blazej Santini Aichl, thus starting the period of the premises changes into one of the most significant church seats of that era. Building of the Pilgrimage Church of St John of Nepomuk on Zelena hora (Green Hill) became the height of their common efforts. The Church was festively consecrated in 1722. In 1994 it was listed with the UNESCO World Cultural Heritage Sites as the first self-standing building within Czech lands.



The monastery was finally dissolved during the rule of the Emperor Josef II in 1784. In 1930 the castle became the property of Chlumeck branch of the Kinsky family. The family has restituted the property in 1991.

Owners of the premises after the monastery dissolution

As soon as the monastery was dissolved, all the property came under administration of the Church Fund. In 1826 it was bought in an auction by Josef Vratislav from Mitrovice. Hereafter, the domain was undertaken by the prince F. J. Dietrichstein-Proskau-Leslie and was assigned to the countess Clotilda Clam-Gallas, born Dietrichstein, in 1862. Eleanor Kinsky, born Clam-Gallas, mother of the present owner, undertook the property in 1930. Her son, Radslav Kinsky, has restituted the estate in 1991.



Fresco from the Convent Church (15th century). Panoramic picture of the monastery (18th century).

Jaroslav Heyrovský (1890 – 1967) - 120 years anniversary



Jaroslav Heyrovský was born on 20th December 1890 in Prague as fifth child of Leopold Heyrovský and his wife Klára, née Hanel. Both his father and grandfather were lawyers; however, young Jaroslav did not show any interest in that family line. From his early childhood he was attracted by natural objects, mineral, botanical and animal.

In 1904 the recently introduced Nobel Prize for chemistry was awarded to the English physical chemist William Ramsay for his discovery and isolation of the rare gas elements. Jaroslav became inspired by the Ramsay's experiments, described in the press, to that extent, that he firmly decided he must become physical chemist. After maturity examination in 1909 he registered at the Faculty of Philosophy of the Prague University for the study of physics, mathematics and chemistry. During the first year at the university he discovered that there was no special subject of physical chemistry, and he begged his father to allow him to continue his studies at the London University College where William Ramsay was teaching. There he still could attend Ramsay's lectures until 1913, when the great scientist retired. In his position at University College Ramsay was followed by professor F.G.Donnan, who was specialized in electrochemistry. Jaroslav, who in that year gained the title Bachelor of Science (BSc), became Donnan's demonstrator for the year 1913-14, which decided about his orientation towards electrochemistry.

The intensive work in that direction was interrupted in 1914 by the outbreak of the First World War, after the student went home for summer holidays. Instead of returning to London he was enrolled in the Austro-Hungarian army to serve as dispensing chemist and radiologist in military hospitals.

After the end of the war, he was able to pass doctorate examinations and to defend his PhD thesis at the Prague University. The examination in physics was conducted by professor Bohumil Kučera, author of the method of measuring surface tension of polarized mercury by weighing drops of mercury from dropping mercury electrode. Next day after the examination Heyrovský visited Kučera's laboratory to get acquainted with his experimental set-



up and the satisfied professor advised the student to continue in research of the method. Heyrovský replaced collecting, counting, drying and weighing the drops of mercury by measuring the drop-time, which is also proportional to surface tension. He found that from electrocapillary curves the values of "decomposition voltage" of compounds of various metals could be determined. Of these results he lectured at a meeting of the Union of Czech Mathematicians and Physicists in spring 1921, still in presence of professor Kučera, who shortly after that passed away prematurely.

In order to gain more electrochemical data about the dropping mercury electrode system Heyrovský decided to measure, besides the drop-time, also **the current passing through the mercury drops at each value of applied voltage**. The first measurement of this kind was done on 10th February 1922 and it came out, that from the thus gained current / voltage curve one can determine both quality and quantity of substances dissolved in the solution into which the electrode drops. That day can be hence considered as the birthday of polarography, although the term „polarography“ was coined later. The work on electrolysis with dropping mercury electrode was

published first in Czech in 1922 by Chemické Listy, an enlarged English version appeared one year later in Philosophical Magazine.

Aware of the disadvantage of the time-consuming manual recording of the curves point-by-point, Heyrovský together with M. Shikata from Japan (who joined him to learn about this new method) suggested automation of the method with photographic recording of the curves. For the automatic instrument they introduced the term “polarograph”, i.e., apparatus drawing course of electrochemical polarization.

Since 1922 Heyrovský was director of the newly established Department of physical chemistry, in 1926 he became full professor of that subject, first at Charles University. He had many students and coworkers from Czechoslovakia as well as from abroad (Wiktor Kemula from Poland, from Italy Giovanni Semerano, from USSR Emilia Varasova, from USA O.H.Müller, from France Edgar Verdier etc.).

After the 2nd World War in Czechoslovakia a specialized Polarographic Institute was founded in April 1950 under directorship of Jaroslav Heyrovský. Today's the J. Heyrovský Institute of Physical Chemistry of Academy of Sciences of the Czech republic is its direct follower.



Heyrovský himself was lecturing on polarography in many countries. Since 1934 he was repeatedly suggested for Nobel Prize for the discovery and development of polarography, finally in 1959 several simultaneous proposals were accepted, and in December that year the Swedish king transmitted the **Nobel prize for chemistry to Heyrovský** in Stockholm (foto). In that way Jaroslav Heyrovský's whole life's dedicated work got its highest appreciation.

He died in Prague on March 27th 1967. (Until now, he is the only Czech who received this prize for sciences; the second Czech Nobel prize winner was Jaroslav Seifert, poet, for literature.)

Heyrovský Discussion meetings (1967 - 2007)

Since 1967 his pupils and followers organise every year a small international meeting, called Heyrovský Discussion. The purpose of the Discussions is to bring together, on invitation by the Organizing Committee, a limited group of specialists in a particular field of electrochemistry, and to

enable them to exchange ideas and views on their research problems in an informal and friendly atmosphere. This was the way how polarography was developing under the guidance of Professor Heyrovský between the I. and II. world wars at Charles University in Prague; hence the name of this scientific gathering. Every year a different subject has been selected for the Discussion. The following topics were discussed so far :

- 1967 Adsorption at Electrodes and its Influence upon Electrode Processes
- 1968 Adsorption and Processes on Catalytic Electrodes
- 1969 Mechanism of Redox Reaction Proper
- 1970 Intermediates and Products of Electrode Reactions
- 1971 Products and Intermediates of Redox Reactions
- 1972 New Principles in Electroanalytical Chemistry
- 1973 Deposition and Oxidation of Metals
- 1974 Electrochemistry in Non-Aqueous Solvents
- 1975 Electrochemical Phenomena in Biological Systems
- 1976 Redox Reactions of Coordination Compounds
- 1977 New Horizons in Polarography
- 1978 Electrochemical Energy Conversion
- 1979 Electrochemistry in Environmental Protection
- 1980 Electrochemical Phenomena on Membranes and Biomembranes
- 1981 Fundamentals of Preparative Organic Electrolysis
- 1982 New Principles in Electroanalysis
- 1983 Photochemical Stimulation of Redox Reactions
- 1984 Electrochemical Processes in Two-Phase Liquid, Microemulsion and Micellar Systems
- 1985 Recent Aspects of Electrocatalysis
- 1986 New Aspects of Electrochemical Materials Fundamentals
- 1987 Ecoelectrochemistry
- 1988 Electrochemistry of Separation and Synthetic Processes at Liquid/Liquid Interfaces
- 1989 Catalytic Homogeneous Processes Combined with Electrochemical Charge or Group Transfer
- 1990 Electrochemistry on Organized Molecular and Polymolecular Structures
- 1992 Electroanalysis and the Environment
- 1993 Progress in Organic and Organometallic Electrochemistry
- 1994 Electrochemical Processes on Liquid Membranes
- 1995 Electrochemistry of Biologically Active Compounds and Their Models
- 1996 Advanced Techniques in Electrochemistry
- 1997 Electrochemistry at Liquid/Liquid Interface
- 1998 Electrochemistry for Analytical Separations
- 1999 Organic Electrochemistry
- 2000 Nanostructures on Electrodes
- 2001 Chemistry on Polarised Liquid-Liquid Interfaces
- 2002 Electrochemical Impedance Analysis
- 2003 Electrochemistry of Biological Systems and Their Models
- 2004 Applications and Methodologies in Electrochemistry on Liquid-Liquid Interfaces
- 2005 Electrocatalysis in Nanoscale
- 2006 Electrochemical Impedance Analysis
- 2007 Electrochemistry of molecules with multiple redox centers
- 2008 Electrochemical Impedance Spectroscopy
- 2009 Liquid-liquid Electrochemistry - from Fundamentals to Applications
- 2010 Electrochemistry of Organic Molecules and Coordination Compounds**

