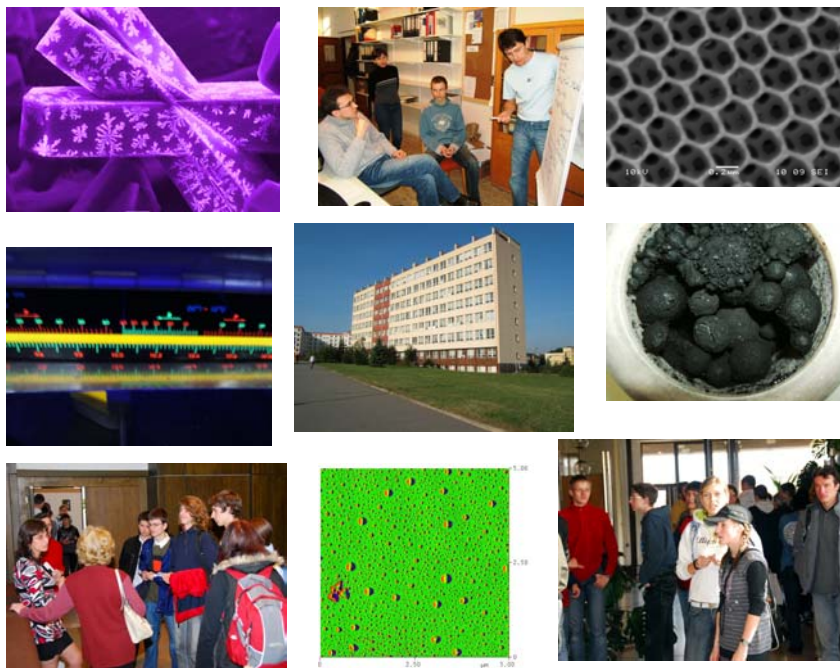


Ústav fyzikální chemie J. Heyrovského AV ČR, v.v.i.



Seminář studentů ÚFCH JH

21. -22. května 2008

Konferenční centrum Liblice



Dolejškova 3, 182 23 Praha 8, T.:266 052 011, F.: 286 582 307,
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Seminář studentů ÚFCH JH

Liblice, 21.-22.5.2008

Kategorie I (17 studentů)

Studenti magisterského studia a diplomanti

Ferus Martin (diplomant, školitel S. Civiš)
Kamas Michal (magisterské studium, šk. S. Civiš)
Kociánová Radana (diplomantka, školitel J.Ludvík)
Kubelík Petr (diplomant, školitel S. Civiš)
Ončák Milan (diplomant, školitel P.Slavíček)
Profant Václav (diplomant, školitel M. Fárník)
Sovová Kristina (magisterské studium, šk.S. Civiš)
Šimková Ludmila (diplomantka, školitel J.Ludvík)
Veis Libor (diplomant, školitel J. Pittner)
Vlk Josef (bakalářské studium, školitel J. Čejka)
Zvěřinová Radka (diplomantka, školitel S: Záliš)

Studenti 1. ročníku PGS

Bek David (školitel J. Čejka)
Janečková Radmila (školitel Z. Zelinger)
Kolesníková Lucie (školitel Š. Urban)
Kubů Martin (školitel J. Čejka)
Mašát Milan (školitel O. Votava)
Skřínský Jan (školitel Z. Zelinger)

Hodnotící komise

Předsedající:

Doc. Martin.Hof, Dr. rer.nat. DSc.

Členové komise:

RNDr. Patrik Španěl, Dr. rer.nat.

Mgr. Michal Horáček, Ph. D.

Ing. Petr Krtil, CSc.

Kategorie II (10 studentů)

Studenti 2. ročníku PGS

Bulíčková Jana (školitel L. Pospíšil)
Grigorová Eva (školitel Z. Zelinger)
Kalousek Vít (školitel J. Rathouský)
Macháň Radek (školitel M. Hof)
Procházková Dana (školitel J. Čejka)
Sathu Naveen Kumar (školitel Z. Sobalík)

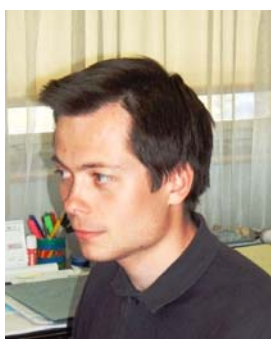
Studenti 3. ročníku PGS

Brabec Jiří (školitel J. Pittner)
Demel Jan (školitel J. Čejka)
Kiran Bhaskaran Nair (školitel J. Pittner)
Kulakowska Anna (školitel M. Hof)



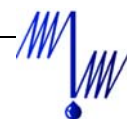


**Seminář studentů
ÚFCH JH 2008**



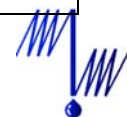
POZOR ZMĚNA - PROGRAM - Středa 21.5.2008 - odjezd autobusem z parkoviště před ústavem v 11:30 hodin !!!!!!!!.

Čas	Předsedající	Přednášející	Název
12:30	Registrace a ubytování		
13:00	OBĚD		
14:15	Zahájení semináře studentů		
14:20	<u>Jan DĚMEL</u>	Libor VEIS (diplomant, školitel J. Pittner)	AB INITIO CALCULATIONS WITH SINGLE-REFERENCE AND BRILLOUIN-WIGNER MULTIREFERENCE COUPLED CLUSTERS METHODS
14:40		Martin FERUS (diplomant, školitel S. Civiš)	CHARAKTERIZACE VÝBOJE V ATMOSFÉRE METHANU A HELIA POMOCÍ ČASOVĚ ROZLIŠENÉ SPEKTROMETRIE S FOURIEROVOU TRANSFORMACÍ
15:00		Ludmila ŠIMKOVÁ (diplomantka, školitel J. Ludvík)	ELEKTROCHEMICKÉ STUDIUM INTRAMOLEKULÁRNÍCH REDOX REAKCÍ 2,2-DINITROETHEN-1,1-DIAMINU VE VODNÉM PROSTŘEDÍ
15:20		Vít KALOUSEK (II. ročník, školitel J. Rathouský) Petr	PHOTOCATALYTIC DECOMPOSITION OF FATTY DEPOSITS ON ORGANIZED MESOPOROUS LAYERS OF TiO ₂
15:40	PŘESTÁVKA NA KÁVU		
16:00	<u>Eva GRIGOROVÁ</u>	Petr KUBELÍK (diplomant, školitel S. Civiš)	ČASOVĚ ROZLIŠENÁ FT SPEKTROSKOPIE VÝBOJE VE SMĚSI He - C ₂ N ₂
16:20		Václav PROFANT (diplomant, školitel M. Fárník)	NANOPARTICLES STUDY IN MOLECULAR BEAMS – PYRROLE, IMIDAZOLE AND PYRAZOLE CLUSTERS
16:40		Radka ZVĚŘINOVÁ (diplomantka, školitel S. Zálíš)	EXPERIMENTAL AND THEORETICAL STUDY OF Cr AND Fe AMINOCARBENE COMPLEXES
17:00		Josef VLK (bakalářské studium, školitel J. Čejka)	SYNTHESIS OF ACYLFERROCENE DERIVATIVES BY FRIEDEL-CRAFTS ACYLATION OVER ZEOLITES
17:20	PŘESTÁVKA		
17:40	<u>Libor VEIS</u>	Milan ONČÁK (diplomant, školitel P. Slavíček)	PHOTOCHEMISTRY OF HYDROGEN HALIDES ON SMALL WATER PARTICLES
18:00		Milan MAŠÁT (I. ročník, školitel O. Votava)	CHARACTERIZATION OF HIGH - PREASSURE GLOW DISCHARGE IN SUPERSONIC RADICAL SOURCE
18:20		Radmila JANEČKOVÁ (I. ročník, školitel Z. Zelinger)	ROTATIONAL SPECTROSCOPY OF THE ν_{21} , ν_3 , ν_4 AND ν_6 BANDS OF THE FORMALDEHYDE H ₂ ¹² C ¹⁶ O IN THE FREQUENCY RANGE 150 – 660 GHz
18:40		David BEK (I. ročník, školitel J. Čejka)	[RuCl ₂ (p-cymene)] ₂ IMMOBILIZED ON MESOPOROUS MOLECULAR SIEVES SBA-15 AS CATALYST FOR ROMP
19:00	Ukončení prvního dne semináře		
19:30	VEČEŘE – začátek v 19:30		



PROGRAM - Čtvrtek 22.5.2008

Čas	Předsedající	Přednášející	Název
8:15	Zahájení druhého dne semináře studentů		
8:20	<u>Radek MACHÁŇ</u>	Michal KAMAS <i>(magisterské studium, školitel S. Civiš)</i>	VZNIK ORGANICKÝCH MOLEKUL INICIOVANÝ PROCESY O VYSOKÉ HUSTOTĚ ENERGIE V METHANOVÝCH ATMOSFÉRÁCH
8:40		Radana KOCIÁNOVÁ <i>(diplomantka, školitel J.Ludvík)</i>	ELEKTROCHEMICKÉ STUDIUM INTRAMOLEKULÁRNÍCH REDOX REAKCÍ 2,2- DINITROETHEN-1,1-DIAMINU V APROTICKÉM PROSTŘEDÍ
9:00		Kristina SOVOVÁ <i>(magisterské studium, školitel S. Civiš)</i>	STUDIUM PRODUKTŮ TERMÁLNÍHO ROZKLADU POLYETHYLEN TEREFTALÁTU METODOU VYSOCE ROZLIŠENÉ SPEKTROSKOPIE S FOURIEROVOU TRANSFORMACÍ, SELECTED ION FLOW TUBE MASS SPECTROMETRY A PLYNOVOU CHROMATOGRAPHII
9:20		Martin KUBŮ <i>(I. ročník, školitel J. Čejka)</i>	SYNTHESIS AND CHARACTERIZATION OF TNU-9 AND SSZ-74 TYPE OF ZEOLITES
9:40	PŘESTÁVKA NA KÁVU		
10:00	<u>Jiří BRABEC</u>	Lucie KOLESNÍKOVÁ <i>(I. ročník, školitel Š. Urban)</i>	MICROWAVE SPECTROSCOPY OF RADICALS
10:20		Jana BULÍČKOVÁ <i>(II.ročník, šk. L. Pospíšil)</i>	FULLERENE AS A REDOX MEDIATOR IN AQUEOUS MEDIUM
10:40		Jan SKŘÍNSKÝ <i>(I.ročník, školitel Z. Zelinger)</i>	THE SUB-MILLIMETRE WAVE SPECTROSCOPY OF THE C ₂ S RADICAL
11:00		Radek MACHÁŇ <i>(II. ročník, školitel M. Hof)</i>	INTERACTION OF α -HELICAL PEPTIDES WITH PHOSPHOLIPID BILAYERS STUDIED BY MODEL PEPTIDE LAH ₄
11:20	PŘESTÁVKA NA KÁVU A ZÁKUSEK		
11:45	<u>Anna KULAKOWSKA</u>	Naveen Kumar SATHU <i>(II.ročník, školitel Z. Sobalík)</i>	THE ROLE OF CRYSTAL SIZE ON OXIDATIVE DEHYDROGENATION OF PROPANE OVER Fe-ZSM-5
12:05		Eva GRIGOROVÁ <i>(II. ročník, šk.Z. Zelinger)</i>	ANALYSIS OF ν_4 BAND OF FCO ₂ RADICAL OBTAINED BY FTIR SPECTROSCOPY
12:25		Dana PROCHÁZKOVÁ <i>(II. ročník, školitel J. Čejka)</i>	ACYLATION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE WITH ORGANIC ANHYDRIDES OVER ZEOLITES
12:45	PŘESTÁVKA		
13:00	<u>Jana BULÍČKOVÁ</u>	Jiří BRABEC <i>(III.ročník, školitel J.Pittner)</i>	COMPUTER-AIDED SYNTHESIS OF MULTIREFERENCE COUPLED CLUSTER METHODS CODE
13:20		Anna KULAKOWSKA <i>(III.ročník, školitel M. Hof)</i>	THE BINDING OF PROTHROMBIN TO THE SUPPORTED PHOSPHOLIPID MEMBRANES
13:40		Jan DEMEL <i>(III.ročník, školitel J.Čejka)</i>	HETEROGENEOUS CATALYSTS FOR PALLADIUM CATALYSED COUPLING REACTION
14:00		Bhaskaran N. KIRAN <i>(III.ročník, školitel J.Pittner)</i>	IMPLEMENTATION OF STATE-SPECIFIC MULTI- REFERENCE MUKHERJEE COUPLED CLUSTER THEORY
14:20 14:30	Ukončení prezentací SLAVNOSTNÍ OBĚD		
16:00 17:00	Vyhlášení výsledků a ukončení Semináře studentů Odjezd do Prahy (autobusem z parkoviště u zámku)		





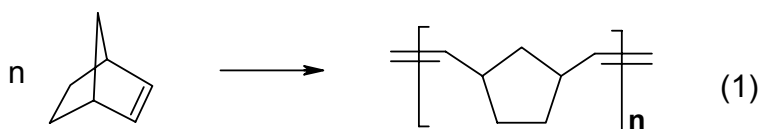
[RuCl₂(p-cymene)]₂ IMMOBILIZED ON MESOPOROUS MOLECULAR SIEVES SBA-15 AS CATALYST FOR ROMP

Ing. David Bek

Prof. Ing. Jiří Čejka, DrSc.

Metathesis of unsaturated compounds is important reaction, which is applied in petrochemistry, in preparation of polymers or synthesis of fine chemicals. Ru complexes are the most effective metathesis catalysts in contrast to other transition metal catalysts. Mesoporous sieves represent advantageous support for heterogeneous catalysts including metathesis ones [1] due to large surface areas, high void volumes and narrow pore size distributions of mesopores. By immobilization of suitable Ru complexes on mesoporous molecular sieves new metathesis catalysts can be prepared with following advantages: i) easy separation of catalyst leading to products free of catalyst residues, ii) reusability, iii) high activity and selectivity.

New heterogeneous metathesis catalyst has been prepared by immobilization of [RuCl₂(p-cymene)]₂ on siliceous mesoporous molecular sieves SBA-15 ($S_{\text{BET}} = 915 \text{ m}^2/\text{g}$, $V = 1.10 \text{ cm}^3/\text{g}$, $d = 6.3 \text{ nm}$). The catalyst with 1wt% of Ru, was prepared by stirring of dried SBA-15 with [RuCl₂(p-cymene)]₂ in CH₂Cl₂. Activity of the catalyst was tested in ring opening metathesis polymerization (ROMP) of 2-norbornene (1) as a model reaction.



After catalyst activation with trimethylsilyldiazomethane, the yields of high molecular weight polynorbornene ($M_w = 2.8\text{--}7.4 \cdot 10^5$) up to 77 % were obtained (1 h, 60°C). Filtration test proved that the catalytic activity is bound to the solid phase. The polymer structure corresponding with equation (1) was proved by IR and NMR spectroscopy. Catalyst could be easily separated from reaction mixture in contrast to the corresponding homogeneous system [2] and, therefore, the final polymer with reduced amounts of catalyst residues was obtained.

[1] H. Balcar, J. Čejka, in *Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials*, Y. Imamoglu, V. Dragutan (eds.), Springer 2007, pp. 151-166.

[2] A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* 30, 3127-3136, (1997).



IMPLEMENTATION OF STATE-SPECIFIC MULTIREFERENCE MUKHERJEE COUPLED CLUSTER THEORY

Mgr. Kiran Bhaskaran Nair

Mgr. Jiří Pittner, Dr. rer.nat.

State-specific multireference coupled cluster theory is one of the most successful method for studying quasi degenerate molecular systems which require a multideterminantal treatment even for qualitatively correct description. One successful approach is state-specific multireference Mukherjee Coupled-Cluster (MkCC)[1] method. Unlike the Brillouin-Wigner Coupled-Cluster (BWCC)[2], which has been studied extensively at our institute, MkCC is rigorously size-extensive, which refers to the linear scaling of the energy with the number of non interacting particles. However the structure of equations in MkCC equations is more complex than in BWCC, since its coupling terms include cluster amplitudes corresponding to different sets of cluster amplitudes.

MkCCSD has been effectively implemented in the Aces2 Program Package, which can be used for the study of real systems. Present implementation is able to handle arbitrary number of both closed shell and open shell reference configurations. MkCCSD has now being employed to study systems where BWCC had problems. Future works include implementation of triexcitations and a parametrized version.

References

1. U. S. Mahapatra, B. Datta, and D. Mukherjee, J. Chem. Phys. 110,6171(1999).
2. J. Pittner, P. Nachtigall, P. Čársky, J. Mášik, I. Hubač, I. J. Chem. Phys. 110, 10275(1999).



COMPUTER-AIDED SYNTHESIS OF MULTIREFERENCE COUPLED CLUSTER METHODS CODE

Mgr. Jiří Brabec

Mgr. Jiří Pittner Dr. rer. nat.

The implementations of the most methods in quantum chemistry are based on numerical solving of equation systems. It means large number of operations and long computation time. Therefore the implementation must be optimized and, if possible, parallel. Because of their complexity, advanced high accurate QCH methods have to be implemented automatically, not by hand. With an automatic code synthesis, it is possible to perform various optimizations of the calculation and test several approaches to the solution.

Multireference coupled clusters methods belong to the most accurate quantum chemical methods. When these methods include higher term of the cluster operator, the source code can be very difficult to write by hand and optimization. Now, the state specific multireference Brillouin-Wigner coupled cluster method with contributions from single and double excitations has been implemented to the NWCHEM package. Next step is extending this implementation for higher contributions and implementing new MR CC methods.



FULLERENE AS A REDOX MEDIATOR IN AQUEOUS MEDIUM

Ing. Jana Bulíčková

Doc. RNDr. Lubomír Pospíšil, CSc.

Fullerene (C_{60}) is soluble in aprotic solvents and can be reduced in six consecutive one-electron redox steps yielding very reactive redox states of C_{60} . The creation of an inclusion complex of fullerene enables the reaction of C_{60} in aqueous medium. Encapsulation of C_{60} in the cavity of cyclodextrin yields sufficient solubility of the resulting complex in the aqueous medium and at the same time the redox character of C_{60} is preserved [1, 2, 3].

We report on the electrochemical conversion of gaseous dinitrogen to ammonia at ambient pressure and 60°C mediated by reduced fullerene inside a molecular cavity of γ -cyclodextrin in aqueous solution [4].

Our cyclic voltammetric experiments show that the reduced fullerene form of C_{60}^{2-} of the $[C_{60}-(\gamma CD)_2]$ complex mediates the N_2 reduction to ammonia. The formation of NH_3 was confirmed by the preparative electrolysis performed under nitrogen atmosphere and at the electrode potential of the second redox step i.e. at -1.2V. The fixation reaction required elevated temperature of 60°C. Electrogenerated ammonia was detected by photoacoustic, high-resolution IR spectroscopy and UV-Vis spectroscopy. Major part of ammonia is retained in the solution probably bound in the cyclodextrin cavity. The experimental evidence favors the catalytic pathway, most probably through the dissociation mechanism.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (A400400505 and KJB400400603) and the Ministry of Education (LC510 and COST OC140).

- [1] Anderson, T.; Nilson, M.; Sundahl, M.; Westman, G.; Wennerstram, O. *J. Chem. Soc., Chem. Commun.* 1992, 604-606
- [2] Kutner, W.; Boulas, P.; Kadish, K. M. *J. Electrochem. Soc.* 1992, 139, 243C (Abstr. Soc. Meeting, St. Louis, May 1992, 659FUL).
- [3] Priyadarsini K. I., Mohan H., Tyagi A. K., Mittal J. P.: *J. Phys. Chem.* 98, 4759 (1994).
- [4] Pospíšil L., Bulíčková J., Hromadová M., Gál M., Civiš S., Cihelka J., Tarábek J.: *Chem. Commun.* 2270 (2007).



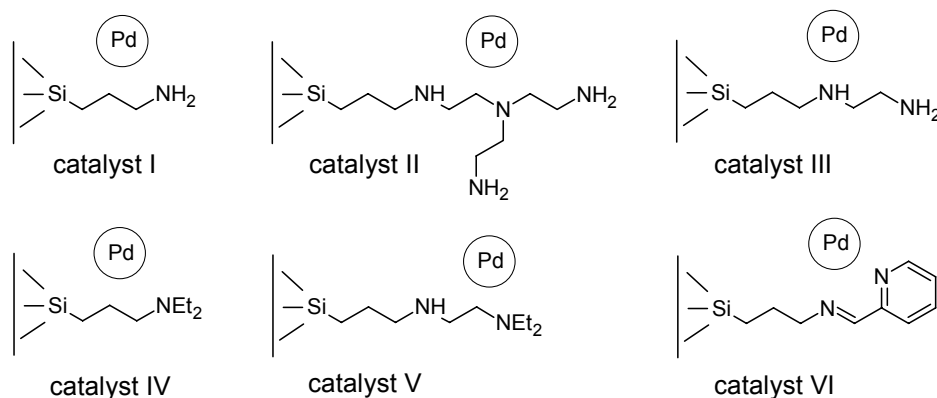
HETEROGENEOUS CATALYSTS FOR PALLADIUM CATALYSED COUPLING REACTION

RNDr. Jan Demel

Prof. Ing. Jiří Čejka, DrSc.

Palladium-catalyzed coupling reactions are well established as efficient and reliable tool for the construction of new carbon-carbon bonds. One of the challenges in this field is the development of highly active heterogeneous catalysts. Many research groups study new ways of preparation of simple supports that would not only bind palladium species but also stabilize palladium active species during the reaction. This target could be achieved by modification of solid material by donor groups such as phosphine, sulfanyl or various nitrogen containing groups.

In our work we have prepared series of mesoporous molecular sieves modified by pendant amino groups and treated those materials with palladium(II) acetate. The series comprises from already in the literature reported groups (catalysts I, III, IV and VI) with some newly prepared ones (catalysts II and V). Catalysts were tested in the model Heck reaction of butyl acrylate with bromobenzene to give butyl cinnamate. The reactions were done under microwave irradiation at 165 °C in *N,N*-dimethylacetamide.



The most active were catalysts I, V and VI having conversions after 30 minutes 84, 90 and 94 %, respectively. The amount of leached palladium during the reaction was lowest for catalyst V. Catalyst V can also be recovered by simple filtration and reused but the achieved conversion was only 34 %. This decrease in the activity can be attributed to the growth of palladium nanoparticles during the reaction as documented by X-ray powder diffraction and HR-TEM.



CHARAKTERIZACE VÝBOJE V ATMOSFÉŘE METHANU A HELIA POMOCÍ ČASOVĚ ROZLIŠENÉ SPEKTROMETRIE S FOURIEROVOU TRANSFORMACÍ

Bc. Martin Ferus

Doc. RNDr. Svatopluk Civiš, CSc.

Časově rozlišená FT spektrometrie spojuje výhody klasické metody (zejména široký spektrální rozsah a vysoké rozlišení) s časovým měřením v mikrosekundových krocích. V rámci jednoho měření tak získáváme soubor časově rozlišených spekter v širokém časovém i spektrálním rozsahu. V blízké infračervené oblasti od 2000 cm^{-1} do 4000 cm^{-1} bylo s rozlišením $0,05\text{ cm}^{-1}$ pomocí upraveného spektrometru Bruker IFS 120 HR změřeno časově rozlišené spektrum modulovaného výboje v pozitivním sloupci v atmosféře methanu a helia.

Ve výboji byla nalezena emisní spektra molekulárních radikálů CH, C₂, atomárních linií H, C a molekulárního vodíku. Na základě analýzy spekter byla zkoumána molekulární dynamika reakcí probíhajících ve výboji.

Z experimentálních dat plyne, že methan je srážkou s elektrony a heliem v metastabilním stavu destruován až na uhlík a vodík. Radikály CH rekombinují za vzniku acetyleny, který je dehydrogenován až na radikál C₂.

Fitováním exponenciálního vyhasínání radikálů jsme obdrželi experimentální doby života jednotlivých částic v plazmě. Tyto doby jsou vlivem vzájemných interakcí jednotlivých specií v plazmatu odlišné od teoretických hodnot nebo hodnot naměřených ve speciálních aparaturách, které nerespektují kolizní podmínky ve výbojové plazmě.

Z intenzit linií He a radikálu CH jsme s časovým rozlišením stanovili vibrační, rotační a excitační teplotu. Z výsledků jsme určili, kdy systém dosahuje termodynamické rovnováhy.



ANALYSIS OF ν_4 BAND OF FCO_2 RADICAL OBTAINED BY FTIR SPECTROSCOPY

ing. Eva Grigorová

ing. Z. Zelinger CSc., Dr. S. Bailleux

FCO_2 radical belongs to significant atmospheric radicals, because it is probably produced in the stratosphere by degradations of HCFCs and HFCs. It is the most stable member amongst carboxy radicals of the type XCO_2 [$\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CF}_3, \text{OCF}_3$].

Radical FCO_2 is an asymmetric rotor with Ray's asymmetry parameter equal to +0.39. The radical FCO_2 belongs to C_{2v} point group in the ground electronic state X^2B_2 .

The ν_4 unperturbed, fundamental band of the FCO_2 radical in the ground electronic state X^2B_2 was measured by Fourier – transform infrared spectroscopy and its infrared spectrum has not been fully analyzed till now. The ν_4 band is CO_2 asymmetric stretching mode, b-type band with the center of the band in 1094.142 cm^{-1} .

The infrared spectrum of the ν_4 band is very dense, in which fine splitting of the ro-vibrational levels occurs due to unpaired electron. More than 3300 ro-vibrational transitions have been assigned. Rotational constants, quartic centrifugal constants and fine constants of the first excited state have been determined by detailed analysis for the first time.



.ROTATIONAL SPECTROSCOPY OF THE ν_2 , ν_3 , ν_4 AND ν_6 BANDS OF THE FORMALDEHYDE $\text{H}_2^{12}\text{C}^{16}\text{O}$ IN THE FREQUENCY RANGE 150 – 660 GHz

Radmila Janečková

Ing. Zdeněk Zelinger, CSc.

Completely new rotational spectrum of H_2CO in the 2^1 , 3^1 , 4^1 and 6^1 vibrational excited states was investigated in Lille where the measurements were performed in the millimeter and submillimeter region 150 – 660 GHz.

Formaldehyde is one of the most extensively studied molecule playing important role in atmospheric chemistry, chemistry of combustions, photochemistry of the troposphere etc. There are many reasons for its interest and also a reliable prediction of the rotational spectra is important from spectroscopic, atmospheric and astrophysical point of view. Formaldehyde is one of the most abundant and one of the first polyatomic molecule detected in interstellar space (1968) and identified in several cometary objects at submillimeter wavelengths – all its isotopic species have been detected.

The spectrum between 150 and 660 GHz was measured in Lille with a millimeter-wave source-modulated spectrometer using backward-wave oscillators (BWO) as a source and a He-cooled InSb bolometer as a detector. The frequency accuracy of the measurements is generally estimated to be better than 30 kHz. The formaldehyde was freshly prepared before the measurements – powder of CH_2O was heated on 200 °C to get a gas phase reaction product.

One of the aims of the present study is a more complete description of the microwave spectrum in the excited vibrational states for possible astrophysical applications. The Cologne database involves only rotational spectrum within ground vibrational state for various isotopic species of formaldehyde and this study will contribute to this database by new lists of rotational lines in the excited states ν_2 , ν_3 , ν_4 and ν_6 in the millimeter-wave and submillimeter-wave region.



PHOTOCATALYTIC DECOMPOSITION OF FATTY DEPOSITS ON ORGANIZED MESOPOROUS LAYERS OF TiO₂

Ing. Vít Kalousek

Ing. Jiří Rathouský, CSc.

At present we counter the consequences of the extensive soiling of the external surfaces of building structures in municipal cities. Another very important general issue in a vast range of technologies is the requirement to render the surface of a number of products self-cleaning or at least easy-to-clean. Such a distinguished property would substantially enhance the utility value of the products and would improve the cleanness of the environment and the quality of life. One of the promising possibilities how to solve this task is to cover their surface with a photocatalytically active layer.

We have shown that mesoporous layers of TiO₂ are especially effective in the decomposition of liquid or solid layers of fatty deposits. The mesoporosity ensures fast transport of O₂ and H₂O, which are viable for the photocatalytic degradation of deposits. This transport is often significantly hindered by the compact layer of the dirt. Typically such layers are 200-500 nm in thickness and their pore size ranges from 6-8 nm.

We have performed a systematic study into the photocatalytic decomposition of thin layers of oleic acid. This compound is a suitable model substance because of its ability of netting and low volatility. Further it is contained in a number of products of everyday life and has been suggested as an international standard for testing the photocatalytic activity. We have found that mesoporous layers of TiO₂ are able to remove oleic acid or to convert it to highly hydrophilic compounds by illumination with weak UV light (power of 1 mW/cm²). These hydrophilic compounds are easy to wash-off. Furthermore even high molecular weight products of carbonization of oleic acid at 200 °C were removed/transformed within 24 hours of illumination.



VZNIK ORGANICKÝCH MOLEKUL INICIOVANÝ PROCESY O VYSOKÉ HUSTOTĚ ENERGIE V METHANOVÝCH ATMOSFÉRÁCH

Bc. Michal Kamas

Doc. RNDr. Svatopluk Civiš, CSc.

Základní myšlenkou této studie bylo potvrdit hypotézu vzniku složitějších látek ze směsi jednoduchých plynů. Tento jejich vznik je iniciován procesy o vysoké hustotě energie, které mají simulovat dopady mimozemských těles do planetární atmosféry.

Jodový laser PALS (Prague Asterix Laser System), je jedinečným zdrojem energie, protože poskytuje energie stovek joulů v pulsech kratších jedné nanosekundy. Do směsi $\text{CH}_4\text{-N}_2\text{-D}_2\text{O}$, bylo akumulováno 30 takových laserových pulzů.

Nestabilní částice vznikající při laserovém pulzu byly sledovány pomocí optické emisní spektroskopie, byla zjištěna přítomnost C_2 a CN radikálů. Stálé produkty v plynné fázi byly po ozáření směsi detegovány infračervenou absorpční spektroskopií s Fourierovou transformací, kterou jsme dokázali přítomnost kyanovodíku a acetyleny. Další analýzou plynné fáze byla aplikace metody proudové trubice s vybranými ionty, touto metodou byla potvrzena přítomnost kyanovodíku i acetyleny, dále bylo detegováno dalších více než 10 organických sloučenin.

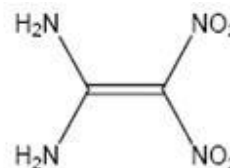


ELEKTROCHEMICKÉ STUDIUM INTRAMOLEKULÁRNÍCH REDOX REAKCÍ 2,2-DINITROETHEN-1,1-DIAMINU V APROTICKÉM PROSTŘEDÍ

Radana Kociánová

Doc. RNDr. Jiří Ludvík, CSc.

Mezi významné organické molekuly s více redox centry, jejichž vzájemné interakce hrají skutečně klíčovou úlohu v jejich vlastnostech, jsou výbušniny. Moderní výbušniny jsou z hlediska redox dějů velmi pozoruhodné látky. Jde zpravidla o molekuly, které nesou silně oxidativní a současně i silně reduktivní centra. Aby mohly pracovat za nepřístupu kyslíku, jejich žádanou reakcí není hoření, ale intramolekulární redox děj, kdy je molekula sama sebou zoxídována, resp. zredukována za vzniku plynných produktů. Jejich vývoj spolu s uvolněným teplem pak představuje důvod účinnosti těchto látek.



Jeden z hlavních směrů vývoje výbušnin je v dnešní době hledání takových sloučenin, které mají vysoký výkon a současně nízkou citlivost k nárazu. Mezi tyto výbušniny můžeme zařadit i **FOX-7** (2,2-Dinitroethen-1,1-diamin), který byl poprvé syntetizován v roce 1998. I když byla tato látka již podrobně testována z hlediska svých explozivních vlastností, detailnějšímu studiu jejích chemických vlastností (včetně elektrochemického chování) dosud nebyla věnována pozornost. Dostupná literatura se zabývá zejména otázkami její syntézy, která zatím zůstává velkým problémem. Praktické využití této látky je z toho důvodu dosud vzdálené. O to lákavější je výzkum mechanismu intramolekulárních redox interakcí této molekuly, pro který je velmi vhodný elektrochemický přístup.

Náplní mojí dosavadní práce bylo nejprve charakterizovat elektrochemicky tuto látku v aprotickém, tedy bezvodém prostředí. Zabývala jsem se nejprve její redukcí za využití standardních elektrochemických metod (dc-polarografie, cyklická voltametrie, preparativní elektrolýzy a coulometrie). Ačkoli redukce dvou nitroskupin představuje u běžných nitrolátek spotřebu minimálně osmi elektronů, tato látka se v aprotickém prostředí na rtuťové kapkové elektrodě redukuje pouze ve dvou jedoelektronových krocích, které navíc vykazují známky reverzibility. Tyto reakce jsou však doprovázeny množstvím následných reakcí, jejichž detailní mechanismus bude náplní dalšího studia. V každém případě však lze říci, že elektrochemická redukce neprobíhá „stechiometricky“, příjem elektronu molekulou je zřejmě pouze startovacím mechanismem řady intramolekulárních dějů, které vlastně představují „zpomalenou explozi“. Právě vznik pouze plynných produktů by mohl být vysvětlením skutečnosti, proč ani po opakovaných preparativních elektrolýzách za různých podmínek nebyl dosud identifikován žádný organický produkt.



MICROWAVE SPECTROSCOPY OF RADICALS

Ing. Lucie Kolesniková

prof. RNDr. Štěpán Urban, CSc.

A participation of radicals in chemical reactions, atmospheric processes, and the interstellar medium is well known. Thus their high resolution spectra (e.g. microwave spectra) are useful or even indispensable to monitor these species, to understand the mechanisms of chemical reactions and composition of the various environments.

Since radicals are usually short-lived, it is desirable to generate them inside the cell during the spectroscopic measurements. In our experiment, a pyrolysis of a suitable precursor was used. Many transition lines of other molecular species were observed in our spectra. Therefore the identification of the radical lines was supported using an external magnetic field affecting only the radical species by the molecular Zeeman effect.

In this study, the rotational spectra of two radicals (fluoroformyloxy radical $\text{FCO}_2\cdot$ and fluorosulfate radical $\text{FSO}_3\cdot$) were measured using the Prague millimeterwave spectrometer. These radicals are of the atmospheric interest, for example the $\text{FCO}_2\cdot$ radical may be produced by stratospheric degradations of HCFCs and HFCs. Both the radicals contain one unpaired electron and one nucleus with nonzero spin that cause the fine and hyperfine splittings of the rotational levels. The measured rotational spectra with these effects were analyzed in terms of the matrix elements of rotational, fine and hyperfine Hamiltonians. An interesting feature observed in the fluorosulfate radical rotational spectra was a significant A_1 - A_2 splitting that is manifested by a measurable doubling of $K = 3$ transitions.

The radicals $\text{FCO}_2\cdot$ and $\text{FSO}_3\cdot$ were measured in the frequency regions 130 – 242 GHz and 93 – 280 GHz, respectively. The set of rotational, centrifugal distortion, fine and hyperfine constants was derived from obtained transition frequencies.



ČASOVĚ ROZLIŠENÁ FT SPEKTROSKOPIE VÝBOJE VE SMĚSI He - C₂N₂

Bc. Petr Kubelík

Doc. RNDr. Svatopluk Civiš, CSc.

Metoda časově rozlišené spektroskopie s Fourierovou transformací byla použita pro získání spekter částic vznikajících v elektrickém výboji ve směsi He – C₂N₂. Použité experimentální nastavení poskytuje spektrální rozlišení 0,025 cm⁻¹ a časové rozlišení 1 μs. Během jednoho měření bylo zaznamenáno 30 časově posunutých spekter.

Ve směsi He a C₂N₂ byl generován CN radikál. Emisní časově rozlišená spektra umožnila detekci několika nových elektronických pásů CN radikálu, které nebyly dosud pozorovány. Jedná se o přechody mezi A²Π – X²Σ⁺ v molekule CN.

Vzhledem k tomu, že v minulých letech byly analyzovány vibračně rotační přechody CN v základním stavu (X²Σ⁺) pro různé vibrační stavy (až do v = 10), byli jsme schopni analyzovat i elektronické přechody mezi stavem A.

A-X elektronické přechody společně s vibračně rotačními pásy CN v základním stavu byly změřeny v oblasti 1800 až 9000 cm⁻¹. Dohromady bylo analyzováno 7 pásů 0-3, 1-4, 2-5, 4-7, 5-8 a 6-9, Δv = 3 sekvence.

Časově rozlišená FT spektroskopie umožnila separaci dlouze žijících vibračních pásů v základním elektronickém stavu od krátce žijících elektronických přechodů.

Dále byly získány experimentální závislosti emise CN, C₂, N, C a He na čase. Tyto závislosti byly proměřeny pro různé energetické přechody. Na jejich základě bylo možné stanovit experimentální doby života výchozích energetických hladin. Analýzou intenzit spektrálních linií byly stanoveny rotační, vibrační a excitační teploty a jejich časový vývoj během vyhasínání výboje.

Na základě časově rozlišených experimentálních dat bylo možné studovat dynamiku jednotlivých relaxačních procesů a jejich vzájemnou posloupnost.



SYNTHESIS AND CHARACTERIZATION OF TNU-9 AND SSZ-74 TYPE OF ZEOLITES

Ing. Martin Kubů

Prof. Ing. Jiří Čejka, DrSc.

Zeolites and crystalline molecular sieves are unique porous solids because of their catalytic properties as well as sieving characteristics. These materials have found a wide range of commercial applications, especially in hydrocarbon conversions, gas drying and separation, and recently in fine chemical syntheses. Although many different zeolites and related materials have been revealed and their use is well established, there is still interest in searching for novel zeolite structures. It might contain new types of pores, ensuring improvement of current technologies by giving enhanced selectivities in these processes and also to facilitate entirely new processes based on shape selectivity properties.

My PhD thesis is focused on the syntheses of novel TNU-9 zeolite and SSZ-74 using linear di-quaternary alkylammonium ions as structure-directing agents (SDAs). These SDAs are not commercially available and have to be synthesized. Synthesized zeolites were characterized by X-ray powder diffraction, scanning electron microscopy, nitrogen adsorption isotherms and FTIR spectroscopy.

TNU-9 was synthesized under hydrothermal conditions at the expense of a lamellar precursor over a very narrow range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and NaOH/SiO_2 ratios and in the presence of 1,4-bis-(N-methyl-N-pyrrolidinium) butane and Na^+ ions as SDAs.

High silica molecular sieve SSZ-74 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio greater than 100) using a 1,6-bis-(N-methyl-N-pyrrolidinium) hexane as SDA was synthesized under hydrothermal conditions in fluoride media.

Both materials with 10 member ring channel system seem to exhibit high hydrothermal stability as well as acidity showing unique properties.

Further study will be centered on the characterization of porous system of these zeolites and they will be tested mainly in n-butene skeletal isomerization and toluene alkylation with isopropyl alcohol.



THE BINDING OF PROTHROMBIN TO THE SUPPORTED PHOSPHOLIPID MEMBRANES

Mgr. Anna Kułakowska

Doc. Dr. rer.nat. Martin Hof, DSc.

Prothrombin is a vitamin-K dependent proenzyme abundant in blood, acting in the blood coagulation cascade. The interaction of coagulation factors with the phospholipid membranes is of paramount importance for haemostasis.

In the current project, study the binding of bovine prothrombin to Supported Phospholipid Bilayers (SPBs). The binding studies are performed by the Two-Color Fluorescence Correlation Spectroscopy (FCS) method. The analysis of FCS data yields the dissociation equilibrium constants for prothrombin binding to phospholipid membranes of different phosphatidylcholine content.

In the study of the kinetics we also endeavor to employ the concept based on the newly developed technique of Fluorescent Lifetime Correlation Spectroscopy (FLCS).



INTERACTION OF α -HELICAL PEPTIDES WITH PHOSPHOLIPID BILAYERS STUDIED BY MODEL PEPTIDE LAH₄

Mgr. Radek Macháň

Doc. Dr. rer.nat. Martin Hof, DSc.

α -helices are among the most frequent secondary structures of peptides interacting with biological membranes (so called membrane-active peptides) and membrane binding domains of proteins. Membrane-active peptides have received a lot of interest thanks to their important biological functions including potent antibiotic activity (antimicrobial peptides – AMPs). Due to the complexity of biological membranes, model systems (like supported phospholipid bilayers – SPBs or large unilamellar vesicles – LUVs) allowing controlled variations of properties are very convenient for such studies. Charge and hydrophobicity are important determinants of membrane-activity in peptides. Therefore, B. Bechinger designed a model peptide LAH₄ whose charge can be varied by changes in pH. This results in changes in peptide orientation with respect to the bilayer.^[1]

In the present study, effects of LAH₄ on phospholipid bilayers at different pH values were studied by several optical methods. Its influence on the lateral mobility of lipids within an SPB and on the stability of LUVs suspensions were characterized by fluorescence correlation spectroscopy. Changes of hydration and local viscosity within the bilayer following changes in orientation of peptide molecules were measured by solvent relaxation technique. Results obtained for the model peptide provide deeper insight into the interaction of α -helices with phospholipid bilayers and will be useful for understanding results of experiments with novel α -helical AMPs.

[1] Bechinger B. *J. Mol. Biol.* (1996) **263**: 768-775.



CHARACTERIZATION OF HIGH - PREASSURE GLOW DISCHARGE IN SUPERSONIC RADICAL SOURCE

Mgr. Milan Mašát

Mgr. Ondřej Votava, Ph. D.

Molecular radicals are highly reactive species which play important role in broad range of chemical reactions in atmosphere. They play important role in decomposing organic pollutants in troposphere, in nitrogen oxides chemistry or in tropospheric ozone generation. Knowledge of physical and chemical properties of these molecules is important for understanding these atmospheric processes.

Due to their high reactivity, molecular radicals have to be generated and studied in-situ. In our experiment the radicals are produced by stable precursor dissociation in an electric discharge followed by a supersonic expansion into vacuum. This method can create a molecular beam with a high concentration of internally cooled molecular radicals.

The main goal of our work is the characterization of molecular free radical production in a high pressure glow discharge with subsequent supersonic expansion. We develop methods for generation of specific radicals and their characterization with a high-resolution laser spectroscopy.

In our present development we have observed two-mode behavior of the discharge properties in dependence on the carrier gas pressure. We have also observed that this behavior heavily influences radical generation. Detailed experimental characterization of this phenomenon and its theoretical modeling will be presented.



PHOTOCHEMISTRY OF HYDROGEN HALIDES ON SMALL WATER PARTICLES

Milan Ončák

RNDr. Petr Slavíček, PhD.

Chemistry of the polar stratosphere has witnessed a large increase of interest in last three decades, mainly in connection with discovery of the Antarctic ozone hole. The exceptional chemistry of the polar stratosphere region results due to the unique meteorology: During the winter, polar vortex develops, stays relatively isolated in the stratospheric region and allows building up of the photochemically active products. In particular, polar stratospheric clouds (PSC) are formed and many atmospheric species (e.g. HCl, HBr, ClONO₂, HNO₃) are adsorbed on their surface. In the following heterogeneous reactions, halogen molecules X₂ are produced. These are then photolyzed during the polar summer, producing halogen radicals which catalyze ozone cleavage.

Photochemistry of the HCl and HBr molecules on the water clusters (H₂O)_n ($n \approx 500$) has been recently investigated by photodissociation experiment in group of Dr. Michal Fárník in J. Heyrovský Institute: Water clusters were doped with one HX molecule, excited by a 193 nm laser and kinetic energy distribution of the dissociated hydrogen atoms was measured. In this way, photochemical behavior of hydrogen halides on PSC may be explored under well-defined conditions.

In this study, photochemistry of small HX(H₂O)_n (X = F, Cl, Br; $n = 1-5$) clusters has been investigated by methods of theoretical chemistry. Acidic dissociation in the ground state was described by the quantum chemical calculations; electronic absorption spectra were modeled employing multi-dimensional reflection principle; finally, photodynamics of the clusters was investigated by quantum *ab initio* molecular dynamics.

Based on the theoretical results, experimental findings can be interpreted. It is suggested that electronic absorption in 193 nm region strongly increases after the acidic dissociation of hydrogen halide on the water particle. After the excitation, charge transfer to solvent takes place and formed halogen radical is released from the cluster. From the electronic absorption spectra calculations and atmospheric photon flux data, this alternative source of reactive Cl and Br radicals is shown to be of comparable importance to direct photolysis of Cl₂ and Br₂ molecules (with photolysis rate ratio about 1:20 and 1:10, respectively).



NANOPARTICLES STUDY IN MOLECULAR BEAMS – PYRROLE, IMIDAZOLE AND PYRAZOLE CLUSTERS

Bc. Václav Profant

Mgr. Michal Fárník, Ph. D.

Pyrrrole, imidazole and pyrazole molecules are one of the simplest heteroatomic compounds with great biological relevance. They are basic elements of many important biological structures, e.g. photosynthetic dyes (chlorophylls, phycobilisomes), oxygen carriers (hemoglobin, myoglobin), amino acids (proline, hydroxyproline, histidine) and their derivatives (histamine, indole), and are also structurally close to the bases of the nucleic acids.

A low luminescent quantum yield explained by rapid internal conversion is typical for these molecules. This is an important biological consequence since the photon energy dissipates and molecule is not susceptible to the potentially harmful reactions in excited states.

Thanks to this properties pyrrole, imidazole and pyrazole attracted a lot of attention of both theoreticians and experimentalists. They have been studied by various methods of optical and laser spectroscopy and their structures computed by methods of ab initio calculations with purpose to find an interpretation of their UV absorption spectra and after-excitation dynamics. However, this research was focused on single molecules, so it didn't cover influences of solvent on photolysis.

In our experiment we prepare molecular beams containing clusters of observed molecules. Clusters means bulks of particles connected together by weak bonds like hydrogen or Van der Waals' bonds. Molecular beam is created by supersonic expansion of gas into vacuum. By using elastic collisions with secondary beam and consecutive velocity selection we are able to create beam with clusters of certain size.

Clusters are studied using several methods. In the scattering experiment we examine their fragments after electron impact ionization and determine the structure of clusters. In the photodissociation experiment we study UV photolysis of clusters and measure their mass spectra and kinetic energy distribution of hydrogen fragments, witch gives us information about dissociation paths.



ACYLATION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE WITH ORGANIC ANHYDRIDES OVER ZEOLITES

Ing. Dana Procházková

Prof. Ing. J. Čejka DrSc.

Ing. M. Bejbllová PhD.

Acylation of olefins with carboxylic acid derivatives is an interesting reaction and resulting unsaturated ketones are versatile intermediates in the preparation of more elaborated compounds. But, olefin acylation was not yet satisfactorily applied in organic synthesis, in contrast to the analogous acylation of aromatics. The problem is that acylation of olefins is the consequence of the formation of reactive intermediates, which undergo different transformations by reactions as additions, eliminations and isomerizations. Friedel-Crafts acylation is a reaction, in which an active and selective heterogeneous catalysts could replace the conventional homogeneous system. Zeolites have been found to be viable alternatives to liquid acids in numerous reactions in recent years.

This work is aimed to study the acylation of cyclohexene and 1-methylcyclohexene with organic anhydrides over zeolites. The effect of the chain length of the anhydride in cyclohexene acylation over zeolite Beta with Si/Al ratio 37.5 was studied. In addition, the effect of the structure and Si/Al ratio of zeolite on the activity and selectivity in acylation of cyclohexene and 1-methylcyclohexene with propionic anhydride was investigated.

Catalytic tests were carried out in a liquid phase in a multi-experiment work station StarFish at temperature 80 °C and atmospheric pressure. Acetic, propionic, butyric, isobutyric, caproic, and 2-ethylbutyric anhydrides were used as acylating agents. Zeolites Mordenite, Beta and USY with different Si/Al ratio were employed as catalysts. Reaction products were analyzed by gas chromatography and mass spectrometry.

It was found that with increasing chain-length of acylating agent cyclohexene conversion decreases. The decrease in the conversion is probably due to a decrease in the diffusivity of bulky products obtained with increasing molecular size of anhydride. Cyclohexene conversions decreased in the order: acetic 82 % > propionic 78 % > butyric 69.3 % > hexanoic 69.3 % > isobutyric and 2-ethylbutyric 63 %.

Cyclohexene acylation resulted in the formation of α,β -unsaturated ketone. Reaction is complicated by the formation of side products, β,γ -unsaturated ketone, cyclohexylester of carboxylic acid, diacylcyclohexene and acylcyclohexylester of carboxylic acid. Acylation of 1-methylcyclohexene preferentially takes place in the allylic position. Methyl substituent prevents subsequent reactions. The highest conversions were achieved over zeolite Beta with Si/Al ratio 37.5 with propionic anhydride (cyclohexene conversion 78.7 %, 1-methylcyclohexene conversion 60.7 %). Selectivities to cyclohexylethyl ketone were up to 45 % (40% cyclohexene conversion). Selectivities to ethyl-(3-methylcyclohex-2-en-yl) ketone were about 90 % (40% 1-methylcyclohexene conversion).



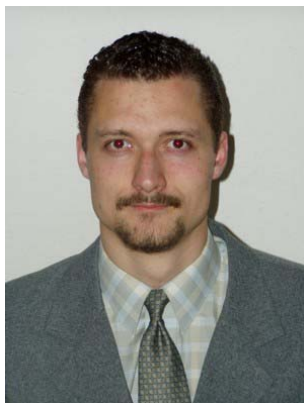
THE ROLE OF CRYSTAL SIZE ON OXIDATIVE DEHYDROGENATION OF PROPANE OVER Fe-ZSM-5

Mgr. Naveen Kumar Sathu

Ing. Zdeněk Sobalík, CSc.

Catalytic oxidative dehydrogenation of propane by N_2O (ODHP) over Fe-zeolite catalysts represents a potential process for simultaneous functionalization of propane and utilization of N_2O waste as an environmentally harmful gas. The isolated Fe sites stabilize the atomic oxygen formed and prevent its recombination to a molecular form, and facilitate its transfer to a paraffin molecule. A major drawback of Fe-zeolites in ODHP with N_2O is their deactivation by accumulated coke, leading to a rapid decrease of the propene yield.

N_2O -mediated Oxidative dehydrogenation of propane has been studied over a series of Fe/ZSM-5 catalysts. The effect of crystal size on the ODHP has been investigated using parent zeolite samples having size 100nm, 1x2 μ m, 1x3 μ m, and 3x6 μ m. Fe/ZSM-5 catalysts were prepared with the same iron content using impregnation method followed by steam treatment. The steam treated or un-treated catalysts displayed different catalytic activities in N_2O decomposition and ODHP. Results show that the nano-sized ZSM-5 zeolite expressed superior catalytic activity and higher stability at longer time on stream compared to micron-sized zeolites. The correlation between catalytic performance and trend to deactivation caused by coke deposition has been further analysed using temperature programmed oxidation (TPO) of spent catalysts. TPO results shown that coke deposition significantly depend on the crystal size of the parent zeolite. Similar propene yields, same catalytic profiles of fresh and regenerated catalysts show that hydrothermal treatment and regeneration of spent catalysts in presence of oxygen stream does not change the local environment of iron species. Among all the catalysts tested the nano-sized ZSM-5 zeolite exhibits higher resistance to deactivation by pore blockage compared to the micron-sized ZSM-5 zeolites. The advantage of the nano-size ZSM-5 zeolite has been attributed to its shorter channels and higher relative number of pore mouth openings which could: (i) suppress diffusion limitation for reactants, (ii) decrease retention of desired products in zeolite channels and thus eliminate consequent reactions, (iii) decrease pore blocking compared to the micro-sized ZSM-5 zeolites. The comparable propene yield over the fresh and repetitively regenerated samples shows practical potential for regeneration of a spent catalyst.



THE SUB-MILLIMETRE WAVE SPECTROSCOPY OF THE C₂S RADICAL

Ing. Jan Skřínský

Ing. Zdeněk Zelinger, CSc.; Dr. Stefan Bailleux

The spectrum of the linear C₂S radical in its ground electronic state (³Σ⁻) has been measured in the sub-millimetre wave region in PhLAM laboratory in Lille.

The C₂S radical is an interstellar specie occurs in the TMC-1, TMC-2, SGR B2 and IRC sources. This radical plays an important role in the chemical formation of the dark clouds.

In the laboratory the C₂S radical was generated in a DC glow discharge using a CS₂/Ar mixture cooled with a flow of liquid nitrogen. The sub-millimeter wave radiation was provided by two phase-locked backward-wave oscillators. A liquid helium-cooled InSb bolometer was used as detector. More than forty rotational transition frequencies have been recorded between 426 GHz – 659 GHz spectral region. Line profiles have been evaluated by using of non-linear regression function and by the Pearson profile function.

Results of the measurement are a basis for the determination of molecular constants. The future step is the prediction for astronomical detection in 1 THz spectral region. The combination of laboratory measured spectra together with the astronomically observed frequencies of C₂S radical lead to better understanding of carbon and sulfur chemistry of the interstellar molecular clouds.



STUDIUM PRODUKTŮ TERMÁLNÍHO ROZKLADU POLYETHYLEN TEREFTALÁTU METODOU VYSOCE ROZLIŠENÉ SPEKTROSKOPIE S FOURIEROVOU TRANSFORMACÍ, SELECTED ION FLOW TUBE MASS SPECTROMETRY A PLYNOVOU CHROMATOGRÁFIÍ

Bc. Kristýna Sovová

Doc. RNDr. Svatopluk Civiš, CSc.

Průmyslová produkce polyethylen tereftalátu (PET) má za poslední desetiletí vzrůstající tendenci. Množství použitého a nevytříděného plastu končí na skládkách, ve spalovnách nebo domácích topeništích. Je proto velmi důležité zjistit, jaké látky vznikají při spalování a rozpoznat jejich účinky na lidské zdraví a životní prostředí jako celek.

V této práci byly spáleny vzorky PET materiálu ve speciálním spalovacím zařízení, které odpovídá německé normě DIN 53 436 při teplotách 500°C, 800°C (v proudu vzduchu). Bylo provedeno také nekontrolované spalování, které neodpovídalo normě. Plynné produkty byly analyzovány třemi různými analytickými metodami: vysoce rozlišenou spektroskopií s Fourierovou transformací (FTIR), selected ion flow tube mass spectrometry (SIFT-MS) a plynovou chromatografií s hmotnostní spektrometrií (GC-MS). Oxid uhličitý, methan, ethylen, acetylen, formaldehyd a acetaldehyd byly detegovány metodou FTIR. Voda, methan, acetaldehyd, ethylen, formaldehyd, methanol, aceton, benzen, kyselina tereftalová, styren (ethenylbenzen), ethanol, toluen (methylbenzen), xylen (dimethylbenzen), ethylbenzen, naphthalen, biphenyl a phenol byly kvantifikovány pomocí SIFT-MS a GC-MS. Produkty nekontrolovaného spalování byly analyzovány pouze metodou FTIR, která umožnila rozlišit rotačně-vibrační strukturu pásů formaldehydu ($2779,90$ a $2778,48$ cm^{-1}) a propanu, který byl identifikován díky charakteristické vibraci CH_3 skupin při $2977,00$ a $2962,00$ cm^{-1} .

Výsledky této studie ukazují, že nekontrolované hoření v proudu vzduchu vede k formování produktů, které jsou podobné produktům vznikajícím při kontrolovaném hoření za teploty 500 °C. Při teplotě 800 °C vzniká především oxid uhličitý, voda a těžší uhlovodíky o nižší koncentraci než v případě 500°C.

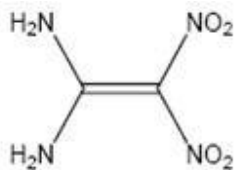


ELEKTROCHEMICKÉ STUDIUM INTRAMOLEKULÁRNÍCH REDOX REAKCÍ 2,2-DINITROETHEN-1,1- DIAMINU VE VODNÉM PROSTŘEDÍ

Ludmila Šimková

Doc. RNDr. Jiří Ludvík, CSc.

Molekuly látek, které patří mezi moderní průmyslové výbušniny, musí mít z chemického hlediska velmi specifické vlastnosti: aby mohly fungovat i za nepřístupu vzduchu, musí v jedné molekule obsahovat jak silně reduktivní, tak i silně oxidativní centra. Právě interakce těchto dvou opačných redox center v rámci jedné molekuly vede k intramolekulární redox reakci, která - pokud je dostatečně rychlá a pokud při ní vznikají plyny - se projeví velkým účinkem.



Logický vývoj ve výzkumu výbušnin je hledání nových explosiv, které by měly vysoký výkon a nízkou citlivost vůči iniciaci. Jednou z takovýchto látek, která byla poprvé syntetizována v r. 1998, je organická sloučenina 2,2-dinitroethen-1,1-diamin. V literatuře je často označována jako FOX-7. Jiný název, se kterým je možno se u této sloučeniny setkat, je zkratka DADNE, neboli 1,1-diamino-2,2-dinitroethylen, někdy zkracováno na DANE.

Tyto molekuly jsou zajímavé však nejen z hlediska praktického použití, ale zejména z hlediska základního výzkumu molekul s více redox centry. Velmi pozoruhodná - zejména z hlediska redukčního mechanismu - je zde zejména kombinace dvou snadno redukovatelných geminálních nitroskupin se dvěma aminoskupinami, které dohromady vytváří elektronový "push-pull" delokalizovaný systém.

Protože se ale současně jedná o potenciální výbušninu, mechanismus řetězce redox reakcí během exploze je velmi složitý, navíc prakticky nezkoumatelný. Jednou z možností, jak se pokusit tuto řadu reakcí zpomalit, případně zastavit a tím nahlédnout do způsobu iniciace a do sledu jednotlivých kroků může být právě elektrochemický přístup.

Redukce ve vodném, tedy protickém prostředí má zde ten význam, že mechanismu intramolekulárních redox reakcí (vedoucích k jakémusi "zpomalenému výbuchu" v nádobce) konkuruje vnější protonizace a tedy redukce spojená s hydrogenací. To se projevilo tím, že zatímco polarografické experimenty odhalily v celém rozsahu pH osm redukčních dějů s celkovou spotřebou 18 elektronů na jednu molekulu FOX-7, preparativní elektrolýza vedoucí k úplné konverzi vykazovala pouze spotřebu šesti, resp. čtyř elektronů.

Pozoruhodné jsou i další získané výsledky, jako např. závislost vzájemného poměru limitních proudů na koncentraci látky, nebo otázka produktů elektrolýz.



AB INITIO CALCULATIONS WITH SINGLE-REFERENCE AND BRILLOUIN-WIGNER MULTIREFERENCE COUPLED CLUSTERS METHODS

Bc. Libor Veis

Mgr. Jiří Pittner Dr. rer. nat.

The single-reference coupled clusters (CC) method is nowadays one of the most commonly used ab initio methods. The main reasons for this fact are its reliability and accuracy. Especially coupled cluster single double (CCSD) and coupled cluster single double (triple) [CCSD(T)] methods are very wide-spread and used by computational chemists as „black box“ tools.

Single-reference methods however fail in the situations where the static correlation is important (description of dissociation, diradical species etc.). In these cases, use of multireference methods, which correctly describe static correlation, is necessary. One of the things in which we are interested in our laboratory is the development and implementation of new multireference coupled clusters methods concretely multireference Brillouin-Wigner coupled clusters (MR BWCC) methods.

In my lecture, the results of calculations performed in terms of my diploma thesis at the Charles University will be presented.

First system, which will be discussed, is the molecule of boron nitride (BN). This molecule is due to the multireference character of its lowest-lying singlet state suitable for testing of performance of newly developed multireference methods. The results of calculations of singlet-triplet separation and vibrational frequencies and anharmonicities of two lowest-lying electronic states performed with different kinds of MR BWCC methods will be presented and critically compared with experimental data and available results of other ab initio methods.

Second system is a set of fused small-ring hydrocarbons from Balaji and Michl's paper¹. These improbable-looking structures were studied mainly by means of single-reference CCSD(T) method. The existence of local minima on potential energy surfaces was proven at this level of theory and several spectroscopic characteristics (IR, Raman and NMR spectra) were calculated. Thermal isomerization of one of the structures (tricyclo[2.1.0.0^{2,5}]pentane) studied by means of CASPT2, MR BWCCSD and MR BWCCSD(T) methods will also be presented.

References:

¹Balaji, V.; Michl, J. *Pure Appl. Chem.* **1988**, *60*, 189-194.



SYNTHESIS OF ACYLFERROCENE DERIVATIVES BY FRIEDEL-CRAFTS ACYLATION OVER ZEOLITES

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Derivatives of ferrocene, especially ferrocenylenones (FCNs), are important starting materials for the synthesis of polymers. FCNs are used as dienophiles in Diels-Alder reactions and as dipolarophiles in 1,3-dipolar cycloaddition reactions. Syntheses of hetero- and carbocyclic-ferrocene derivatives are also based on the use of FCNs.

Syntheses of FCNs are carried out in different ways. Common method is Friedel-Crafts acylation reaction. This method is successfully employed in the syntheses of adamantanoyl-, cinnamoyl-, and 4-chlorbenzoylferrocene using homogeneous catalysts. In the case of ferrocene acylation with acryloyl chloride using AlCl_3 as the catalyst reaction usually resulted in the formation of corresponding ferrocenophan-1-one.

The preparation of non-symmetrical ketones by the reaction of acyl chlorides and ferrocene in the presence of zeolite catalysts is described. Friedel-Crafts acylation of ferrocene was carried out in a Heidolph Synthesis 1 (16-parallel reactor) in a liquid phase under atmospheric pressure, at the reaction temperature of 140 °C. As acylating agents were used chlorides of acryloic, adamantanoic, 4-chlorbenzoic, cinnamoic and benzoic acid and anhydride of benzoic acid. Zeolites BEA, MFI and USY with different Si/Al ratio were used as catalysts.

This way of preparation of ferrocene derivatives is alternative method for conventional homogeneous catalysis. The higher pore size of zeolite was used, the higher conversion of ferrocene was found due to faster transport of reactants to active sites and products from channel system. The conversion was also influenced by the reactivity of acylating agents. The highest ferrocene conversion was achieved with benzoyl chloride and lowest with 4-chlorbenzoyl chloride.

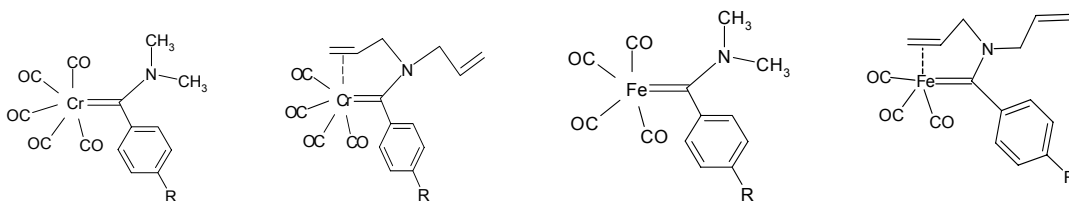


EXPERIMENTAL AND THEORETICAL STUDY OF Cr AND Fe AMINOCARBENE COMPLEXES

Radka Zvěřinová

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A series of Fischer-type carbene complexes (with electrophilic character of carbene carbon atom $(^{-})M - C^{(+)}R_2$) was studied experimentally by electrochemical (polarography, cyclic voltammetry) and spectroscopical (IR and UV-Vis) methods. Formulas of the complexes are shown below, R = OCH₃, CH₃, H, Cl, COOCH₃, CF₃.



Experimental results were influenced by various factors: by the central metal nature and its coordination number, by the phenyl ring substitution, by bonding possibilities of ligands. Electrochemical methods were found to be the most sensitive to structural changes.

Optimized structures, MO energies, vibrational analyses and excited states were calculated using Gaussian 03 program package and hybrid B3LYP functional. The excited state calculations were performed by TD-DFT and solvent effect was described by a continuum polarized model CPCM.

Correspondence between calculated results and experimental data was very good for redox potentials and IR frequencies while some additional refinement was necessary for UV-Vis spectra.

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