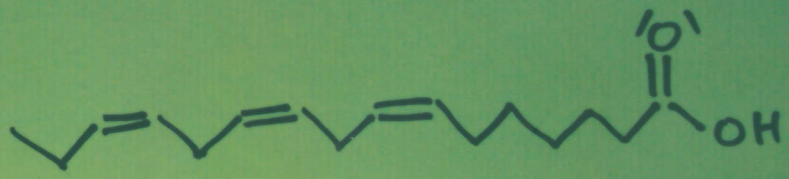
Efnafræðifélag Íslands
The Icelandic Chemical Society



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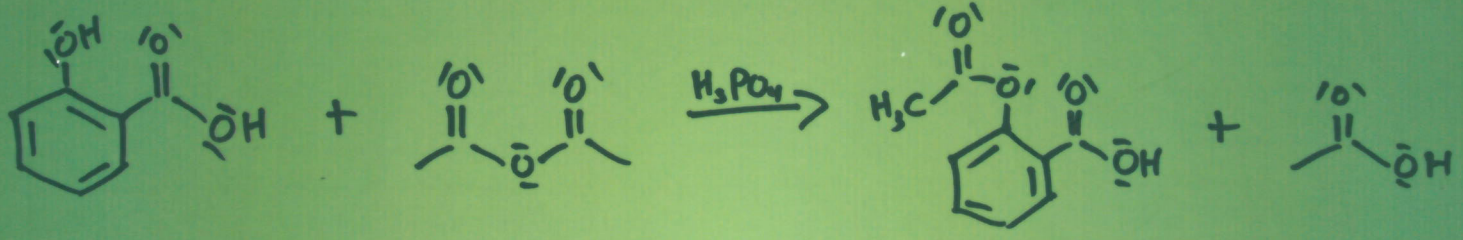

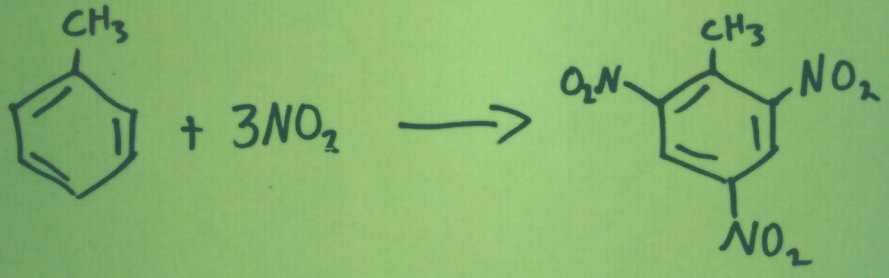

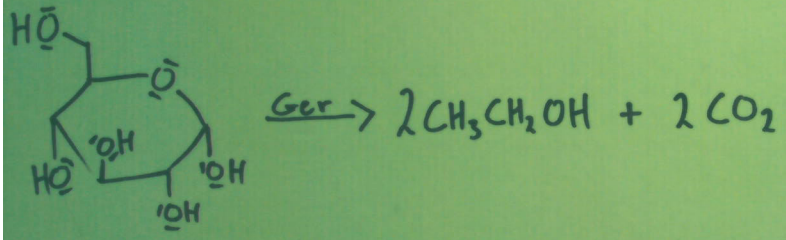

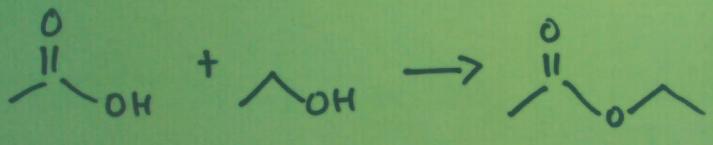

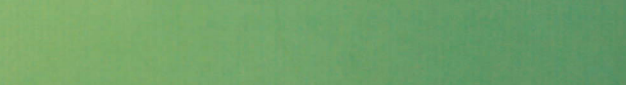

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Actavi

HVÍTA HÚSIÐ / SÍA - Actavis 311120

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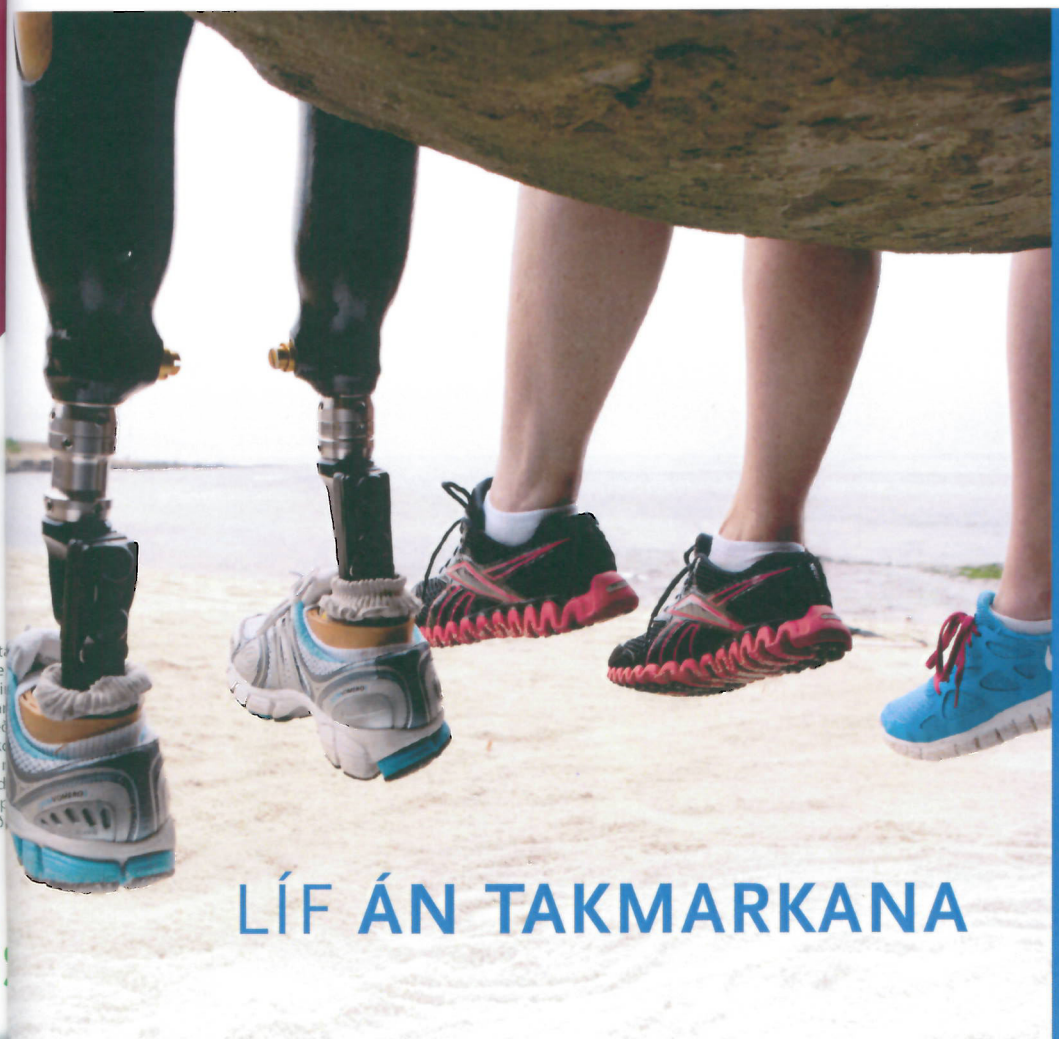

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Hlutverk Össurar er að gera fólki sem lifir með líkamlegri fötlun af völdum sjúkdóma eða aflimunar kleift að njóta sín til fulls með bestu stoð- og stuðningstækjum sem völ er á.

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Dagskrá

Tími	Fyrirlesari	Titill
09:00 - 09:10	Margrét Þorsteinsdóttir	Setning
09:10 - 09:40	Hörður Filippusson	Lífefnavinnsla. Fortíð nútíð - framtíð
09:40 - 10:10	Ásgeir Ívarsson	Íslenskur efnaiðnaður í fortíð, nútíð og framtíð
10:10 - 11:20	**Kaffihlé/Veggspjöld**	
11:20 - 11:40	Katrín Lilja Sigurðardóttir	Efnafræði fyrir börn á öllum aldri
11:40 - 12:00	Ragnheiður Rósarsdóttir og Elva Björt Pálsdóttir	Þróun í Kvennó- tími nemenda er dýrmætur
12:00 - 13:00	**Hádegismatur**	
13:00 - 13:20	Stefán Jónsson	Efnafræðirannsóknir hjá Actavis: Niðurbrot lyfjaefna í lyfjavörum
13:20 - 13:40	Finnur Freyr Eiríksson	Notkun massagreina á klíniskum rannsóknastofum
13:40 - 14:00	Giuseppe Paglia	Ion mobility-mass spectrometry: using collision-cross sections of common metabolites to support metabolomics applications
14:00 - 14:20	Kennet Joelsson	The future separates from the past
14:20 - 15:00	Gísli Bragason	Framleiðsla á áli hjá Norðuráli
15:00 - 15:40	**Kaffihlé/Veggspjöld**	
15:40 - 16:00	Sigríður Ólafsdóttir	Traust, ást og einkvæni. Efnafræði tilfinninga
16:00 -	Vilhelm Anton Jónsson	Villi naglbítur
16:00 - 17:00	**Veggspjaldakynningar og mixer**	
17:00 - 19:00	**Hlé/Spa**	
19:00	**Árshátíð Efnís**	

Schedule

Time	Lecturer	Title
09:00 - 09:10	Margrét Þorsteinsdóttir	Introduction
09:10 - 09:40	Hörður Filippusson	Biochemicals industry in Iceland. Past – present – future
09:40 - 10:10	Ásgeir Ívarsson	Icelandic chemicals industry. Past, present and future
10:10 - 11:20	**Coffee break/Posters**	
11:20 - 11:40	Katrín Lilja Sigurðardóttir	Chemistry for children of all ages
11:40 - 12:00	Ragnheiður Rósarsdóttir og Elva Björt Pálsdóttir	A step forward in Kvennó- making the best use of the students time in school
12:00 - 13:00	**Hádegismatur**	
13:00 - 13:20	Stefán Jónsson	Chemistry research at Actavis: Degredation of chemicals in pharmaceuticals
13:20 - 13:40	Finnur Freyr Eiríksson	The use of mass spectrometers in clinical laboratories
13:40 - 14:00	Giuseppe Paglia	Ion mobility-mass spectrometry: using collision-cross sections of common metabolites to support metabolomics applications
14:00 - 14:20	Kennet Joelsson	The future separates from the past
14:20 - 15:00	Gísli Bragason	Aluminum production at Norðurál
15:00 - 15:40	**Coffee break/Posters**	
15:40 - 16:00	Sigríður Ólafsdóttir	Trust, love and monogomy. The chemistry of feelings.
16:00 -	Vilhelm Anton Jónsson	Villi naglbítur
16:00 - 17:00	**Poster session and mixer**	
17:00 - 19:00	**Break/Spa**	
19:00	**Efnís Gala**	

Ágrip fyrirlestra
Lecture abstracts

Fyrirlestur 1

Lífefnavinnsla á Íslandi
Fortíð - nútíð - framtíð?

Hörður Filippusson

Raunvísindastofnun Háskólans, Lífefnafræðistofa, Dunhaga 3, IS-107 Reykjavík

Í þessu erindi verður litið yfir sögu síðustu áratuga með tilliti til þeirra hugmynda sem settar hafa verið fram og tilrauna til aðgerða á sviði lífefnavinnslu, einkum með tilliti til vinnslu úr innlendum hráefnum.

Árið 1973 skipaði iðnaðarráðuneytið Lyfja- og líf-efnavinnslunefnd sem skilaði áliti ári síðar. Nefndin taldi að lífefnaiðnaður ætti sér mjög bjarta framtíð enda væri hér fyrir hendi mikið magn hráefna, innyfli fiska, hvala og sláturdýra, sem úr mætti vinna margvísleg verðmæt efni. Nefndin setti fram all-margar tillögur að rannsóknum til undirbúnings slíkum iðnaði. Á næstu tveim til þrem áratugum eða svo var rannsóknaverkefnum byggðum á mörgum af þessum hugmyndum hrint í framkvæmd.

Um áratug síðar er mikil gróska orðin í rannsóknum á sviði lífefnatækni, studd af verulega auknum opinberum framlögum til rannsókna og erlendum styrkjum. Nýstofnaður Tæknisjóður á vegum Rannsóknaráðs setti í gang líftækniáætlun. Norræn líftækniáætlun var í gangi 1988-1990 og kom mjög við sögu hér. Af þessu leiddi mikilsverða upp-byggingu innviða, tækjabúnaðar, aðstöðu og þekk-ingar á þeim rannsóknastofum sem þátt tóku í verk-efnum á þessu sviði, einkum við Háskóla Íslands, Rannsóknastofnun fiskiðnaðarins og Iðntæknistofn-un.

Um svipað leyti hafði erfðatækni vaxið mjög fiskur um hrygg og líftækni byggð á beitingu hennar, en sú þróun átti eftir að valda geysimiklum breytingum á allri lífefnavinnslu og minnka mikilvægi náttúrlegra hráefna fyrir framleiðslu próteinafurða.

Hér á landi spruttu upp fjölmörg fyrirtæki sem meira eða minna byggðu á niðurstöðum þeirra rannsóknaverkefna sem unnið hafði verið að á áðurnefndum stofnunum.

Fjallað verður stuttlega um nokkur þessara fyrirtækja og hvernig þeim hefur reitt af. Hvaða lífefnavinnsla er stunduð á Íslandi nú? Hvaða breytingar hafa orðið á umhverfi slíkra fyrirtækja og áherslum þeirra?

Á lífefnaiðnaður framtíð fyrir sér á Íslandi?

Lecture 1

Biochemicals industry in Iceland
Past - present - future?

Hörður Filippusson

University of Iceland Science Institute, Biochemistry Department, Dunhaga 3, IS-107 Reykjavík, Iceland

This lecture will attempt to give an overview of the recent decades with respect to the ideas which have been proposed and the attempts which have been made towards the production of biochemicals in Iceland, especially extraction from local raw materials.

In 1973 the Ministry for Industry formed a committe to look at the production of pharmaceuticals and biochemicals in Iceland. The committe reported a year later. It concluded that the future of biochemicals production in Iceland was very bright as a great deal of raw material, the inner organs of fish, whales and slaughterhouse animals, was in plentiful supply and a variety of valuable compounds could be isolated from them. The committee suggested various research programmes which would be necessary as preparation for such industries. Over the following two to three decades many of these ideas became the basis of actual research programmes.

A decade or so later we find a vigorous research effort in the field of biochemical technology, supported by substantially increased government funding for research as well as foreign grant money. A newly established Technical Fund under the Research Council established a biotechnology funding plan. A Nordic biotechnology plan was in operation during 1988-1990 and had a substantial influence here. This led to an important increase in infrastructure, equipment, facilities and expertise, in the laboratories participating in these projects, in particular at the University of Iceland, the Fisheries laboratories and te Industrial Technology Institute .

At about tis time gene technology had become an increasingly powerful tool and biotechnology based on it. This development was to destined to caus immense changes in everything concerning production of biochemicald and decrease the importance of natural raw materials as sources of biochemical compounds.

In Iceland a substantial number of commercial enterprises were started up as a more or less direct result of the research programmes of the aforementioned institutions.

In this lecture we will mention briefly some of these companies and how they have succeeded. What biochemicals are being produced in Iceland at present. What changes have occurred in the environment in which such companies find themselves and in the direction they have taken.

Is there a future for biochemicals production in Iceland?

Fyrirlestur 3

Efnafræði fyrir börn á öllum aldri

Katrín Lilja Sigurðardóttir

Raunvísindastofnun Háskóla Íslands, Dunhaga 3, 107 Reykjavík, Ísland

Efnafræði er sú fræðigrein sem hefur fengið viðurnefnið "The central science" sem mætti þýða sem "hin miðlæga vísindagrein". Ástæðan fyrir nafngiftinni er meðal annars sú að fræðigreinin tengir saman eðlisvísindi og lífvísindi.

Efnafræðikunnátta er grundvöllur fyrir velgengni í fjölmörgum öðrum námsgreinum, en þrátt fyrir greinilegt mikilvægi greinarinnar er raunin sú að á Íslandi geta nemendur lokið leikskóla, grunnskóla og framhaldsskóla án þess að læra stakan staf í efnafræði. Sú staðreynd er merki þess að þörf sé á almennri hugarfarsbreytingu skólayfirvalda gagnvart efnafræði.

Fjallað verður um efnafræði sem fræðigrein og stöðu hennar innan skólakerfisins. Jafnframt verður rætt um hvernig hægt sé að vekja áhuga barna og hvernig kennslu sé best háttað fyrir yngstu kynslóðina. Einstök verkefni sem ýta undir jákvætt hugarfar gagnvart efnafræði verða einnig til umfjöllunar og má þar helst nefna Háskóla unga fólksins, Sprengjugengið og hina árlegu Landskeppni framhaldsskólanna í efnafræði og Ólympíukeppni í efnafræði.

Chemistry for children of all ages

Katrín Lilja Sigurðardóttir

Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland

Chemistry is often called "The central science" because it connects all the other sciences together. Therefore, Chemistry should be a fundamental subject in the education of Icelandic children. For some reasons it is not. In fact, some people have never learned a single word in chemistry throughout their whole school attendance. But how can this be changed?

It is obvious that the attitude towards chemistry in general needs to change. In Iceland, there are some projects that are already making a big difference for that matter, e.g. "The university for the youth", "Sprengjugengið", and The Annual Domestic Trial in Chemistry and the International Chemistry Olympiads. But it is also necessary to take a look at the status of Chemistry within the school system.

Fyrirlestur 4

Þróun í Kvennó
-tími nemenda er dýrmætur

Elva Björt Pálsdóttir og Ragnheiður Erla Rósarsdóttir

Kvennaskólinn í Reykjavík
Fríkirkjuvegi 9

Uppúr aldamótum vorum við hér í Kvennó orðnar langþreyttar á hversu erfitt var að fá nemendur til að læra (vinna). Við vorum með hefðbundið fyrirlestraform(glærur og tafla) með dæma- og verklegum tímum inná milli. Einnig var ætlast til heimavinnu en þar var allur gangur á skilum.

Eftir nokkrar pælingar ákváðum við að kúvenda kennslunni, nú skyldu nemendur læra að læra. Kynningin fjallar um hvernig við komum þessu á koppinn og hvernig þetta hefur þróast á þessum 8 árum sem eru liðin síðan við byrjuðum.

A step forward in Kvennó
- making the best use of the students time in school

Elva Björt Pálsdóttir og Ragnheiður Erla Rósarsdóttir

Kvennaskólinn í Reykjavík
Fríkirkjuvegi 9

A couple of years after the turn of the century it was getting too obvious that the students time in school was not very efficiently used. We had been teaching with traditional methods, lectures (PP and board) with problem solving and experimental work now and then. We assigned homework which was not always handed in.

After a lot of thinking we decided to do things radically different. We were going to teach our students how to learn chemistry with their own devices. This presentation shows how we did that and how this method has evolved over the last 8 years.

Fyrirlestur 5

Efnafræðirannsóknir hjá Actavis: Niðurbrot lyfjaefna í lyfjavörum.

Stefán Jónsson

Department Manager, Actavis Reykjavikurvegur 76-78, 220 Hafnarfjordur

Farið verður yfir helstu tegundir niðurbrotsferla lyfjaefna í lyfjavörum, og ljósi varpað á þann mun sem gjarnan er á niðurbrotsefnahvörfum og þeim efnahvörfum sem við þekkjum úr efnasmíðamiðuðu námsefni okkar í lífrænni efnafræði. Nokkur dæmi verða tekin um niðurbrotsefni lyfja sem sannkennd hafa verið hjá Actavis, og um tilraunir til efnasmíða á þeim.

Fyrirlestur 6

Notkun massagreina á klínískum rannsóknastofum

Finnur Freyr Eiríksson

Lækna- og lyfjafræðideild, Háskóli Íslands, Reykjavík, Ísland

Mikilvægi massagreina á klínískum rannsóknarstofum hefur aukist mikið síðustu ár. Meðal annars má rekja þá þróun til þess að notkun massagreina hefur verið gerð auðveldari á undanförnum árum. Þá hefur það verið aðkallandi að massagreinar séu í meira mæli notaðir á klínískum rannsóknarstofum til þess að hægt sé að mæla nákvæmlega þau lífmörk sem þarf við annaðhvort sjúkómsgreiningar eða mælingar til að styðjast við stýringu á lyfjagjöf. Vökvaskilja tengd raðtengdum massagreini (LC-MS/MS) er framúrskarandi greiningartækni með frábæra valvísi, næmni og mikil afköst. Við aðferða þróun á LC-MS/MS þarf að hámarka margar breytur til að ná fram hámarks næmni og sértækni. Með því að notast við efnatölfræði er hægt að draga verulega úr tíma sem þarf við aðferðaþróun á LC-MS/MS.

Í þessum fyrirlestri verður dregin fram miklvægi massagreina á klínískum rannsóknarstofum. Þá verða einnig gefin dæmi um nytsemi massagreina við sjúkdómsgreiningar og við stýringu lyfjameðferðar sjúklinga.

Fyrirlestur 7

Ion mobility-mass spectrometry: using collision-cross sections of common metabolites to support metabolomics applications.

Giuseppe Paglia

Center for Systems Biology, University of Iceland, Reykjavik, Iceland

Metabolomics aims to measure the complete set of small metabolites (metabolome) present in biological samples. The development of reproducible analytical workflows for measuring and monitoring the metabolome is one of the major analytical challenges of this century.

Ion mobility spectrometry (IMS) is a gas phase electrophoretic tecnique, which separates molecules according to their charge, shape and size as well as their interaction with a buffer gas.

Charge, shape and size of an ion define its collision cross section (CCS), which is the area interacting with buffer gas moleucules. This is a chemical information directly related with the chemical structure of a given metabolite.

The IMS separation occurrs in the milliseconds timeframe making it compatible with mass spectrometry (MS) detection.

Hyphenated techniques coupling liquid chromatography (LC)-MS with ion mobility are a promising field in metabolomics, providing ion mobility-derived information in addition to retention time and mass, resulting in an increased peak capacity and specificity.

Here we explore the use of IM-MS in combination with LC in metabolomics, as well as the reproducibility of the procedures for deriving CCS and the possibility of building new databases containing mobility information.

Fyrirlestur 8

The Future Separates From The Past

Kennet Joelsson

Sales Specialist High Resolution MS, Waters Sverige AB

Imagine a lab where all analytical scientists can acquire high-quality mass spectral data. On their own. Within their existing workflow's. Across every sample. Without training. A lab where uncertainty about compounds is replaced by fast, efficient conformation and confidence that comes with crossing LC/MS divide like never before. Now imagine all this happening at the push of a button. This is where its get interesting.

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Fyrirlestur 9

Framleiðsla á áli hjá Norðuráli

Gísli Bragason

Norðurál ehf. Grundartanga

Álframleiðsla í dag fer aðallega fram með Hall/Héroult aðferðinni. Sú aðferð var þróuð af Bandaríkjamanninum Charles Martin Hall og Frakkanum Paul Louis Toussaint Héroult. Aðferðina þróuðu þeir hvor í sínu lagi og sóttu báðir um einkaleyfi fyrir henni árið 1886. Hún felst í því að leysa súrál upp í fljótandi krýólíti (Na_3AlF_6) í járndeiglu, setja forskaut úr kolum ofan í blönduna og hleypa á straumi. Aðferðin í dag er enn sú sama þó svo að tæknileg útfærsla á rafgreiningarkerjum hafi tekið framförum.

Til þess að framleiða 1 tonn af áli þarf um 2 tonn af súráli, 0,5 tonn af kolefni, 11 kg af álflúoríði og 13,5 MWst af raforku. Nauðsynlegt er að nota flúor í álframleiðslu til þess að leysa súrál upp við viðunandi hitastig, þ.e.a.s. um 950°C í stað 2100°C sem er bræðslumark súráls. Vegna hárrar staðalspennu áls er nauðsynlegt að hafa forskautin úr kolefni og „fórna" því til þess að fá hreint ál. Ef forskautin væru úr málmi myndu þeir málmar, sem hægt væri að nota, afoxast við bakskautið og blandast álinu en með forskautum úr kolefni rýkur koltvíoxíð í burtu og eftir verður hreint ál. Álver framleiða því koltvíoxíð í miklu magni en koltvíoxíð sem verður til í álverum á Íslandi, og öðrum álverum sem nota raforku frá vatnsaflsvirkjunum, er þó margfalt minna en það sem verður til við framleiðsu áls þar sem kol, olía eða gas er notað við raforkuframleiðslu.

Aluminium production at Nordural

Gísli Bragason

Norðurál ehf. Grundartanga

Aluminium production today is primarily performed with the Hall/Héroult method. That method was developed by the American Charles Martin Hall and Frenchman Paul Louis Toussaint Héroult. They developed the method separately and patented it both in 1886. It comprises solving alumina in liquid cryolite (Na_3AlF_6) in an iron crucible, insert coal-anode into the mixture and apply current. The method today is still the same even though the technical details of the electrolysis cells has progressed.

In order to produce one tonne of aluminium, about 2 tons of alumina, 0.5 tons of carbon, 11 kg of aluminum fluoride and 13.5 MWh of electric power is needed. It is necessary to use aluminum fluoride in order to dissolve the alumina at an acceptable temperature, ie at 950°C instead of 2100°C which is the melting point of alumina. Because of the high standard voltage of aluminium it is necessary to make anodes out of carbon and then "sacrifice" the carbon in order to obtain pure aluminium. If anodes were made out of metal, the metals which could be used would be reduced at the cathode and mixed with the aluminium, but with anodes made out of carbon the carbon dioxide will evaporate, leaving pure aluminium. Smelters therefore produce carbon dioxide in large quantities but carbon dioxide arising from smelters in Iceland, and other plants that use electricity from hydropower stations, is far less than from smelters that use electricity generated from burning coal, oil or gas.

Fyrirlestur 10

Traust, ást og einkvæni. Efnafræði tilfinninga

Sigríður Ólafsdóttir

SÓL ráðgjöf, Frostaskjóli 89, 107 Reykjavík

Í erindinu verður fjallað um nýlegar rannsóknir á áhrifum nónapeptíðhormónanna oxytocin og arginín-vasopressin á félagshegðun og tilfinningar. Bæði hormón eru fáanleg á nefúðaformi og því einfalt að nota í rannsóknir á mönnum og bera saman við lyfleysu. Lýst verður nokkrum tilraunum og teknar saman helstu hugmyndir um hlutverk hormónanna hjá dýrum og mönnum.

The talk will describe recent studies on the effects of the nonapeptide hormones oxytocin and arginine-vasopressin on emotions and social behavior. Both hormones are available as nasal spray and are convenient for use in placebo controlled human studies. A few studies will be described in some detail and ideas on the role of these hormones in animals and humans will be summarized.

Selected bibliography

Bos, Peter A., et al. "Acute effects of steroid hormones and neuropeptides on human social–emotional behavior: a review of single administration studies."*Frontiers in Neuroendocrinology* 33.1 (2012): 17-35.

Graustella, Adam J., and Colin MacLeod. "A critical review of the influence of oxytocin nasal spray on social cognition in humans: evidence and future directions." *Hormones and behavior* 61.3 (2012): 410-418.

Kosfeld, Michael, et al. "Oxytocin increases trust in humans." *Nature* 435.7042 (2005): 673-676.

Zak, Paul J., Angela A. Stanton, and Sheila Ahmadi. "Oxytocin increases generosity in humans." *PLoS One* 2.11 (2007): e1128.

Williams, Jessie R., et al. "Oxytocin administered centrally facilitates formation of a partner preference in female prairie voles (Microtus ochrogaster)." *Journal of neuroendocrinology* 6.3 (1994): 247-250.

Ágrip veggspjalda
Poster abstracts

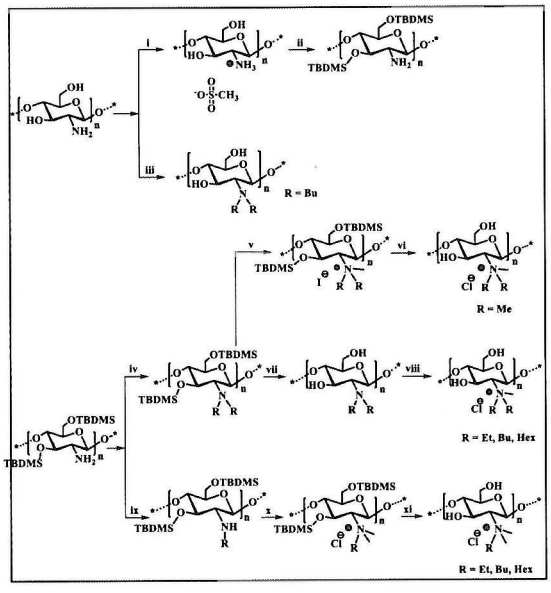
Veggspjald 1

Impact of chain length on Antibacterial activity and Hemocompatibility of Quaternary chitosan derivatives

Priyanka Sahariah[a], Berglind Eva Benediktssdóttir[a], Martha Hjálmarsdóttir[b], Olafur Eysteinn Sigurjonsson[c], Knud J. Jenssen[d], Már Másson[a,*]

[a]Faculty of Pharmaceutical Sciences, School of Health Sciences, University of Iceland, Hofsvallagata 53, IS-107 Reykjavík, Iceland
[b]Department of Biomedical Science, Faculty of Medicine, University of Iceland, Stapi, Hringbraut 31, 101 Reykjavík, Iceland
[c]The Blood Bank, Landspitali University Hospital, Reykjavik, Iceland
[d]Faculty of Life Sciences, Department of Basic Sciences and Environment, University of Copenhagen, Copenhagen, Denmark

A highly efficient method for regioselective modification of chitosan biopolymer using a simple reductive amination procedure to yield N,N-dialkyl chitosan derivatives was developed. Four different dialkyl derivatives namely di-methyl, di-ethyl, di-butyl and di-hexyl were synthesized with the aid of 3,6-O-di-TBDMS chitosan[1] as a precursor. The reaction involved treatment of the protected chitosan with the aldehyde forming the imine followed by reduction to get the mono alkyl derivative, which was then subjected to similar treatment once again to have the dialkylated product. The use of the TBDMS protected chitosan enabled the reaction to be performed in organic solvent simplifying the method and resulting in 100% substitution.



Scheme 1: Reagents and conditions : (i) methanesulfonic acid, water, 10°C; (ii) TBDMS chloride, imidazole, DMSO, N_2, room temperature; (iii) Sodiumtriacetoxyborohydride, AcOH, DCM, 40 °C; (iv)aldehyde, $NaBH_4$, DCM, room temperature, (v) TBAF (1 M), NMP, 50 °C. (vi) MeI, NMP, 40°C; (vii) aldehyde, triethylamine, DCM, 45°C; (viii) Sodiumtriacetoxyborohydride, AcOH, DCM, rat; (xi) TBAF (1 M), NMP, 50 °C. Note : Chitosan has 2% N-acetylation that has been omitted for clarity.

Dialkylation reaction in absence of the protecting groups i,e. on native chitosan (unmodified chitosan) was performed under acidic conditions[2] which resulted in lower degree of substitution. N-methylation and quaternisation of the dialkyl chitosan derivatives was attempted under different reagents and conditions. With the protected dialkyl compound only a very low degree of quaternisation was obtained due to the sterric hindrance provided by the highly bulky tertiarybutyldimethylsilyl groups. However, a high degree of quaternisation of these derivatives could be achieved by using MeI as reagent and NMP as solvent after the removal of the protecting groups. The quaternisation reaction yielded compounds which carried permanent positive charges on the polymer backbone and showed good aqueous solubility, making them suitable for antimicrobial testing. The degree of substitution was calculated from the integrals of ^{1}H-NMR spectrum and all the derivatives were characterized using ^{1}H-NMR, IR and COSY spectrum. These quaternary derivatives were then investigated for antibacterial efficacy against two gram-positive and two gram-negative bacterial species using the MIC and the MLC values. Toxicity of the compounds was evaluated by treatment against human red blood cells. The amount of hydrophobicity in terms of chain length necessary for optimum activity against each bacterial strain has been optimized.

References

[1] Song, W.L., et al., Functionalized superhydrophobic biomimetic chitosan-based films. Carbohydrate Polymers, 2010. 81(1): p. 140-144.
[2] Muzzarelli, R.A.A. and F. Tanfani, The N-permethylation of chitosan and the preparation of N-trimethyl chitosan iodide. Carbohydrate Polymers, 1985. 5(4): p. 297-307.

Veggspjald 2

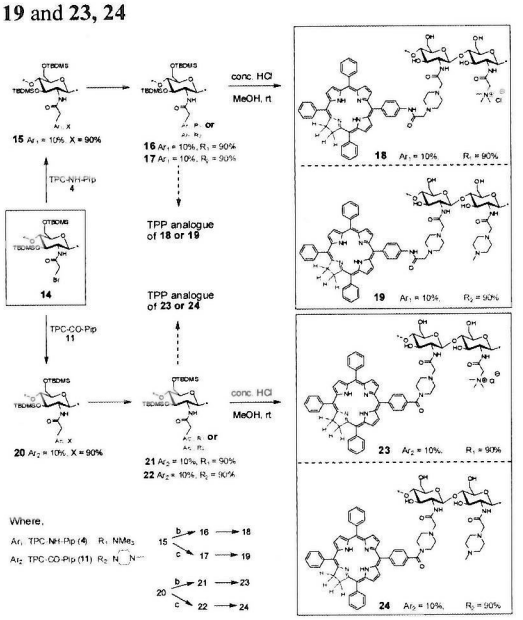
Synthesis and Characterization of meso-Tetraphenylchlorin Tethered Chitosan Based Nanocarriers for Photochemical Internalization

Vivek Gaware[†], Monika Håkerud[††], Sigríður Jónsdóttir[†††], Anders Høgset[††], Kristian Berg[††], Már Másson[†*]

[†] University of Iceland, Reykjavík, Iceland
[††] PCI Biotech AS, N-1366 Lysaker, Norway
[†††] The Norwegian Radium Hospital, N-0310 Oslo, Norway

Four amphiphilic *meso*-tetraphenylchlorin (TPC) conjugated chitosan carriers [$TPC_{NP0.1}$-CS-$TMA_{0.9}$ (**18**), $TPC_{NP0.1}$-CS-$MP_{0.9}$ (**19**), $TPC_{CP0.1}$-CS-$TMA_{0.9}$ (**23**), and $TPC_{CP0.1}$-CS-$MP_{0.9}$ (**24**)] were synthesized and evaluated for *in vitro* and *in vivo* study for use in the photochemical internalization[1] (PCI) in cancer therapy. Our, earlier in vitro study based on amphiphilic meso-tetraphenylporphyrin (TPP) conjugated chitosan showed promising results for PCI,[2] therefore, in the current study we have synthesized chlorin conjugated chitosan which unlike porphyrin, could absorb light in red region and thus allow deep tissue penetration and effective treatment of large lesions in vivo. The protocol for synthesis of two monofunctional hydrophobic chlorin photosensitizers, 5-(*p*-aminophenyl)-10,15,20-triphenylchlorin [$TPC(p\text{-}NH_2)_1$] and 5-(*p*-carboxyphenyl)-10,15,20-triphenylchlorin [$TPC(p\text{-}CO_2H)_1$] was optimized. The monofunctional photosensitizers were covalently attached to 3,6-di-O-*tert*-butyldimethylsilyl-chitosan (DiT-BDMS-CS) with 0.10 degree of substitution. Trimethylammoniumyl (TMA) and/or 1-methylpiperazinyl (MP) moieties were then introduced with 0.9 degree of substitution to give fully water soluble final TPC-CS carriers (**18**, **19**, **23** and **24**) after TBDMS deprotection as shown in Scheme 1. Dynamic light scattering results confirmed the formation of nanoparticles with a 100-400nm diameter. These carriers could be activated at 650 nm (red region) light and are thus suitable candidates for use in PCI for cancer treatment. These compounds were evaluated *in vitro* for light induced transfection of EGFP-N1 in HCT116/LUC cells and showed enhancement of transfection. The carriers were also evaluated in preliminary *in vivo* experiments using tumor bearing Hsd:Athymic nude-*Foxn1*^{nu} female mice. Pictures of illuminated tumor-bearing mice treated with the carriers **24** and **19** either alone or together with the cytotoxic anti-cancer drug bleomycin can be seen in Figure 2. Untreated animals and animals injected with $TPCS_{2a}$ + bleomycin were used as controls. The nanocarriers induced a strong PCI effect; and seemingly stronger than the photosensitiser $TPCS_{2a}$ which is currently under clinical development for cancer treatment. The nanocarriers also showed substantial selectivity and are therefore promising for PCI in cancer therapy.

Scheme 1. Synthesis of TPC-chitosan nanocarriers **18**, **19** and **23**, **24**



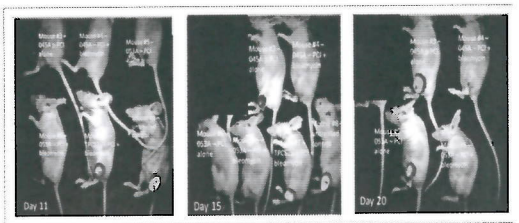


Figure 2. *In vivo* bioluminescence imaging after PCI treatment of tumor-bearing animals with TPC-chitosan conjugates (**24** and **19**) and bleomycin. The treatment for each animal and the time point for imaging (days after photosensitizer injection) are indicated.

References:
[1] K Berg et al. Cancer Res. **1999,** 59 (6), 1180-1183.
[2] V Gaware et al. J Med Chem **2013,** 56 (3), 807-819.

Veggspjald 3

Stöðgun nautatrypsín með leysanlegum kítófásykrakrossteningum og efnabreytingum á yfirborði með glúkósamíni

Jóhann Gretar Kröyer Gizurarson og Hörður Filippusson

Raunvísindastofnun Háskólans, Lífefnafræðistofa, Dunhaga 3, 107 Reykjavík

Á síðustu áratugum, hefur orðið vaxandi eftirspurn eftir stöðugari ensímum fyrir ýmis not í líftækni og lyfjageiranum sem og í iðnaði.

Krosstenging ensíma við kolhýdratafjölliður hefur verið tiltölulega vinsæl krosstengingaraðferð. Glýkósýlering á óglýkósýleruðum ensímum getur leitt til mikillar breytingar á eðli þeirra, en kosturinn við krossteningu er að ensímin verða oft stöðugri gagnvart hita and sjálfmeltu (í tilfelli próteasa) o.s.frv. geymsluþol eykst gjarnan líka. Helsti ókostur þessarar aðferðar er töpuð virkni.

Það er talið að krosstengjandi kolhydröt auki stífni sameindanna, minnki snertingu óskautaðra amínósýruleifa við leysinn o.s.frv. Efnatengingar á yfirborði með einvirkum eða fásykrum sem ekki valda krosstengingum stöðga ensím á svipaðan hátt en einnig gæti „preferential hydration"-fyrirbærið lagt stöðgununni lið.

Í okkar rannsóknum hefur markmiðið verið að stöðga trypsín sameindir með krossteningu kítófásykra (kítósan) sem og efnateningar á yfirborði ensímsins með glúkósamíni til samanburðar. Kítósanið sem notast var við í þessu rannsóknarverkefni er óeinsleit blanda af 4-8 glúkósamín-/N-asetýlglúkósamínleifum.

Báðar gerðirnar af breytta trypsíninu voru búnar til með því að láta frjálst trypsín hvarfast við kítófásykrunar í návist 1-Eþýl-3(dímeþýlamínóprópýl)- karbódíímið og N-hýdróxysúlfósúkkínímið í lítt súrum böffer í 24 klst. Þetta hvarf kúplar saman súrar amínósýruleifar á yfirborði trypsínsameinda við amínóhóp/a glúkósamín og kítófásykranna.

Tvö mismunandi hlutföll krosstengdra ensíma voru valin fyrir verkefnið, 1:5 og 1:10 ensím:kítósan. Rannsóknir á stöðugleika breyttu trypsínsameindanna gagnvart háum hita og úreu (karbamíð/þvagefni), mótstöðu gagnvart sjálfmeltu, Michaelis Menten hraðfræði, virkni við mismunandi sýrustig, mati á mólmassa breyttu trypsínsameindanna og breytingum á annars stigs byggingu voru rannsakaðar eða er ennþá verið rannsaka.

Þrátt fyrir að rannsóknargögnin séu ekki tilbúin að fullu, lofa niðurstöður úr stöðugleikamælingum og sjálfmeltumælingum góðu. Krosstenging kítófásykra af þessari gerð virðist vera stöðugleikaaukandi fyrir trypsín við fyrrgreindar aðstæður.

Poster 3

Stabilization of bovine trypsin by soluble chitooligosaccharide crosslinking and surface modification with glucosamine

Jóhann Grétar Kröyer Gizurarson and Hörður Filippusson

Raunvísindastofnun Háskólans, Lífefnafræðistofa, Dunhaga 3, Reykjavík

Over the past decades, there has been a growing demand for high stability enzymes for miscellaneous biotechnological, pharmaceutical and industrial purposes.

Crosslinking enzymes with carbohydrate polymers has been a rather popular crosslinking method. Glycosylation of naturally occuring unglycosylated enzymes can change their functionality dramatically, the advantages of this is that the enzyme may become more stable toward heat, autolysis (in case of proteinases) etc. as well as it can improve storage stability. However, the most common disadvantage of this method is reduced activity.

It is thought that crosslinker carbohydrate polymers increase the structural rigidity of the enzyme, reduce the exposure of nonpolar residues toward the solvent etc. Surface modification with monofunctional or non-crosslinking oligosaccharide stabilize enzyme similarily as crosslinking, although preferential hydration may also be a contributing factor.

In our research the aim has been to provide increased stability to trypsin molecules by crosslinking with chitooligosaccharide (chitosan) and by surface modification with glucosamine for comparison. The chitosan used in this research are heterogenous mixture of 4-8 glucosamine/N-acetylglucosamineresidues.

Both preparations were made by letting native trypsin react with the oligosaccahride or glucosamine in the presence of 1-Ethyl-3-(Dimethylaminopropyl)carbodiimide and N-Hydroxysulfosuccinimide in sligthly acidic buffer for 24h. This reaction couples acidic residues on the trypsin surface to amino group/s on the chitooligosaccharide and on the glucosamine.

Two different ratios of crosslinked enzyme were chosen for this study 1:5 and 1:10 enzyme:chitosan. Studies on stability in high temperature and urea (carbamide) , susceptibility toward autolysis, Michaelis Menten kinetics, pH profiles, estimation of molecular size of the preperations and conformational characterization have been conducted or are ongoing.

Although the study has not been completed yet the results on the temperature stability and autolysis are promising. Chitooligosaccharides seem to be a good stabilizing crosslinker for trypsin under the aforementioned conditions.

Veggspjald 4

Nýsmíði og greining afleiða af 1,3,5-trísílasýklóhexani

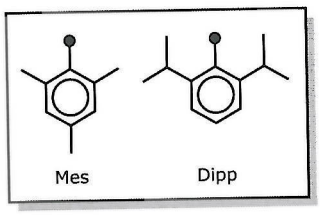
Ísak Sigurjón Bragason†*, Ingvar Helgi Árnason†, Yosiyuki Mizuhata‡, Norihiro Tokitoh‡

† Háskóli Íslands, Raunvísindastofnun, Dunhaga 3, 107 Reykjavík
‡ Kyoto University, Institute for Chemical Research, Gokasho Uji-city, Kyoto

Ýmsir hraðafræðilega stöðgaðir mónósílaarómatar og nokkrir dísílaarómatar hafa verið smíðaðir[1–8]. Forsendur hraðafræðilegrar stöðgunar kísilatómanna í þessum efnum er álagning gríðarlega rúmfrekra hópa eins og Tbt (Tbt = 2,4,6-tris[bis(trímetýlsílýl)metýl]fenýl)[1] og Bbt (Bbt = 2,6-bis[bis(trímetýlsílýl)metýl]-4-[tris(trímetýlsílýl)metýl]fenýl)[2].

Þrátt fyrir að stöðug trísílabensen hafi ekki enn verið smíðuð hafa tilraunir bent til myndunar 1,3,5-trísílabensens í hvörfum hliðarmálmjóna og sýklópentadíenýlhliðarmálmjóna við 1,3,5-trísílasýklóhexan í gasfasa[9]. Að auki benda niðurstöður reiknirannsókna til að myndun slíkra sameinda sé varmafræðilega hagkvæm[10, 11].

Við höfðum áhuga á smíði hraðafræðilega stöðgaðs 1,3,5-trísílabensens. Sökum innbyrðis nálægðar kísilatómanna í slíkri sameind er ekki vænlegt að nota gríðarlega rúmfreka hópa eins og Tbt eða Bbt. Í ljósi þessa leituðum við leiða við nýsmíði forefnis fyrir 1,3,5-trísílabensen úr 1,3,5-trísílasýklóhexani, sem stöðgað væri með minni, en þó rúmfrekum, hópum (Mynd 1).



Mynd 1: Rúmfrekir hópar sem valdir voru til stöðgunar kísilatómanna í efnasmíðum okkar.

Ný 1,3,5-trísílasýklóhexön með ýmsum sethópum voru smíðuð og greind með NMR og einkristallagreiningum. Þessar rannsóknir náðu hámarki þegar það heppnaðist að smíða 1,3,5-tríklóró-1,3,5-tris(Dipp)-1,3,5-trísílasýklóhexan, sem við teljum vera álitlegan forvera 1,3,5-trísílabensens (Skema 1).

Heimildir

[1] Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; von Ragué Schleyer, P.; Jiao, H. *Journal of the American Chemical Society* **1997**, *119*, 6951–6952.

[2] Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *Journal of the American Chemical Society* **1999**, *121*, 11336–11344.

[3] Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angewandte Chemie International Edition* **2000**, *39*, 634–636.

[4] Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256–258.

[5] Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024–4026.

[6] Tokitoh, N.; Shinohara, A.; Matsumoto, T.; Sasamori, T.; Takeda, N.; Furukawa, Y. *Organometallics* **2007**, *26*, 4048–4053.

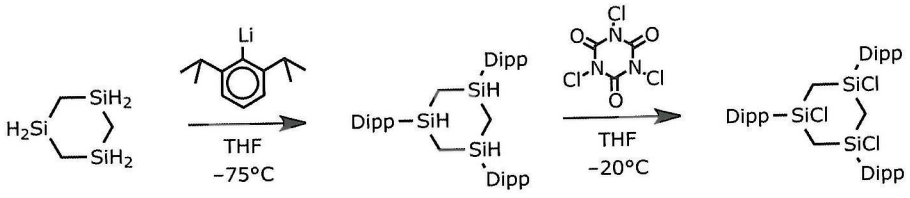
[7] Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. *Journal of the American Chemical Society* **2007**, *129*, 7766–7767, PMID: 17542592.

[8] Sen, S. S.; Khan, S.; Nagendran, S.; Roesky, H. W. *Accounts of Chemical Research* **2012**, *45*, 578–587.

[9] Bjarnason, A.; Arnason, I. *Angewandte Chemie International Edition in English* **1992**, *31*, 1633–1634.

[10] King, R. A.; Vacek, G.; Schaefer III, H. F. *Journal of Molecular Structure: THEOCHEM* **1995**, *358*, 1–14.

[11] Baldridge, K. K.; Uzan, O.; Martin, J. M. L. *Organometallics* **2000**, *19*, 1477–1487.



Skema 1: Leið að smíði 1,3,5-trísílabensen forvera með 1,3,5-trísílasýklóhexan sem upphafsefni.

Poster 4

Synthesis and analysis of derivatives of 1,3,5-trisilacyclohexane

Ísak Sigurjón Bragason†*, Ingvar Helgi Árnason†, Yosiyuki Mizuhata‡, Norihiro Tokitoh‡

† University of Iceland, Science Institute, Dunhaga 3, 107 Reykjavík
‡ Kyoto University, Institute for Chemical Research, Gokasho Uji-city, Kyoto

Several kinetically stabilized monosilaaromatics and some disilaaromatics have been synthesized[1–8]. Kinetic stabilization of the silicon centres in these substances is achieved through the addition of extremely bulky groups such as Tbt (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)[1] and Bbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl)[2].

Stable trisilabenzenes have not yet been synthesized. However, experimental evidence exist suggesting the formation of a 1,3,5-trisilabenzene in gas-phase reactions of transition metal ions and cyclopentadienyl transition metal ions with 1,3,5-trisilacyclohexane[9] and indeed theoretical studies indicate the formation of such a compound to be thermodynamically feasible[10, 11].

We were interested in the synthesis of a kinetically stabilized 1,3,5-trisilabenzene. However, due to the close proximity of the three silicon centres in such a compound, kinetic stabilization through addition of the extremely bulky Tbt and Bbt groups is not feasible. In light of this we sought a synthetic route from 1,3,5-trisilacyclohexane to a precursor for 1,3,5-trisilabenzene stabilized with smaller, yet bulky substituents (Figure 1).

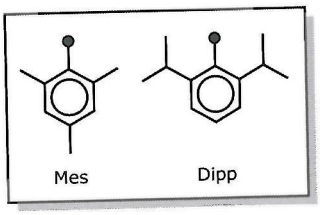


Figure 1: Bulky groups selected for stabilization of the silicon centres in our synthetic trials.

Several novel substituted 1,3,5-trisilacyclohexanes were synthesized and characterized by NMR and X-ray crystallographic techniques. This research culminated in the successful synthesis of 1,3,5-trichloro-1,3,5-tris(Dipp)-1,3,5-trisilacyclohexane (Dipp = 2,6-di(isopropyl)phenyl), which we believe is a promising precursor to 1,3,5-trisilabenzene (Scheme 1).

References

[1] Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; von Ragué Schleyer, P.; Jiao, H. *Journal of the American Chemical Society* **1997**, *119*, 6951–6952.

[2] Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *Journal of the American Chemical Society* **1999**, *121*, 11336–11344.

[3] Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angewandte Chemie International Edition* **2000**, *39*, 634–636.

[4] Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256–258.

[5] Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024–4026.

[6] Tokitoh, N.; Shinohara, A.; Matsumoto, T.; Sasamori, T.; Takeda, N.; Furukawa, Y. *Organometallics* **2007**, *26*, 4048–4053.

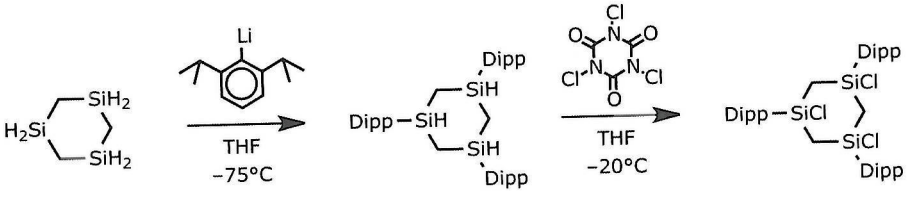
[7] Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. *Journal of the American Chemical Society* **2007**, *129*, 7766–7767, PMID: 17542592.

[8] Sen, S. S.; Khan, S.; Nagendran, S.; Roesky, H. W. *Accounts of Chemical Research* **2012**, *45*, 578–587.

[9] Bjarnason, A.; Arnason, I. *Angewandte Chemie International Edition in English* **1992**, *31*, 1633–1634.

[10] King, R. A.; Vacek, G.; Schaefer III, H. F. *Journal of Molecular Structure: THEOCHEM* **1995**, *358*, 1–14.

[11] Baldridge, K. K.; Uzan, O.; Martin, J. M. L. *Organometallics* **2000**, *19*, 1477–1487.



Scheme 1: A successful synthetic route from 1,3,5-trisilacyclohexane to promising precursor to 1,3,5-trisilabenzene.

Veggspjald 5

Myndun Mólybdenum Súlfíðó Komplex í Brottnámshvarfi Brennisteins

Jóhanna M. Grétarsdóttir, Sigríður G. Suman*

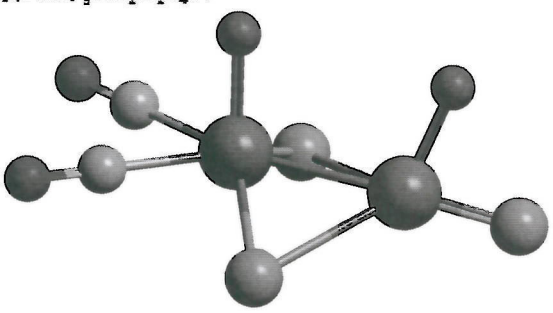
Raunvísindastofnun, Háskóli Íslands, Dunhagi 3, 107 Reykjavík, Ísland

Formáli

Cýaníð er efni sem er notað í iðnaði. Ef einstaklingur kemst í snertingu við of mikið magn af cýaníði gætir áhrifa eitrunar fljótt. Banvænn skammtur leiðir til dauða á innan við 20 mínútum. Meðferðarúrræði eru af skornum skammti og er þróun á skilvirkri meðferð því mikilvæg fyrir heilsu almennings. Mólybdenum komplexar sem innihalda óstöðug brennisteinsatóm virka oft sem skaðlausir brennisteinsgjafar í líffræðilegum kerfum. Þessi eiginleiki mólybdenum komplexa gerir þá hentuga í hvötun afeitrunar á cýaníðeitrun í mönnum.

Niðurstöður

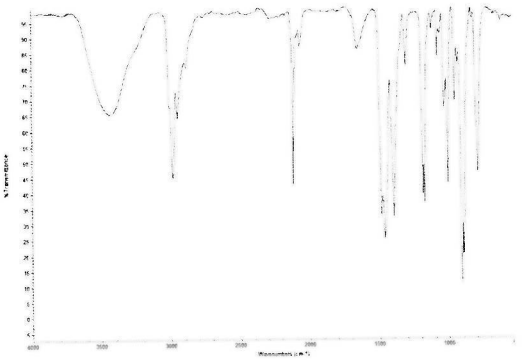
$(Et_4N)_2[(CN)_2Mo_2O_2S_3]$ (Mynd 1) var smíðað með auðvelda hvarfinu á Et_4NCN við $[(DMF)_3Mo_2O_2S_4]$.



Mynd 1. Módel af byggingunni á $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$. [1]

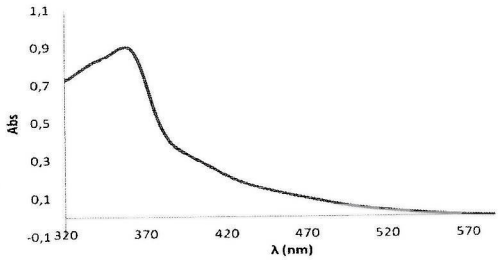
$(Et_4N)_2[(CN)_2Mo_2O_2S_3]$ hefur mólmassann 632.6176 gmól^{-1}. ESI MS staðfesti byggingu komplexins. Mæling í neikvæðu sviði sýndi topp við 501.8835 m/z, sem er í samræmi við anjón komplexins með hleðsluna -1.

Innrautt róf komplexins sýnir Mo – O teygjur við 891 og 904 cm^{-1} , Mo = S_t við 487 cm^{-1}, Mo – S_b við 468 cm^{-1} og C – N við 2116 cm^{-1} (Mynd 2).



Mynd 2. IR róf af $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$.

UV-vis róf af komplexinum sýnir topp við 358 nm (mynd 3). Gleypnifasti komplexins er 4665 L mol^{-1} cm^{-1}.



Mynd 3: UV-vis róf af $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$.

Heimildir

[1] D. Coucouvanis*, A. Toupadakis, A. Hadjikyriacou. Inorg. Chem. (1988) , Vol. 27, No. 19.

Poster 5

Formation of Molybdenum Sulfido Complex in a Sulfur Abstraction Reaction

Johanna M. Gretarsdottir, Sigridur G. Suman*

Science institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland

Introduction

Cyanide poisoning is rapid and treatment options are limited. An efficient mass treatment for cyanide poisoning is essential for public health. Molybdenum sulfur complexes containing labile sulfur atoms often serve as non-toxic sulfur donors in biological systems. This property makes molybdenum complexes suitable for the bioinorganic catalysis of cyanide detoxification.

Results

$(Et_4N)_2[(CN)_2Mo_2O_2S_3]$ (Figure 1) was synthesized by the facile reaction of Et_4NCN with $[(DMF)_3Mo_2O_2S_4]$.

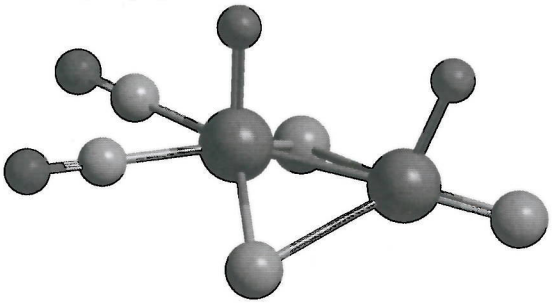


Figure 1. A model of the structure of $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$. [1]

$(Et_4N)_2[(CN)_2Mo_2O_2S_3]$ has the molecular weight of 632.6176 $gmol^{-1}$. ESI MS verified the structure of the complex. Negative scan mode showed a peak at 501.8835 m/z, which is consistent with the monoanion of the complex.

The infrared spectra of the complex shows Mo – O vibrations at 891 and 904 cm^{-1}, Mo = S_t at 487 cm^{-1}, Mo – S_b at 468 cm^{-1} and C – N at 2116 cm^{-1} (Figure 2).

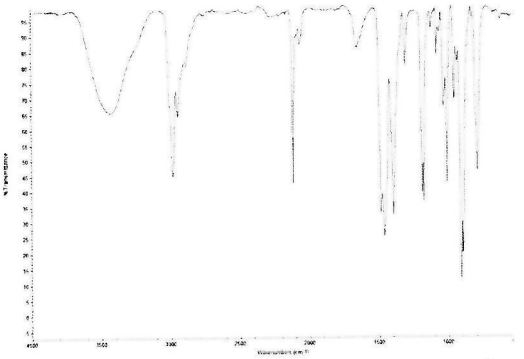


Figure 2. IR spectrum of $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$.

UV-vis spectrum of the complex shows a peak at 358 nm (Figure 3). The molar absorbtivity of the complex is 4665 L mol^{-1} cm^{-1}, which is consistent with a charge transfer transition.

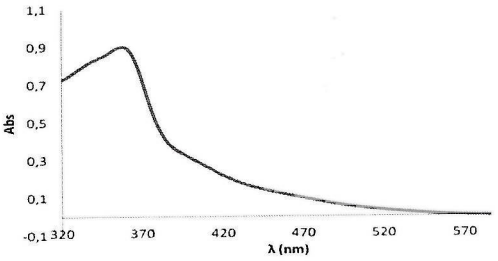


Figure 3: UV-vis spectrum of $(Et_4N)_2[(CN)_2Mo_2O_2S_3]$.

References

[1] D. Coucouvanis*, A. Toupadakis, A. Hadjikyriacou. Inorg. Chem. (1988), Vol. 27, No. 19.

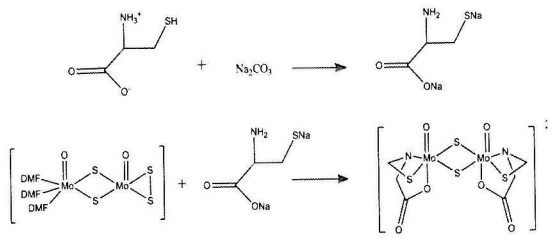
Veggspjald 6

Litrófsgreining á efnahvörfum $[Mo_2O_2S_4(DMF)_3]$ við Cysteine í lausn

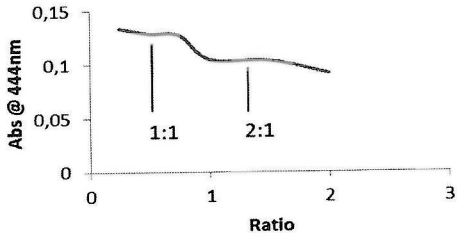
Jón Petur Gunnarsson, Sigridur G. Suman

Raunvísindastofnun, Háskóli Íslands, Dunhagi 3, 107 Reykjavik, Ísland

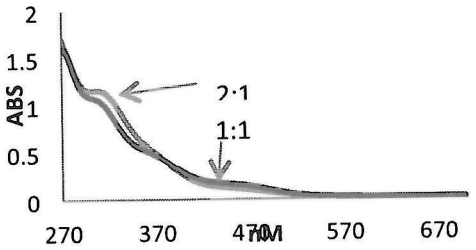
Cysteine er líffræðilega mjög mikilvægt mólekúl og hefur umtalverðan styrk í blóði. Það er mjög mikilvægt að skilja efnahvörf þess við [Mo2O2S4(DMF)3] í lausn. Rannsókn á efnahvarfi Na2Cysteins í lausn við [Mo2O2S4(DMF)3] voru framkvæmdar til að to ákvarða hvarftíman cysteins, sem og að ákvarða fjölda og eðli myndefna. Niðurstöður okkar sýna að hvarfinu líkur á tveimur klst. Lausnir voru útbúnar og látnar ná jafnvægi við staðalaðstæður. Niðurstöður úr mælingum lausnanna gáfu mettunarferla sem voru greindir.Greining sýndi að cysteine myndar 1:1 og 2:1 komplexa með $(Mo2O2S4)^{2+}$ jóninni. Hlutfallslegur styrkur cysteins og complex ræður hvort myndefnið myndast.



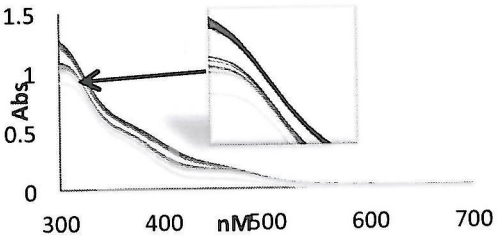
Mynd 1. Efnasmíði á Na salti af cysteine og hvarfi þess við við molybdenum komplex, [Mo2O2S2(S2)(DMF)3].



Mynd 2. Sýnir gleypni (@444nm) á móti hlutfalli Na_2Cysteine og $[(DMF)_3Mo_2O_2S_4]$.



Mynd 3. Sýnir mynd hlutfalls á milli $[(DMF)_3Mo_2O_2S_4]$ og Na_2Cysteine.



Mynd 4. Gröf af Na_2cysteine hvarfi við komplex 2,hægt er að sjá hvernig hvarfið ágerist, efsta línan er frá 10 sek eftir að Na_2Cystein er bætt út í og neðsta lína sýnir 24 tímum eftir að Na2Cysteini.

Niðurstöður:

Efnafræði molybdenum komplexsins við Na2Cysteine var rannsakað með mismunadi hlutföllum af Na2cysteine til að reyna að finna 1:1 komplex.

Heimildir:

[1] D. Coucouvanis, A. Toupadakis, J. D. Lane, S. M. Koo, C. G. Kim, and A. Hadjikyriacou, 1991. *J. Am. Chem. Soc. 1991, 113, 5271-5282*, Michigan.

[2] B. H. Sörbo, Acta Chem. Scand. 7, 1129 (1953).

[3] Nature, 219, 267-268,1968, A. Kay, P.C.H Mitch

Poster 6

Spectroscopic Study of the Solution Chemistry of $[Mo_2O_2S_4(DMF)_3]$ with Cysteine

Jón Petur Gunnarsson, Sigridur G. Suman*

Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland

Cysteine is a biologically important molecule and has significant concentration in blood. For the evaluation of a potential drug, it is important to understand its reaction chemistry with potential inhibitors in blood. As a first approximation, we undertook studies of the reaction of Na_2cysteine with the $[Mo_2O_2S_4(DMF)_3]$ complex. Equilibrium studies were conducted to determine the time it takes for the reaction with cysteine to complete. Our results show that the reaction is completed in 2 hours. The selectivity of the reaction of cysteine with was also probed by determining number and types of species formed in solution as a function of concentration of cysteine. Saturation curves analyzed in the equilibrium studies showed that 1:1 and 2:1 complexes with cysteine were formed, depending on the ratio of complex to cysteine employed.

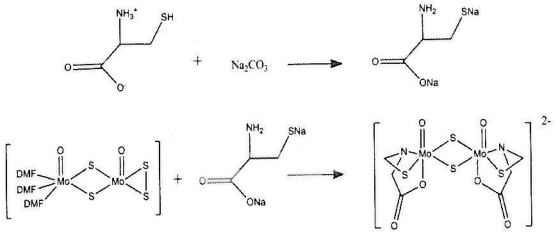


Figure 1. *Synthesis of sodium salt of cysteine and its reaction with the molybdenum complex, $[Mo_2O_2S_2(S_2)(DMF)_3]$.*

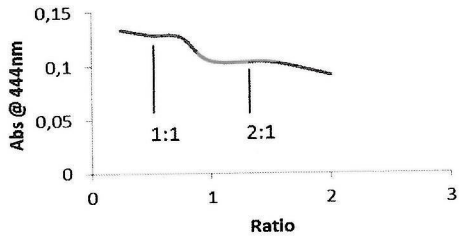


Figure 2. *Shows absorbance (444nm) as a function of the ration of Na_2cysteine to (1).*

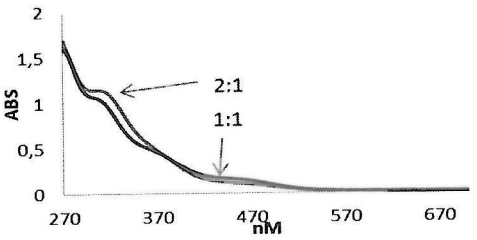


Figure 3. *Shows the electronic spectra of the two complexes formed between (1) and Na_2cysteine.*

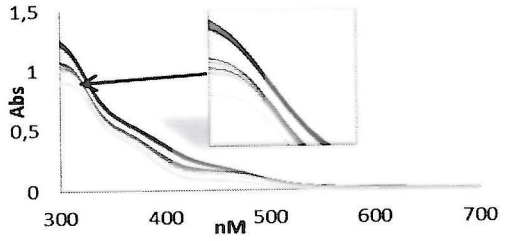


Figure 4. *Example graph of Na_2cysteine reacting with (1), the reaction was monitored as it progressed, the top line is from 10 sek after Na_2cystein injection and the bottom line is at 24 hour time point after injection.*

Conclusion:

Reaction chemistry of molybdenum complexes with Na_2cysteine was explored using various ratios of Na_2cysteine to try and find the 1:1 Complex. Saturation curves prepared in equilibrium studies showed that both 1:1 and 2:1 complexes of $[Mo_2O_2S_4(DMF)_3]$ with cysteine are formed, depending on the ratio of complex to cysteine employed.

References

[1] D. Coucouvanis, A. Toupadakis, J. D. Lane, S. M. Koo, C. G. Kim, and A. Hadjikyriacou. 1991. *J. Am. Chem. Soc. 1991, 113, 5271-5282*, Michigan.

[2] B. H. Sörbo, Acta Chem. Scand. 7, 1129 (1953).

[3] Nature. 219, 267-268,1968, A. Kay, P.C.H Mitchell

Veggspjald 7

Hraðafræði skiptihvarfs $[Mo_2O_2S_2(SCN)_4]^{2-}$ við síaníð.

Þorvaldur Snæbjörnsson[†], Sindri Frostason[†], Sigríður G. Suman*[†]

[†]Science Institute, University of Iceland, Dunhagi 3

Síaníð eitrun er hröð og meðferðarúrræði eru fá, sem veldur hárri tíðni dauðsfalla. Þau meðferðarúrræði í boði eru byggð á bindingu síaníðs við málm, svo sem Fe(III) í methemoglóbíni eða kóbalamín og afleiður þess, svo sem hydroxíkóbalamín og kóbinamíð [1]. Þessar meðferðir eru hlutfallslegar og binda venjulega eina eða tvær síaníð sameindir. Notkun tvímálma komplexa tvöfaldar fjölda bundinna síaníð sameinda á hverja komplex sameind.

Þíósíanat er aðlaðandi tengill fyrir síaníð-eitrunarmeðferð því það er skaðlaust myndefni í umbreytingu síaníðs af rhodanese enzíminu [2].

Við smíðuðum titilsameindina með fjórum þíósíanat tenglum og skoðuðum skiptihvarf þeirra við síaníð í DMF lausn með það að markmiði að meta skiptihvarfhraðan og myndunarfasta fyrir $[Mo_2O_2S_2(CN)_4]^{2-}$ anjónina. Hvarflok voru ákvörðuð með litrófsgreiningu rafeindarófs.

Figure 1. Sýnir hvarfið sem skoðað var með hraðafræðilegum rafeindarófsmælingum

Litrófsgreining yfir breitt bil bylgjulenda gerði okkur kleift að sjá breytingu tenglanna við molybdenum kjarnann.

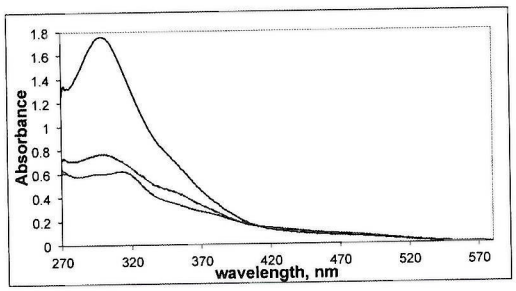


Figure 2. Sýnir niðurstöður fyrir hraðafræðilegar rafeindarófsmælingar. Efsti ferillinn er mæling á $[Mo_2O_2S_2(SCN)_4]^{2-}$ fyrir viðbót síaníðs. Seinni ferillinn er mæling skömmu eftir viðbót síaníðs, ath. hvernig síðustu fjóru mælingarnar eru allar eins.

Hratt efnahvarf er mikilvægt í fjarlægingu síaníðs, og því mældum við hraðafasta efnahvarfsins með rafeindarófsmælingum. Hraðafræðilegar mælingar voru framkvæmdar með upphafshraða aðferð. Markmiðið var að ákvarða hvarfhraða $[Mo_2O_2S_2(SCN)_4]^{2-}$ við síaníð, hraðafasta þess og hvarfstig. Hraða lögmálið er sýnt í jöfnu (1). Hraðafastinn var mældur sem $k_{obs} = 8 \cdot 10^{11} M^{-2} \cdot s^{-1}$.

$$Rate = k_{obs}[Mo_2O_2S_2(SCN)_4]^m[CN]^n \quad (1)$$

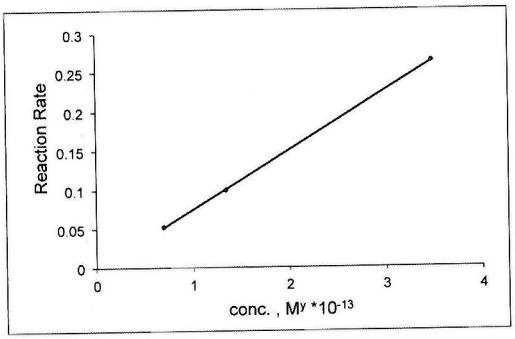


Figure 3. Graf hvarfhraða (reaction rate) sem fall af styrk (conc.) eins og sýnt í jöfnu (1). $y = m + n$

Við höfum sýnt að með því að breyta tenglaumhverfi $[Mo_2O_2S_2]^{2+}$ miðjunnar er hægt að binda mikið af síaníði mjög hratt. Okkar hraðafasti er sambærilegur hraðaföstum skiptihvarfs sem mældir voru fyrir kóbalamín með þíósíanati og síaníði [3].

Heimildir

[1] M. Brenner et al., *Ann Emerg Med.*, **2010**, 55, 352-363.

[2] M. S. Alphey et al., *J. Biol. Chem.*, **2003**, 278 (48), 48219-48227.

[3] M. Panda, N. C. Robinson, Biochem., 43:10009-10018, 1995.

Poster 7

Kinetics of the exchange reaction of $[Mo_2O_2S_2(SCN)_4]^{2-}$ with cyanide.

Thorvaldur Snæbjörnsson[†], Sindri Frostason[†], Sigridur G. Suman*[†]

[†]Science Institute, University of Iceland, Dunhagi 3

Cyanide poisoning is rapid and treatment options are limited, and thus the survival rate is low. Available cyanide treatments are based on cyanide binding to a metal such as Fe(III) in methemoglobin, or in cobalamin and its derivatives such as hydroxocobalamin and cobinamide[1]. These treatments are stoichiometric and normally bind one or two cyanide molecules.
A different approach, using bimetallic complex increases the number of cyanide molecules bound per mole of complex twofold.

Thiocyanate is a nontoxic, attractive ligand for a cyanide poisoning treatment because it is a natural metabolite formed in the conversion of cyanide by the rhodanese enzyme [2].

We synthesized the title molecule with four thiocyanate ligands and studied the exchange reaction of the thiocyanate ligands with cyanide in DMF in our efforts to evaluate the ligand exchange reaction rate and formation constant for the $[Mo_2O_2S_2(CN)_4]^{2-}$ anion. The completion of the ligand exchange was verified spectroscopically using UV/visible (fig. 2).

Figure 1. Shows the reaction studied in a kinetic UV/visible measurement.

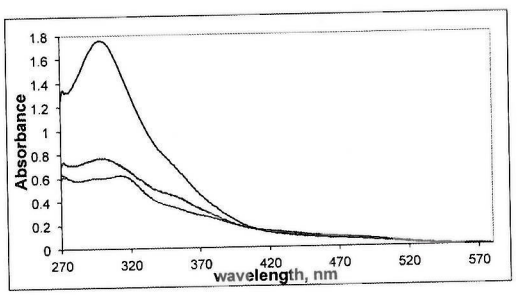


Figure 2. Shows the results for kinetic UV/visible measurements. Topmost curve represents $[Mo_2O_2S_2(SCN)_4]^{2-}$ before addition of CN^-. Second curve is moments after addition of four equivalents of CN^-, note how the last

Rapid reaction is important for cyanide removal, therefore we undertook measuring the rate constant for this reaction using UV/visible spectroscopy.
Kinetic measurements were performed using initial rates method. The goal was to determine the rate of reaction of $[Mo_2O_2S_2(SCN)_4]^{2-}$ with cyanide, its rate constant as well as its order of reaction. The rate law is shown in eq. (1). The rate constant was found to be $k_{obs} = 8 \cdot 10^{11} M^{-2} \cdot s^{-1}$.

$$Rate = k_{obs}[Mo_2O_2S_2(SCN)_4]^m[CN]^n \quad (1)$$

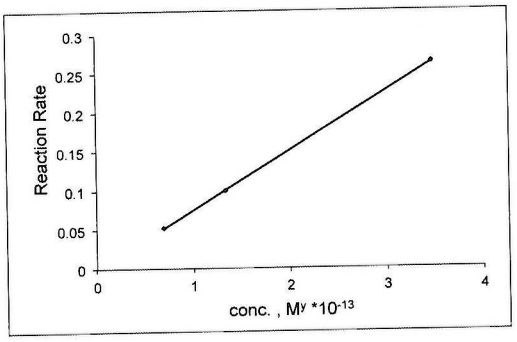


Figure 3. Plot of reaction rate as a function of concentration as shown in eq. (1). $y = m + n$.

We have shown that by changing the ligand environment of the $[Mo_2O_2S_2]^{2+}$ center it was possible to bind a lot of cyanide very quickly. Our observed rate constant is comparable to exchange reaction rate constants measured for cobalamine with thiocyanate and cyanide[3].

Heimildir

[1] M. Brenner et al., *Ann Emerg Med.*, **2010**, 55, 352-363.

[2] M. S. Alphey et al., *J. Biol. Chem.*, **2003**, 278 (48), 48219-48227.

[3] M. Panda, N. C. Robinson, Biochem., 43:10009-10018, 1995.

Development of a Novel Electrophoretic Deposition (EPD) Method for Depositing Chitosan on Titanium Implants

Markéta Foley[1], Ramona Lieder[1,2], Joseph T. Foley[1], Gissur Örlygsson[3] and Ólafur E. Sigurjónsson[1,2]

[1]School of Science and Engineering, Reykjavík University
[2]REModel Lab, The Blood Bank, Landspítali University Hospital
[3]Department of Materials, Biotechnology and Energy, Innovation Center Iceland

INTRODUCTION

Titanium and titanium alloys are frequently utilized in clinical treatment of orthopaedic injuries. Considerable research has focused on improving bone attachment to implants by coating titanium with biomaterials. Chitosan, a partially deacetylated form of chitin, is a promising coating agent under investigation[1]. Electrophoretic deposition (EPD) is currently being explored as a technique for applying bioactive coatings to implant surfaces[2].

EXPERIMENTAL METHODS

In this study, an EPD method was developed to coat titanium with chitosan. The titanium surface was pre-treated by sand-blasting and/or acid etching to obtain desired surface roughness. Chitosan (DD 87%) was solubilized in acetic acid (0,4 - 1% v/v). EPD was performed using a titanium cathode under constant voltage conditions with generated electric fields ranging from 0.5 to 6 V/cm. Coated surfaces were characterized by light microscopy, water contact angle measurement, SEM, and AFM.

RESULTS AND DISCUSSION

Preliminary results suggest that EPD is well-suited for depositing chitosan onto titanium implants (Figure 1). No detachment was observed when coated titanium was incubated in cell culture medium during a 3-week study. Obtained coatings were porous due to gas bubble entrapment at the cathode. Furthermore, electric field fringing effects led to increased deposition along plate edges. Future work will focus on minimizing porosity by using pulse-width modulation in place of constant voltage EPD. To reduce fringing effects and assist in reduction of porosity, a new EPD chamber with a vertical inter-electrode axis and a special sample mounting has been designed. Furthermore, in vitro cell culture experiments with MC3T3-E1 mouse pre-osteoblasts are planned to analyse cell bioactivity.

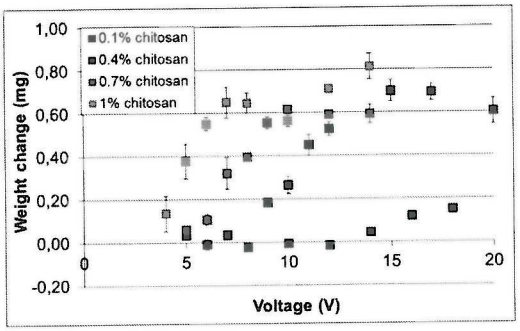


Figure 1: Weight changes experienced by titanium electrodes as a function of applied voltage during the EPD process. The weight change represents the mass of chitosan deposited on the electrode. Error bars 1 σ.

CONCLUSION

EPD is well-suited for attaching chitosan to titanium. Chitosan was successfully deposited onto differently pre-treated titanium surfaces of varying roughness.

REFERENCES

1. M.R. Leedy et al., Adv. Polym. Sci. 244 (2011) 129-165.

2. A.R. Boccaccini et al., J. R. Soc. Interface 7 (2010) S581-S613.

ACKNOWLEDGMENTS

The authors would like to thank the Icelandic Research Fund (grant no. 090007023) and the Landspítali University Hospital research fund for providing financial support to this project, and Heiðdís Rut Hreinsdóttir and Andrew Marc for engaged project work.

Veggspjald 9

Framleiðsla kísil-nanóvíra með málmhvataðri ætingu

Birgir H. Hallgrímsson[1], Kristján Leósson[2], Halldór G. Svavarsson[1]*

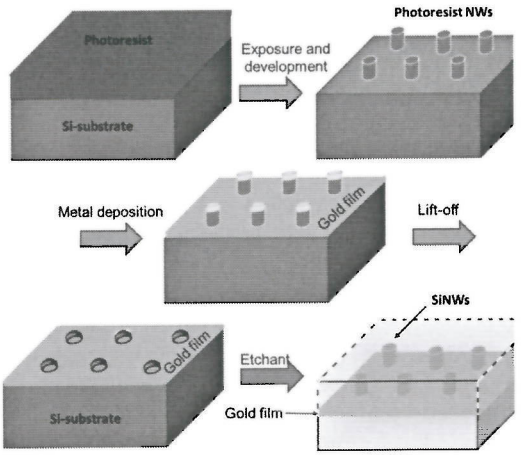
[1]Háskólinn í Reykjavík – Tækni- og Verkfræðideild
[2]Háskóli Íslands – Raunvísindastofnun
**halldorsv@ru.is*

Byggingareiningar í örsmæðar stærð munu gegna stóru hlutverki í framtíðarþróun á sviði skynjaratækni og orkuvinnslu. Vírar með þvermál á nm stærðarbili (NWs) hafa til dæmis verið framleiddir með notkun á sviði sólarhlaða, hitarafmagns-tóla og Raman mögnunar (surface enhanced Raman scattering; SERS) í huga. Hér er lýst notkun málmhvataðrar ætingar [1] við framleiðslu kísil nanóvíra (SiNWs). Aðferðin byggir á mjög stefnuháðri rafefnafræðilegri ætingu kísilskífa í snertingu við málmhvata. Með aðferðinni er unnt að fá þéttar breiður af einkristalla kísilvírum með hátt lengdar-breiddar hlutfall. Ætingin fer fram í þynntri lausn af flúrsýru (HF) og mildum oxara á borð við H_2O_2 og á sér stað á þeim hluta kísilskífunnar sem er í beinni snertingi við málmhvatann. Sé sett þunnt lag af nanó-mynstruðum málmhvata á kísilskífuna mun ætta svæðið hafa sömu útlínur og málm mynstrið. Gull (Au), silfur (Ag) og platína (Pt) eru best þekktu málmhvatarnir. Ein leið til að setja nanó málmmynstur á stór svæði (tugi cm^2) er að nota laser bylgjuvíxlverkunar litógrafíu (LIL) [2] en með slíkri aðferð er hægt að mynda stórar breiður af lotubundnu ein- og tvívíðu mynstri með lotur allt niður í fáa tugi nm í stærð.

Framleiðsla SiNWs fór fram með samþættri notkun málmhvataðri ætingu og laser bylgjuvíxlverkunar litografíu. SiNWs voru búnir til úr 2" einkristalla (100) kísilskífu, 350 μm að þykkt, í eftirfarandi skrefum:

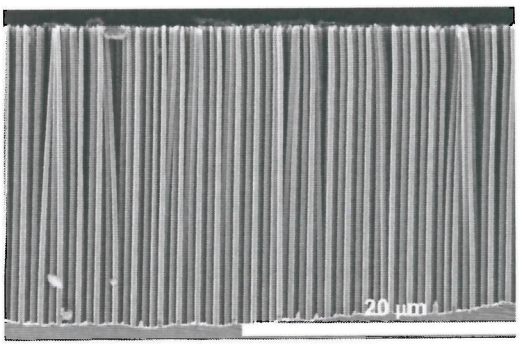
1. kísilskífan húðuð með ljósvirkum fjölliðum (photoresist)
2. víxlverkunar mynstri frá útfjólubláu laser ljósi varpað á kísilskífuna
3. sá hluti fjölliðanna sem ljósi var varpað á fjarlægður með framköllunar vökva
4. 20 nm þykkri Au-lagi húðað á skífuna
5. fjölliðunar mynstur fjarlægt með leysi (Lift-off)
6. kísilskífu dýft í ætilausn (HF, H_2O_2, H_2O).

Skýringateikningar af framleiðsluferlinu eru sýndar í Mynd 1. Rafeindasmásjár- (SEM) mynd af SiNWs eftir 60 mín. ætingu er sýnd í Mynd 2.



Mynd 1. Skýringarmynd af framleiðslu SiNWs með málmhvataðri ætingi. Ætingin á sér stað á samskeytum kísils og Au-málmhvatans.

Í Mynd 2 er lota víranna 500 nm, þvermál 300 nm og hæð um 20 μm.



Mynd 2. Þversnið af SiNWs sem fengust eftir 60 mín. Ætingu. Lota víranna er 500 nm, þvermál um 300 nm og lengd um 20 μm. Lengdar-breiddar hlutfallið ~ 70.

References

[1] Zhang et al, (2008). Preparation of large-area uniform silicon nanowires arrays through metal-assisted chemical etching. *Journal of Physical Chemistry*, **122** (12), 4444-4450.

[2] Svavarsson et al, (2011). Fabrication of Large Plasmonic Arrays of Gold Nanocups Using Inverse Periodic Templates. *Plasmonics*, **6** (4), 741-744.

Poster 9

Fabrication of silicon nanowires with metal catalyzed etching

Birgir H. Hallgrimsson[1], Kristjan Leosson[2], Halldor G. Svavarsson[1]*

[1]Reykjavik University – School of Science and Engineering
[2]University of Iceland – Science Institute
*Corresponding author: *halldorsv@ru.is*

Nanostructured devices hold great potential for the future advances in sensing technology and energy harnessing. Nanowires (NWs) have for instance been fabricated with surface enhanced Raman scattering (SERS), photovoltaic and thermoelectric applications in mind. Here, a fabrication of silicon NWs (SiNWs) using a newly developed technique, metal assisted etching (MAE) [1] will be described. The technique is based on highly anisotropic electrochemical etching with the aid of catalytic metal. MAE is capable of giving densely packed arrays of high aspect-ratio single-crystal SiNWs with tunable dimensions. A catalysed etching of a bulk Si-wafer in a water-based solution of hydrofluoric acid (HF) and a mild oxidizer (typically H_2O_2) is taking place in the vicinity of the metal catalyst. The etched part of the silicon will have exactly the same shape as the outlines of a nanoscale patterned film of a catalytic metal. The best known catalysts are gold (Au), silver (Ag) and platinum (Pt). A large scale nano-patterned metal film was deposited by means of so-called laser interference lithography (LIL) [2]. LIL is a maskless lithography technique capable of patterning large areas of 1-dimensional (1D) or 2D arrays, with dimensions down to few tens of nm.

Here, a fabrication of periodic arrays of silicon nanowires (SiNWs), using combined techniques of LIL and MAE, is introduced.

The SiNWs wera prepared from 2" single crystalline (100) Si wafer in the following chronological steps:

1. spin coating with positive photoresist (PR)
2. exposure to an interference pattern from a continuous-wave ultra-violet laser system.
3. removal of exposed PR (developing)
4. deposition of 20 nm thick Au-film
5. removal of remnant PR (Lift-off)
6. catalyzed etching of the Si in the vicinity of the gold pattern

A schematic presentation of the process is given in Fig. 1. An example of SiNWs is visualized in the scanning electrons microscope (SEM) image in Fig. 2.

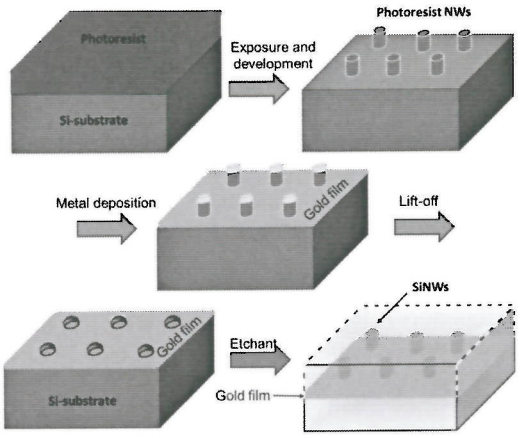


Figure 1. A schematic of the Metal Assisted Etching. The sample is immersed in hydrofluoric acid and the area under the gold film is etched.

The wires have diameter of 300 nm and height of roughly 20 μm.

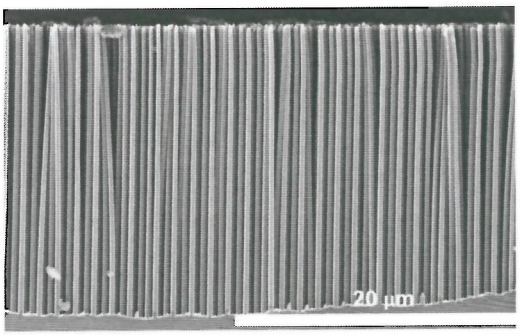


Figure 2. A cross-sectional SEM image of silicon nanowires with a diameter of 300 nm and a period of 500 nm. 60 min etching time. Aspect ratio ~ 70.

References

[1] Zhang et al, (2008). Preparation of large-area uniform silicon nanowires arrays through metal-assisted chemical etching. *Journal of Physical Chemistry,* **122** (12), 4444-4450.

[2] Svavarsson et al, (2011). Fabrication of Large Plasmonic Arrays of Gold Nanocups Using Inverse Periodic Templates. *Plasmonics*, **6** (4), 741-744

Veggspjald 10

Rannsóknir á stellingajafnvægi 1-methyl-1-germacyclohexane: Lághita kjarnarófsmælingar

Nanna Rut Jónsdóttir*†, Ingvar Árnason†, Sigríður Jónsdóttir†, Ágúst Kvaran† og Ragnar Björnsson‡

† Raunvísindastofnun Háskóla Íslands, Dunhagi 3, 107 Reykjavik
‡ Max-Planck Institute for Chemical Energy Conversion, Stiftstrasse 32-34, 45470 Mülheim an der Ruhr, Germany

Rúmefnafræði cyclohexans hefur verið rannsökuð ítarlega og er stellingajafnvægi einsetinna hringja vel þekkt. Rannsóknir á sexhringjum sem innihalda önnur atóm úr flokki 14 í lotukerfinu eru hins vegar mun skemur á veg komnar. Á síðustu árum hafa ýmsar afleiður að setnum kísilhringjum verið rannsakaðar og nýverið hófust rannsóknir á setnum germaníumhringjum. Áður hafa verið birtar niðurstöður á rannsóknum á stellingajafnvægi 1-methyl-1-germacyclohaxane. Niðurstöður mælinga með lághita kjarnarófsmælingum (DNMR) bentu til þess að sethópurinn væri frekar í áslægu stellingunni eða í hlutföllunum 60/40 % áslæg/ þverlæg [1, 2]. Í þessu verkefni er þessi rannsókn endurgerð og mælingar framkvæmdar með þeim aðferðum sem hafa reynst vel við sams konar mælingar á setnum kísilhringjum. Efnasmíðar á 1-methyl-1-germacyclohexan voru framkvæmdar og stellingajafnvægi þess skoðað með áherslu á jafnvægi milli áslægs og þverlægs stólforms sameindarinnar með DNMR mælingum. Niðurstöður NMR mælingarinnar sýndu að hlutfallið milli áslægs og hliðlægs stellingarforms var 44/56 mól % við 114 K sem samsvarar að A gildi ($A = G_{ax} - G_{eq}$) sé 0.06 kcal mól^{-1}.

Mynd 1: Þverlæg og áslæg stelling 1-methylgermacyclohexan

Meðalvirkjunarorkan ($\Delta G^{\ddagger}$) fyrir 106-134 K var reiknuð 5.0±0.1 kcal mól^{-1}. Þessar niðurstöður eru í góðu samræmi við skammtafræðilega reiknuðu gildin A gildi uppá 0.02 kcal mól^{-1} og Δ E = 0.01 kcal mól^{-1} við 0 K [3].[3]

Heimildir

[1] Takeuchi, Y.; Ichikawa, Y.; Tanaka, K.; Kakimoto, N. *Bull. Chem. Soc. Jpn* **1988**, *61*, 2875–2880.

[2] Takeuchi, Y.; Shimoda, M.; Tanaka, K.; Tomoda, S.; Ogawa, K.; Suzuki, H. *J. Chem. Soc. Perkin Trans. II* **1988**, *1*, 7–13.

[3] Jonsdottir, N. R.; Ágúst Kvaran,; Jonsdottir, S.; Arnason, I.; Bjornsson, R. *Structural Chemistry* **2013**, *24*, 769–774.

Poster 10

Conformational properties of 1-methyl-1-germacyclohexane: Low temperature NMR measurements

Nanna Rut Jonsdottir†*, Ingvar Arnason†, Sigridur Jonsdottir†, Agust Kvaran† and Ragnar Bjornsson‡

† Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik
‡ Max-Planck Institute for Chemical Energy Conversion, Stiftstrasse 32-34, 45470 Mülheim an der Ruhr, Germany

The steriochemistry of cyclohexane have been investigated thoroughly and the conformational properties of monosubstituted cyclohexanes are well known. Far less research has been reported on six-membered rings containing heavier element from group 14 in the periodic table. In recent years several derivatives of substituted silacyclohexanes have been investigated at the Science Institute and investigation on conformational properties of monosubstituted germacyclohexanes started recently. Previously reported research on 1-methyl-1-germacyclohexane where the result from dynamic magnetic resonance (DNMR) measurements showed axial preference in the ratio 60/40 % axial/equatorial [1, 2]. The aim of this study was to reexamine the conformational properties of the compound and use experimental and theoretical methods that have proven successful in investigation on substituted silacyclohexanes. The methyl substituted germacyclohexane was synthesized and the conformational behaviour of the compound, in terms of axial and equatorial chair conformers, was investigated by means of dynamic nuclear magnetic resonance (DNMR) measurements.

Figure 1: Equatorial and axial conformers for 1-methyl-1-germacyclohexane.

The result from the NMR experiment showed the axial/equatorial ratio to be 44/56 mol % at 114 K corresponding to an A value ($A = G_{ax} - G_{eq}$) of 0.06 kcal mol $^{-1}$. The average free energy of activation ($\Delta G^{\ddagger}$) for the temperature range 106-134 K was found to be 5.0±0.1 kcal mol^{-1}. These results are in good agreement with the quantum chemical calculated values, A value of 0.02 kcal mol^{-1} and ΔE of 0.01 kcal mol^{-1} at 0 K [3].

References

[1] Takeuchi, Y.; Ichikawa, Y.; Tanaka, K.; Kakimoto, N. *Bull. Chem. Soc. Jpn* **1988**, *61*, 2875–2880.

[2] Takeuchi, Y.; Shimoda, M.; Tanaka, K.; Tomoda, S.; Ogawa, K.; Suzuki, H. *J. Chem. Soc. Perkin Trans. II* **1988**, *1*, 7–13.

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Veggspjald 11

Ósamhverfar hreyfingar í samhverfu tvíeininga ensími koma í ljós við tölvureikninga á kvikum sveigjanleika. Gott dæmi er kuldavirkur alkalískur fosfatasi úr Vibrio kaldsjávarörveru.

Ásgeirsson, B.[1], Renzetti, G.[2], Invernizzi, G.[2], Papaleo, E.[2]

[1]Raunvísindastofnun háskólans, Dunhagi 3, 107 Reykjavik, Ísland (bjarni@hi.is).
[2]Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126, Milan, Italy.

Síkvikar hreyfingar próteina hafa áhrif á virkni og stöðugleika þeirra með áhrifum á stellingajafnvægi. Ósamgildir milliatóma- kraftar leika lykilhlutverk í slíkum hreyfanleika. Heildaráhrifin eru m.a. háð netskipan í víxlverkunum og samskiptum milli einstakra amínósýra. Samskipti og samtaka hreyfingar yfir skil á milli undireininga geta auk þess drifið hvötunarferlið á ósamhverfan hátt, líkt og hefur verið spáð fyrir um í tilfelli tveggja eininga í alkalískum fosfatasa (AP). Í því tilfelli eru umskipti í byggingu líklega hraðatakmarkandi fyrir hvötunarferlið en ekki efnafræðilegu breytingarnar. Við höfum rannsakað hér þær kviku hreyfingar sem vænta má í kuldavirkum AP úr örverunni *Vibrio splendidus* AP (VAP). Hermireikningar (e. multiple all-atom explicit solvent molecular dynamics simulations) voru nýttir til að framkalla ýmsa mælikvarða sem nýta má til að meta mynstur kvikra hreyfinga og þær leiðir sem slík boð gætu bortist innan undireininga og milli eininganna tveggja í lokamynd ensímsins. Samanburður á einingunum tveimur leiddi í ljós ólíka dreifingu tengsla innan eininganna á hverjum tíma og einnig voru þátttakendur í samtaka hreyfingum ólíkir (Mynd 1). Netgreining hópa frá hvarfstöð og í ytri hluta sameindarinnar var rakin og sýndi sú athugun að flutningur upplýsinga fór eftir ólíkum leiðum í einingunum tveimur. Í VAP reyndust fá tengi liggja yfir skilin milli undireiniganna og víxl-verkandi samtaka hreyfingar voru einnig fáar. Niðurstöðurnar gefa tilgátunni um víxlvirkni hvarfstöðva (e. half-of-site mechanism) stuðning í tilfelli VAP, líkt og áður var haldið fram og þá byggt á tilraunum með ensímum úr *E. coli* og spendýri. Aðferðir okkar gætu hentað rannsóknum á öðrum tvíeininga ensímum.

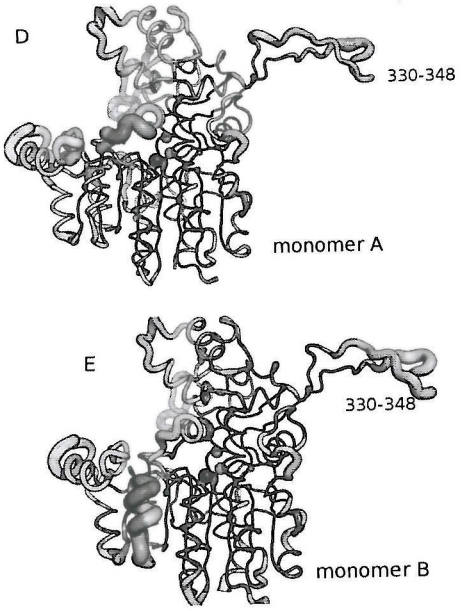


Figure 1. The average rmsf per-residue profiles were calculated (whole trajectory, 10 ns) and are mapped on the 3D structure of monomer A(D) and B (E) of the cold-active *Vibrio* alkaline phophatase after a structural alignment of the two subunits. The cartoon shade of color and thickness are proportional to the Cα rmsf values.

References

[1] Papaleo E, Renzetti G, Invernizzi G, Ásgeirsson B. Dynamics fingerprint and inherent asymmetric flexibility of a cold-adapted homodimeric enzyme. A case study of the *Vibrio* alkaline phosphatase. *Biochim Biophys Acta (BBA) - General Subjects.* 2013;1830(4):2970-2980.

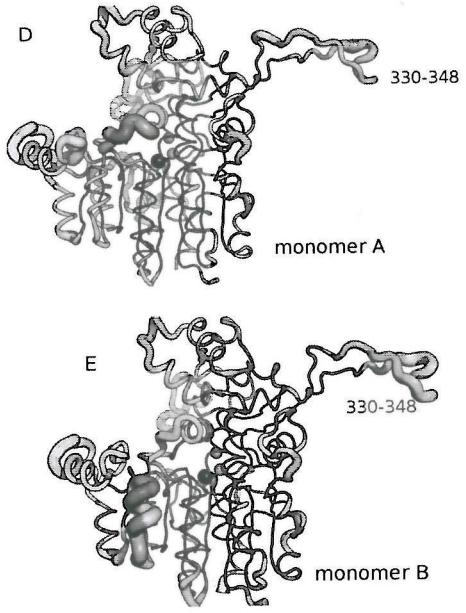
Poster 11

Asymmetric flexibility of a homodimeric enzyme as shown by molecular dynamics computations. A case study of the cold-active Vibrio alkaline phosphatase.

Ásgeirsson, B.*[1], Renzetti, G.[2], Invernizzi, G.[2], Papaleo, E.[2]

[1] Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland (bjarni@hi.is).
[2] Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126, Milan, Italy.

Protein dynamics influence protein function and stability by modulating conformational changes. Non-covalent intramolecular interactions play a key role for such motions. The total effect will depend on the underlying networks of communicating residues within the structure. Interactions and coupled motions over the interface between subunits may further drive the catalytic cycle asymmetrically, as has been suggested for the dimeric alkaline phosphatase (AP). In this case, a conformational change might be the rate-limiting step rather than the chemical transformations. Here, we present a characterization of the dynamic properties of the cold-adapted *Vibrio splendidus* AP (VAP). Multiple all-atom explicit solvent molecular dynamics simulations were employed in conjunction with different metrics to analyze the dynamics patterns and the paths of intra- and intermolecular communication. The comparison of the dynamic patterns of the two subunits in the dimeric structure pointed out a different distribution of intramolecular interactions and correlated motions (Fig 1). The paths of long-range communications mediated from the catalytic residues to distal sites were also characterized, suggesting a different information flow in the two subunits. VAP displayed a low number of intersubunit interactions and coupled motions between the two halves were also few. Our results provide a structural rationale to support the half-of-site mechanism for VAP as previously proposed for some other APs. The methods may lead to characterization of asymmetric dynamics in other homodimeric enzymes.



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Veggspjald 12

Truflanir í (2+n) REMPI rófum vetnis joðíðs

Helgi Rafn Hróðmarsson, Huasheng Wang, Ágúst Kvaran

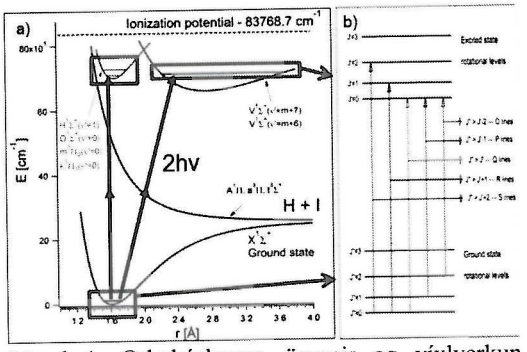
Raunvísindastofnun Háskóla Íslands, Dunhaga 3, 107 Reykjavík

Tvívíð (2D) fjölljóseinda-jónunar (e. resonance enhanced multi-photon ionization) gögn fyrir HI, sem innihéldu tveggja ljóseinda örvanir í Rydberg og jónparaástönd á 69 000–71 500 cm^{-1} sviðinu voru skráð með HI sameindastraumi. Til örvunar var notaður púslaður „excimer" leysir ásamt litleysi og tíðnitvöfaldara. Geislanum var beint í jónunarklefa á milli fráhrindi og aðdráttar platna. Jónir sem mynduðust með fjölljóseinda örvunum var beint inn í flugtímamassagreini (e. time of flight mass spectrometer) og þær greindar með MCP-greini (e. micro-channel plates detector). Kvörðun leysisins var byggð á sjáanlegum (2 + 1) joð atóma REMPI toppum. Nákvæmni bylgjutalna kvörðuninnar var yfirleitt í kringum ± 0.5 cm^{-1} á bylgjutalnaskala leysigeislans og því í kringum ± 2.0 cm^{-1} á bylgjutalnaskala tíðnitvöfaldaðrar tveggja-ljóseinda-örvunar.

Í þessum tilraunum var HI sameind örvuð úr grunnástandi sínu upp í örvað Rydberg ástand eða jón-para ástand. Ef sameindin er örvuð upp í Rydberg ástand, þá getur örvaða sameindin annað hvort örvast frekar og í kjölfarið jónast og myndað sameindajónina HI^+, eða sameindin getur víxlverkað við fráhrindandi ástönd og í kjölfarið klofnað ótímabært (e. predissociation). Frekari örvanir leiða þá til myndunar atómjónanna H^+ og I^+. Þ.a.l. þar sem Rydberg ástönd og jónparaástönd eru bundin ástönd, þá er hægt að greina snúnings byggingar (e. rotational structures) þeirra í REMPI litrófsgreiningum.

Á síðustu árum hafa nokkrar greinar verið birtar sem leggja áherslu á víxlverkun örvaðra ástanda og ljóssundrunarferla í HCl [1-4] og HBr[1,5,6]. Flestar rannsóknir sem framkvæmdar hafa verið á HI, hafa hins vegar lagt áherslu á beinar litrófsgreiningar Ryberg og jónpara ástanda þar sem engin áhersla hefur verið lögð á truflanir í rófunum að undanskilinni einni nýlega birtri grein um nýjar athuganir í REMPI rófi HI[7]. Í henni voru nýfundin Rydberg ástönd og jónpara ástönd tilkynnt og önnur sem einungis höfðu sést í gleypnirófum[8], en ekki REMPI rófum[9]. Minnst var á nokkur tilfelli truflanna, sér í lagi truflanir í $k^3\Pi_1(v' = 1)$ ástandinu, sem var talið vera truflað af $V^1\Sigma^+(v' = m + 7)$ jónpara ástandinu.

Nokkur Rydberg ástönd og jónpara ástönd voru skoðuð og mæld magnbundið m.t.t. truflana, m.a. $H^1\Sigma^+(v' = 1)$, $m^3\Pi_2(v' = 0)$, $R^1\Pi_1(v' = 0)$, $O^1\Sigma^+(v' = 0)$, og $k^3\Pi_1(v' = 1)$ Rydberg ástöndin og jónpara ástöndin $V^1\Sigma^+(v' = m + 6)$ og $V^1\Sigma^+(v' = m + 7)$ (Mynd 1).



Mynd 1. Orkubúskapur, örvanir og víxlverkun ástanda í HI. Rydberg ástönd eru grænmerkt og jónparaástönd blámerkt.

Truflanir vegna víxlverkana ástanda koma fram sem styrkleika flökt, línu hliðranir og línuvíddar breikkanir, en bæði fjær-hermandi (e. off-resonance) og nær-hermandi (e. near-resonance) víxlverkanir er að finna á milli Rydberg ástanda og jónpara ástanda.

References

[1] J. Long, H. Wang, and Á. Kvaran, J. Chem. Phys. **138** (2013).
[2] A. Kvaran, K. Matthiasson, and H. S. Wang, J. Chem. Phys. **131** (2009).
[3] Á. Kvaran *et al.*, J. Chem. Phys. **129** (2008).
[4] S. Kauczok *et al.*, J. Chem. Phys. **133** (2010).
[5] J. Long *et al.*, J. Chem. Phys. **136** (2012).
[6] J. Long, H. Wang, and Á. Kvaran, J. Mol. Spectrosc. **282** (2012).
[7] H. R. Hróðmarsson, H. Wang, and Á. Kvaran, Journal of Molecular Spectroscopy **290** (2013).
[8] D. S. Ginter, M. L. Ginter, and S. G. Tilford, J. Mol. Spectrosc. **92** (1982).
[9] S. T. Pratt, and M. L. Ginter, J. Chem. Phys. **102** (1995).

Poster 12

Perturbations in the (2+n) REMPI spectra of HI

Helgi Rafn Hróðmarsson, Huasheng Wang, Ágúst Kvaran

Raunvísindastofnun Háskóla Íslands, Dunhaga 3, 107 Reykjavík

Mass resolved resonance enhanced multiphoton ionization data for HI, for two-photon resonance excitations to Rydberg and ion-pair states in the 69 600–71 500 cm^{-1} region was recorded with a HI molecular beam, created by jet expansion of a pure sample through a pulsed nozzle. Excitation radiation was generated by pulsed excimer laser-pumped dye laser systems and frequency doubled radiation was focused on the molecular beam inside an ionization chamber between a repeller and extractor plates. Ions formed by multiphoton excitations were directed into a time-of-flight tube and detected by a micro-channel plates (MCP's) detector. Laser calibration was based on observed (2 + 1) iodine atom REMPI peaks. The accuracy of the absolute wavenumber calibration was typically found to be about ± 0.5 cm^{-1} on the laser wavenumber scale, hence about ± 2.0 cm^{-1} on the frequency doubled two-photon excitation scale.

In these experiments, a HI molecule is excited from the ground state to an excited Rydberg state or ion-pair state. If excited to a Rydberg state, the molecule can either be further excited to yield the molecular ion HI^+ or it can interact with a repulsive state and predissociate and thus further excitation yields only the atomic fragments, H^+ and I^+. Therefore, since Rydberg and ion-pair states are bound states, one can identify their rotational structures in REMPI spectroscopy (Figure 1).

In recent years, a number of papers have been published, which place emphasis on state interactions, energy transfers and photo dissociation processes, in HCl[1-10]-4] and HBr[10-12]. Whereas most of the studies of HI, however, have focused on spectral assignments and the energetics of the Rydberg and ion-pair states, no emphasis has been placed on spectral perturbations with the exception of a recently published paper on new observations in the REMPI of HI[13]. Therein, new Rydberg and ion-pair states were presented as well as Rydberg and ion-pair states that had been observed in absorption spectroscopy[14], and REMPI[15]. A few cases of perturbations were addressed, particularly that of the $k^3\Pi_1(v' = 1)$ state, which was concluded to being perturbed by the $V^1\Sigma^+(v' = m + 7)$ ion-pair state.

Several Rydberg states and ion-pair states were observed and measured quantitatively in terms of spectral perturbations, including the $H^1\Sigma^+(v' = 1)$, $m^3\Pi_2(v' = 0)$, $R^1\Pi_1(v' = 0)$, $O^1\Sigma^+(v' = 0)$, and $k^3\Pi_1(v' = 1)$ Rydberg states and the $V^1\Sigma^+(v' = m + 6)$ and $V^1\Sigma^+(v' = m + 7)$ ion-pair states (Figure 1).

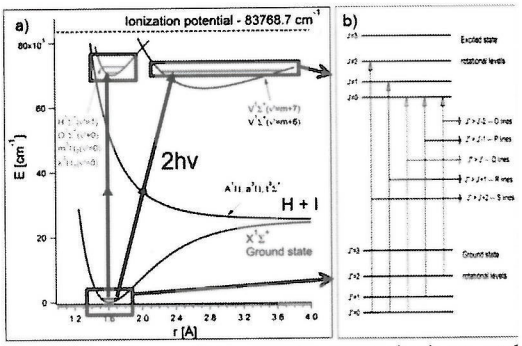


Figure 1. Energetics, resonance excitations and state interactions for HI. Rydberg states are marked green and ion-pair states are marked blue.

Perturbations due to state interactions result in intensity variations, line-shifts and line-width broadenings, but both off-resonance and near-resonance interactions are observed between Rydberg states and ion-pair states.

References

[1] J. Long, H. Wang, and Á. Kvaran, J. Chem. Phys. **138** (2013).
[2] A. Kvaran, K. Matthiasson, and H. S. Wang, J. Chem. Phys. **131** (2009).
[3] Á. Kvaran *et al.*, J. Chem. Phys. **129** (2008).
[4] S. Kauczok *et al.*, J. Chem. Phys. **133** (2010).
[5] J. Long *et al.*, J. Chem. Phys. **136** (2012).
[6] J. Long, H. Wang, and Á. Kvaran, J. Mol. Spectrosc. **282** (2012).
[7] H. R. Hróðmarsson, H. Wang, and Á. Kvaran, Journal of Molecular Spectroscopy **290** (2013).
[8] D. S. Ginter, M. L. Ginter, and S. G. Tilford, J. Mol. Spectrosc. **92** (1982).
[9] S. T. Pratt, and M. L. Ginter, J. Chem. Phys. **102** (1995).

Veggspjald 13

Possible reasons for Pt being inefficient in electrochemically reducing CO_2 into hydrocarbons

Javed Hussain, Hannes Jónsson and Egill Skúlason

Science Institute, University of Iceland, Dunhagi 3, VR-III, 107 Reykjavik, Iceland

The increasing energy demand, global climate change and foreseeable reduction in fossil fuel availability has sparked interest to develop ways of producing synthetic fuel. One option is conversion of CO_2 to methane or methanol. The best-known catalyst for reducing CO_2 to hydrocarbons is copper but the reason why platinum or other similar metals are inactive for this reaction has been puzzling. Density functional theory (DFT) calculations have been used to model the electrochemical reduction of CO_2 on various metals, in particular Pt and Cu to compare the two. The energy and structure of various intermediates is determined and the onset potential for reduction estimated. To identify the reasons for the low catalytic activity of Pt in comparison with Cu we analyze: i) the reaction mechanisms, ii) influence of water bilayer, iii) CO coverage and iv) H_2 formation rate. By understanding in detail the requirements for a good catalyst for electrochemical reduction of carbon dioxide (CO_2) to hydrocarbons we hope to be able to predict alternative catalysts that work even better than pure Cu.

Veggspjald 14

Computational Screening of Transition Metal Nitride Catalysts for Electrochemical Ammonia Formation

Y. Abghoui, A.L. Garden, V.F. Hlynsson, S. Björgvinsdóttir, H. Ólafsdóttir, E. Skúlason

Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland

Computational screening of transition metal nitrides is presented for electrochemical synthesis of ammonia at room temperature and ambient pressure. Density functional theory (DFT) calculations were used to calculate the free energy profile for the reduction of surface nitrogen atom in order to find promising candidates amongst a wide range of nitride catalysts worthwhile being tested experimentally. Surface and vacancy stability, detailed catalytic activity, defect poisoning and onset potential required for ammonia formation were considered in this study. The most promising candidates turned out to be CrN, VN and ZrN at (100) facets of rocksalt structure that should be able to make ammonia at around -0.22 V, -0.29 V and -0.53 V vs. NHE, respectively. At these potentials, the nitrides are stable and they would not be decomposed to their metal forms. The (110) facets of zincblende structure of FeN is also promising candidate capable of making ammonia at -0.5 V vs. NHE. From the latter structure RuN and OsN can make reduction of molecular nitrogen to ammonia as well, but they should need higher temperature to speed up the reaction and higher pressures to fill the N-vacancy in order to make ammonia electrochemically.

Veggspjald 15

Co^{III}-komplex með þrípeptíði: Mögulegur hvati fyrir fjölliðanir?

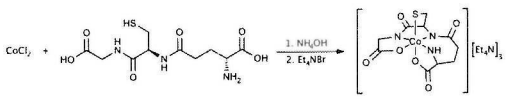
Ester Eyjólfsdóttir, Sigríður G. Suman

Raunvísindastofnun Háskólans, Dunhaga 3, 107 Reykjavík

Sýnt hefur verið fram á að hliðarmálmar seint í lotukerfinu hvata samfjölliðun (copolymerization) koltvíoxíðs og epoxíða, þar sem fjölkarbónöt myndast [1]. Koltvíoxíð er hentugur foveri fyrir fjölliðanir þar sem það er ekki eitrað og hægt er að nýta það beint úr útblæstri frá iðnaði, sem gerir notkun þess ódýra og umhverfisvæna. Rannsóknum á samfjölliðunum með koltvíoxíði hefur þó nánast aðeins verið beint að epoxíðum, þrátt fyrir að vel sé þekkt að hvatar með hliðarmálmum geti einnig fjölliðað etýlen og önnur α-ólefín [2].

Hluti af vinnu þeirri sem fram fer í rannsóknarhópi Dr. Suman snýst um að finna nýja tegund hvata sem geta virkjað koltvíoxíð fyrir fjölliðun með α-ólefínum, þar sem pólýesterar myndast.

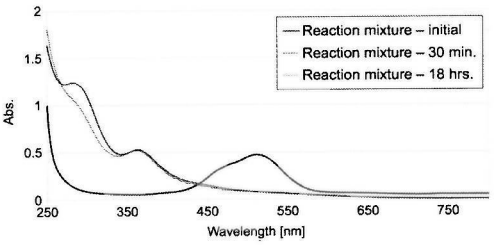
Á veggspjaldi þessu munum við kynna smíði og greiningar á komplex þar sem Co(III) er tengt þrípeptíðinu glútaþíoni (skema 1).



Skema 1.

Glútaþíon er samsett úr amínósýrunum glýsíni, sisteini og glútamati. Með því að nota peptíð eða peptíð afleiður sem tengla vonumst við til að geta gert fjölliðanir við lægri hita og þrýsting en vanalegt er. Einnig stefnum við að því að notast við málma sem eru algengir í náttúrunni og ekki eitraðir.

Við notuðumst við rafeindaróf til að fylgjast með framgangi hvarfsins, og til að ákvarða oxunarstig og girðiumhverfi málmsins. Einnig var innrauð litrófsgreining notuð til að reyna að meta hversu margar, ef ekki allar, girðistöðvar glútaþíons væru bundnar málminum.



Mynd 1. Rafeindaróf af hvarfi $CoCl_2$ við glútaþíon.

Heimildir

[1] G.W. Coates, D.R. Moore. Angew. Chem. Int. Ed. (2004) *43*, 6618 – 6639.

[2] S.D. Ittel, L.K. Johnson, M. Brookhart. Chem. rev. (2000) *100*, 1169 – 1203.

Poster 15

Tripeptide complex with Co^{III}: A potential copolymerization catalyst?

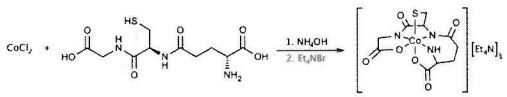
Ester Eyjolfsdottir, Sigridur G. Suman

Science institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland

It has been shown that late transition metal catalysts are effective in the copolymerization of CO_2 and epoxides, to form polycarbonates [1]. CO_2 is an ideal synthetic feedstock because it is nontoxic and can be retrieved from industrial waste streams, which makes it both abundant and inexpensive. Research into copolymerization with CO_2 has, however, almost exclusively been focused on using epoxides as comonomers, although it has been shown that first row late transition metal catalysts can also efficiently polymerize ethylene and other α-olefins [2].

Part of the work in Dr. Suman's research group is focused on developing a new class of catalysts that are able to activate CO_2 for copolymerization with α-olefins, to form polyesters.

We hereby present the synthesis and preliminary structural analysis of a Cobalt(III) complex with glutathione (scheme 1).



Scheme 1.

Glutathione is a tripeptide consisting of the amino acids glycine, cysteine and glutamate. By using peptide derived ligands we hope to achieve catalytic activity at lower reaction temperatures and pressures than is common for polymerization reactions. We would also like to focus on metals that are abundant, and therefore inexpensive, and nontoxic, making the process environmentally friendly.

We used UV-Visible spectroscopy to monitor the extent of reaction, and to determine the oxidation state and spatial environment of the central cobalt atom. Infrared spectroscopy was utilized to assess which, if not all, of the possible coordination sites in glutathione were bonded to cobalt.

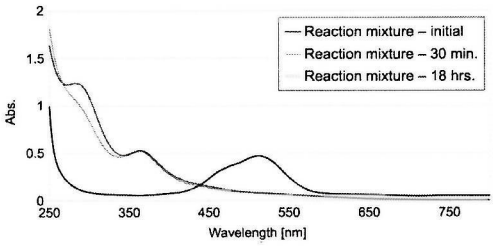


Figure 1. Electronic spectra of the reaction shown in scheme 1, recorded at different reaction times.

References

[1] G.W. Coates, D.R. Moore. Angew. Chem. Int. Ed. (2004) *43*, 6618 – 6639.

[2] S.D. Ittel, L.K. Johnson, M. Brookhart. Chem. Rev. (2000) *100*, 1169 – 1203.

Veggspjald 16

Stabilization, dissociation and rearrangement, triggered by low-energy electron attachment to tetrafluoro-*para*-benzoquinone

B. Ómarsson and Oddur Ingólfsson

Science institute, University of Iceland, Dunhagi 3, 107 Reykjavík Iceland
odduring@hi.is

Quinones are a class of organic compounds that exhibit extraordinary electron transfer properties. Quinone derivatives play a key role in charge-transfer mechanisms behind the production of ATP[1] and is thus found in almost every cell in the human body. These derivatives are also abundant in nature where plastoquinones play a pivotal role in electron transfer processes[2,3] in photosynthesis.

Here, we present our results form dissociative- and non-dissociative electron attachment to tetrafluoro-*para*-benzoquinone (TFQ). We report an extensive and complex fragmentation pattern and discuss the main fragmentation channels with respect to the reaction path and thermochemical thresholds. The observed fragmentation reactions can at large be described through two dissociation series, i.e., the formation of $[TFQ - CO - nF]^-$ (n = 0, 1, 2 or 3) and $[TFQ - 2\,CO - nF]^-$ (n = 0, 1, 2, 3 or 4). The most striking fragment in DEA to TFQ, observed at incident electron energy as low as ~2.7 eV, is the formation of C_4^- which requires the formation of two, neutral, F_2CO molecules followed by recombination of the remaining moiety to form an anionic 4-carbon chain.

In addition to the complex dissociation channels, TFQ forms a long-lived metastable molecular anion at unusually high incident electron energy in electron attachment under single collision conditions. This rare ability which is common to quite a few quinone-derivatives[4-6] is also observed in electron attachment to para-benzoquinone[7-10]. In order to explain the formation of the negative ion at this high energy we apply transition state calculations for both p-BQ and TFQ and explore possible stabilization of the molecular anion through isomerization reactions, and discuss stabilization through intramolecular vibrational energy redistribution (IVR) in relation to the electronic structure of these compounds.

References

[1] H. Inouye and E. Leistner, The Quinonoid Compounds: Volume 2 (1988) 1293 (2010).
[2] A. Trebst, Philosophical Transactions of the Royal Society B: Biological Sciences **284**, 591 (1978).
[3] J.-D. Rochaix, BBA - Bioenergetics **1807**, 375 (2011).
[4] O. G. Khvostenko, V. G. Lukin, and E. E. Tseplin, Rapid Commun. Mass Spectrom. **26**, 2535 (2012).
[5] P. M. Collins, L. G. Christophorou, E. L. Chaney, and J. G. Carter, Chem. Phys. Lett. **4**, 646 (1970).
[6] S. A. Pshenichnyuk, A. S. Vorob'ev, N. L. Asfandiarov, and A. Modelli, J. Chem. Phys. **132**, 244313 (2010).
[7] L. G. Christophorou, J. G. Carter, and A. A. Christodoulides, Chem. Phys. Lett. **3**, 237 (1969).
[8] C. D. Cooper, W. T. Naff, and R. N. Compton, J. Chem. Phys. **63**, 2752 (1975).
[9] M. Allan, Chem. Phys. **81**, 235 (1983).
[10] O. G. Khvostenko, P. V. Shchukin, G. M. Tuimedov, M. V. Muftakhov, E. E. Tseplin, S. N. Tseplina, and V. A. Mazunov, Int. J. Mass. Spectrom. **273**, 69 (2008).

Veggspjald 17

Interactions of low-energy electrons to hexafluoroacetylacetone, trifluoroacetylacetone and acetylacetone

B. Ómarsson, S. Engmann and Oddur Ingólfsson

Science institute, University of Iceland, Dunhagi 3, 107 Reykjavík Iceland
odduring@hi.is

Beta-diketones are a versatile class of compounds that exist in a keto-enol equilibrium. In the gas phase, the enol form, stabilized by a hydrogen bond between the carbonyl oxygen and the alcohol hydrogen, is usually the more stable conformer. β-diketones can complex almost any metal in the periodic table of elements and are their complexes are common precursor molecules in focused electron beam induced deposition. Motivated by our earlier studies on Pd and Cu complexes of hexafluoroacetylacetone (HFAc)[1] we have conducted detailed experimental study on the interaction of low energy electrons with hexafluoro- (HFAc), trifluoro (TFAc) and native (Ac) acetylacetone.

Here we, briefly, report the extensive and complicated fragmentation patterns observed from a crossed electron-/molecular beam study on the dissociative and non-dissociative electron attachment (DEA, NDEA) to HFAc, TFAc, and Ac. In the case of HFAc and TFAc we observe rich fragmentation patterns, which is in many cases promoted by the formation of neutral HF. This is in good agreement to earlier DEA studies we have conducted on fluorinated benzene derivatives[2,3] where we showed that reaction channels, otherwise energetically impossible, are made accessible through the exothermic formation of HF. The dominating dissociation channel observed in DEA to HFAc and TFAc is in fact the formation of $[M - HF]^-$ observed at 0 eV incident electron energy. Also observed, through the 0 eV resonance is the formation of $[M - 2HF]^-$ and the formation of FHF^-. From Ac however we only observe a few fragments all with comparably low intensity and mostly governed by single bond dissociations.

References

[1] S. Engmann, B. Ómarsson, M. Lacko, M. Stano, Š. Matejčík, O. Ingólfsson, J. Chem. Phys Accepted.

[2] B. Ómarsson, E. H. Bjarnason, O. Ingólfsson, S. Haughey, and T. A. Field, Chem. Phys. Lett. **539-540**, 7 (2012).

[3] B. Ómarsson, E. H. Bjarnason, S. A. Haughey, T. A. Field, A. Abramov, P. Klüpfel, H. Jónsson, and O. Ingólfsson, Phys. Chem. Chem. Phys. **15**, 4754 (2013).

Veggspjald 18

Rjúfandi rafeindaálagning tetra-brómíða og klóríða flokks IV

F. H. Ómarsson, B. Reynisson, O. Ingólfsson

Raunvísindastofnun, Háskóli Íslands, Dunhaga 3, 107 Reykjavík, Ísland

Tetrahalíð efna úr flokki IV eru mikilvæg í iðnaði. Kísil- og germaníum-halíð eru forverar í framleiðslu hálfleiðara og ljósleiðara en kolefnisflúríð og klóríð eru notuð víða í kælikerfum. Áhrif hinna síðastnefndu efna á loftslagið hafa þó dregið úr notkun þeirra á síðari árum. Fjölhæfir eiginleikar halíða úr flokki IV voru hvati fyrir víðtækri gagnasöfnun okkar um flokkinn á sviði anjónamyndunnar gegnum rafeindaálagningu. Í ljósi fyrri mælinga á tetraflúríð flokks IV[1] beindum við athygli okkar að tetrabrómíðum og tetraklóríðum.

Mælingar byggja á því að gasfasa agnageisli þverar rafeindageisla. Rafeindageislinn er einlitur og fæst úr trochoidal rafeinda monochromator. Anjónaniðurbrot mynduð í árekstrum agna við rafeinda eru numin af fjórpóla massagreini(Hiden, HAL EPIC1000). Orkuskalin var kvarðaður með mælingum á þremur niðurbrotum af vel skilgreindri orku: 0eV úr afleiðu SF_6; SF_6^- og 4.4eV og 8.2eV úr niðurbroti CO_2 í O^-. Orku upplausn mælinga(150 meV) var ákvörðuð sem breidd topps í hálfu hámarksgildi fyrir mælingu SF_6^-.

Fjöldi mældra jóna voru skráð sem fall af orku rafeinda fyrir öll möguleg niðurbrot. Líkt og í fyrri rannsóknum[1] er markmiðið að safna áreiðanlegum gildum birtingar orku(e. appearance energy) og orku við hámarksútslag. Þegar unnið er með hliðstæðar sameindir innan flokks má búast við reglubundnum mynstrum. Sérstök áhersla verður því á samanburðargreiningu. Mælingar eru langt á leið komnar en til stendur að kynna brot af niðurstöðum.

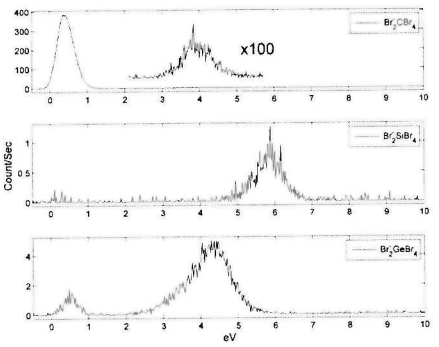


Figure 1. Rjúfandi rafeindarálagningarróf Br_2^- niðurbrota úr hvarfi CBr_4, $SiBr_4$ and $GeBr_4$. Hærri orka tengjarofs fyrir $SiBr_4$ er í samræmi við rafsækni miðatóma í sameindum.

Heimildir

[1] E.H. Bjarnason et al. Int. J Mass Spectrom. 339-340 (2013) 45-53.

Poster 18

Dissociative electron attachment of group IV tetrachlorides and bromides

F. H. Ómarsson, B. Reynisson, O. Ingólfsson

Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland

Tetrahalides of group IV elements are important compounds in industry. Silicon and germanium halides are precursors in production of semiconductors and fibre optics while carbon fluorides and chlorides have applications in refrigeration. In recent years however, concerns about their polluting nature has stunted their use. Motivated by the diverse applications of group IV halides we set out to gather comprehensive data on the series in the field of negative ion formation through electron attachment. Building on an earlier study on the group IV tetrafluorides [1] we've set the focus on the tetrabromides and tetrachlorides.

In the experimental set-up a gas phase molecular beam crosses an electron beam, generated by an trochoidal electron monochromator. Anionic fragments formed in the collision region are detected by a commercial quadropole mass spectrometer(Hiden, HAL EPIC1000). The energy scale was calibrated with a three point calibration from the formation of SF_6^- from SF_6 at $\approx$0 eV and the formation of O^- from CO_2 at XY and XY eV. The energy resolution (150 meV) was estimated from the FWHM of the SF_6 signal.

The ion yield was recorded as a function of electron energy for each possible ion. As in earlier research [1] we intend to gather accurate appearance energy for fragments in the series as well as their peak energies. Working with congeners is potentially a rich field for patterns so our attention will be on comparative analysis. Measurements are currently underway and preliminary results will be presented.

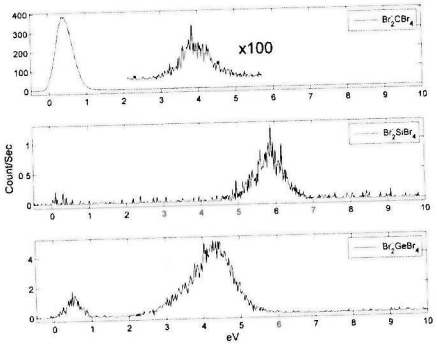


Figure 1. DEA spectra of Br_2^- fragments from dissocitation of CBr_4, $SiBr_4$ and $GeBr_4$. The higher energy needed for dissociation of $SiBr_4$ is in agreement with electron affinty trends of the group.

Heimildir

[1] E.H. Bjarnason et al. Int. J Mass Spectrom. 339-340 (2013) 45-53.

Veggspjald 19

Rjúfandi rafeindaálagning CF_4 skoðuð með hraðasneiðmyndun

**Frímann H. Ómarsson*, Oddur Ingólfsson*, Ewelina Szymanska† Nigel Mason†
E. Krishnakumar‡**

*Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland
†Department of Physical Sciences, The Open University, Walton Hall, MK7 6AA, Milton Keynes, UK
‡Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

Þegar hlutlaus sameind grípur lágorkurafeind myndast svokölluð tímabundin neikvæð jón. Þessi jón er yfirlett mynduð í örvuðu ástandi og leitar strax leiða til að slaka. Ef hún gerir það með því að rjúfa efnatengi kallast ferlið rjúfandi rafeindaálagning og myndast við það ein anjón og eitt eða fleiri óhlaðin niðurbrot. Með tækni sem nýlega hefur verið þróuð, hraðasneiðmyndun, má fá ýmsar upplýsingar um ferlið, s.s. um hrondreifingu neikvæðu jónanna og hreyfiorku þeirra. Með hraðasneiðmyndun fást upplýsingar um horndrefinguna á öllum skalanum samtímis, þ.e. 0-360°. Tæknin byggir á því að eftir myndun jónanna er þeim leyft að blása út í Newton-kúlu í um 200 ns áður en þeim er hraðað í flugtímamassagreini. Neminn á massagreininum bæði staðsetningarnæmur og púlsaður. Með því að taka sneið úr miðju Newton-kúlunnar fást upplýsingar um horndrefingu jónanna og radíus dreifingarinnar er háður hreyfiorku þeirra. Horndreifinguna má svo máta við föll sem fást með forskrift frá Azria og fél. [2] sem útvíkkuðu módel sem sett var fram af O'Malley og Taylor [3]. Út frá þessu fást upplýsingar um samhverfu neikvæðu jónarinnar. Á þessu veggspjaldi verða kynntar niðurstöður á mælingum á CF_4. Með gögnunum má sýna fram á að sameindin afmyndast frá T_d niður í C_{3v} samhverfu eftir álagningu rafeindarinnar vegna Jahn-Teller áhrifa. Þetta má bæði sjá út frá horndreifingu jónanna sem og hreyfirokudreifingu CF_3^- jónanna [4].

Heimildir

[1] D. Nandi, V. S. Prabhudesai, E. Krishnakumar, and A. Chatterjee, Rev. Sci. Instrum., 76 053107, (2005).

[2] R. Azria, Y. Le Coat, G. Lefevre, and D. Simon, J. Phys B: At. Mol. Phys., 12, 1–10, (1979).

[3] T. F. O'Malley and H. S. Taylor, Phys. Rev, 176, 1–15, (1968).

[4] F. H. Ómarsson, E. Szymanska, N. J. Mason, E. Krishnakumar, O. Ingólfsson, Phys. Rev. Lett., 111, 063201, (2013).

Poster 19

Symmetry of resonances in Dissociative Electron Attachment to CF_4 studied by Velocity Slice Imaging

**Frímann H. Ómarsson*, Oddur Ingólfsson*, Ewelina Szymanska† Nigel Mason†
E. Krishnakumar‡**

*Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavk, Iceland
†Department of Physical Sciences, The Open University, Walton Hall, MK7 6AA, Milton Keynes, UK
‡Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

Velocity Slice Imaging is a powerful technique, which recent application in Dissociative Electron Attachment (DEA) studies, has revealed details that are not accessible with conventional experimental methods [1]. In VSI a pulsed electron beam interacts with a perpendicular molecular beam, and through the kinetic energy release in the DEA process the fragment ions produced expand to form a Newton sphere. The spatial ion density of this sphere reflects the angular distribution of the fragments formed. Hence, by recording the central slice of the Newton sphere of ions, their angular distribution can be obtained simultaneously over the whole (0-360°) angular range. Furthermore, due to conservation of momentum, the kinetic energy release in the process can be directly obtained from the radial extent of the spheres expansion. In the current experiment the Newton sphere is allowed to bloom out for few hundred nano-seconds after the electron pulse and is then extracted towards a position sensitive detector (PSD) at the end of a time-of-flight (TOF) tube. The bias on the PSD is pulsed so that a thin central slice of the Newton sphere can be recorded each time. By using a polyatomic extension [2] of the theoretical diatomic model proposed by O'Malley and Taylor [3] the angular distributions may be fitted to obtain information on the symmetry of the resonances involved in the respective DEA processes. Here the VSI-DEA apparatus will be described as well as results from measurements on CF_4. The VSI data provides an unprecedented insight into the quantum superposition of the target and product states in the DEA process, and we argue that the symmetry of both these sates, T_d and C_{3v} respectively are reflected in the angular distributing of the fragment ions. Furthermore, the strong coupling of the electronic and nuclear kinetic energy, provided through the Jahn-Teller effect, in this highly symmetrical molecule is also reflected in the kinetic energy release (KER) in the CF_3^- formation through DEA [4].

References

[1] D. Nandi, V. S. Prabhudesai, E. Krishnakumar, and A. Chatterjee, Rev. Sci. Instrum., 76 053107, (2005).

[2] R. Azria, Y. Le Coat, G. Lefevre, and D. Simon, J. Phys B: At. Mol. Phys., 12, 110, (1979).

[3] T. F. O'Malley and H. S. Taylor, Phys. Rev, 176, 115, (1968).

[4] F. H. Ómarsson, E. Szymanska, N. J. Mason, E. Krishnakumar, O. Ingólfsson, Phys. Rev. Lett., 111, 063201, (2013).

(2+n) REMPI LJÓSEINDALITRÓFSGREINING: VÍXLVERKUN ÁSTANDA OG LJÓSHVÖTUÐ NIÐURBROT Á CH_3Br

ARNAR HAFLIÐASON, HUASHENG WANG, AND ÁGÚST KVARAN*

**Raunvísindastofnun, Háskóli Íslands, Dunhagi 3, 107 Reykjavík, Ísland*

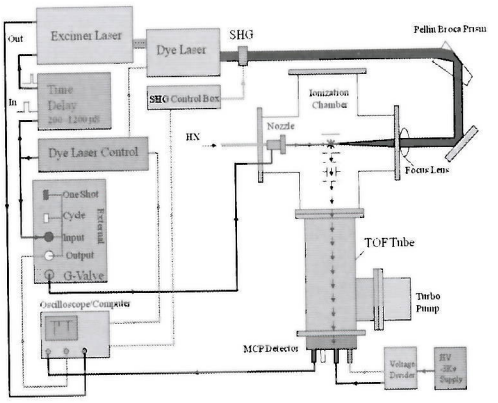
Þetta verkefni er rannsókn á CH_3Br (metýl brómíð) sameindinni, þar sem könnuð verður víxlverkun milli ástanda og myndun á sameindar og atóm niðurbrotum. Gögn tengd massa og tíðni eru tekin saman fyrir fyrirfram ákveðið orkubil, sem gefur 2D REMPI róf. Rannsóknin fer fram á orkubilinu ~ 81 000 cm^{-1} – 85 000 cm^{-1}.

(2+n) REMPI (Resonance-Enhanced Multi Photon Ionization) aðferðin notar orkuháar ljóseindir til að örva rafeindir í sameindinni á orkuhærri ástönd. Til þess er notaður Excimer leysir (Lambda Physik COMPex 205) í samvinnu með litaleysi (ScanMate Pro). Í þessari tilraun er CH_3Br örvað með 2 ljóseindum upp í Rydberg ástönd (CH_3Br + 2 hν → CH_3Br** (Ry)). Frá Rydberg ástandi getur sameindin víxlverkað við t.d., önnur Rydberg ástönd, jónpara ástönd eða rofferilsástönd. Víxlverkun við jónparaástönd geta leitt til rofs sem leiðir til jónpara myndunnar: CH_3Br**, CH_3Br** → CH_3^+ + Br^-. eða þar semvíxlverkun við rofferilástönd leiðir til niðurbrots og myndunar á radikölum: CH_3Br**, CH_3Br** → CH_3 + Br. Sjá má nokkur dæmi um möguleg niðurbrot á CH_3Br**(Ry) í töflu 1. Jónun á niðurbrotum er síðan greind og skráð, t.d. CH_3^+: CH_3 + 2 hν → CH3**, CH_3** + n hν → CH_3^+ + e^-.

Tafla 1. Niðurbrot frá Rydberg ástöndum.

CH_3Br** → CH_3+Br
CH_3Br** → CH_2 + HBr
CH_3Br** → CH_2 + H + Br
CH_3Br** → CH + H + HBr
CH_3Br** → C + H_2 + HBr

Frá þessu eru gögn um massa og REMPI róf fengin og greining á ýmsum jóna myndunum er skoðuð, t.d., CH_3^+, CH_2^+, CH^+, Br^+. Þetta er gert með notkun á TOF (e. time of flight) massagreini með MCP (e. microchannel plate) skynjara. Merki frá skynjaranum eru leidd í 400MHz sveiflusjá (sjá Mynd 1). Gögn sem innihalda merki um jónamyndun með mismunandi massa og örvunar bylgjutölu getur verið sett fram sem 2D REMPI. Útslag toppanna sem myndast fyrir hverja jón er heildað til að finna út hversu mikið myndaðist af jónum, sem fall af örvunar bylgjutölu, sem gefur 1D REMPI róf [1].



Mynd 1. Uppstilling á mælitækjum fyrir REMPI mælingar. Massaróf er skráð sem fall af örvunarorku til að fá tvívíð (2D) REMPI gögn.

Fengin gögn eru nú unnin. Einblínt er á að finna sönnur um víxlverkun milli ástanda. Ferill sem leiðir til ljóshvataðs niðurbrots á CH_3Br sameindinni er svo ráðinn með hjálp skammtafræðinnar.

References

[1] Kvaran, Á., et al. (2010), *J. Phys. Chem. A* 114: 9991 – 9998

Poster 20

(2+n) REMPI SPECTROSCOPY:

STATE INTERACTIONS AND PHOTOFRAGMENTATIONS OF CH_3Br

ARNAR HAFLIÐASON, HUASHENG WANG, AND ÁGÚST KVARAN*

**Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland*

This research involves experiments on the CH_3Br (methyl bromide) molecule and observations of state interactions and formations of molecular and atomic fragments. A collection of mass and frequency data over a selected energy range is obtained, generating 2D REMPI data. Experiments are performed for the ~ 81 000 cm^{-1} – 85 000 cm^{-1} resonance energy range.

The (2+n) REMPI (Resonance-Enhanced Multi-Photon Ionization) technique uses high-energy photons to excite electrons in molecules, using Excimer laser (Lambda Physik COMPex 205) pumped dye-laser (ScanMate Pro) system. In this experiment CH_3Br is excited with 2 photons to excited Rydberg states (CH_3Br + 2 hv → CH_3Br**(Ry)). Rydberg states then can interact with other states, e.g., other Rydberg states, ion-pair states or repulsive states. Interactions with ion-pair states can lead to dissociations to form ion pairs: CH_3Br** → CH_3^+ + Br^-, whereas interactions with repulsive states can lead to formations of radical fragments: CH_3Br** → CH_3 + Br. Several examples of possible dissociations of CH_3Br**(Ry) are shown in Table 1. Ionization of these fragments is then observed and recorded, e.g., CH_3 + 2 hv → CH3**, CH_3** + n hv → CH_3^+ + e^-.

Table 1. Dissociation of Rydberg states.

CH_3Br** → CH_3+Br
CH_3Br** → CH_2 + HBr
CH_3Br** → CH_2 + H + Br
CH_3Br** → CH + H + HBr
CH_3Br** → C + H_2 + HBr

Thus mass and REMPI spectra are obtained and detection of various ion formations can be observed, e.g., CH_3^+, CH_2^+, CH^+, Br^+, etc. This is done by a TOF (time of flight) mass spectrometer tube and a MCP (microchannel plate) detector, whose signals are fed into a 400MHz storage oscilloscope (see Figure 1). Data involving ion signals for different masses and excitation wavenumbers can be displayed as 2D REMPI spectra. Signal intensities for each ion are integrated to find relative magnitude of ions formed, as a function of excitation wavenumbers, to give 1D REMPI spectra [1].

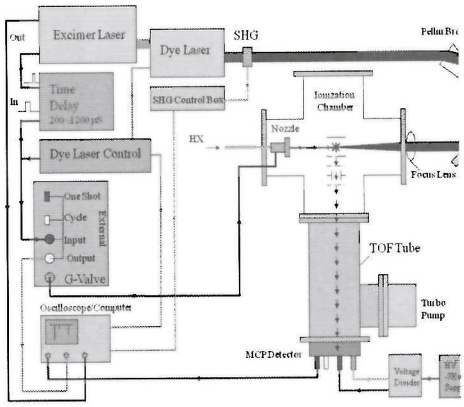


Figure 1. Experimental setup for REMPI measurements. Mass spectra are recorded as a function of resonance excitation energy to obtain two-dimensional (2D) REMPI data.

Data collected is then processed. The focus is on finding evidence of state interactions. The mechanism for the (photo)dissociation of the CH_3Br molecule can then be determined by help of quantum mechanical models.

References

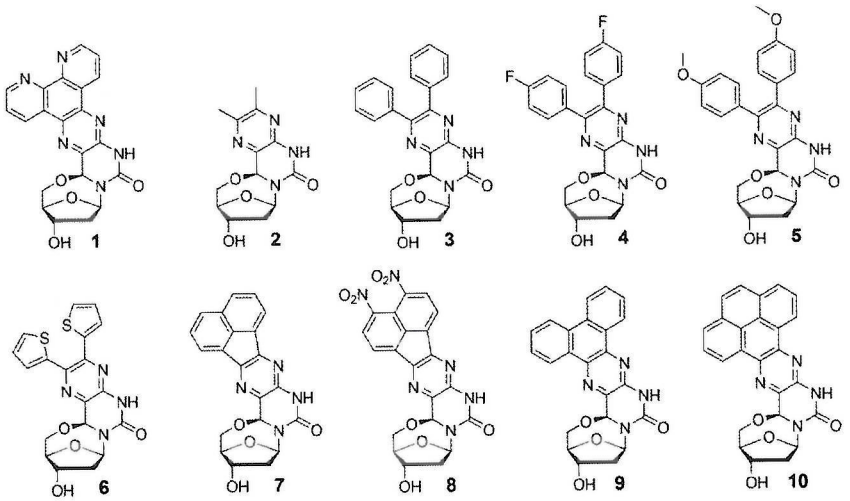
[1] Kvaran, Á., et al. (2010), *J. Phys. Chem. A* 114: 9991 – 9998

Veggspjald 21

5'-6 tengdar flúrljómandi kirnisleifar

Kristmann Gíslason* og Snorri Þór Sigurðsson*

* Raunvísindastofnun, Háskóli Íslands, Dunhagi 3, Reykjavik.



Mynd 1. Byggingar kirnisleifa **1-10**.

Sú staðreynd að kirni eru ekki ljómandi veldur því að rannsóknir á kjarnsýrum með flúrljómunar litrófsgreiningu krefst innleiðingar á flúrljómandi einingum. Sú innleiðingar-aðferð sem veldur minnstum breytingum á náttúrulegri byggingu kjarnsýrunnar er að byggja við náttúrulegu basana til að fá fram flúrljómun. Við höfum áður smíðað 5'-6 tengdu kirnisleifina **1** (Mynd 1) með hvarfi 1,10-fenanþrólín-5,6-díón við 5-amínó-2'-deoxýcýtídín.[1] Þar sem efnasmíðarnar á **1** voru tiltölulega einfaldar ákváðum við að beita sömu aðferð til að smíða flúrljómandi 5'-6-tengdar kirnisleifar. Níu díketónar voru valdir til að smíða kirnisleifar **2-10** (Mynd 1). Safnið reyndist hafa fjölbreytta ljómunareiginleika.

Til að kanna eiginleika flúrljómandi 5'-6-tengdra kirnisleifa í DNA var kirnisleif **9** innleidd á 5'-enda 14-basa fákirnis. Ljósfræðilegir eiginleikar **9** voru rannsakaðir bæði í einstrendu og tvístrendu DNA. Einnig voru eiginleikar **9** rannsakaðir í DNA helix sem innihélt einn brotinn strending til að kanna mögulega innleiðingu 5'-6-tengdra kirnisleifa í innri-stöðu í kjarnsýru-tvístrendingi.

Tilvísanir

[1] K. Gislason and S. T. Sigurdsson, *Eur. J. Org. Chem.* (2010) 4713.

Poster 21

5'-6 locked fluorescent nucleosides

Kristmann Gislason* and Snorri Th. Sigurdsson*

* Science Institute, University of Iceland, Dunhagi 3, Reykjavik.

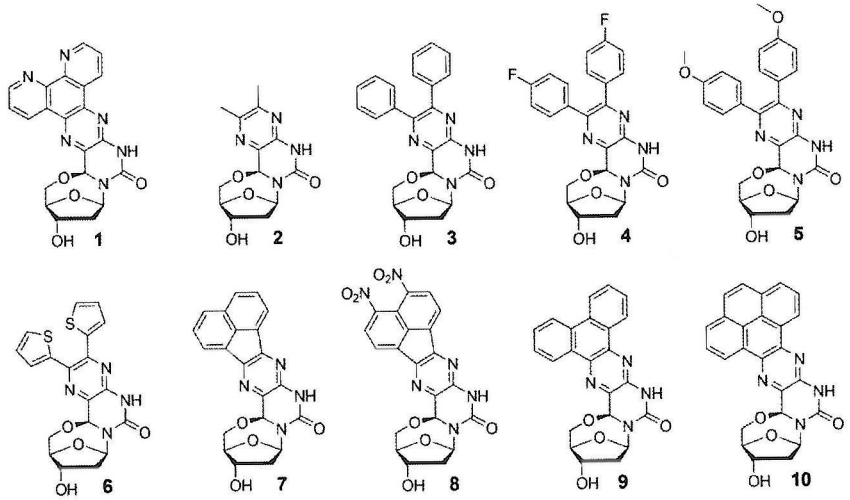


Figure 1. Structures of nucleosides **1-10**.

Due to the non-emissive nature of nucleotides, fluorescence spectroscopic studies of nucleic acids require incorporation of chromophores. The least invasive method to achieve this is to expand the structure of one of the natural bases to obtain a chromophore. We have previously synthesized 5'-6 locked nucleoside **1** (Figure 1) containing a 1,10-phenanthroline moiety by condensation of 1,10-phenanthroline-5,6-dione to 5-amino-2'-deoxycytidine.[1] Due to the simplicity of the synthetic approach we decided to apply the same method to synthesize fluorescent 5'-6-locked nucleosides. Nine commercially available diketones were chosen to obtain 5'-6-locked fluorescent nucleosides **2-10** (Figure 1). The group displayed varied photophysical properties, such as absorption and emission maxima, extinction coefficients and quantum yields.

To study the properties of fluorescent 5'-6-locked nucleosides in DNA, nucleoside **9** was phosphitylated and incorporated at the 5'-end of a model 14-mer oligonucleotide. The photophysical properties of **9** were determined in both single-stranded and double-stranded DNA. Also, the properties of **9** were determined in a nicked DNA helix to study the possibility of incorporating 5'-6-locked nucleosides at internal positions in nucleic acid double helixes.

References

[1] K. Gislason and S. T. Sigurdsson, *Eur. J. Org. Chem.* (2010) 4713.

Veggspjald 22

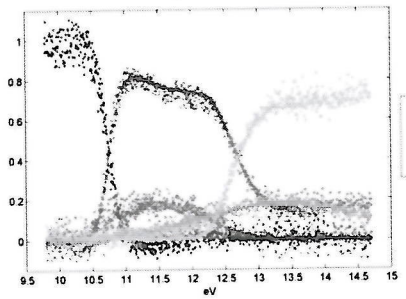
Niðurbrot 1-halo-kísilhringhexana: Mælingar, tölvureikningar og hermun

Katrín Lilja Sigurðardóttir[φ]*, Ingvar H. Árnason[φ], Andras Bodi[†], Ragnar Björnsson[#]

[φ]Raunvísindastofnun Háskóla Íslands, Dunhaga 3, 107 Reykjavík
[†] Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[#]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

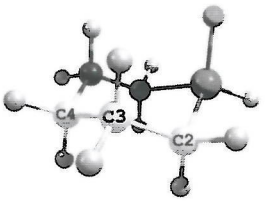
Stellingajafnvægi setinna kísilinnihaldandi sexhringja hafa verið rannsökuð ítarlega af Ingvari Árnasyni og rannsóknarteymi hans við Raunvísindastofnun Háskóla Íslands [1]. Til ad öðlast dýpri skilning á þessum sameindum var ákveðið ad mæla þröskuldsorku fyrir niðurbrot einsetinna halógen kísilsexhringja, $(CH_2)_5SiHX$; X = F, Cl, Br, I; með svokölluðum TPEPICO mælingum[2].
Mæliniðurstöður hverrar sameindar innihalda TOF massaróf af jónaðri sameind og þeim niðurbrotseiningum hennar sem eru á jónaformi.

- Þegar réttir massatoppar eru heildaðir og hlutfall þeirra dregið upp sem fall af heildarorku sameindajónarinnar, fæst niðurbrotsferill tiltekinnar sameindar. Til samanburðar við þessa mældu niðurbrotsferla voru orkuferlar fyrir niðurbrotin reiknaðir með skammtafræðilegum aðferðum.



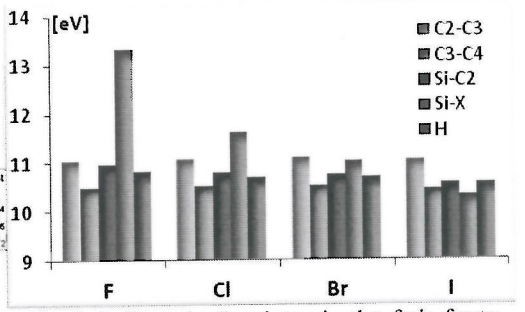
Mynd 1. Niðurbrotsferill $(CH_2)_5SiHCl$.

Niðurbrotsferlar F-, Cl- og Br- setinna hringja reyndust keimlíkir. Við lægsta orkugildi brotnar C_2H_4 eining af, en einnig eru þar sýnileg C_3H_6, H og X = Cl, Br niðurbrot í minna mæli. Við hærri orku brotnar svo önnur C_2H_4 eining af. Niðurbrotsferill I-setins hrings er töluvert ólíkur. Þar klofnar I af við lægstu orku og við hærri orku klofnar af C_2H_4. Þessar niðurstöður eru í megindráttum í góðu samræmi við hina reiknuðu orkuferla fyrir niðurbrotin.
Tengjaorkur fyrir öll möguleg fyrstu niðurbrot á hringnum voru reiknaðar og í ljós kom áhugavert mynstur milli halógenanna fjögurra.



Mynd 2. Sýnir númer kolefnisatóma i hringnum.

Rof C3–C4 tengisins, sem leiðir svo af sér C_2H_4 eða C_3H_6 klofnun, krefst svipaðrar orku fyrir alla fjóra hringina en Si–X tengjaorkan minnkar töluvert með stærð X. Í tilfelli I-setna hringsins er tengjaorka Si–I minni en tengjaorka C3–C4 og skýrir það hvers vegna niðurbrotsferillinn fyrir I-setna hringinn er ólíkur niðurbrotsferlum hringjanna sem setnir eru með F, Cl og Br.



Mynd 3. Samanburður á tengjaorku fyrir fyrsta mögulega tengjarof í sameind.

Á heildina litið er samræmi gott milli mældu ferlanna og þeirra reiknuðu. Hins vegar er ekki mögulegt ad lesa klofnunarorkuna beint af niðurbrotsferlunum. Þá þarf að herma til að fá tölugildi sem má bera saman við reiknuðu gildin. Sem stendur er enn unnið að hermuninni.

Heimildir

[1] Wallevik.S.O., *Conformational behaviour of substituted silacyclohexanes*, M.Sc. thesis, University of Iceland, 2008.
[2] Tomas Baer et al. Phys.Chem. Chem. Phys. 2005, 7, 1507-1513.

Poster 22

Breakdown of 1-halo-silacyclohexanes: Measurements, chemical calculations and modelling

Katrín Lilja Sigurðardóttir[ϕ]*, Ingvar H. Árnason[ϕ], Andras Bodi[†], Ragnar Björnsson[♯]

[ϕ]Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland
[†] Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[♯]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

Conformational properties of substituted Silicon-containing six-membered rings have been investigated thoroughly by Ingvar Arnason's research group at the Science Institute [1]. In order to obtain a deeper thermochemical understanding about these ring systems, we decided to carry out a Threshold Photoelectron Photoion coincidence (TPEPICO)[2] analysis on monohalogenated silacyclohexanes $(CH_2)_5SiHX$; X = F, Cl, Br, I.
The experimental data include TOF mass spectra of the molecular ion and of its ionic fragments. A breakdown diagram is obtained from the mass spectra by integrating the correct TOF mass peaks and plotting their fractional abundance as a function of the parent ion internal energy. For comparison, energy diagrams for the most common breakdown pathways were calculated by computational methods.

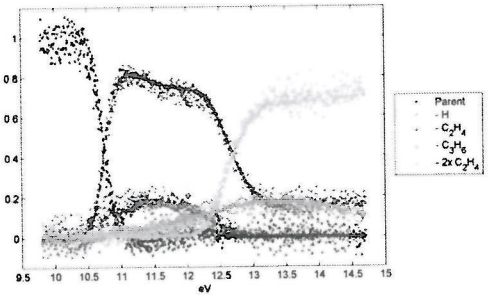


Figure 1. Breakdown diagram for $(CH_2)_5SiHCl$.

The breakdown diagrams are similar for the F-, Cl- and Br-substituted rings. The first dissociation involves the loss of a C_2H_4 fragment and competitive dissociations where the fragments C_3H_6, H or X = Cl or Br are likely to break off the molecule. At higher energies, a consecutive dissociation step is seen with the loss of a second C_2H_4 fragment. The breakdown diagram for the I-substituted ring is different, where the first dissociation is a loss of an I atom and the consecutive step is a loss of a C_2H_4 fragment. This is in good agreement with the calculated energy breakdown diagrams. The bond energy for all possible 1st breakage of all the four rings were calculated, showing some interesting trends for the four different halogens.

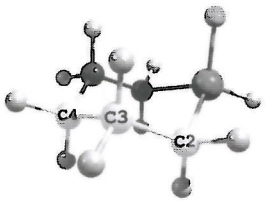


Figure 2. Showing numbering of carbon atoms.

Cleavage of the C3–C4 bond resulting in either C_2H_4 or C_3H_6 loss, requires similar energy for all rings, but the Si-X bond energy decreases considerably as the X atom grows larger. For the I-ring, the calculated Si-I bond energy is lower than the C3–C4 bond energy.

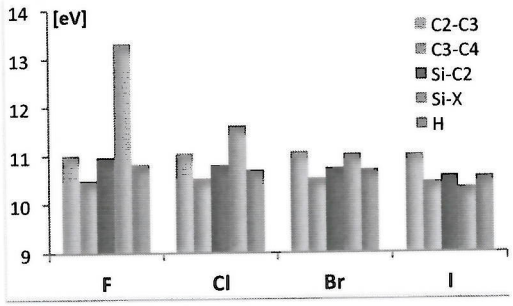


Figure 3. Comparision of the bond energies for all possible 1st breakages.

In general, the appearance of the breakdown curves for all of the four rings are in good accordance with the calculated energy diagrams.
Nevertheless, the bond dissociation energies can not be read directly from the breakdown diagrams. The breakdown processes have to be modelled to obtain values comparable to the
calculated values. At present, the modelling is still being worked on.

References

[1] Wallevik.S.O., *Conformational behaviour of substituted silacyclohexanes*, M.Sc. thesis, University of Iceland, 2008

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Characterisation of human gluconokinase and its proposed impact on human metabolism

Neha Rohatgi and Óttar Rolfsson.

Center for systems biology, University of Iceland, Sturlugata 8, 101 Reykjavik, Iceland.
rohatgineha1989@gmail.com, ottarr@hi.is, s:8450075

Gluconate is a commonly encountered nutrient yet its metabolism in humans is unaccounted for. A gene encoding a gluconokinase was recently identified highlighting an overlooked route of carbon flux into the pentose phosphate pathway. The pathwy is key for cellular redox homeostasis and nucleotide and amino acid anabolism. Here we report the biochemical characterisation of the enzyme along with computational network modelling of its contribution to human energy metabolism. The enzyme, shown to be a dimer, had ATP dependent phosphorylation activity and strict specificity towards gluconate. Isothermal titration calirometry allowed the determination of reaction kinetics. *In vitro* cell assays showed that despite expression of the active enzyme, Hep-G2 and Ht-29 cells do not incorporate gluconate during proliferation implying its source could be endogenous. To gain insight into the role of gluconokinase and the metabolic impact of gluconate we modeled gluconate metabolism using steady state metabolic network analysis. The data indicate that significant flux changes in anabolic pathways linked to the pentose phosphate pathway are induced through a small increase in gluconate concentration. We argue that the enzyme takes part in a previously undiscovered context specific carbon flux route into the pentose phosphate pathway in humans.

TMC homopolymer and other N-alkyl-quaternized chitosan derivatives as Permeation enhancers for bronchial epithelial

Berglind Eva Benediktsdóttir[*], Thórarinn Gudjónsson[†], Ólafur Baldursson[‡] Már Másson[*]

[*]Faculty of Pharmaceutical Sciences, University of Iceland, Hofsvallagata 53, IS-107 Reykjavík, Icelan
[†] Stem Cell Research Unit, University of Iceland, Reykjavik, Iceland
[‡] Landspitali - The National University Hospital of Iceland, Reykjavik, Iceland

The polysaccharide chitosan has been the subject of numerous studies as a potential permeation enhancer, mainly to increase absorption in the intestinal mucosa. The advantages of the chitosan polymer are its mucoadhesive nature, biodegradability and safety in non-parental dosage formulations. Introducing a permanent positive charge, such as with N,N,N-trimethyl chitosan (TMC), increases the aqueous solubility of chitosan at physiological pH. TMC previously studied had different degrees of trimethylation, often accompanied with O-methylation, thereby reducing the water solubility. We have recently used the tert-butyldimethylsilyl protection strategy to synthesize fully trimethylated chitosan without O-methylation in addition to N-alkyl-N,N-dimethyl chitosan derivatives [1]. The aim of the current study [2] was to determine the permeation enhancing effects of these quaternary chitosan derivatives and establish a structure-activity relationship.

VA10 human bronchial epithelial cells were cultured on transwell filters under air-liquid interface. The epithelia were then treated with the chitosan derivatives N,N,N-trimethyl chitosan (TMC), N-propyl-N,N-dimethyl chitosan (QuatPropyl), N-butyl-N,N-dimethyl chitosan (QuatButyl) and N-hexyl-N,N-dimethyl chitosan (QuatHexyl). Transepithelial electrical resistance (TER) for all derivatives, a useful indicator of the function of the tight junctions, decreased in a dose-dependent manner. The decrease was different between derivatives, with TER decreasing slowly for TMC and QuatPropyl but a rapid decrease was observed for QuatButyl and QuatHexyl chitosan derivatives. TMC caused a 55 % decrease in TER, QuatPropyl 73%, QuatButyl 91% and QuatHexyl 90% for the highest concentration (1 mg/mL). The decrease in TER values was associated with increased paracellular permeability of FITC-labeled dextran 4 kDa with the highest increase in permeability obtained after treatment with QuatButyl followed closely by QuatHexyl, than QuatPropyl and finally TMC..

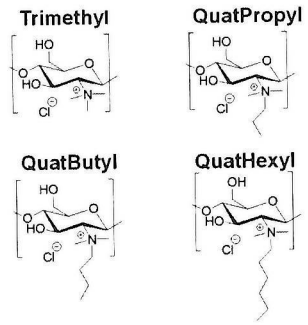

Figure 1. Quaternary chitosan derivatives used in the current study.

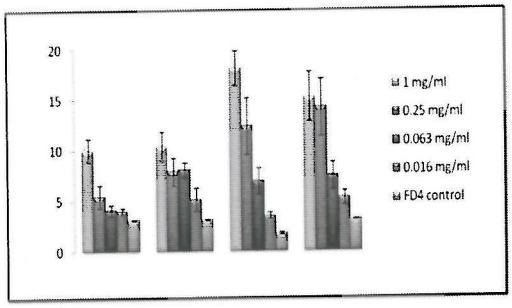

Figure 2. Comparison of FITC-dextran 4 kDa Papp values between the quaternary chitosan derivatives

References

[1] B.E. Benediktsdóttir, V.S. Gaware, Ö.V. Rúnarsson, S. Jónsdóttir, K.J. Jensen, M. Másson, Carbohyd. Polym., 86 (2011) 1451–1460.

[2] Berglind Eva Benediktsdóttir, T. Gudjónsson, Ó. Baldursson, M. Másson, European Journal of Pharmaceutics and Biopharmaceutics - in press, (2013).

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The effect of salt bridges on the properties of aqualysin I, a thermostable subtilisin-like proteinase.

Lilja B. Jónsdóttir[1], Brynjar Ö. Ellertsson[1], Manuela Magnúsdóttir[1], Sigríður H. Thorbjarnardóttir[2] and Magnús M. Kristjánsson*[1]

[1]Department of Biochemistry, Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland.
[2]Institute of Biology, University of Iceland

Aqualysin I (AQUI) is a subtilisin-like serine proteinase (subtilase), from the thermophilic bacterium *Thermus aquaticus*. We have compared the structure and properties of AQUI to homologous subtilases, from microorganisms adapted to lower temperatures, in order to gain a better insight into the molecular mechanisms of temperature adaptation of those enzymes. Such a comparison to a close structural homolog from a psychrophilic marine *Vibrio* sp. (VPR) indicated that the thermostable enzyme contains several additional putative salt bridges, which are not present in the structure of the cold adapted VPR. To test whether these additional salt bridges contribute to thermostabilization of the thermophilic enzyme, we have studied the effects of deleting some of the putative salt bridges from the structure of AQUI by site directed mutagenesis. In most cases the mutations of AQUI involved an exchange to the corresponding residue in VPR. Most mutations had relatively benign effects on the properties of the enzyme with respect to stability and kinetic properties. For the single mutant, AQUI-D17N, in which a putative salt bridge between Asp17 and Arg259 was eliminated, an 8-9 °C decrease in thermal stability was observed, however. In another set of mutants, AQUI-D98S and AQUI-D98G, the turnover number, k_{cat}, was increased twofold when activity was measured against synthetic substrates. These residue exchanges would be expected to weaken a potential Asp98-Arg95-Asp58 ion pair in the protein, as well as to reduce the number of hydrogen bonds involving residue 98 and critical residues of the substrate binding site of the enzyme. These mutations however had no significant effects on the thermal stability of the enzyme.

PEG Functionalized Chitosan Nanocarriers for Light Activated Cancer Therapy - Synthesis and Characterization

Ingólfur Magnússon[a], Elvar Örn Viktorsson[a], Vivek Gaware[a], Már Másson[a,*].

[a]Faculty of Pharmaceutical Sciences, School of Health Sciences, University of Iceland, Hofsvallagata 53, IS-107 Reykjavík, Iceland.

In recent decades, derivatives of natural carbohydrate polymers like chitosan have received attention for their possible utilization in nanoscale drug delivery systems. Such systems could be used to overcome some of the problems associated with many traditional anti-cancer agents, such as low solubility and ineffective tumor targeting [1]. Drug-polymer conjugates have now become well-established nanoscale systems which can be utilized in cancer therapy to improve solubility of lipophilic drugs in order to achieve more specific tumor targeting by taking advantage of the enhanced permeability and retention (EPR) effect [2]

In the current study, lipophilic photosensitizer and polar derivatives of triethyleneglycol (TEG) were attached to the backbone of TBDMS-*O*-protected chitosan. Nucleophilic and electrophilic substitutions were utilized for these reactions and reductive alkylation was also attempted. Two types of nanocarriers were synthesized and one of these had good aqueous solubility.

Characterization methods used in this study included ^{1}H NMR (figure 1), ^{13}C NMR, ^{1}H-^{1}H COSY, FT-IR and Mass spectrometry's. UV- and dynamic light scattering (DLS) experiments were also conducted to obtain data on nanoparticle formation and their characteristics.

The investigations seen in figure 2 showed that the water soluble nanocarriers formed nanoparticles with an average diameter of 216 nm. Z-potential measurements also indicate that the final nanocarrier would be stable in aqueous environment.

Thus it is possible that this nanocarrier could be used in light activated cancer therapy. For example, these carriers could be used to release trapped cancer drugs from endocytic vesicles with a new method called photochemical internalization (PCI).

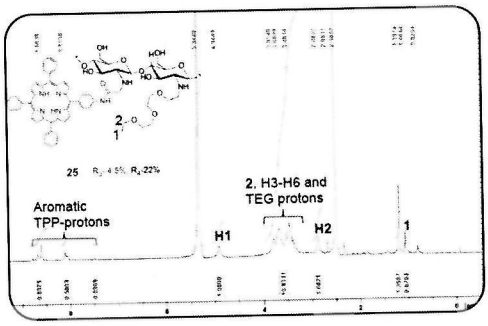

Figure 1. ^{1}H NMR of TEGylated-TPP-piperazine chitosan nanocarrier

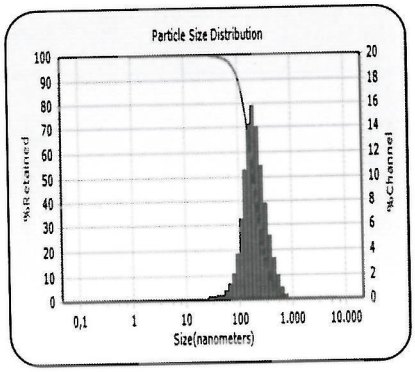

Figure 2. Size distibution measurment of Chitosan nanoparicles measured by DLS

References

[1] Duncan, R. (2006). Polymer conjugates as anticancer nanomedicines. [Review]. Nature Reviews Cancer, 6(9), 688-701.

[2] Brannon-Peppas, L., & Blanchette, J. O. (2004). Nanoparticle and targeted systems for cancer therapy. [Review]. Adv Drug Deliv Rev, 56(11), 1649-1659

Mechanistic Mathematical Modeling of Release from Drug Loaded Silicone Matrix Systems and Transdermal Delivery

Bergþóra S. Snorradóttir[*], Fjóla Jónsdóttir[†], Sven Th. Sigurðsson[†], Freygardur Thorsteinsson[‡] Már Mássona[*]

[*]Faculty of Pharmaceutical Sciences, University of Iceland, Hofsvallagata 53, IS-107 Reykjavík, Icelan
[†]Faculty of Industrial Engineering, Mechanical Engineering and Computer Science, Engineering and Natural Sciences, University of Iceland, Stapi, Hringbraut 31, 101 Reykjavík, Iceland
[‡] Össur hf., Grjóthálsi 5, IS-110 Reykjavik, Iceland

Silicones are biocompatible polymers which have been used for different kinds of applications both medical and non-medical. Silicone matrix formulations have many unique characteristics, they are non-biodegradable polymers, suitable for medical use, drug delivery matrices and in medicated prosthesis. Drug micro- and nanoparticles have been embedded for various types of applications such as birth control implants and transdermal patches. The high stability of the silicone and the biocompatibility offers great advantage as matrix drug formulation and the good reproducibility of drug release from such formulation are advantageous especially when considering modelling drug release from such formulations.

Based on our previous modelling, two non-linear coupled partial differential equations derived from the Noyes-Whitney and Fick´s second law were solved numerically using MATLAB. The aim was a model which could accurately predict the rate of drug release from silicone elastomers, as well as undissolved drug concentration in the material at each point in time (Figure 1). The predictions could be fitted to the experimental data[1]. Drug release from these matrix type systems were conducted with vertical Franz diffusion cells which offers one dimensional diffusion and is advantageous for definition of release profile from the silicone matrix.

Here is also presented further modifications of the numerical modelling of multi-layered silicone membranes with the aim of adding the skin into the model. Therefore offering a model with the option of having multi-layered silicone matrix as well as implicating the skin as one barrier/layer in the numerical modelling.

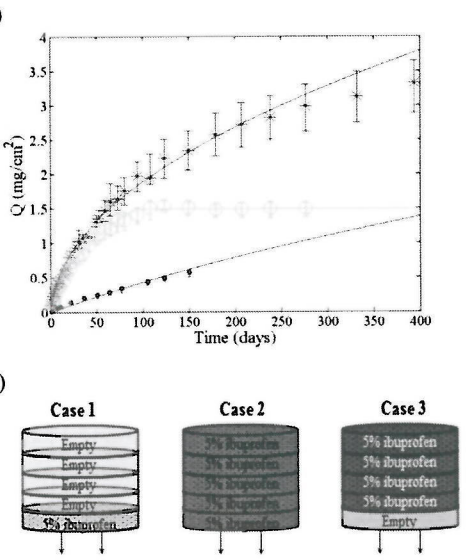

Figure 1. Amount of drug release for ibuprofen; comparison between numerical results and experimental data (a) for three different layer configurations (b).

References

[1] B.S. Snorradóttir, F. Jónsdóttir, S.T. Sigurdsson, F. Thorsteinsson, M. Másson, Eur. J. Pham. Sci., 49 (2013) 671-678.

Hönnun og umbrot: Benedikt Ómarsson og Helgi Rafn Hróðmarsson
Prentun: Háskólaprent ehf.
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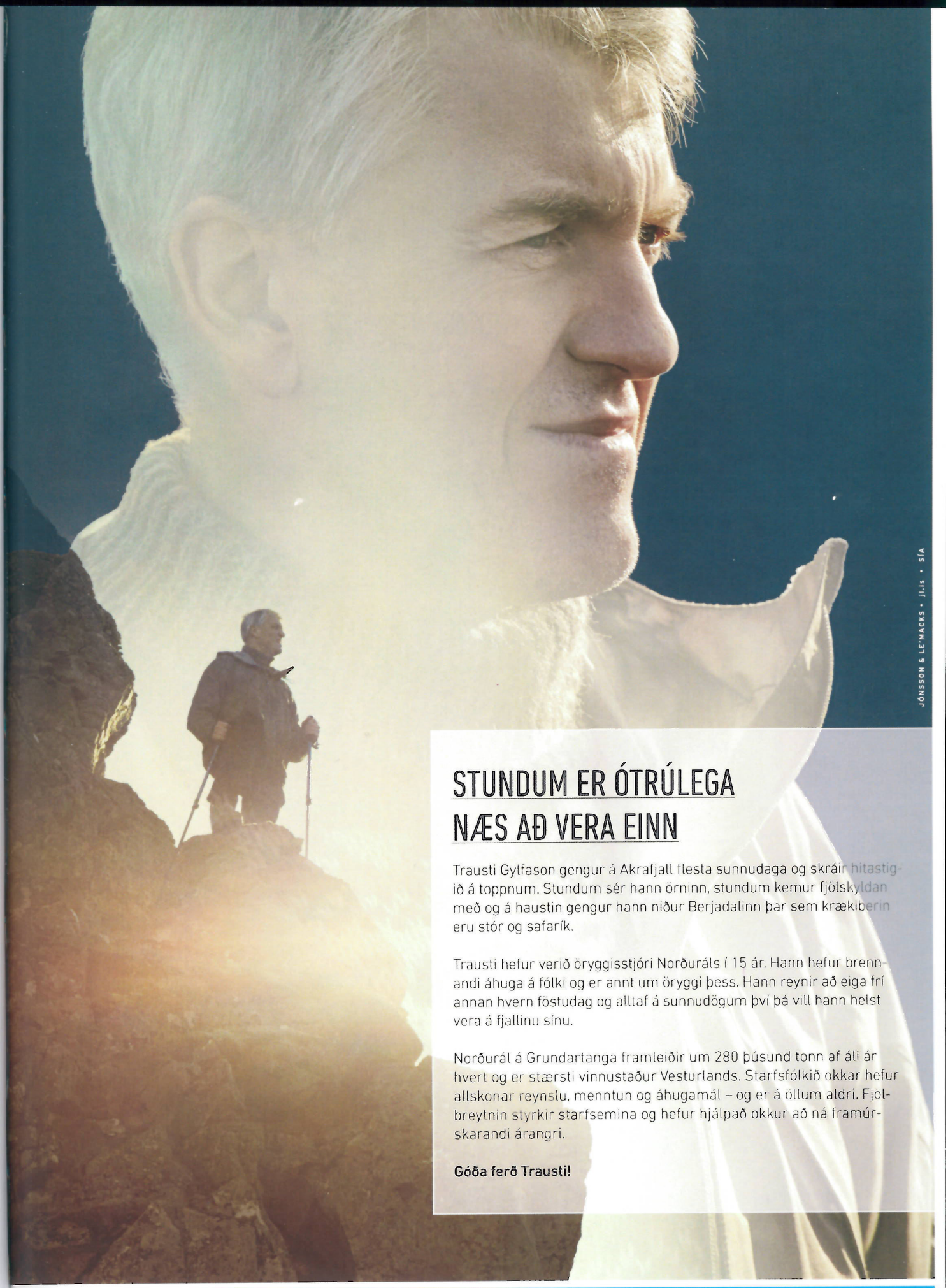

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