Realia et naturalia

DISSERTATIONES
CHIMICAE
UNIVERSITATIS
TARTUENSIS
138

AIKO ADAMSON

Properties of amine-boranes and phosphorus analogues in the gas phase

TARTU ÜLIKOOL · UNIVERSITAS TARTUENSIS · 1632

DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS
138

DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS
138

AIKO ADAMSON

Properties of amine-boranes and phosphorus analogues in the gas phase

UNIVERSITY OF TARTU
PRESS
1632

Institute of Chemistry, Faculty of Science and Technology, University of Tartu.

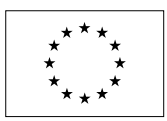
Dissertation is accepted for the commencement of the Degree *of Doctor philosophiae* in Chemistry on June 18, 2014 by the Doctoral Committee of the Institute of Chemistry, University of Tartu.

Supervisor: prof. Peeter Burk (PhD, chemistry),
Institute of Chemistry, University of Tartu, Estonia

Opponent: prof. Holger Bettinger (PhD),
University Tuebingen, Germany

Commencement: August 22, 2014 at 10:00, Ravila 14a, room 1021

This work has been partially supported by Graduate School „Functional materials and technologies" receiving funding from the European Social Fund under project 1.2.0401.09-0079 in University of Tartu, Estonia.



Publication of this dissertation is granted by University of Tartu

ISSN 1406-0299
ISBN 978-9949-32-627-3 (print)
ISBN 978-9949-32-628-0 (pdf)

University of Tartu Press
www.tyk.ee

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original papers, which are referred to in the text by the following numbers:

I Abboud, J-L. M.; Németh, B.; Guillemin, J-C.; Burk, P.; Adamson, A.; Nerut, E. R. Dihydrogen generation from amine/boranes: synthesis, FT-ICR, and computational studies. *Chem. Eur. J.* **2012**, 18, 3981–3991.

II Adamson, A.; Guillemin, J.C.; Burk, P. Acidities of N-Substituted Amine–boranes. *J. Mol. Mod.* **2013**, 19, 5089–5095.

III Adamson, A.; Burk, P. P-substituted phosphine–boranes: Gas phase acidities, basicities and dihydrogen release. A comparison to amine–boranes. *Comp. Theor. Chem.* **2014**, 1032, 12–19.

Author's contribution

Paper I: Performed most of the computational work.
Paper II: Main person responsible for planning and writing the manuscript. Performed all computational work.
Paper III: Main person responsible for planning and writing the manuscript. Performed all computational work.

1. INTRODUCTION

Borane (BH_3, also known as trihydridoboron) forms stable Lewis acid-base complexes with amines and phosphines. It has been revealed that such species exhibit several interesting properties and potential for practical applications, ranging from organic synthesis to hydrogen storage. On the quest to design a complex with the most desirable characteristics for any potential application, it is important to know the intrinsic properties of the species and theoretical methods provide many possibilities in that regard. In recent years theoretical calculations have become a powerful tool as accurate results for relatively large amount of species can be obtained in a reasonable time.

Hydrogen is the simplest chemical element and its concentration in biosphere is notable. A proton is involved in many different processes and the abilities to accept and donate it are of great consequence. Knowledge about properties relating to proton transfer reactions gives us insight into the reactivity of a compound and in the case of amine-boranes, it is also important in the field of energetics as the high gravimetric capacity of hydrogen makes amine-boranes appealing for hydrogen storage.

Chemical hydrogen storage system must be reversible at working conditions, which means that the Gibbs free energy of the hydrogen release must be slightly positive. However, at the present the usage of amine-boranes for that purpose is complicated as several practical and fundamental questions are still un-answered. Although the desired reversibility at practical conditions has not yet been achieved, it is known that the dihydrogen activating properties of boron-nitrogen containing compounds can be used for more than just hydrogen storage.

Computational methods are at their strength in investigation of intrinsic gas-phase properties and interactions, and are therefore ideal for filling the cap of knowledge concerning borane complexes. Systematic investigation of different analogous species does not only gives us information about single complexes, but allows us to gain insight into the overall properties and brings us closer to a complex with the most desirable characteristics.

Substituents play important role in the properties of amine- and phosphine-boranes. So far mostly complexes with small substituents like methyl groups or halogen atoms have been investigated and much less attention is given to complexes with bulkier substituents. The aim of this work is to study computationally the properties of amine- and phosphine-boranes in relation to proton transfer. In the current theses the gas-phase stabilities, acidities and basicities for several complexes are investigated and the effects of substituents are discussed. It has been shown that protonated complexes release hydrogen and the thermodynamics of the reaction is dependent on the species. The results of the presented work can be used as a valuable input for designing future experiments and applications.

2. LITERATURE OVERVIEW

2.1. Gas-phase acidity and basicity

Brønsted acidity and basicity [1–4] are parameters describing the proton donating and accepting ability of a molecule. Proton transfer reactions are of significant importance as a lot of reactions from biochemistry to interstellar chemistry are catalyzed by the proton. Both parameters can be determined in solvents, but there is a fundamental problem – proton is not a free particle in liquid phase. The proton and all other species taking part of the proton transfer reaction are solvated and the solvation depends on solvent. Therefore no intrinsic acidity or basicity can be obtained in solution. This problem can be solved by measuring the acidity or basicity in the gas phase.

The gas-phase acidity and basicity are defined by the following equilibrium reactions:

$$\text{deprotonation} \qquad AH \leftrightarrows A^- + H^+ \tag{1}$$

$$\text{protonation} \qquad BH^+ \leftrightarrows B + H^+. \tag{2}$$

Gas-phase acidity (GA) is the Gibbs free energy change for the reaction 1 and gas-phase basicity (GB) is the Gibbs free energy change for the reaction 2. A closely related term – proton affinity (PA) can be found in literature, which refers to the enthalpy change for reaction 2. It should be noted that by such definitions the higher basicity values correspond to the stronger bases but it is *vice versa* for acidity – higher acidity values mean a less acidic compound (and therefore lower acidity values correspond to a stronger acid).

Gas-phase acidity and basicity can also be determined experimentally. The measurements are conducted in low pressure environment against reference substances with known acidity or basicity values. The basic concept is described by the following proton exchange reaction:

$$AH(g) + A_{ref}^-(g) \rightarrow A^-(g) + A_{ref}H(g). \tag{3}$$

The GA value for AH can be calculated by the following equation:

$$GA(AH) = GA(A_{ref}H) - RT \ln K_p, \tag{4}$$

where R is the universal gas constant, T is absolute temperature and K_p concerns the experimental partial pressures (P) of neutral and ionic species involved:

$$K_p = \frac{P_{A_{ref}H} \times P_{A^-}}{P_{AH} \times P_{A_{ref}^-}}. \tag{5}$$

2.2. Amine-boranes and analogues

Amine-boranes are complexes formed by the association of amines and boranes. The amine acts as a Lewis base and borane acts as a Lewis acid in this addition reaction. The history of such complexes date back more than 200 years as the H_3N-$BF_3$was first synthesized in 1809 by Gay-Lussac [5, 6]. The unsubstituted amine-borane was first prepared many years later in 1955 by Shore and Parry [7]. Since 2000 the complexes have gained much more attention, as countless number of applications has been suggested and several reviews about various aspects of such complexes [8–14] were published. One of the potentially most rewarding usages relates to hydrogen storage as the hydrogen content in ammonia-borane is notably high –19.6 wt % and for this reason the substituted amine-borane is by far the most investigated among such complexes. In addition to the amine-boranes there are several analogues where the Lewis base or acid is replaced; such complexes include hydrazine-boranes [15, 16], phosphine-boranes [17, 18], amine-alanes [19], and phosphine-alanes [20, 21].

It has been shown that substituents greatly affect the acidity and basicity of isolated amines and phosphines [22, 23], same is also true for boranes. For example methyl borane is 47 kcal/mol more stronger acid than free borane [24]. Despite the increasing attention towards the complexes, the substituent effects to the fundamental properties like acidity and basicity have not gained much attention. So far amine-boranes and phosphine-boranes with mostly small substituents like halogens and methyl groups have been investigated and studies concerning the complexes with bigger substituents are very limited.

2.3. Investigated deprotonation reactions

Based on the few works concerning the acidities of substituted borane complexes, a general conclusion can be drawn that the most acidic hydrogens are usually located in the Lewis base [25–28]. For example in the primary and secondary amine-boranes the acidity center is the N-H group [27] and in tertiary trimethyl amine-borane the C-H acts like an acidity center [25]. However it is important to note that there are several more theoretical acidity centers in these species. Both computations and experiments have shown that in the case of some substituents the alternative deprotonations may lead to drastic intramolecular changes, and as a result, some complexes are not stable towards the deprotonation [25, 26].

The common nominator for all complexes studied so far is that the acidity of the Lewis base is greatly enhanced by the complexation, this is true for amine-boranes (up to 47 kcal/mol [27]), phosphine-boranes (up to 26 kcal/mol [26]), and phosphine-alanes (up to 44 kcal/mol [28]).

More than ten years ago some complexes which included trimethyl amine-borane and trimethyl amine-borane were investigated by Ren *et al* [25]. It was found experimentally that the acidity of trimethyl amine-borane is between water and naphthalene and the gas-phase acidity value of 384.0 ± 2.0 kcal/mol

was assigned to the complex. They estimated that the coordination of Me_3N by BH_3 increases the C-H acidity by about 18 kcal/mol. It was also reported that due to an elimination reaction resulting in the removal of an ethyl group, experimental acidity for trimethyl amine-borane could not be determined. Beside the work of Ren *et al* there are three major papers that deal with the acidities of such complexes and are thus also related to our study.

Very recently the experimental gas-phase acidities measured by ESI-MS and Cooks kinetic method were published [27]. In this work the investigated amine-boranes were bulkier and the experiments were in a good agreement with G4 calculations. One important aim of this study was to determine the transition states of the reactions that lead to intramolecular changes. The $PhCH_2NH_2BH_3$ complex was used as a model to compare N-H deprotonation and a possible intramolecular reaction starting from B-H deprotonation. It was concluded that the B-H deprotonation is energetically too demanding.

Gas-phase acidities for six P-substituted phosphine-boranes with a bit bulkier substituents ($MePH_2BH_3$, Me_3PBH_3, $c\text{-}PrPH_2BH_3$, $PhPH_2BH_3$, $BnPH_2BH_3$, $ClCH_2PH_2BH_3$) have been also investigated – both experimentally and computationally [25, 26]. It is reported that the addition of BH_3 increases the acidity of phosphines by 20 to 30 kcal/mol. Studied complexes included chloromethyl phosphine-borane which was reported to be unstable in anionic form both experimentally and computationally [26].

It has been found that the AlH_3 enhances the acidity of phosphines even more than borane [28].From the mentioned works, only three similarly substituted complexes ($H_3X\text{-}YH_3$, $MeXH_2\text{-}YH_3$ and $PhXH_2\text{-}YH_3$, where X=N or P and Y=B or Al) can be found for which the acidity values of amine-borane, phosphine-borane and phosphine-alane species are known. The gas phase complexation free energies and the acidity values for those complexes (and additionally for unsubstituted complex) are presented on Tables 1 and 2. In all the complexes the substitution is made in the Lewis base. It should be noted that the values presented on Tables 1 and 2 are obtained with different methods and are therefore not completely comparable, but some general conclusions can still be drawn. Although only primary substituted complexes are compared, it can be seen that amines are the most stable among the complexes. Replacing the amine with phosphine reduces the stability of complex notably and the free energy of the complexation reaction becomes even more positive if we move on to phosphine-alanes. The trends in acidity are the opposite, phosphine-alanes are the most acidic, followed by phosphine-boranes and amine-boranes. It is explained that the anionic alane complexes are more stable than corresponding borane complexes due to the enhanced stability of the deprotonated alane species, as the delocalization of the P lone pair is more favorable in the presence of the P-Al bond compared to the P-B bond [28].

Table 1. The complexation free energies (in kcal/mol) for some Lewis acid base complexes.

R	RNH_2BH_3	RPH_2BH_3	RPH_2AlH_3
H	–18,6[a]	–12,2[c]	–5,6[c]
Me	–23,0[a]	–13,4[b]	–10,4[c]
c-Pr	–17,0[a]	–13,4[b]	–10,2[c]
Ph	–13.8[a]	–12,0[b]	–8,9[c]

a – values calculated with G4 method taken from ref [27], b – values calculated with B3LYP/6–311++G(3df,2p) method taken from ref [26], c – values calculated with G4 method taken from ref [28]

Table 2. The gas-phase acidity values (in kcal/mol) for some Lewis acid base complexes.

R	RNH_2BH_3	RPH_2BH_3	RPH_2AlH_3
H	349,8[d]	329,7[c]	317,1[c]
Me	349,5[a]	328,9[b]	325,2[c]
c-Pr	344,6[a]	337,1[b]	323,5[c]
Ph	326.7[a]	328,9[b]	316,9[c]

a – experimental values taken from ref [27], b – experimental values taken from ref [26], c – values calculated with G4 method taken from ref [28], d – value calculated with G4 method taken from ref [27]

It can be summarized that although there are some results concerning the complexes under question, the number of substituents studied is usually small and the substitutions selected are similar. Therefore no comprehensive comparisons based on broader bases can be made.

2.4. Investigated protonation reactions

The protonation center of amine-boranes is clearly located on the boron moiety and the resulting structure can be described as a dihydrogen connected to the rest of the complex ($RNH_2BH_2^+$ •• H_2) [29]. As an example, Figure 1 describes the structure of protonated amine-borane calculated by Patwari at the MP2 6-311++G(d,p) level [29]. This structure is important as possible practical applications involve the activation of hydrogen and such processes include dihydrogen-boron interaction. Related to the complex presented on Figure 1, it was found that the PA of the amine-borane is 191.7 kcal/mol and N-methyl substitutions increase the value (up to 200.2 kcal/mol for trimethyl amine-borane) [29].

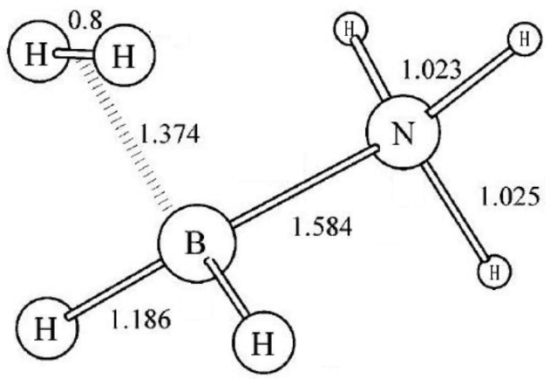


Figure 1. Protonated amine-borane structure as calculated by Patwari at the MP2/6-311++G(d,p) level [29].

So far proton affinities of complexes with only relatively small substituents have gained attention. More than ten years ago Skancke, Gaffoor, Anane and others [29-36] have published several works about the consecutively substituted borane complexes and about their proton affinities. For a series of methyl and halogen substituted amine- and phosphine-boranes it was found that successive addition of methyl groups to amines and phosphines increased the stability of the complexes [31, 33] and the consecutive fluorination of amine in amine-boranes decreased both the stability and proton affinity [35]. The trends in the series of chlorine substitutions in amine-boranes were analogous [32], but switching from amines to phosphines gave unexpected results [35, 36]. Despite the seeming similarity between amines and phosphines, the stability of fluorinated phosphine-boranes changed differently. In the series of H_3BPHnF_{3-n} (n = 0, 1, 2, and 3), the proton affinity decreases (from 186.8 kcal/mol for n = 3 to 158.8 kcal/mol for n = 0 at the G2MP2 level), while the complexation energy increases (values of 21.1 kcal/mol, 27.5 kcal/mol, 28.9 kcal/mol and 22.9

kcal/mol were assigned to the respective complexes at the G2MP2 level). This phenomenon was explained with hyperconjugation and back donation from BH_3 to phosphine moiety and the sudden decrease in the stability of H_3B-PF_3 was attributed to the repulsion between negatively charged fluorine atoms [35, 36].

2.5. Practical applications: amine-boranes as dihydrogen sources and activators

The fact that the hydrogen content in amine boranes is notably high has led to several investigations of their use as a dihydrogen source. It has been found that amine-boranes exhibit the property called dihydrogen bonding, where a metal-hydrogen [37, 38] or in this case a boron-hydrogen bond acts as a hydrogen acceptor to acidic groups [39, 40]. This can be observed for example in ammonia-borane where the B-H••H-N structure is present in dimers which are aligned head to tail. Such interaction is energetically favorable (over 5 kcal/mol of energy per interaction, there are two interactions per one dimer) and ultimately play a part in the release of dihydrogen.

The thermal decomposition of ammonia-borane can occur in solid state and in solvent. The simplest view to the separation of dihydrogen includes three steps [41]. The first steps corresponds to the formation of $(H_2N\text{-}BH_2)_X$, second to the formation of $(HN\text{-}BH)_X$, and third to the formation on BN. The first product $(H_2N\text{-}BH_2)_X$ is polymeric and very unstable. It decomposes and the resulting $(HN\text{-}BH)_X$ is a mixture of poorly defined polymeric substances consisting of boron, nitrogen and hydrogen. A more detailed view to the mechanism has been provided by Shaw et al [42] who used MAS NMR spectroscopy. Based on the observations another model consisting of three steps was proposed, including: induction, nucleation and growth. The most important step is the nucleation where the diammoniate of diborane (DADB) is generated (presented on Figure 2). The DADB can then react with ammonia-borane to release H_2 and oligomerize. It has been found that although the decomposition pathways are different in solution, the DADB still plays a role [43]. Unfortunately, it has been detected that the thermal dihydrogen release in not a reversible process [44].

There have been several computational studies on the mechanisms of the decomposition of amine-borane. Most studies deal with gas-phase reactions onto which the solvent effects are imposed. The overall picture is rather complicated as several alternative pathways with close activation energies are found. It should be noted that the thermodynamics of dehydrogenation of ammonia-borane in gas phase on coupled cluster level has been calculated [45]. According to those results the release of hydrogen from ammonia-borane is exothermic by -5.1 kcal/mol and the dehydrogenation from the resulting amino-borane is endothermic by 31.4 kcal/mol.

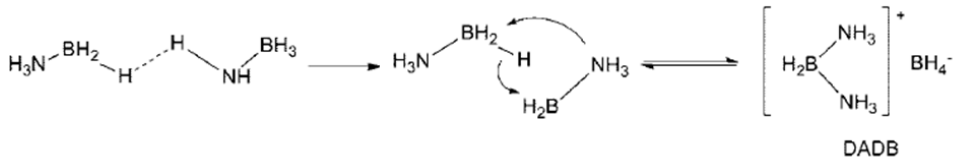


Figure 2. Theformation of DADB during the dihydrogen release reaction from ammonia-borane proposed by Shaw *et al* [42]. Figure is taken from ref [14].

Systems containing amine or phosphine together with borane group can be also used to activate dihydrogen for hydrogenation of imines and enamines [46–50]. The use of such compounds has many benefits as alternative transition-metal catalysts are expensive and toxicity concerns must be addressed. In this kind of dihydrogen activator the concept of dihydrogen bond is used. A molecular tweezer composing of a frustrated Lewis pair forms the core of the system [50, 51]. Amine group acts as a Lewis base and boron as an acid. In normal circumstances they would form a complex, but in the tweezer they are separated by a link that sterically prevents the B-N interaction. In the activation process the tweezer captures a H_2 between the boron and nitrogen and a N-H •• H-B dihydrogen bond is formed. One of the possible tweezers investigated by Sumerin *et al* is presented on Figure 3.The hydrogens captured can now be used to hydrogenate different species (imines and enamines for example). Such structures are experimentally verified and can be used to activate dihydrogen even from other amine-boranes [50, 52].

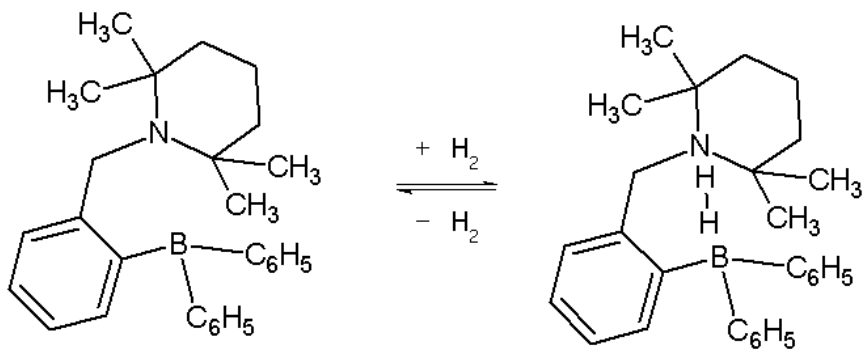


Figure 3. A molecular tweezer is capable of binding and releasing dihydrogen. Figure is taken from ref [50].

3. METHODOLOGY

Calculations in this work were performed by Gaussian 09[53] program package. A density functional theory method B3LYP [54] and an ab initio MP2 method [55–59] both with 6-311+G(d,p) [60-63] bases set were used. Both methods were in a good agreement and for the sake of simplicity, in the current thesis mostly MP2 results are used in discussion. In special cases where two or more acidity centers were close in energy, additional G2MP2 [64] calculations were performed. Vibrational analyses for zero-point energies and thermal corrections were carried out. All stationary points were found to be true minima (NImag=0). For all species full conformational search was done, for protonated and deprotonated species all possible protonation and deprotonation centers were investigated and only the most stable structures were used. For a free proton, the Gibbs free energy value of 0.01 au (ca. 0.0627 kcal/mol) was used; derived from statistical thermodynamics under standard state (298.15 K and 1 atm) conditions. Enthalpy:

$$H(H^+) = U + pV = \frac{5}{2}RT, \tag{6}$$

where U is internal energy, p is pressure, V is volume, R is the universal gas constant, and T corresponds to absolute temperature. Entropy:

$$S(H^+) = R \ln\left(\frac{e^{\frac{5}{2}}k_B T}{p\Lambda^3}\right), \tag{7}$$

where k_B is Boltzmann constant and the thermal De Broglie wavelength Λ can be obtained as follows:

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}, \tag{8}$$

where h is Planck's constant and m is the mass of the proton. Gibbs free energy:

$$G(H^+) = H(H^+) + TS(H^+). \tag{9}$$

In the case of complexation energies and dihydrogen removal reaction, basis set superposition error (BSSE) was calculated using the counterpoise method of Boys and Bernardi [66-68]. The BSSE estimations for both methods were quite constant, the values for MP2/6-311+G(d,p) calculations were approximately 4–5 kcal/mol for complexation reactions and about 2 kcal/mol for dihydrogen removal.

To investigate the electronic structure of some complexes in more detail, Bader's Atoms in Molecules (AIM) [69] analysis was performed using AIMAll program package [70]. The AIM analyzes is based solely on the wave function

obtained for a given molecule and therefore it's dependency on the chosen method and bases set are rather small (only on the extent how well can the wave function be described using the chosen bases set). The wave function is used to calculate the electron density of the system as a function of the three spatial coordinates.

The AIM approach allows to analyze the electron density in terms of topology. The critical points and topologic parameters are used to characterize the interactions between atoms and assess the strength of the bonds present in a molecule. For example, if we trace the maximum electron density between two nuclei, we obtain a bond path that characterizes the shape of the bond. Two important characteristics of the AIM analysis are the electron density (ρ) and the laplacian of the electron density ($\nabla^2\rho$) in the bond critical point (BCP, where the electron density is minimal along the bond path). Electron density at the BCP indicates the amount of electrons involved in the bond formation and higher density refers to a stronger bond. The laplacian of the electron density in the BCP characterizes the curvature of the electron density distribution and is an indicator of bond covalency. Negative values generally refer to more covalent interactions.

4. RESULTS AND DISCUSSION

4.1. Investigated complexes and complexation energies

We have studied the gas-phase stabilities, acidities, basicities and dihydrogen release from protonated species for several substituted amine-boranes, phosphine-boranes and for hydrazine-boranes. Variety of different substituents were used in the Lewis base, resulting in primary, secondary and tertiary species. The substituents included methyl, trifluoroethyl, 2-chloroethy, allyl, propargyl, adamantyl, benzyl, phenyl, propyl, c-propyl, dimethyl, ethenyl-methyl, trimethyl, ethenyldimethyl. Some cyclical structures (pyridine/ phosphorine, aziridine, azetidine, pyrrolidine) were also used as Lewis bases.

The stabilities of the complexes were calculated as the Gibbs free energy change (ΔG) for the complexation reaction, for example in case of amine-boranes:

$$R_1R_2R_3N + BH_3 \rightarrow R_1R_2R_3N\text{-}BH_3. \quad (10)$$

Based on the previously published data about primary substituted complexes it was possible to conclude that the amine-boranes are generally more stable than phosphine-boranes (with the exception of halogen substitutions). Our comparative calculations based on eleven amine-boranes and phosphine boranes revealed that although this is generally true, there are some exceptions. According to our results the ΔG for the complexation reaction for amine-boranes was from –14.1 to –22.1 kcal/mol and –6.6 to –22.2 kcal/mol for phosphine-boranes. The results for all eleven complexes can be found in Table 3 and are more thoroughly discussed in article III. The $\Delta\Delta G$ values comparing complexes with the same substituents varied from –1.7 to 11.3 kcal/mol and it is evident from those values that some phosphine boranes can be more stable than corresponding amine boranes. The substituent that makes the phosphine complex more stable compared to respective amine-borane is phenyl. The reason why phenyl phosphine-borane is more stable than the amine counterpart comes from the relative instability of the latter. The conjugation of the free electron pair is much better in aniline than it is in phenyl phosphine. As a result the electron pair is harder to access and while the complexation itself is favorable, some of the delocalization is lost. It is reported in article III that the differences can also be observed analyzing the geometries of the species as the H-N-H angle in aniline decreases much more in the complexation process than it is typical for amines. No untypical geometry changes occur in the case of phenyl phosphine complexation. NBO charges tell the same story as in aniline 1.904 electrons are located in the orbital occupied by the lone pair of nitrogen and upon complexation, the value increases to 1.992 electrons. In phenyl phosphine the electron occupancy change is negligible.

Table 3. Calculated complexation free energies at the MP2/6-311+G(d,p) level. Table is taken from article III.

Lewis base in complex	phosphine-borane	amine-borane	Δ
Ammonia/phosphine	–8.3	–14.1[a]	5.8
Methyl amine/phosphine	–13.4	–18.4[a]	5.0
Cyclopropyl amine/phosphine	–14.1	–17.3[a]	3.2
Adamantyl amine/phosphine	–13.9	–16.5[a]	2.6
2-Chloroethyl amine/phosphine	–12.2	–15.2[a]	3.0
Trifluoroethyl amine/phosphine	–11.3	–15.4[a]	4.1
Phenyl amine/phosphine	–13.8	–12.1[a]	-1.7
Benzyl amine/phosphine	–13.0	–18.2[a]	5.2
Dimethyl amine/phosphine	–18.1	–21.0[a]	2.9
Pyridine/phosphorine	–6.6	–17.9[a]	11.3
Trimethyl amine/phosphine	–22.2	–22.1[a]	-0.1

It is also noteworthy that phosphorine-borane is much less stable (the Gibbs energy of complex is only -6.6 kcal/mol) towards dissociation compared to other phosphine complexes. The reason behind this unexpected instability can be found in its electronic structure. Phosphorine is the analogue of pyridine in which the nitrogen is replaced by phosphorus and while the free electron pair in pyridine is located in the highest occupied molecular orbital (HOMO) the same pair in phosphorine is related to lower energy molecular orbitals [71]. As a result the free electron pair is harder to access and phosphorine is much worse Lewis base.

In addition to the regular substitutions we have also investigated hydrazine-borane and hydrazine-bisborane. Hydrazine-borane can be considered as an amine-borane with specific substitution that enables the formation of a bisborane and will be discussed separately from rest of the amine-boranes in this work. Similarly to amine-boranes the both mentioned hydrazine complexes are stable in the gas phase, the calculated Gibbs free energy for the first BH_3 addition is -17.1 kcal/mol, and -15.8 kcal/mol for the addition of second BH_3.

4.2. Acidity and deprotonated structures

We have investigated the deprotonation reactions of nineteen amine-boranes, eleven phosphine-boranes and two hydrazine-boranes. It can be concluded that the most favorable acidity center in complexes involving primary and secondary amines or phosphines is expectedly located on the nitrogen or on phosphorus and the tertiary substituted ones behave like C-H acids, with the exception of pyridine- and phosphorine-boranes. According to the additional G2MP2

calculations the B-H hydrogens in phosphorine-borane are 5.5 kcal/mol and in pyridine-borane 0.5 kcal/mol more acidic than the C-H hydrogens (article III).

Phosphine-boranes can generally be considered more acidic than amine-boranes. There is a significant difference in the charge distribution comparing amine and phosphine complexes, as the acidity centers have different charges. The nitrogen in amine-boranes holds a negative charge, while phosphorus in phosphine-boranes is strongly positive (the average charge on phosphorus in neutral phosphine-borane is 1.02 and it decreases to 0.47 in deprotonated species) and can help to stabilize the negative charge left by deprotonation. The acidity values vary from 327.3 to 349.1 kcal/mol for the N-H group and from 323.0 to 340.9 kcal/mol for P-H group, respectively. The phenyl substitution is the only known exception to the generalization that phosphine-boranes are more acidic – aniline-borane is more acidic than its phosphine counterpart, as the stabilizing effect from charge delocalization in the phenyl phosphine complex is smaller.

The substitutions change the acidities of phosphine- and amine-boranes differently. The substitutions in amine-boranes clearly increase the N-H acidity as the acidities of all substituted complexes are higher than the acidity of ammonia-borane (with the exception of methyl substitution, where the difference is negligible). This is not the case for phosphine-boranes as the alkyl substitutions tend to decrease the acidity. For example, compared to unsubstituted phosphine-borane the methyl substitution decreases the acidity by 6.7 kcal/mol, cyclopropyl by 2.9 kcal/mol, adamantyl by 2.1 kcal/mol, and dimethyl by 9.1 kcal/mol.

All deprotonation centers in all complexes were investigated and it was found that in some cases some amine-boranes went through intramolecular changes, i.e. rearranged to different chemical species (article II) if B-H deprotonated species were taken as the starting points for optimization. The resulting structures were energetically more favorable compared to the regular deprotonated structures without changes. Martin-Comer et al. [27] also came across this phenomena and based on the transitions states obtained for deprotonation reactions for benzyl amine-borane, concluded that the B-H deprotonation is energetically too demanding. Their theoretical work was supplemented by experiment and explains most of the dissociations we also encountered. However, the questions about 2-chloroethylamine-borane and ethenyldimethyl amine-borane still remain. For those two complexes the energy difference between the “unchanged” and “changed” deprotonated structures were the largest (article II).It can be said that hydrazine-borane and hydrazine-bisborane also belong into this group, as the decomposition reactions starting from B-H deprotonation result in energetically very favorable structures (ca. 37 kcal/mol in both cases, compared to unchanged N-H deprotonated structures).Similarly to amine complex the 2-chloroethyl phosphine-borane was also found to be unstable towards deprotonation (article III).The instability of the related 2-chloromethyl species has been previously reported [26]. It was found that the

chlorine ion dissociates from the deprotonated structures and we observed the same result in both deprotonated 2-chloroethyl substituted complexes.

Stabilities of Lewis acid base complexes are dependent on the amount of electrons donated by the base to the acid. That in turn is dependent on the substituents which also affect the acidity. In the complexes studied in current work the substituents are directly connected to the electron pair donor which is in most cases also the acidity center and therefore the dependency is notably high. For example, if we have a substituent with strong electron withdrawing ability it would make the complex less stable, as electrons are withdrawn from the donor-acceptor bond, but at the same time the charge withdrawing ability would enhance the acidity, as the charge is delocalized from the deprotonation center. Based on this reasoning, it can be concluded that the complexes with very high acidity would be unstable and to design more acidic species an alternative deprotonation center should be introduced.

4.3. Basicity and protonated structures

The protonated structure of the complexes studied in this work can be described as H_2 connected to the rest of the positively charged complex ($R_1R_2R_3X$-$BH_2^+\cdot\cdot H_2$) and is therefore similar to the geometry described earlier by Patwari (Figure 1.) It can be stated that the boron moiety is clearly the most favored protonation center. If we compare the proton acceptor abilities of amine- and phosphorine-boranes, it can be said that the values are quite close, although the amine complexes are somewhat more basic (ca. 5 kcal/mol) as the basicities of phosphine-boranes vary from 181.8 to 193.1 kcal/mol (article III), while the same values for amine-boranes vary from 180.2 to 198.1 kcal/mol (article I). The substitutions tend to increase the basicity and the only investigated exception was the electron withdrawing trifluoroethyl group. The overall enhancement is dependent on the size of substituents and number of substitutions as increase in both parameters also increases the basicity.

The bond paths are one of the most interesting features of the complexes in this study. The dihydrogen with boron forms a 3-center-2-electron bond. The bond shapes in the species are rather unusual and depend on the type of the complex. The Baders AIM analysis has revealed that the bond paths in amine complexes (hydrazine-borane included) and phosphine-complexes are different. The difference is illustrated in Figure 4 taken from article III. In amine-complexes there are three notably curved bond paths forming a cycle, while in phosphine-boranes the boron interacts with the bond critical point in H_2.

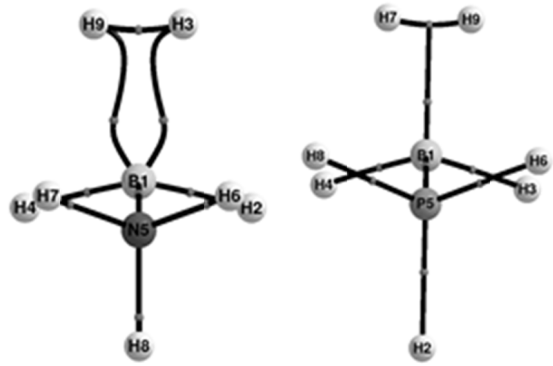


Figure 4. Bond paths and bond critical points (dots on bond paths) in protonated ammonia-borane (curved topology) and phosphine-borane (T-shaped topology). Picture taken from article III.

It was stated earlier that amine-boranes are generally more basic than respective phosphine-boranes, but few exceptions can be mentioned. Our research revealed that in some cases the substitution effects can be more important than the electronic differences coming from nitrogen/phosphorus atom and in some cases it is vice versa. Below some complexes with more interesting substitutions are discussed (more detailed discussion can be found in articles I–III).

It should be noted that the basicity gap between amine and phosphine complexes gradually decreases upon consecutive methyl substitution from 6.4 kcal/mol to none. It can be concluded that substituents have greater effect to the basicities of phosphine-boranes than for amine-boranes. This is somewhat expected as the basicities of phosphine-boranes tend to be smaller and it is easier to enhance the basicity of a low basicity compound than increase the basicity of an already highly basic compound.

Other interesting case is the pair consisting of pyridine-borane and phosphorine-borane. In this species the change of nitrogen for phosphorus has a considerable effect. The basicity difference between the two is untypically large, 12.0 kcal/mol in the favor of the pyridine-complex. It can be noted that the Gibbs free energy for the protonation reaction of phosphorine-borane is one of the lowest among the studied phosphine complexes while the value assigned to pyridine complex is the highest among amine-borane complexes. Neutral phosphorine-borane was relatively unstable compared to pyridine-borane and our results show that the addition of the proton increases the energy gap even more.

AIM analyses revealed that protonated phenyl substituted complexes have a special structure. As an example the most stable conformer of protonated benzyl amine-borane is presented on Figure 5 (taken from article I). In benzyl substituted complexes a conformation exists where the distance between H_2 and benzene ring is rather small (2.4 A in benzyl amine-borane) and a direct

interaction is possible. The resulting geometry can be described as H_2 captured between the positively charged boron and a negative π-system and is closely related to the concept of molecular tweezers [50, 72]. It was found that this kind of interaction is also present in other protonated borane complexes containing a suitably placed substituent involving π-system, like in $HCCCH_2NH_2BH_3$ and $H_2CCHCH_2NH_2BH_3$ (article I).

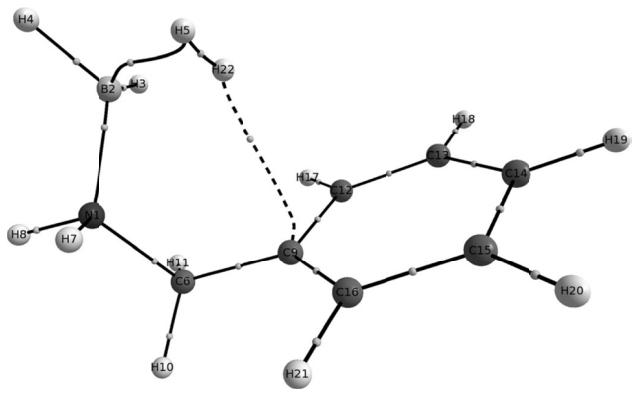


Figure 5. Bond paths in protonated benzyl amine-borane. Taken from article I.

The protonated structure of hydrazine-borane is very similar to amine-boranes described in Figure 4. Bulkier carbon based N-substitutions in amine-boranes usually increase the basicity and electron withdrawing groups have the opposite effect (article I). The second nitrogen in hydrazine-borane can be viewed as an electron withdrawing group and as a result the basicity of hydrazine-borane (183 kcal/mol) is somewhat smaller than the basicity of ammonia-borane (185.4 kcal/mol). The attachment of the second BH_3 supports the formation of a considerably different protonated structure. The additional link in the backbone of the species allows a formation of a cyclic structure which is presented in Figure 6. The structure resembles the structure of protonated benzyl amine-borane as the H_2 is captured between positively charged boron and negatively charged hydrogen. The basicity of the bis-BH3 complex (172.8 kcal/mol) is considerably lower than the basicity of any investigated amine or phosphine-complex.

Figure 6. Bond paths in protonated hydrazine-bisborane.

The special case of protonated cyclopropyl substituted complexes should be mentioned. In such complexes the protonation on the cycle initiates irreversible intramolecular changes leading to the destruction of the cycle and resulting in energetically more favored structure. By definition a reversible equilibrium protonation reaction is needed for the gas phase basicity determination and therefore no true basicity value can be assigned to cyclopropyl substituted complexes.

4.4. The release of H_2 from protonated structures

The protonated structures of complexes under study could be described as di-hydrogen connected to the rest of the molecule. Looking at such structure an obvious question arises – how strongly is the H_2 connected. The dissociation under investigation is described by the following reaction:

$$R_1R_2R_3X\text{-}BH_2^+ \bullet\bullet H_2 \rightarrow R_1R_2R_3X\text{-}BH_2^+ + H_2 \qquad X= N, P. \qquad (11)$$

It has been calculated (article I and article III) and shown experimentally (article I) that the removal of H_2 is clearly an exergonic process. The main driving force for the dihydrogen removal is entropy. The entropy term in the given conditions ranges from 7 to 9 kcal/mol which means that in most cases the reaction enthalpy is close to zero or even slightly positive.

Our calculation show that the Gibbs free energies values for the H_2 release from protonated complexes vary from –5.3 to –11.0 kcal/mol for amine-boranes, from 0.1 to –8.1 kcal/mol for phosphine-boranes and are especially large for hydrazine-borane and hydrazine-bisborane (–20.9 and –27.2 kcal/mol respectfully). The only investigated case where the reaction was not exergonic (0.1 kcal/mol) was the hydrogen release from methyl phosphine-borane. On the other end of the spectrum phosphorine/pyridine-borane and benzyl substituted

complexes can be found. Phosphorine- and pyridine-borane release dihydrogen much more favorably because the resulting $C_5H_5X\cdots BH_2^+$(X= P, N) structures are close to planar and the charge is thus well delocalized.

The benzyl substituted complexes are an example of a special case. The structures of protonated benzyl substituted complexes were discussed above and it was described that the $H_2$is captured into structure similar to molecular tweezers. At the first glace such interaction could hinder the release of H_2 as the interaction can make the dissociation energetically more expensive, but this is not the case. When a H_2 is removed a new interaction is formed. The interactions both before and after H_2 removal are illustrated on Figure 7 taken from article III. Data from AIM analyses and shorter interaction distances show that the new C-B_π interaction is considerably stronger than the old H_{H2}-B_π interaction. This is also the reason why the dihydrogen release from benzyl substituted complexes is unexpectedly favored.

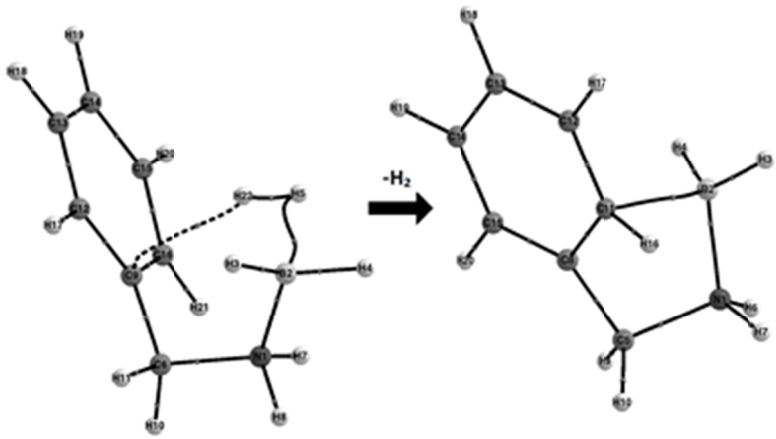


Figure 7. The bond paths protonated benzylamine-borane before and after dihydrogen removal.

The dihydrogen release from protonated hydrazine-borane and hydrazine-bisborane leads to the formation of cycles. After the removal of H_2 from hydrazine-borane an empty orbital is left on boron and there is a free electron pair on second nitrogen. As a result an intramolecular Lewis complexation reaction takes place and a three membered cycle is formed and 20.9 kcal/mol of energy is released. In protonated hydrazine-bisborane the H_2 was captured between the negatively charged hydrogen and a positive boron (B-H••H2••B). Similarly to benzyl substituted complexes, after the dihydrogen release a new direct interaction (B••H••B) can form. Compared to hydrazine-borane the interaction is a bit different as it involves a five membered ring that includes a 3-

centre-2-electron B-H-B bond. The H_2 release from protonated hydrazine-bisborane is exceptionally exergonic as the ΔG is –27.2 kcal/mol.

From the hydrogen storage perspective the dihydrogen release from the complexes studied tends to be too exergonic and irreversible under conditions used in this work. Although phosphorus is heavier, replacing the nitrogen with phosphorus could be a step into right direction as the replacement with heavier atom is not disadvantage if we consider the potential for dihydrogen activation.

5. CONCLUSIONS

Variety of substituted amine-borane and phosphane-borane complexes were studied using computational B3LYP/6-311+G** and MP2/6-311+G** methods. The substituents included alkyl, alkene, alkyne and aryl groups as well as halogen atoms and sterically strained systems. Both used methods gave concurrent results and were in good agreement with the known experimental data. The complexation energies, gas-phase acidities, basicities and the energies for dihydrogen dissociation from protonated species were calculated.

A formation of neutral complex is thermodynamically favored process for all studied systems. Amine-boranes are generally more stable than the respective phosphine-boranes and substituents tend to increase the stability of both types of complexes. The N-H and P-H are the most favorable acidity centers. The acidity value for the N-H group ranges from 327.3 to 349.1 kcal/mol and the acidity value for the P-H group ranges from 323.0 to 340.9 kcal/mol. The tertiary substituted complexes have to act like C-H acids and are therefore less acidic.

The most favorable basicity center is in both type of complexes located on the boron moiety. The resulting structure $R_1R_2R_3X\text{-}BH_2^+ \bullet\bullet H_2$ can be described as dihydrogen loosely connected to the rest of positively charged complexes. The interactions connecting the H_2 can be characterized as 3-center 2 electron bonds. Baders Atoms in Molecules approach has revealed that the bond paths involved in this interaction are different for amine-boranes and phosphine-boranes.

The dihydrogen release from protonated species is an exergonic process driven by entropy. The Gibbs free energy values for the process range from –5.3 to –11.0 kcal/mol for amine-boranes and from 0.1 to –8.1 kcal/mol for phosphine-boranes. The investigation of interactions revealed that a suitably placed substituent may lead to the formation of a so called “molecular tweezer”. For example in benzyl substituted complexes the H_2 is captured between the positive boron and negatively charged π-system. Unexpectedly, the interactions causing the “tweezer” also increase the exergonicity of the H_2 release, as a new and stronger direct link between the π-system and boron is formed upon dihydrogen removal. The hydrogen removal for hydrazine-boranes was found to be extremely exergonic.

SUMMARY IN ESTONIAN

Amiin-boraanide ja nende fosforanaloogide omadused gaasifaasis

Käesoleva töö raames uuriti arvutuslike B3LYP/6-311+G** ja MP2/6-311+G** meetoditega amiin- ja fosfiin-boraan komplekse. Amiinides ning fosfiinides kasutati erinevaid asendajaid – alküül, alkeen, alküül jaarüülrühmi, kloori ning fluori aatomeid sisaldavaid gruppe ning steeriliselt pingestatud süsteeme. Mõlemad kasutatud meetodid andsid kokkulangevaid tulemusi, mis olid omakorda kooskõlas ka teadaolevate eksperimentaalsete andmetega. Kõigile uuritud kompleksidele arvutati komplekseerumisenergia, gaasifaasiline happelisus, gaasifaasiline aluselisus ning protoneeritud kompleksist H_2 eraldumisele vastava reaktsioonivabaenergia.

Kõigi uuritud komplekside moodustumine oli termodünaamiliselt soodne protsess. Võib teha üldised järeldused, et amiin-boraanid on stabiilsemad kui vastavad fosfiin-boraanid ning asendajad suurendavad reeglina mõlemat tüüpi komplekside stabiilsust. N-H and P-H vesinikud on vastavalt amiin ja fosfiin kompleksides kõige happelisemad. N-H vesiniku happelisus amiin-boraanis varieerub 327.3 kcal/mol kuni 349.1 kcal/mol ja P-H vesiniku happelisus fosfiin-boraanis varieerub 323.0 kcal/mol kuni 340.9 kcal/mol.

Uuritud komplekside energeetiliselt soodsaim aluselisuse tsenter paikneb boraanis. Protoneerumise tulemusel tekib kompleks $R_1R_2R_3X\text{-}BH_2^+ \bullet\bullet H_2$, mida võib kirjeldada kui positiivset laetud kompleksi, mis on nõrgalt seotud vesiniku molekuliga. Nimetatud struktuuris moodustavad kaks elektroni kolm sidet ning Baderi laengutiheduse topoloogiline analüüs näitab, et vastavates interaktsioonides ilmnevadamiin-boraane ja fosfiin-boraane võrreldes tähelepanuväärsed erinevused.

Vesiniku eraldumine protoneeritud kompleksidest on eksergooniline protsess, selle põhjuseks on entroopia. Eraldumisreaktsiooni Gibbsi vabaenergia muut varieerub amiin-boraanide puhul –5.3 ja –11.0 kcal/mol vahel ning fosfiin-boraanide korral 0.1 kcal/mol ja –8.1 kcal/mol vahel. Asendusrühmade mõju uurimine antud kompleksides näitas, et teatud omadustega asendajate korral omandab protoneeritud kompleks konformatsiooni, kus vesinik on haaratud positiivselt laetud boori ja negatiivselt laetud π elektrone sisaldava süsteemi vahele. Kirjeldatud struktuur esineb näiteks protoneeritud bensüülamiin-boraanis. Ootamatult muudab selline interaktsioon vesiniku lahkumise energeetiliselt veelgi soodsamaks. Uurimise tulemusena selgus, et selle põhjuseks on uus otsene ja tugevam side, mis tekib boori ja negatiivselt laetud π süsteemi vahele.

REFERENCES

1. Brønsted, J. N. Recl. Trav. Chim. Pays-Bas 1923, 42, 718.
2. Brønsted, J. N. Chem. Rev. 1928, 5, 231.
3. Lowry, T. M. Chem. Ind. (London) 1923, 42, 43.
4. Lowry, T. M. Chem. Ind. (London) 1923, 42, 1048.
5. Gay-Lussac, J. L.; Thenard, J. A. Mem. Phys. Chim. Soc. D'Arcueil 1809, 69, 204–220.
6. Gay-Lussac, J.L.; Thenard, J. A. Mem. Phys. Chim. Soc D'Arcueil 1809, 2, 317–331.
7. Shore, S. G.; Parry, R. W. J. Am. Chem. Soc. 1955, 77, 6084.
8. Carboni, B.; Monnier, L. Tetrahedron 1999, 55, 1197.
9. Baxter, E. W.; Reitz, A. B. Org. React. 2002, 59, 1.
10. Carboni, B.; Carreaux, F. Sci. Synth. 2004, 6, 455.
11. Takrouri, K.; Dembitsky, V. M.; Srebnik, M. Stud. Inorg. Chem. 2005, 22, 495.
12. Jabbour, A.; Smoum, R.; Takrouri, K.; Shalom, E.; Zaks, B.; Steinberg, D.; Rubinstein, A.; Goldberg, I.; Katzhendler, J.; Srebnik, M. Pure Appl. Chem. 2006, 78, 1425.
13. Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. Chem. Rev. 2010, 110, 4023–4078.
14. Staubitz, A.; Robertson, A. P. M.; Manners, I. Chem. Rev. 2010, 110, 4079–4124.
15. Hügle, T.; Kühnel, M. F.; Lentz, D. J. Am. Chem. Soc. 2009, 131, 7444–7446.
16. Goubeau, J.; Ricker, E. Z. Anorg. Allg. Chem. 1961, 310, 123–142.
17. Besson, A. Comptes Rendus 1890, 110, 516.
18. Gamble, E. L.; Gilmont, P. J. Am. Chem. Soc. 1940, 62, 717.
19. Ashby, E. C. J. Am. Chem. Soc. 1964, 86, 1882–1883.
20. Sircoglou, M.; Saffon, N.; Miqueu, K.; Bouhadir, G.; Bourissou, D. Organometallics 2013, 32, 6780–6784.
21. Alton, E. R.; Montemayor, R. G.; Parry, R. W. Inorg. Chem. 1974, 13, 2267–2270.
22. Rosenstock, H.M.; Draxl, K.; Steiner, B.W.; Herron, J.T. "Ion Energetics Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. Linstrom, P.J.; Mallard, W.G. National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved May 17, 2013).
23. Radisic, D.; Xu, S. J.; Bowen, K. H. Chem. Phys. Lett. 2002, 354, 9–13.
24. Gamez, J. A. ; Guillemin, J-C.; Mo, O.; Yanez, M. Chem. Eur. J. 2008, 14, 2201.
25. Ren, J.; Workman, D. B.; Squires, R. R. J. Am. Chem. Soc. 1998, 120, 10511.
26. Hurtado, M.; Yanez, M.; Herrero, R.; Guerrero, A.; Davalos, J. Z.; Abboud, J-L. M.; Khater, B.; Guillemin, J-C. Chem. Eur. J. 2009, 15, 4622.
27. Martín-Sómer, A.; Lamsabhi, A. M.; Yáñez, M.; Dávalos J. Z.; González, J. R. R.; Guillemin J-C. Chem. Eur. J. 2012, 18, 15699–15705.
28. Martín-Sómer, A.; Lamsabhi, A.M.; Mó, O.; Yáñez, M. J. Phys. Chem. A 2012, 116, 6950–6954.
29. Patwari, G.N. J. Phys. Chem. A 2005, 109, 2035–2038.
30. Skancke, A.; Skancke, P. N. J. Phys. Chem. 1996, 100, 15079–15082.
31. Gaffoor, F.; Ford, T.A.; Spectrochim. Acta Part A 2008, 71, 550–558.
32. Anane, H.; El Houssame, S.; El Guerraze, A.; Guermoune, A.; Boutalib, A.; Jarid, A.; Nebot-Gil, I.; Tomás, F. Cent. Eur. J. Chem. 2008, 6, 400–403.
33. Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. Chem. Phys. Lett. 1998, 287, 575–578.

34. Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. J. Mol. Struct. (Theochem) 1998, 455, 51–57.
35. Anane, H.; El Houssame, S.; El Guerraze, A.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. J. Mol. Struct. (Theochem) 2004, 709, 103–107.
36. Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. Chem. Phys. Lett. 2000, 324, 156–160.
37. Stevans, R. C.; Bau, R.; Milstein, R.; Blum, O.; Koetzle, T. F. J. Chem. Soc. Dalton Trans. 1990, 1429.
38. Vander Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. J. Am. Chem. Soc. 1990, 112, 4381.
39. Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. J. Am. Chem. Soc. 1999, 121, 6337.
40. Richardson, T. B.; Gala, S. D.; Crabtree, R. H.; Siegbahn, P. E. M. J. Am. Chem. Soc. 1995, 117, 12875.
41. Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. Thermochim. Acta 1978, 23, 249.
42. Stowe, A. C.; Shaw, W. J.; Linehan, J. C.; Schmid, B.; Autrey, T. Phys. Chem. Chem. Phys. 2007, 9, 1831.
43. Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. Angew. Chem., Int. Ed. 2008, 47, 7493.
44. Baitalow, F.; Wolf, G.; Grolier, J. P. E.; Dan, F.; Randzio, S. L. Thermochim. Acta 2006, 445, 121.
45. Dixon, D. A.; Gutowski, M. J. Phys. Chem. A 2005, 109, 5129.
46. Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Science 2006, 314, 1124–1126.
47. Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Angew. Chem. Int. Ed. 2007, 46, 8050–8053.
48. Chase, P. A.; Stephan, D. W. Angew. Chem. Int. Ed. 2008, 47, 7433–7437
49. Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. Angew. Chem. Int. Ed. 2008, 47, 7543–7546.
50. Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. J. Am. Chem. Soc. 2008, 130, 14117–14119.
51. Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. J. Organomet. Chem. 2009, 694, 2654 –2660.
52. Guo, Y.; He, X.; Li, Z.; Zou, Z. Inorg. Chem. 2010, 49, 3419.
53. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

54. Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
55. Head-Gordon, M.; Pople, J. A.; Frisch, M. J. Chem. Phys. Lett. 1988, 153, 503.
56. Saebø, S.; Almlöf, J. Chem. Phys. Lett. 1989, 154, 83.
57. Frisch, M. J.; Head-Gordon, M.; Pople, J. A. Chem. Phys. Lett. 1990, 166, 275.
58. Frisch, M. J.; Head-Gordon, M.; Pople, J. A. Chem. Phys. Lett. 1990, 166, 281.
59. Head-Gordon, M.; Head-Gordon, T. Chem. Phys. Lett. 220 (1994) 122.
60. McLean, D.; Chandler, G. S. J. Chem. Phys. 1980, 72, 5639.
61. Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. J. Chem. Phys., 1980, 72, 650.
62. Binning Jr. R. C.; Curtiss, L. A. J. Comp. Chem. 1990, 11, 1206.
63. Frisch, M. J.; Pople, J. A.; Binkley, J. S. J. Chem. Phys. 1984, 80, 3265.
64. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. J. Chem. Phys. 1991, 94, 7221–30.
65. Curtiss, L. A.; Raghavachari, K.; Pople, J. A. J. Chem. Phys., 1993, 98, 1293–98.
66. Boys, S. F.; Bernardi, F. Mol. Phys. 1970, 19, 553–566.
67. Simon, S.; Duran, M.; Dannenberg, J. J. J. Chem. Phys. 1996, 105, 11024–11031.
68. Sordo, J.A. J. Mol. Struct. (Theochem) 2001, 537, 245–251.
69. Bader, R. F. W. Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.
70. Keith, T. A. AIMAll, Version 11.04.03, (aim.tkgristmill.com).
71. Márkl, G. Phosphorous Sulfur 1977, 3, 77–108.
72. Chen, C. W.; Whitlock H. W. Jr. J. Am. Chem. Soc., 1978, 100, 4921–4922.

ACKNOWLEDGEMENTS

I am very grateful to Peeter Burk for his professional supervision and guidance. I appreciate the support from my research group and would also like to thank my co-authors from Madrid and Rennes. Advice concerning some linguistic and formatting questions from Kairi Raabe must be mentioned.

I acknowledge the support from the Estonian Science Foundation (Grant No. 8809) and the Estonian Ministry of Education and Research Targeted Financing Project No. SF0180120s08. My work was inspired by an Integrated Exchange Program 'PARROT' co-financed by the Estonian Science Foundation and the French Ministry of Foreign Affairs. In addition, the work has been partially supported by graduate school "Functional materials and technologies" receiving funding from the European Social Fund under project 1.2.0401.09-0079 in Estonia.

PUBLICATIONS

CURRICULUM VITAE

Name: Aiko Adamson
Born: 07.06.1986
Citizenship: Estonian
E-mail: adamson@ut.ee

Education:

2010–present	University of Tartu, Faculty of Science and Technology, Institute of Chemistry, PhD Student
2008–2010	University of Tartu, Faculty of Science and Technology, Institute of Chemistry, *M.Sc.* (theoretical and computational chemistry)
2005–2008	University of Tartu, Department of Chemestry, *B.Sc*, (chemistry)
2002–2005	Nõo Real Gymnasium
1993–2002	Co-educational Gymnasium of Paide

Work Experience:

2014–present	University of Tartu, Faculty of Science and Technology, Institute of Chemistry, Testing Centre, specialist
2013–present	Quretec OÜ, analyst/software developer

Publications:

1. Abboud, J-L. M.; Németh, B.; Guillemin, J-C.; Burk, P.; Adamson, A.; Nerut, E. R. Dihydrogen generation from amine/boranes: synthesis, FT-ICR, and computational studies. *Chem. Eur. J.* **2012**, 18, 3981–3991.
2. Adamson, A.; Guillemin, J.C.; Burk, P. Acidities of N-Substituted Amine–boranes. *J. Mol. Mod.* **2013**, 19, 5089–5095.
3. Adamson, A.; Burk, P. P-substituted phosphine–boranes: Gas phase acidities, basicities and dihydrogen release. A comparison to amine–boranes. *Comp. Theor. Chem.* **2014**, 1032, 12–19.

ELULOOKIRJELDUS

Nimi: Aiko Adamson
Sündinud: 07.06.1986
Kodakondsus: Eesti
E-post: adamson@ut.ee

Hariduskäik:

2010–...	Tartu Ülikool, Loodus- ja tehnoloogiateaduskond, Keemia instituut, doktorant.
2008–2010	Tartu Ülikool, Loodus- ja tehnoloogiateaduskond, Keemia instituut, *M.Sc.* (teoreetiline- ja arvutikeemia)
2005–2008	Tartu Ülikool, Füüsika-keemiateaduskond, Keemia instituut, *B.S* (keemia)
2002–2005	Nõo Reaalgümnaasium
1993–2002	Paide Ühisgümnaasium

Teenistuskäik:

2014–...	Tartu Ülikool, Loodus ja tehnoloogiateaduskond, Keemia instituut, Katsekoda, spetsialist
2013–...	Quretec OÜ, analüütik–tarkvara arendaja

Publikatsioonid:

1. Abboud, J-L. M.; Németh, B.; Guillemin, J-C.; Burk, P.; Adamson, A.; Nerut, E. R. Dihydrogen generation from amine/boranes: synthesis, FT-ICR, and computational studies. *Chem. Eur. J.* **2012**, 18, 3981–3991.
2. Adamson, A.; Guillemin, J.C.; Burk, P. Acidities of N-Substituted Amine–boranes. *J. Mol. Mod.* **2013**, 19, 5089–5095.
3. Adamson, A.; Burk, P. P-substituted phosphine–boranes: Gas phase acidities, basicities and dihydrogen release. A comparison to amine–boranes. *Comp. Theor. Chem.* **2014**, 1032, 12–19.

DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

1. **Toomas Tamm.** Quantum-chemical simulation of solvent effects. Tartu, 1993, 110 p.
2. **Peeter Burk.** Theoretical study of gas-phase acid-base equilibria. Tartu, 1994, 96 p.
3. **Victor Lobanov.** Quantitative structure-property relationships in large descriptor spaces. Tartu, 1995, 135 p.
4. **Vahur Mäemets.** The ^{17}O and ^{1}H nuclear magnetic resonance study of H_2O in individual solvents and its charged clusters in aqueous solutions of electrolytes. Tartu, 1997, 140 p.
5. **Andrus Metsala.** Microcanonical rate constant in nonequilibrium distribution of vibrational energy and in restricted intramolecular vibrational energy redistribution on the basis of slater's theory of unimolecular reactions. Tartu, 1997, 150 p.
6. **Uko Maran.** Quantum-mechanical study of potential energy surfaces in different environments. Tartu, 1997, 137 p.
7. **Alar Jänes.** Adsorption of organic compounds on antimony, bismuth and cadmium electrodes. Tartu, 1998, 219 p.
8. **Kaido Tammeveski.** Oxygen electroreduction on thin platinum films and the electrochemical detection of superoxide anion. Tartu, 1998, 139 p.
9. **Ivo Leito.** Studies of Brønsted acid-base equilibria in water and non-aqueous media. Tartu, 1998, 101 p.
10. **Jaan Leis.** Conformational dynamics and equilibria in amides. Tartu, 1998, 131 p.
11. **Toonika Rinken.** The modelling of amperometric biosensors based on oxidoreductases. Tartu, 2000, 108 p.
12. **Dmitri Panov.** Partially solvated Grignard reagents. Tartu, 2000, 64 p.
13. **Kaja Orupõld.** Treatment and analysis of phenolic wastewater with microorganisms. Tartu, 2000, 123 p.
14. **Jüri Ivask.** Ion Chromatographic determination of major anions and cations in polar ice core. Tartu, 2000, 85 p.
15. **Lauri Vares.** Stereoselective Synthesis of Tetrahydrofuran and Tetrahydropyran Derivatives by Use of Asymmetric Horner-Wadsworth-Emmons and Ring Closure Reactions. Tartu, 2000, 184 p.
16. **Martin Lepiku.** Kinetic aspects of dopamine D_2 receptor interactions with specific ligands. Tartu, 2000, 81 p.
17. **Katrin Sak.** Some aspects of ligand specificity of P2Y receptors. Tartu, 2000, 106 p.
18. **Vello Pällin.** The role of solvation in the formation of iotsitch complexes. Tartu, 2001, 95 p.

19. **Katrin Kollist.** Interactions between polycyclic aromatic compounds and humic substances. Tartu, 2001, 93 p.
20. **Ivar Koppel.** Quantum chemical study of acidity of strong and superstrong Brønsted acids. Tartu, 2001, 104 p.
21. **Viljar Pihl.** The study of the substituent and solvent effects on the acidity of OH and CH acids. Tartu, 2001, 132 p.
22. **Natalia Palm.** Specification of the minimum, sufficient and significant set of descriptors for general description of solvent effects. Tartu, 2001, 134 p.
23. **Sulev Sild.** QSPR/QSAR approaches for complex molecular systems. Tartu, 2001, 134 p.
24. **Ruslan Petrukhin.** Industrial applications of the quantitative structure-property relationships. Tartu, 2001, 162 p.
25. **Boris V. Rogovoy.** Synthesis of (benzotriazolyl)carboximidamides and their application in relations with *N*- and *S*-nucleophyles. Tartu, 2002, 84 p.
26. **Koit Herodes.** Solvent effects on UV-vis absorption spectra of some solvatochromic substances in binary solvent mixtures: the preferential solvation model. Tartu, 2002, 102 p.
27. **Anti Perkson.** Synthesis and characterisation of nanostructured carbon. Tartu, 2002, 152 p.
28. **Ivari Kaljurand.** Self-consistent acidity scales of neutral and cationic Brønsted acids in acetonitrile and tetrahydrofuran. Tartu, 2003, 108 p.
29. **Karmen Lust.** Adsorption of anions on bismuth single crystal electrodes. Tartu, 2003, 128 p.
30. **Mare Piirsalu.** Substituent, temperature and solvent effects on the alkaline hydrolysis of substituted phenyl and alkyl esters of benzoic acid. Tartu, 2003, 156 p.
31. **Meeri Sassian.** Reactions of partially solvated Grignard reagents. Tartu, 2003, 78 p.
32. **Tarmo Tamm.** Quantum chemical modelling of polypyrrole. Tartu, 2003. 100 p.
33. **Erik Teinemaa.** The environmental fate of the particulate matter and organic pollutants from an oil shale power plant. Tartu, 2003. 102 p.
34. **Jaana Tammiku-Taul.** Quantum chemical study of the properties of Grignard reagents. Tartu, 2003. 120 p.
35. **Andre Lomaka.** Biomedical applications of predictive computational chemistry. Tartu, 2003. 132 p.
36. **Kostyantyn Kirichenko.** Benzotriazole – Mediated Carbon–Carbon Bond Formation. Tartu, 2003. 132 p.
37. **Gunnar Nurk.** Adsorption kinetics of some organic compounds on bismuth single crystal electrodes. Tartu, 2003, 170 p.
38. **Mati Arulepp.** Electrochemical characteristics of porous carbon materials and electrical double layer capacitors. Tartu, 2003, 196 p.

39. **Dan Cornel Fara.** QSPR modeling of complexation and distribution of organic compounds. Tartu, 2004, 126 p.
40. **Riina Mahlapuu.** Signalling of galanin and amyloid precursor protein through adenylate cyclase. Tartu, 2004, 124 p.
41. **Mihkel Kerikmäe.** Some luminescent materials for dosimetric applications and physical research. Tartu, 2004, 143 p.
42. **Jaanus Kruusma.** Determination of some important trace metal ions in human blood. Tartu, 2004, 115 p.
43. **Urmas Johanson.** Investigations of the electrochemical properties of polypyrrole modified electrodes. Tartu, 2004, 91 p.
44. **Kaido Sillar.** Computational study of the acid sites in zeolite ZSM-5. Tartu, 2004, 80 p.
45. **Aldo Oras.** Kinetic aspects of dATPαS interaction with $P2Y_1$ receptor. Tartu, 2004, 75 p.
46. **Erik Mölder.** Measurement of the oxygen mass transfer through the air-water interface. Tartu, 2005, 73 p.
47. **Thomas Thomberg.** The kinetics of electroreduction of peroxodisulfate anion on cadmium (0001) single crystal electrode. Tartu, 2005, 95 p.
48. **Olavi Loog.** Aspects of condensations of carbonyl compounds and their imine analogues. Tartu, 2005, 83 p.
49. **Siim Salmar.** Effect of ultrasound on ester hydrolysis in aqueous ethanol. Tartu, 2006, 73 p.
50. **Ain Uustare.** Modulation of signal transduction of heptahelical receptors by other receptors and G proteins. Tartu, 2006, 121 p.
51. **Sergei Yurchenko.** Determination of some carcinogenic contaminants in food. Tartu, 2006, 143 p.
52. **Kaido Tämm.** QSPR modeling of some properties of organic compounds. Tartu, 2006, 67 p.
53. **Olga Tšubrik.** New methods in the synthesis of multisubstituted hydrazines. Tartu. 2006, 183 p.
54. **Lilli Sooväli.** Spectrophotometric measurements and their uncertainty in chemical analysis and dissociation constant measurements. Tartu, 2006, 125 p.
55. **Eve Koort.** Uncertainty estimation of potentiometrically measured ph and pK_a values. Tartu, 2006, 139 p.
56. **Sergei Kopanchuk.** Regulation of ligand binding to melanocortin receptor subtypes. Tartu, 2006, 119 p.
57. **Silvar Kallip.** Surface structure of some bismuth and antimony single crystal electrodes. Tartu, 2006, 107 p.
58. **Kristjan Saal.** Surface silanization and its application in biomolecule coupling. Tartu, 2006, 77 p.
59. **Tanel Tätte.** High viscosity $Sn(OBu)_4$ oligomeric concentrates and their applications in technology. Tartu, 2006, 91 p.

60. **Dimitar Atanasov Dobchev**. Robust QSAR methods for the prediction of properties from molecular structure. Tartu, 2006, 118 p.
61. **Hannes Hagu**. Impact of ultrasound on hydrophobic interactions in solutions. Tartu, 2007, 81 p.
62. **Rutha Jäger.** Electroreduction of peroxodisulfate anion on bismuth electrodes. Tartu, 2007, 142 p.
63. **Kaido Viht.** Immobilizable bisubstrate-analogue inhibitors of basophilic protein kinases: development and application in biosensors. Tartu, 2007, 88 p.
64. **Eva-Ingrid Rõõm.** Acid-base equilibria in nonpolar media. Tartu, 2007, 156 p.
65. **Sven Tamp.** DFT study of the cesium cation containing complexes relevant to the cesium cation binding by the humic acids. Tartu, 2007, 102 p.
66. **Jaak Nerut.** Electroreduction of hexacyanoferrate(III) anion on Cadmium (0001) single crystal electrode. Tartu, 2007, 180 p.
67. **Lauri Jalukse.** Measurement uncertainty estimation in amperometric dissolved oxygen concentration measurement. Tartu, 2007, 112 p.
68. **Aime Lust.** Charge state of dopants and ordered clusters formation in CaF_2:Mn and CaF_2:Eu luminophors. Tartu, 2007, 100 p.
69. **Iiris Kahn**. Quantitative Structure-Activity Relationships of environmentally relevant properties. Tartu, 2007, 98 p.
70. **Mari Reinik.** Nitrates, nitrites, N-nitrosamines and polycyclic aromatic hydrocarbons in food: analytical methods, occurrence and dietary intake. Tartu, 2007, 172 p.
71. **Heili Kasuk.** Thermodynamic parameters and adsorption kinetics of organic compounds forming the compact adsorption layer at Bi single crystal electrodes. Tartu, 2007, 212 p.
72. **Erki Enkvist.** Synthesis of adenosine-peptide conjugates for biological applications. Tartu, 2007, 114 p.
73. **Svetoslav Hristov Slavov**. Biomedical applications of the QSAR approach. Tartu, 2007, 146 p.
74. **Eneli Härk.** Electroreduction of complex cations on electrochemically polished Bi(*hkl*) single crystal electrodes. Tartu, 2008, 158 p.
75. **Priit Möller.** Electrochemical characteristics of some cathodes for medium temperature solid oxide fuel cells, synthesized by solid state reaction technique. Tartu, 2008, 90 p.
76. **Signe Viggor.** Impact of biochemical parameters of genetically different pseudomonads at the degradation of phenolic compounds. Tartu, 2008, 122 p.
77. **Ave Sarapuu.** Electrochemical reduction of oxygen on quinone-modified carbon electrodes and on thin films of platinum and gold. Tartu, 2008, 134 p.
78. **Agnes Kütt.** Studies of acid-base equilibria in non-aqueous media. Tartu, 2008, 198 p.

79. **Rouvim Kadis.** Evaluation of measurement uncertainty in analytical chemistry: related concepts and some points of misinterpretation. Tartu, 2008, 118 p.
80. **Valter Reedo.** Elaboration of IVB group metal oxide structures and their possible applications. Tartu, 2008, 98 p.
81. **Aleksei Kuznetsov.** Allosteric effects in reactions catalyzed by the cAMP-dependent protein kinase catalytic subunit. Tartu, 2009, 133 p.
82. **Aleksei Bredihhin.** Use of mono- and polyanions in the synthesis of multisubstituted hydrazine derivatives. Tartu, 2009, 105 p.
83. **Anu Ploom.** Quantitative structure-reactivity analysis in organosilicon chemistry. Tartu, 2009, 99 p.
84. **Argo Vonk.** Determination of adenosine A_{2A}- and dopamine D_1 receptor-specific modulation of adenylate cyclase activity in rat striatum. Tartu, 2009, 129 p.
85. **Indrek Kivi.** Synthesis and electrochemical characterization of porous cathode materials for intermediate temperature solid oxide fuel cells. Tartu, 2009, 177 p.
86. **Jaanus Eskusson.** Synthesis and characterisation of diamond-like carbon thin films prepared by pulsed laser deposition method. Tartu, 2009, 117 p.
87. **Marko Lätt.** Carbide derived microporous carbon and electrical double layer capacitors. Tartu, 2009, 107 p.
88. **Vladimir Stepanov.** Slow conformational changes in dopamine transporter interaction with its ligands. Tartu, 2009, 103 p.
89. **Aleksander Trummal.** Computational Study of Structural and Solvent Effects on Acidities of Some Brønsted Acids. Tartu, 2009, 103 p.
90. **Eerold Vellemäe.** Applications of mischmetal in organic synthesis. Tartu, 2009, 93 p.
91. **Sven Parkel.** Ligand binding to 5-HT_{1A} receptors and its regulation by Mg^{2+} and Mn^{2+}. Tartu, 2010, 99 p.
92. **Signe Vahur.** Expanding the possibilities of ATR-FT-IR spectroscopy in determination of inorganic pigments. Tartu, 2010, 184 p.
93. **Tavo Romann**. Preparation and surface modification of bismuth thin film, porous, and microelectrodes. Tartu, 2010, 155 p.
94. **Nadežda Aleksejeva.** Electrocatalytic reduction of oxygen on carbon nanotube-based nanocomposite materials. Tartu, 2010, 147 p.
95. **Marko Kullapere.** Electrochemical properties of glassy carbon, nickel and gold electrodes modified with aryl groups. Tartu, 2010, 233 p.
96. **Liis Siinor.** Adsorption kinetics of ions at Bi single crystal planes from aqueous electrolyte solutions and room-temperature ionic liquids. Tartu, 2010, 101 p.
97. **Angela Vaasa.** Development of fluorescence-based kinetic and binding assays for characterization of protein kinases and their inhibitors. Tartu 2010, 101 p.

98. **Indrek Tulp.** Multivariate analysis of chemical and biological properties. Tartu 2010, 105 p.
99. **Aare Selberg.** Evaluation of environmental quality in Northern Estonia by the analysis of leachate. Tartu 2010, 117 p.
100. **Darja Lavõgina.** Development of protein kinase inhibitors based on adenosine analogue-oligoarginine conjugates. Tartu 2010, 248 p.
101. **Laura Herm.** Biochemistry of dopamine D_2 receptors and its association with motivated behaviour. Tartu 2010, 156 p.
102. **Terje Raudsepp.** Influence of dopant anions on the electrochemical properties of polypyrrole films. Tartu 2010, 112 p.
103. **Margus Marandi.** Electroformation of Polypyrrole Films: *In-situ* AFM and STM Study. Tartu 2011, 116 p.
104. **Kairi Kivirand.** Diamine oxidase-based biosensors: construction and working principles. Tartu, 2011, 140 p.
105. **Anneli Kruve.** Matrix effects in liquid-chromatography electrospray mass-spectrometry. Tartu, 2011, 156 p.
106. **Gary Urb.** Assessment of environmental impact of oil shale fly ash from PF and CFB combustion. Tartu, 2011, 108 p.
107. **Nikita Oskolkov.** A novel strategy for peptide-mediated cellular delivery and induction of endosomal escape. Tartu, 2011, 106 p.
108. **Dana Martin.** The QSPR/QSAR approach for the prediction of properties of fullerene derivatives. Tartu, 2011, 98 p.
109. **Säde Viirlaid.** Novel glutathione analogues and their antioxidant activity. Tartu, 2011, 106 p.
110. **Ülis Sõukand.** Simultaneous adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} on peat. Tartu, 2011, 124 p.
111. **Lauri Lipping.** The acidity of strong and superstrong Brønsted acids, an outreach for the "limits of growth": a quantum chemical study. Tartu, 2011, 124 p.
112. **Heisi Kurig.** Electrical double-layer capacitors based on ionic liquids as electrolytes. Tartu, 2011, 146 p.
113. **Marje Kasari.** Bisubstrate luminescent probes, optical sensors and affinity adsorbents for measurement of active protein kinases in biological samples. Tartu, 2012, 126 p.
114. **Kalev Takkis.** Virtual screening of chemical databases for bioactive molecules. Tartu, 2012, 122 p.
115. **Ksenija Kisseljova**. Synthesis of aza-β^3-amino acid containing peptides and kinetic study of their phosphorylation by protein kinase A. Tartu, 2012, 104 p.
116. **Riin Rebane.** Advanced method development strategy for derivatization LC/ESI/MS. Tartu, 2012, 184 p.

117. **Vladislav Ivaništšev.** Double layer structure and adsorption kinetics of ions at metal electrodes in room temperature ionic liquids. Tartu, 2012, 128 p.
118. **Irja Helm.** High accuracy gravimetric Winkler method for determination of dissolved oxygen. Tartu, 2012, 139 p.
119. **Karin Kipper.** Fluoroalcohols as Components of LC-ESI-MS Eluents: Usage and Applications. Tartu, 2012, 164 p.
120. **Arno Ratas.** Energy storage and transfer in dosimetric luminescent materials. Tartu, 2012, 163 p.
121. **Reet Reinart-Okugbeni**. Assay systems for characterisation of subtype-selective binding and functional activity of ligands on dopamine receptors. Tartu, 2012, 159 p.
122. **Lauri Sikk.** Computational study of the Sonogashira cross-coupling reaction. Tartu, 2012, 81 p.
123. **Karita Raudkivi.** Neurochemical studies on inter-individual differences in affect-related behaviour of the laboratory rat. Tartu, 2012, 161 p.
124. **Indrek Saar.** Design of GalR2 subtype specific ligands: their role in depression-like behavior and feeding regulation. Tartu, 2013, 126 p.
125. **Ann Laheäär.** Electrochemical characterization of alkali metal salt based non-aqueous electrolytes for supercapacitors. Tartu, 2013, 127 p.
126. **Kerli Tõnurist.** Influence of electrospun separator materials properties on electrochemical performance of electrical double-layer capacitors. Tartu, 2013, 147 p.
127. **Kaija Põhako-Esko.** Novel organic and inorganic ionogels: preparation and characterization. Tartu, 2013, 124 p.
128. **Ivar Kruusenberg.** Electroreduction of oxygen on carbon nanomaterial-based catalysts. Tartu, 2013, 191 p.
129. **Sander Piiskop.** Kinetic effects of ultrasound in aqueous acetonitrile solutions. Tartu, 2013, 95 p.
130. **Ilona Faustova**. Regulatory role of L-type pyruvate kinase N-terminal domain. Tartu, 2013, 109 p.
131. **Kadi Tamm.** Synthesis and characterization of the micro-mesoporous anode materials and testing of the medium temperature solid oxide fuel cell single cells. Tartu, 2013, 138 p.
132. **Iva Bozhidarova Stoyanova-Slavova.** Validation of QSAR/QSPR for regulatory purposes. Tartu, 2013, 109 p.
133. **Vitali Grozovski**. Adsorption of organic molecules at single crystal electrodes studied by *in situ* STM method. Tartu, 2014, 146 p.
134. **Santa Veikšina**. Development of assay systems for characterisation of ligand binding properties to melanocortin 4 receptors. Tartu, 2014, 151 p.
135. **Jüri Liiv.** PVDF (polyvinylidene difluoride) as material for active element of twisting-ball displays. Tartu, 2014, 111 p.

136. **Kersti Vaarmets.** Electrochemical and physical characterization of pristine and activated molybdenum carbide-derived carbon electrodes for the oxygen electroreduction reaction. Tartu, 2014, 131 p.
137. **Lauri Tõntson**. Regulation of G-protein subtypes by receptors, guanine nucleotides and Mn^{2+}. Tartu, 2014, 105 p.