

## Final report on the K 105417 project

Phosphorus and silicon chlorides are key intermediates in the production of phosphanes and silanes, which are of industrial importance, however, their hydrolysis encumbers their use. Since recent reports on phosphorus trichloride dissolved in certain ionic liquids showed that the hydrolysis is slowed down, the aim of the proposal was a detailed investigation of the hydrolysis reactions of these main group element halides, and to explore the effect and properties of ionic liquids, as well as the modification of the electronic structures of phosphorus and silicon containing compounds, to make them less vulnerable against hydrolysis. To this end we decided to carry out quantum chemical calculations to explore the mechanism of the hydrolysis reaction in detail, in particular to see the effect of the number of the reactant water molecules on the reaction rate, as well as the effect of the interactions with other molecules as solvents. On the basis of these informations synthetic work was also planned to verify the conclusions drawn from the calculations.

First we have carried out theoretical calculations on the simplest chlorophosphanes ( $\text{H}_2\text{P}\text{Cl}$  and  $\text{PCl}_3$ ) and chlorosilane ( $\text{H}_3\text{SiCl}$ ) with different amount (1-5) of water molecules, to establish the thermodynamics and the kinetics of the hydrolysis reactions. We have used different levels of the theory for these model systems, to check the reliability of our calculations. Both the thermodynamics and the kinetics of the reactions showed dependence on the number of the participating water molecules. With small number of water molecules the reaction is endergonic, while in case of 4 or 5 water molecules the reaction becomes exoergic, in accordance with the stabilization of the byproduct chloride ion by the solvate shell. Even more importantly the reaction barrier decreases significantly for both the phosphorus and the silicon halides with the increasing amount of reactant molecules, which are able to form a hydrogen bonded network facilitating a proton relay during the hydrolysis reaction. While there is a significant drop in the barriers between one and two reactant water molecules, the change between four and five reactant water molecules is small (*Struct. Chem.* 2015). In fact we were able to locate two pathways, one with inversion, while the other with retention of the configuration about silicon. For water as solvent an ab initio molecular dynamics study on a system containing 58 water molecules and one chlorosilane has shown 2 kcal/mol Gibbs free energy reaction barrier. Further studies were carried out on the practically more important substituted chlorosilanes (*Struct. Chem.* 2017, pp. 333-343). While the effect of the increasing number of water molecules is similar to that of the parent compound, the barriers – which correlate with the energy of the  $\sigma^*_{\text{SiCl}}$  orbital energy - are generally smaller than for the parent  $\text{H}_3\text{SiCl}$  in case of electronegative substituents, but slightly increase for organic groups. The inversion and the retention pathways have comparable barriers (10 – 18 kcal/mol) with four water molecules, while in case of a single reactant water molecule the barrier is 20-25 kcal/mol, for a pathway with configurational retention. The increasing steric bulk of the substituents increases the barrier for each reaction pathway (*Struct. Chem.* 2017, pp. 333-343). Since the key factor in the reduction of the barrier is the formation of a hydrogen bonded network for proton relay, we considered a cage compound, and have shown the significant

increase of the reaction barrier. To get experimental evidence on the reaction mechanism, we decided to synthesize a chiral chlorosilane, which – upon reacting with water under conditions, where water monomers are favoured as in some IL's or in DMSO – we expected the formation of the product with the retention of the configuration, as followed by CD spectroscopy. While the chiral PhMe<sup>t</sup>BuSiCl could be synthesized and purified, but upon dissolving the compound in the rigorously dried solvents no CD spectra could be obtained, as an apparent consequence of racemization, which might be a follow up reaction of the hydrolysis. The reaction barriers were systematically larger in case of the phosphorus compounds, than for the silyl-chloride, and this behavior was in accordance with the fact that while in the literature the hydrolysis of chlorophosphane could be hindered in some ionic liquids, and also we were able to reproduce this behavior, chlorosilanes in the same ionic liquids showed rapid hydrolysis under the same conditions. Altogether we were not able to find conditions where the hydrolysis of chlorosilanes could be slowed down sufficiently.

Apart from the study of the hydrolysis reactions we also investigated aminolysis of CF<sub>3</sub>PF<sub>2</sub> and CCl<sub>3</sub>PF<sub>2</sub> substituted phosphanes (*Heteroatom. Chem. 2017*). The two compounds showed a distinctly different behavior. While in the reaction of CF<sub>3</sub>PF<sub>2</sub> and Me<sub>2</sub>NH the expected product CF<sub>3</sub>PFNMe<sub>2</sub> was formed, in case of CCl<sub>3</sub>PF<sub>2</sub> the products were HCCl<sub>3</sub> and Me<sub>2</sub>NPF<sub>2</sub>, which has turned out to be the thermodynamically controlled product, according to our calculations. This reaction pathway (with P-C bond breaking) is blocked by a large barrier for both compounds. While the difference of the gas phase reaction barriers between the two investigated reactants is not significant, using a PCM solvent model a sizeable reduction was observed, in accordance with the ionic nature of the transition structure. Thus, the observations can be explained by the different boiling points of the reactants, allowing for a gas phase reaction for the CF<sub>3</sub> substituted system, while a condensed phase reaction for the CCl<sub>3</sub> analogue.

The beneficial effect of the ionic liquids on the hydrolysis reaction is attributable to the reduction of water clustering due to strong hydrogen bond formation or by other weak interaction such as pnictogen or tetrel bond formation. The formation of strong hydrogen bonds is related to carbene formation from the cationic component. Following our earlier work on the imidazolium based carbene formation from the ethyl-methylimidazolium acetate ionic liquid, we summarized the available results on the carbene like reactivity in ionic liquids. In case of strongly basic anionic components such as acetate, or hydrogen carbonate carbene like reactivity was observed including carbene organocatalytic effects, metal complex, or adduct formation (eg. with carbon-dioxide) directly from the ionic liquid (*Top. Curr. Chem. 2013*). Apart from the known examples several new possibilities were outlined by variation of the cationic and anionic components of the ionic liquids. For example in a systematic study on the stabilization energies, and dissociation reaction energies of different nucleophilic carbenes (*RSC. Adv. 2013*) we have shown that most importantly oxazol-2-ylidenes, and very probably also selenazol-ylidenes might even be synthesized, or can be used as a component of an ionic liquid, under conditions, where the clustering of water can be reduced, according to the calculations of hydrolysis reaction barriers. In a combined theoretical/experimental work we were able to show that under strongly basic conditions in the reaction between ethyl-methylimidazolium-acetate and supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) at high temperature (130 °C) not the already known 2-CO<sub>2</sub> adduct but the 4-CO<sub>2</sub> adduct - which is derived from the abnormal carbene – could be obtained (*Chemistry - European Journal 2014*). Counterintuitively, the strong basicity in the

consequence of the presence of the normally acidic CO<sub>2</sub>! Carbon-dioxide as sc-CO<sub>2</sub> forms a separate phase from the ionic liquid, and is able to dissolve acetic acid (which was detected in the sc-CO<sub>2</sub> phase), thus increasing the basicity of the IL phase. As we have shown that the hydrogen-bond formation in ionic liquids is significant in imidazolium based ionic liquids even in the presence of 2-methyl substitution owing to the possible formation of the “deoxy-Breslow intermediate” by deprotonation of the 2-methyl group, which can also be described as a carbene (:CR<sub>2</sub>) adduct of imidazole-2-ylidene, we decided to investigate the electronic structure, possible tautomerization and the stability of this class of compounds. Since the behavior of the main group elements is of central importance for us, we also investigated the structure of the imidazole-ylidene adducts with different carbene analogues (:O, :S, :NR, :PR, and :SiR<sub>2</sub>). While for the second row elements (O, N, C) the double bonded resonance structure is dominant, for the heavier elements, and in particular for the Si compound the ylidic resonance structure is the most important form (*RSC. Adv. 2015*). The ylidic form is stabilized by the  $\pi$ -electron donation of two amino nitrogens, the donation becoming effective by the low lying empty orbital of the heavy atom. Ylides can tautomerize to substituted carbenes, and since the adduct formation yielding in the ylide can be at normal (2) or at abnormal (4) positions of the imidazole ring, altogether 4 isomers can be considered. In a noteworthy way the relative stability of two substituted (4-NR<sub>2</sub> and 4-PR<sub>2</sub>) carbenes is close to the 4-NR and 4-PR zwitterionic structures, giving indeed rise for tautomerization (*RSC. Adv. 2015*). While this tautomerization was known for the N-compound, the 4-PR zwitterionic structure could be synthesized by our cooperation partner in Bonn for the first time, and we investigated its highly polar electronic structure and complexing ability (of the tautomeric carbene) in detail (*Angew. Chem. 2013*). Not only the zwitterionic compound could be synthesized, but utilizing a similar protocol, the phosphine derivative of imidazole-2-thion could also be obtained. While the electronic structure of the imidazole thione unit is not perturbed significantly by the phosphane substitution, the polarizing effect of two imidazole-thione unit on the phosphane allows to stabilize the formation of both phosphonium cation, and more importantly the phosphanide anion (in an analogous manner as the above discussed zwitterionic phosphor analogue of the deoxy-Breslow intermediate), giving rise to a rather complex chemical behavior (*Eur. J. Inorg. Chem., 2016*). The significant stability of these intermediates allows to plan new synthetic pathways.

The formation of the zwitterionic electronic structure in the phospho analogue of the deoxy-Breslow intermediate was attributed to the electron donor effect of the two nitrogen lone pairs of the imidazole moiety, resulting in an inverse electron distribution (negative charge at phosphorus). The effect of a single amino substituent in an >N-C=P unit is also similar, although it is not as pronounced as exerted by the two nitrogens in case of the imidazole substitution. Nevertheless, in the planar and highly aromatic 1,3-azaphospholes the  $\pi$ -electron density at phosphorus becomes sufficiently large to form a  $\pi$ -complex with HgCl<sub>2</sub>, instead of the in plane  $\sigma$ -complexation, which is the usual complexation mode of the  $\sigma^2$ P-Ligands (*Dalton Transactions 2014*). Also Ag<sup>+</sup> is complexed in an out of plane mode, forming a  $\mu^2$ -bound dimeric P-complex. The  $\mu^2$ -P- and the bent  $\eta^1$ -P-coordination mode was also characteristic for 1,3-benzazaphosphole copper(I) halide complexes (*Inorg. Chem., 2015*), resulting in a mixture of different compounds including dimers and higher oligomers, in accordance with our calculations, which indicate small energy difference between monomers dimers and tetramers. CuOAc complexes were also formed in a  $\mu^2$ -P-coordination mode (*Dalton Transactions 2015*). Likewise for the CuHal complexes the monomer (which is most stable as an out of plane complex, according to our calculations) is in equilibrium with

dimers and higher oligomers according to the calculations and this is also in agreement with the dynamic behavior of the NMR spectra. A tetrameric complex could be crystallized, and characterized by X-ray diffraction. A noteworthy feature of this multinuclear complex is the cuprophilic interaction, which was clearly shown by the presence of bond critical points between Cu atoms, and the Wiberg bond indexes between 0.13 and 0.19 for the different Cu – Cu pairs. The results were summarized in a review (*Phosphorus, Sulfur, Silicon* 2015). In case of the related aromatic triazaphosphole, rhenium complexation takes place at nitrogen (and not at phosphorus), forming a chelate with the other nitrogen of the substituent 2-pyridine. A noteworthy feature of this ligand is its fluorescence with high quantum yield. This contrasts with the weak fluorescence of the 3- and 4-pyridyl substituted isomers, (*Chemistry - European Journal*, 2015, pp. 11096-11109), which is due to the non-planarity of the latter compounds, and the rather high rotational barrier of the 2-pyridyl derivative. The apparently smaller steric need of the N in plane lone pair in comparison with CH and also with the P lone pair was proven, by analyzing the rotational barriers in phenyl-phosphinines and phenyl-pyridines, together with establishing the position of their in-plane lone pairs by analyzing the second derivatives of the electron density (*Struct. Chem.* 2017, pp. 1243-1253). Strong fluorescence could also be observed in case of a phosphole modified PAH, which could be utilized to make a white emitting OLED (*Chemistry - European Journal*, 2015, pp. 6547-6556). The electronic properties of these P-modified PAH's can conveniently be tuned by the chemical modification at the phosphorus atom, by the variation of the LUMO energy, while having little effect on the HOMO (which contains the phosphorus atom in the nodal plane). Further modifications of the spectral properties could be made by complexation (*Organometallics* 2017) utilizing the phosphorus lone pair. Complexation was achieved by a single P-modified PAH for Au and Re, or by two ligands for Au, Cu and Pd. The TD DFT calculations could be successfully used to assign the spectra of the complexes, including the effect of the ligand interaction in case of the  $ML_2$  systems. The results on the rapidly developing field of phosphorus-modified polycyclic aromatic hydrocarbons were summarized in a minireview (*ChemPhysChem.* 2017, 2618-2630).

Apart from phosphorus heterocycles, we also investigated silicon containing possibly aromatic heterocyclic compounds. In a detailed computational study of the substituent effects on the five membered ring silolide anion (*Struct. Chem.* 2014, pp. 377-387) we have concluded that silyl substitution at the 2- and 5-positions lowers the inversion barrier at the ring Si substantially, yielding a nearly planar five membered ring. The structure shows high aromaticity, with the significant involvement of a non-classical resonance form. The 2,5-bis-silyl substitution is realizable in case of the silolide (silacyclopentadienyl) dianion (*Phosphorus, Sulfur, Silicon*, 2014). In a further work, which is not related to the project, we have investigated computationally the mass spectroscopic fragmentation behavior of alkyl halogenides (*Struct. Chem.* 2014 pp 659-665) by acknowledging the present project.