

CENTRE OF MOLECULAR AND MACROMOLECULAR STUDIES  
POLISH ACADEMY OF SCIENCES

DIVISION OF STRUCTURAL CHEMISTRY



DOCTORAL THESIS  
SUMMARY

THEORETICAL STUDIES OF MECHANISM OF  
THE CATALYTIC NUCLEOPHILIC  
SUBSTITUTION AT SILICON

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ŁÓDŹ 2019

The aim of the thesis is research on the nucleophilic substitution at silicon, in particular catalyzed by fluoride anion, conducted by theoretical methods. Nucleophilic substitution is one of the main types of reaction for this element – one that is still an active research field due to the ambiguity and inconclusiveness of many experimental results obtained.

**Chapter 1** is a brief introduction encompassing an outline of silicon chemistry research history as well as of the so-far accepted mechanism of nucleophilic substitution for reactions engaging a silicon atom.

**Chapter 2** is an introduction to the subject of the thesis, describing properties of silicon as a chemical element and briefly characterizing properties of its hypervalent compounds.

**Chapter 3** is a discussion of concepts and methods applied in computational chemistry. Introduced were concepts of potential energy hypersurface and its stationary points as well as the formalism of *ab initio* methods on the example of Hartree-Fock method. On this basis, the formalism used in density functional theory (DFT) was introduced, which is the method used in this thesis. Long-range and dispersion corrections as well as orbital analysis are briefly discussed. The description of the thermodynamic relationships, intermolecular interactions and impact of the implicit (continuous medium approximation) and explicit (ONIOM method) solvent close the chapter.

**Chapter 4** is devoted to nucleophilic substitution reaction. The  $S_N$  reaction for carbon and silicon is briefly described and the differences between them are discussed. The review of experimental data serves a more comprehensive - than in Chapter 1 - discussion of addition-elimination as the so-far accepted nucleophilic substitution mechanism involving hypervalent silicon compounds. Its energy profile and theoretical interpretation of experimental stereochemical results are presented. Nucleophilic catalysis is presented on the example of hydrolysis and alcoholysis of halosilanes, hydrolysis of alkoxysilanes and condensation of silanols whereas the catalytic effect of fluoride ion is discussed on the example of the role of TBAF in the formation of silsesquioxane cages.

**Chapter 5** is entirely devoted to the results obtained in the process of selecting the appropriate density functional for organosilicon compounds on the example of chlorosilane condensation reaction and homofunctional silanol-to-disiloxane condensation. Compliance tests of the obtained thermodynamic functionals and geometric parameter values in relation to reference results covered 12 density functionals used in various chemical issues and 5 basis sets. As the reference values experimental results, or ones derived from high-level quantum mechanical calculations, were adopted.

**Chapter 6** is a presentation of research on the identity nucleophilic substitution for alkyl- and alkoxyfluoro- and -chlorosilanes, including i. a. groups characterized by high steric hindrance and having great practical significance in silicon chemistry (phenyl and tert-butyl substituent), which allowed determining the influence of steric effects of substituents on the possible mechanism of catalysis with fluoride ions. Reactions in the gas phase and solvents (methanol, water) comprised attack of the nucleophile from the opposite to the leaving group as well as the side attack.

**Chapter 7** presents energy effects associated with the nucleophilic addition of fluoride ion to alkylalkoxysilanes. The results obtained allowed revision of the existing literature assumptions regarding the role of fluoride ion as a catalyst of the nucleophilic substitution involving silicon atom. The research included fluoride anion in the form of a „naked” anion as well as one associated with an organic ( $\text{Me}_4\text{N}^{(+)}$ ) and inorganic ( $\text{Na}^{(+)}$ ) cation.

**Chapter 8** presents results related to energy alignment of hypervalent silicon compounds conformers that contain Si-F bond in their structure as well as pseudorotation barriers of such compounds and NBO analysis of their intramolecular interactions.

**Chapter 9** focuses on the energetics of the hydrolysis reaction of substituted silanes under neutral conditions. The catalytic role of fluoride ion was studied by comparing the energy results for two possible mechanisms of catalysis - the formation of ion-dipole complexes and pentacoordinated intermediate compounds - with the hydrolysis reaction of these compounds without the fluoride ion participation.

**Chapter 10** presents studies on the energy effects associated with ion encapsulation within silsesquioxane cages (POSS) and with possible mechanisms of encapsulation of fluoride ion inside the archetypal  $\text{T}_8$  cage. The results obtained allowed to propose mechanisms of  $\text{F}^{(-)}$  encapsulation as well as of the fluoride-anion-catalyzed POSS formation.

**Chapter 11** is closure containing the summary of presented results. Bibliography of the thesis comprises 218 entries.