UNIVERSITY OF SZEGED

FACULTY OF SCIENCE AND INFORMATICS
DEPARTMENT OF PHYSICAL CHEMISTRY AND MATERIALS SCIENCE
GRADUATE SCHOOL OF CHEMISTRY

MTA-SZTE Lendület
Computational Reaction Dynamics Research Group

THESES OF DOCTORAL DISSERTATION

Quasi-classical dynamics of ion–molecule systems with a silicon central atom

Dékány Attila Ádám
Supervisor:
Dr. Czakó Gábor
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1 Introduction

One of the primary goals of theoretical chemistry is to gain a detailed understanding of the mechanisms and dynamics of chemical reactions. Using computer simulations, it is possible to study transformations with exceptional detail, even those that are challenging or impossible to investigate through experimental methods.

For classical dynamic simulations of small gas-phase systems, two main approaches can be distinguished. In the direct dynamics method, the forces are calculated at every time step of the simulation using an electronic structure calculation software. While trajectory propagation requires minimal preparation, this approach is computationally expensive, which significantly limits the highest practically feasible theoretical level. In contrast, the alternative method uses a global analytical potential energy surface, which allows individual trajectories to be obtained at very low computational cost. However, constructing the function representing the potential energy surface is a complex and demanding process. Analytical energy surfaces can be developed at coupled-cluster quality for isolated systems with 6–10 atoms. Notable six-atom systems include those of the type $X^- + CH_3Y$, whose most characteristic transformations are bimolecular nucleophilic substitution (S_N2) and proton abstraction. S_N2 reactions can further be divided into inversion and retention product channels.

S_N2 reactions can also be studied in systems with different central atoms, such as nitrogen, phosphorus, or silicon, where distinct chemical properties can be observed. The dynamics investigations of systems with silicon as the central atom is relatively unexplored, and no analytical ion–molecule potential energy surface for silicon-centered systems has been reported to date.

2 Objective

During my PhD research, I aimed to conduct theoretical chemical investigations of the gas-phase reactions of silyl halides with halide ions through multiple interconnected projects.

The objective of the first project was to optimize the characteristic stationary points of S_N2 reactions between methyl or silyl halides and halide ions, perform zero-point vibrational analyses, and calculate their relative energies using coupled-cluster quantum chemical methods.

Additional goals included studying the quasi-classical dynamics of two silicon-centered systems: silyl chloride and fluoride, as well as silyl iodide and fluoride. Developing the corresponding analytical potential energy surfaces was also part of the projects.

With the dynamics simulations, our goal is to determine the reaction probabilities, cross-sections, and energetic properties of the product channels, as well as to discover new reaction mechanisms.

3 Methods

We performed the electronic structure calculations, including geometry optimizations, harmonic zero-point vibrational analyses, and energy calculations, using version 2015.1 of the MOLPRO quantum chemistry software package. The applied electronic structure methods included an explicitly correlated coupled-cluster method, CCSD(T)-F12b, and a composite coupled-cluster method incorporating Brueckner perturbative (T) corrections, CCSD-F12b + BCCD(T) – BCCD. The coupled-cluster methods were used with correlation-consistent basis sets augmented with diffuse functions, specifically aug-cc-pVTZ and aug-cc-pVQZ. For systems containing iodine atoms, we accounted for relativistic effects by employing effective core potentials and using the aug-cc-pVTZ-PP and aug-cc-pVQZ-PP basis sets.

The automation of potential energy surface (PES) development was carried out using the ROBOSURFER program, and the fitting process utilized the PES library by Bastiaan Braams. We employed ManyHF to reduce Hartree–Fock convergence issues during the development of the $SiH_3I + F^-$ PES. For the analysis of trajectory simulations, I developed custom Python programs.

4 Results

T1. We conducted a systematic stationary point comparison for the $AH_3Y + X^-$ [A = C, Si; X, Y = F, Cl, Br, I] type S_N2 reactions at the CCSD(T)-F12b/aug-cc-pVQZ(-PP)//CCSD(T)-F12b/aug-cc-pVTZ(-PP) theoretical level. Additionally, we computed reaction energies for several side reactions using the same theoretical method. The examined side reactions include proton abstraction, hydride ion substitution, and reactions leading to the formation of HY, XHY^-, and XY^- products.

We systematically characterized the stationary points of the S_N2 reactions involving inversion, retention, and double inversion mechanisms for methyl halide and halide ion systems of the type $CH_3Y + X^-$ [X, Y = F, Cl, Br, I], as well as their silicon analogs, $SiH_3Y + X^-$ [X, Y = F, Cl, Br, I]. Geometry optimizations were performed at the CCSD(T)-F12b/aug-cc-pVTZ(-PP) level of theory. Harmonic zero-point vibrational energies were also calculated at the same level, while classical relative energies were obtained using the CCSD(T)-F12b/aug-cc-pVQZ(-PP) method.

In addition to halide ion substitutions, we also calculated classical and adiabatic reaction enthalpies for proton abstraction, hydride ion substitution, and the formation of HY, XHY^-, and XY^- products at the CCSD(T)-F12b/aug-cc-pVQZ(-PP)//CCSD(T)-F12b/aug-cc-pVTZ(-PP) level of theory.

Among the product formations in carbon-centered systems, only halide ion substitutions were found to be exothermic. Proton abstractions involving F^- as the attacking ion, as well as the formation of XHY^- products and most halogen abstractions (resulting in XY^- formation), had reaction enthalpies below 50 kcal/mol, making them accessible at high collision energies. For the silicon analog reactions, halide ion substitutions, proton abstractions with F^- as the attacking ion, hydride ion substitutions, and the formation of SiH_2 + FHI^- were either exothermic or nearly thermoneutral. The remaining proton abstractions and bihalide ion formations had reaction enthalpies below 50 kcal/mol.

T2. We developed an analytical potential energy surface of coupled cluster quality [(CCSD-F12b + BCCD(T) − BCCD)/aug-cc-pVTZ] for the quasi-classical dynamics simulations of the reactions of the SiH_3Cl + F^- system. We showed that the most characteristic reactions include chloride ion substitution and proton abstraction, and we also observed the formation of HCl, H^-, $FHCl^-$, H_2, H_2 + Cl^-, and HF + Cl^- products. The retention chloride ion substitution proved to be active across the entire examined collision energy range (1–40 kcal/mol), with its ratio increasing from 10% to 45% as the collision energy increased.

We developed a full-dimensional analytic permutation-invariant potential energy surface of coupled cluster quality [(CCSD-F12b + BCCD(T) − BCCD)/aug-cc-pVTZ] for the gas-phase reactions of the SiH_3Cl + F^- system to perform quasi-classical dynamics simulations.

On this energy surface, we ran millions of trajectory simulations in the collision energy range of 1–40 kcal/mol. The simulation data were analyzed using custom-developed Python programs, allowing us to identify the most characteristic product formations of the system. These key reactions include chloride ion substitution (SiH_3F + Cl^-), proton abstraction (SiH_2Cl^- + HF), the formation of SiH_2F^- + HCl, $SiHFCl^-$ + H_2, SiH_2FCl + H^-, and SiH_2 + $FHCl^-$ (two-fragment products), as well as SiHF + H_2 + Cl^- and SiH_2 + HF + Cl^- (three-fragment products). By calculating collision energy-dependent integral cross sections, we determined that the chloride ion substitution and proton abstraction channels are the most probable. The cross section for chloride ion substitution reaches up to 1000 bohr^2, while that for proton abstraction is about 400 bohr^2 at the lowest collision energy. For the substitution reactions, we demonstrated that both inversion and retention products are formed across the entire collision energy range. Additionally, the ratio of the cross section for retention products to the total substitution cross section increases from 10% to 45% as the collision energy rises, while the total substitution cross section decreases monotonically.

T3. Based on the analysis of the quasi-classical dynamics simulations of the $SiH_3Cl + F^-$ system, both inversion and retention chloride ion substitutions follow indirect mechanisms, while proton abstraction occurs through both direct and indirect mechanisms. The translational energy distribution of HCl formation clearly indicates an indirect mechanism.

By analyzing the dynamics simulations of the $SiH_3Cl + F^-$ system, we obtained translational and internal energy distributions, providing insight into the direct or indirect nature of the reactions. Direct reactions are characterized by the translational energy of the reactants being transferred to the translational motion of the products, while in indirect reactions, the translational energy is transferred to the internal modes of the products. The energy distributions for both inversion and retention chloride ion substitution, as well as for hydrogen chloride formation, indicated an indirect mechanism. In contrast, the translational and internal energy distributions for proton abstraction exhibited dual maxima, suggesting a mixed mechanism. This implies that proton abstraction occurs via both direct and indirect pathways.

T4. We analyzed in detail the mechanisms of characteristic product formation in the SiH_3Cl + F^- system by utilizing trajectory animations. The dependence of the probability of retention chloride ion substitution on the collision parameter at low collision energies can be explained by the reorientation of the reactants and the resulting energy transfer processes. We described secondary proton abstraction mechanisms in which HCl and H_2 products are formed, as well as a mechanism leading to the formation of H_2 and H_2 + Cl^- through the formation of a complex containing a dihydrogen bond, which is the dominant molecular hydrogen formation pathway at low collision energies.

We investigated the reaction mechanisms of the SiH_3Cl + F^- system using trajectory animations. By analyzing the collision energy-dependent reaction probability of chloride ion substitution at 1 kcal/mol, broken down into inversion and retention channels, we observed that the probability of the inversion channel remains nearly constant over a wide range of collision parameters, while the retention channel probability decreases monotonically, almost linearly. Based on the animations, we provided an explanation for this phenomenon. At low collision energies, the reactants orient themselves in a favorable direction for the formation of the Walden complex (WMIN). At high collision parameters, this process imparts energy to the rotational motion of the formed complex, which then dissociates into an inversion product. At low collision parameters, the translational motion of the reactants excites the bending mode of the F–Si–Cl bond in the developing WMIN complex, allowing it to convert into a front side attacking complex, which dissociates into a retention product.

We also described the proton abstractions of the leaving ions in chloride and hydride ion substitution reactions. The proton abstraction by chloride ions is the dominant mechanism for HCl formation, while hydride ion proton abstraction is one characteristic but not exclusive process for molecular hydrogen formation.

At 1 kcal/mol collision energy, molecular hydrogen forms through a much more complex, multi-step mechanism in which the complex containing a dihydrogen bond, ClDHBMIN, is formed after HCl formation, followed by the loss of H_2. Upon the dissociation of ClDHBMIN, SiHF + H_2 + Cl^- is produced, with SiHF and Cl^- frequently recombining.

T5. We performed quasi-classical dynamics simulations on the SiH_3I + F^- system using a custom-developed, coupled cluster quality [(CCSD-F12b + BCCD(T) − BCCD)/aug-cc-pVTZ(-PP)] potential energy surface, resulting in the discovery of reactions analogous to those in the SiH_3Cl + F^- system. These reactions include inversion and retention iodide ion substitution, proton abstraction, as well as the formation of HI, H^-, FHI^-, H_2, H_2 + I^-, and HF + I^- products. Based on their cross-sections, both the inversion and retention iodide ion substitution, as well as proton abstraction, are the most significant reactions. According to trajectory animations, molecular hydrogen formation also occurs through mechanisms involving proton abstraction by the hydride ion and the formation of a complex containing a dihydrogen bond.

We developed the (CCSD-F12b + BCCD(T) − BCCD)/aug-cc-pVTZ(-PP) quality potential energy surface of the SiH_3I + F^- system, on which we ran quasi-classical dynamic simulations in the 1–80 kcal/mol collision energy range. The simulation analysis was performed using our custom Python programs. We identified iodine analogs for all characteristic product formations previously studied in the SiH_3Cl + F^- system, including iodide ion substitution with both inversion and retention pathways active across the entire collision energy range, proton abstraction, as well as reactions leading to the formation of HI, H^-, FHI^-, H_2, H_2 + I^-, and HF + I^- products.

Based on the integral cross-sections of the reactions, halide ion substitution is the most significant, with a cross section of 1000 $bohr^2$ at 1 kcal/mol collision energy. In the SiH_3Cl + F^- system, we observed that the ratio of the retention substitution cross-section changes between 10% and 45%. In the SiH_3I + F^- system, the ratio of the retention substitution changes in the same proportions with increasing collision energy.

The second largest cross-section reaction is produced by proton abstraction, which exceeds 400 bohr^2 at the lowest collision energy.

Based on trajectory animations, the main mechanisms for molecular hydrogen formation are analogous to those observed in the SiH_3Cl + F^- system: proton abstraction of the leaving ion of hydride ion substitution and the pathway via the formation of a complex containing a dihydrogen bond. The latter mechanism is characteristic at low collision energies.

5 Publications

A list of publications forming the basis of the thesis

Attila Á. Dékány; Gyula Z. Kovács; Gábor Czakó; High-level systematic *ab initio* comparison of carbon- and silicon-centered S_N2 reactions. *J. Phys. Chem. A* 2021, **125**, 9645–9657. DOI: 10.1021/acs.jpca.1c07574
IF_{2021}: 2.944

Attila Á. Dékány; Gábor Czakó; Exploring the versatile reactivity of the F^- + SiH_3Cl system on a full-dimensional coupled-cluster potential energy surface. *J. Chem. Phys.* 2023, **158**, 224303. DOI: 10.1063/5.0153083
IF_{2023}: 3.1

Attila Á. Dékány; Gábor Czakó; Detailed quasiclassical dynamics of the F^- + SiH_3Cl multi-channel reaction. *Phys. Chem. Chem. Phys.* 2024, **26**, 10008–10020. DOI: 10.1039/D4CP00048J
IF_{2023}: 2.9

Balázs J. Molnár; Attila Á. Dékány; Gábor Czakó; Automated potential energy surface development and quasi-classical dynamics for the F^- + SiH_3I system. *J. Chem. Phys.* 2024, **161**, 194306. DOI: 10.1063/5.0238366
IF$_{2023}$: 3.1

$$\sum \mathrm{IF} = 12.044$$

Publication related to the thesis

Attila Á. Dékány; Gábor Czakó; Benchmark *ab initio* proton affinity and gas-phase basicity of α-alanine based on coupled-cluster theory and statistical mechanics. *J. Comput. Chem.* 2022, **43**, 19. DOI: 10.1002/jcc.26767
IF$_{2022}$: 3.0

$$\sum \mathrm{IF} = 3.0$$

$$\sum \sum \mathrm{IF} = 15.044$$

Additional publication

Attila Dékány; Enikő Lázár; Bálint Szabó; Viktor Havasi; Gyula Halasi; András Sápi; Ákos Kukovecz; Zoltán Kónya; Kornél Szőri; Gábor London; Exploring Pd/Al_2O_3 catalysed redox isomerisation of allyl alcohol as a platform to create structural diversity. *Catal. Lett.* 2017, **147**, 1834–1843. DOI: 10.1007/s10562-017-2087-4
IF$_{2017}$: 2.911

$$\sum \mathrm{IF} = 2.911$$

$$\sum \sum \sum \mathrm{IF} = 17.955$$

6 Talks

MTA Reaction Kinetics and Photochemistry Working Group Meeting, online, May 27 2021.
Dékány Attila, Czakó Gábor; Az α-alanin protonaffinitásának és gázfázisú bázicitásának nagy pontosságú elméleti kémiai meghatározása

KeMoMo–QSAR symposium, Szeged, June 2 2022.
Dékány Attila, Czakó Gábor; S_N2 reakciók szilícium centrumon: a $F^- + SiH_3Cl$ rendszer dinamikája

MTA Reaction Kinetics and Photochemistry Working Group Meeting, Balatonvilágos, June 9 2023.
Dékány Attila, Czakó Gábor; A $F^- + SiH_3Cl$ reakció dinamikája analitikus potenciálisenergia-felületen