

## ABSTRACT

Understanding the intricate pathways of chemical reactions requires a detailed examination of the electronic and structural changes that occur at the molecular level. While potential energy surfaces are commonly employed to investigate these transformations, a deeper comprehension arises from tracking how atoms and molecules evolve dynamically over time. This thesis aims to investigate the dynamic evolution of molecular systems, offering insight into the sequence of events that govern reaction mechanisms and outcomes. The focus is on three main reactions: the reactions of chloramine ( $\text{NH}_2\text{Cl}$ ) with alkoxide ions ( $\text{RO}^-$ , where  $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$ ), the mechanism and dynamics of  $\text{NH}_2\text{Cl}$  with methoxide ( $\text{CH}_3\text{O}^-$ ), and the dynamic behavior underlying halophilic reactions.

Chapter 1 provides a concise overview of experimental and computational studies on  $\text{S}_{\text{N}}2$  reactions in both gas and solvent phases. It further compares the energy profiles in different environments and with alternative central atoms. Additionally, the chapter includes an in-depth discussion of several novel mechanistic pathways revealed through experimental and theoretical studies.

Chapter 2 outlines the theoretical methods, quantum mechanical and classical methods, that are utilized to explore the chemical reactions considered in the present study.

Chapter 3 investigates the  $\text{S}_{\text{N}}2@N$  reaction mechanisms in chloramine-alkoxide systems using density functional theory (DFT) and second-order Møller–Plesset perturbation theory (MP2). Back-side nucleophilic attacks by  $\text{RO}^-$  on  $\text{NH}_2\text{Cl}$  were found to proceed through double-well potential energy surfaces with low activation barriers, resembling classic  $\text{S}_{\text{N}}2$  reactions at carbon centers ( $\text{S}_{\text{N}}2@C$ ), but featuring unique hydrogen-bonded intermediates. In contrast, front-side attack pathways exhibited significantly higher activation barriers, while proton-transfer routes appeared relatively flat and energetically less favorable. Interestingly, a novel hydride-transfer mechanism was identified in reactions involving methoxide and ethoxide, leading to highly exoergic products, chloride ions ( $\text{Cl}^-$ ), aldehydes ( $\text{R}'\text{CHO}$ , where  $\text{R}' = \text{H}, \text{CH}_3$ ), and ammonia ( $\text{NH}_3$ ). Benchmark calculations using high-level coupled-cluster level of theory identified CAM-B3LYP as the most accurate and reliable functional for describing the energetics and mechanistic features of these systems.

Chapter 4 reports the *ab initio* chemical dynamics simulations carried out at the MP2(fc)/

aug-cc-pVDZ level that uncovers complex and unconventional  $S_N2@N$  dynamics in the reaction of chloramine with methoxide. Unlike classical  $S_N2@C$  reactions, the dominant pathway involved a proton transfer, forming methanol ( $CH_3OH$ ) and the  $NHCl^-$  anion, in good agreement with experimental observations. Additionally, a distinct hydride-transfer route was identified, leading to the formation of  $NH_3$ , formaldehyde ( $H_2CO$ ), and  $Cl^-$ . These reaction displayed nontraditional dynamic pathways, including roaming-mediated and roundabout mechanisms. In some cases, the  $NH_2$  group underwent inversion, resulting in a stereochemical retention in the product  $CH_3ONH_2$ .

Chapter 5 focuses on the computational exploration of experimental gas-phase studies involving the reaction of carbon tetrachloride ( $CCl_4$ ) with the anions  $CH_2CN^-$  and  $CH_3S(O)CH_2^-$ , which predominantly follow a halophilic pathway, where the nucleophile attacks the Cl atom of  $CCl_4$ . These reactions primarily lead to the formation of trichloromethyl anion ( $CCl_3^-$ ), with only minor products from  $S_N2$  substitution and hydrogen/chlorine (H/Cl) exchange reactions [*J. Am. Soc. Mass Spectrom.*, **2005**, 16, 2045]. Using DFT, MP2, and DLPNO-CCSD(T) methods, the potential energy profiles of these reaction pathways were mapped. Among the tested methods, B3LYP/6-311++G\*\* level of theory was identified as both computationally efficient and sufficiently accurate for these systems. The halophilic pathways were found to be barrierless and kinetically favorable, in contrast to the  $S_N2$  channels, which exhibited activation barriers of 4.34 kcal/mol (for  $CH_2CN^-$ ) and 8.39 kcal/mol (for  $CH_3S(O)CH_2^-$ ). The H/Cl exchange was shown to occur via a stepwise process involving an initial halophilic attack, followed by proton transfer, circumventing the energetically demanding direct exchange route.

In Chapter 6, the *ab initio* trajectory simulations at the B3LYP/6-311++G\*\* level of theory for the  $CCl_4 + CH_2CN^-$  reaction supported the experimental findings, confirming the dominance of the halophilic pathway and the presence of  $S_N2$  products. In halophilic reactions, around 93% of the product energy goes into internal motion (vibrations and rotations), leaving only 7% for translation in the direct mechanism. The indirect mechanism leads to even more internal energy (97%) due to longer interaction time.