Theoretical Investigations of Unimolecular Reaction Dynamics in the Gas Phase

Abstract

Chemical dynamics simulation of reactions is widely used to complement experimental studies and provide an atomic level picture i.e., the time dependent motion of nuclei as the reaction progresses. Such an atomic level viewpoint not only provides a clear understanding of the dynamics but is crucial for controlling chemical reactions using external parameters. Atoms and molecules are quantum mechanical in nature and solving the time dependent Schrödinger equation provides information about the dynamics of a reaction. This approach, known as *quantum dynamics* is limited to systems with fewer number of atoms due to the associated computational complexities. On the other hand, modeling the dynamics of a reaction using classical equations of motion - an approach known as *classical trajectory simulation* - has been widely used for the past several decades for studying dynamics of chemical reactions. Such classical simulations have advantages and limitations which are well known. The success of a trajectory simulation primarily depends on the quality of potentials $V(q_i)$ and gradients $\partial V/\partial q_i$ used for integrating the equations of motion. Traditionally, classical analytical potential energy functions are used in the simulations. Due to the advancement in computational techniques, it is possible today to compute $V(q_i)$ and $\partial V/\partial q_i$ directly from an electronic structure theory in an on-the-fly fashion. Such an approach is called *direct dynamics* and is used in the present thesis work to study unimolecular dissociation dynamics of select reactions.

The first reaction studied was the dissociation of formamide (NH_2CHO) in the gas phase. It is the simplest organic molecule containing an amide functional group which also serves as a prototype to study protein and peptide chemistry. Formamide has been found in Comets and interstellar media and it's decomposition results in smaller molecules such as NH_3, CO, HCN, HNCO, etc. These dissociation products are also considered to be potential precursors for the formation of complex biological molecules such as nucleic acids and nucleobases in early Earth. A few dynamics studies of formamide decomposition exist in the literature however only a few pathways have been characterized in detail. In this work, the unimolecular decomposition of formamide in the electronic ground state was investigated in detail using electronic structure theory, direct chemical dynamics simulations, and Rice-Ramsperger-Kassel-Marcus (RRKM) rate constant calculations. Simulations were performed using density functional B3LYP/aug-cc-pVDZ level of electronic structure theory. The major dissociation products observed were NH_3, CO, H_2, HNCO, H_2O, HCN, and HNC along with products of few minor dissociation channels. The importance of indirect dissociation pathways of formamide involving the low lying isomers (NH_2COH and NH=CH-OH) were also established. Reactivity, atomic level mechanisms, and product branching ratios were investigated as a function of total energy.

Formyl halides i.e., halogen substituted analogues of formaldehyde, HXCO (X = F, Cl, Br, and I) play an important role in the degradation of stratospheric ozone. Motivation for the study of the dissociation of formyl halides is their crucial role in atmospheric chemistry. Dissociation products of formyl halides are known to play an important role in ozone depletion. Chemical dynamics simulations were performed on-the-fly using B3LYP/6-31G* theory with suitable effective core potentials for the halogen atoms. Simulations showed multiple pathways and mechanisms for the dissociation of formyl halides. Major reaction products were HX + CO which formed via direct and indirect pathways. Similar to unsubstituted formaldehyde, roaming was observed in the dissociation of formyl halides. Trajectory lifetime distribution calculations

indicated non-statistical dissociation dynamics for HXCO dissociation.

First step of Formose or Butlerov reaction involves C-C bond formation between two formaldehyde molecules resulting in glycolaldehyde. This reaction happens under basic conditions in solution. A tandem mass spectrometry investigation of dissociation of deprotonated glycolaldehyde in the gas phase, to study the formose reaction in a retrosynthetic point of view, has been reported. In the present work, electronic structure theory calculations and quasi-classical direct chemical dynamics simulations were used to model the gas phase dissociation of the conjugate base of glycolaldehyde. The dynamics simulations were performed on-the-fly using B3LYP theory with the 6-31+G* basis set under collision induced dissociation (CID) conditions. Trajectories were launched with two different deprotonated forms of glycolaldehyde for a range of collision energies mimicking experiments. Reverse formose reaction was observed primarily from the high energy isomer via a non-statistical pathway. Intramolecular hydride transfer was ubiquitous in the trajectories.

In summary, the work reported in the thesis demonstrates the need to perform chemical dynamics simulations for a clear interpretation of the experimental spectra and to establish atomic level understanding of chemical reactions.

…