

Theoretical Investigations of Unimolecular Reaction Dynamics in the Gas Phase

A Thesis submitted by
Anchal Gahlaut

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Indian Institute of Technology Jodhpur
Department of Chemistry
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Conclusions and Future Scope

Central theme of the work presented in the thesis was the study of unimolecular dissociation dynamics using direct classical trajectory simulations. Availability of super-fast computers and efficient algorithms has made it possible to study the atomic level dynamics of chemical reactions to an unprecedented detail. In such studies, classical trajectories are run directly on an *ab initio* or a density functional potential energy surface and the trajectories are unadulterated and accurate to the level of chosen electronic structure theory. Such a detailed atomic level study is required for a successful interpretation of experimental data and also to identify new reaction mechanisms. Such a detailed understanding of chemical reactions in terms of mechanisms and energetics is a must for achieving the long-standing goal of chemists - *mode selective chemistry*. In the present thesis work, detailed atomic level dissociation dynamics of few systems were investigated. These molecules were selected based on their importance in atmospheric and prebiotic chemistry. The first molecule studied was formamide (FM) and the study showed that FM can decompose into several smaller molecules of prebiotic interest and multitude of unimolecular reaction pathways exist. Studies reporting formation of biologically relevant molecules such as amino acids from thermal decomposition of FM are known. Branching ratios of competing one-step concerted and two-step dissociation pathways were found as a function of excitation energy. Role of indirect dissociation pathways of FM via low lying isomers such as NH_2COH and $\text{NH}=\text{CH}-\text{OH}$ were established in the present work. Results were also in consistent with previously reported experimental studies on FM dissociation. Isolated gas phase dissociation of FM was found to be a high temperature process and electronic structure calculations have shown that the energy barriers decrease in the presence of a catalyst. Atomic level dynamics investigation of catalytic dissociation of FM is an avenue yet to be explored. Next, dissociation dynamics of formyl halides HXCO ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) was investigated. Dissociation of these molecules play an important role in combustion and atmospheric chemistry. Detailed dynamics investigation showed the various dissociation pathways of HXCO and the formation of different reaction products. Dissociation pathways via formation of isomers such as HCOX and HOXC are found to be high barrier processes and are not significant in the dynamics. An important finding in this work is that a new radical recombination mechanism via *roaming* of H or X contributed to some extent in the dissociation of formyl halides. Roaming in formaldehyde dissociation is well known in the literature and the same in formyl halides is reported here for the first time. Computed product energy distributions also differentiated the direct and indirect dissociation mechanisms of formyl halides and in consistent with previous studies. Furthermore, lifetime distribution calculations showed non-statistical nature of the decomposition dynamics of formyl halides. Detailed investigation of this non-statistical dissociation of formyl halides is an area of research yet to be explored. FM and HXCO dissociation dynamics were studied following micro-canonical excitation of the corresponding reactant molecules. A slightly different way of exciting a reactant molecule viz., collisional activation was used to study the dynamics of deprotonated glycolaldehyde (GA). GA is the simplest possible sugar and is one of the largest organic molecules detected in interstellar media. The main focus of the study was to probe the formation of formose products from a retero-synthetic point of view and to identify intermediates and reaction channels. Target reaction products were formed primarily from a higher energy isomer of deprotonated GA and the results were in qualitative agreement with experiments.

Ubiquitous intramolecular hydrogen transfers and non-statistical dissociation mechanisms were important findings in the work. One of the objectives of the thesis is to demonstrate the importance of performing atomic level dynamics simulations for establishing reaction mechanisms and this objective has been achieved. The findings presented in the thesis will contribute to increasing our understanding of the unimolecular reaction dynamics.

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