Unimolecular Reaction Dynamics: Mechanisms and Pathways via Chemical Dynamics Simulations

A Thesis submitted by
Sumitra Godara

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Department of Chemistry
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Summary

The objectives of the work presented here are to provide atomic level understanding of select unimolecular reactions in the gas phase using Born-Oppenheimer direct classical trajectory simulations. Detailed investigations of the potential energy surface and the dynamics of three different reactions, relevant in synthetic and atmospheric chemistry, have been performed and reported. By investigating the dynamics with initial conditions mimicking experimental conditions, mechanistic details of these reactions have been significantly enhanced. Decomposition of 3-oxetanone molecule was studied using infrared and mass spectrometry experiments and two different dissociation channels viz., ketene + formaldehyde and ethylene oxide (c-C_2H_4O) + carbon monoxide were identified. Electronic structure theory calculations show a high energy barrier for ethylene oxide formation and RRKM rate constant calculations show smaller rate constants for the same pathway. However, experiments have reported an almost equal yield for the two channels. The present direct dynamics study has resolved the issue by explicitly identifying a new ring-opened ethylene oxide pathway. This pathway is indirect and has comparable barrier to the ketene channel and accounts for the experimental observations. In another work, ground state dissociation chemistry of four halon molecules, CF_2Cl_2, CF_2Br_2, $CHBr_3$, and CH_2BrCl were studied. Simulation results showed that molecular products, in general, were dominant for all the four molecules at the chosen energies. A variety of reaction mechanisms, such as direct dissociation via multi-center transition states, decomposition via isomerization (involving iso-halons), radical recombinations involving roaming, contributed to the formation of molecular products. The present work clearly demonstrates the importance of iso-halons in the dissociation chemistry of halons. Another important finding is the identification of roaming involving halogen atoms. Though the fraction is small, it does contribute to molecular product formations. Curtius rearrangement is the elimination of N_2 from carbonyl azides $RC(O)N_3$ to form isocyanates RNCO. The mechanism of Curtius rearrangement of two carbonyl azides with different substituents (R = CH_3 and F) were investigated under thermal reaction conditions. Previous experimental and theoretical studies have indicated that the mechanism is usually concerted for thermal reactions and both step-wise and concerted under photochemical conditions. The present simulation results showed a dominant concerted mechanism for $CH_3C(O)N_3$ and the operation of both the mechanisms for $FC(O)N_3$ under similar conditions showing that the nature of substituent also contributes to the reaction mechanism. Another important finding in this work is that a small fraction of trajectories of $FC(O)N_3$ system underwent concerted dissociation, but the final isocyanate product isomerized back to the nitrene form, pointing to the operation of an indirect mechanism of nitrene production detected in the experiments. In summary, the work presented in the thesis demonstrates the importance of performing chemical dynamics simulations in order to accurately interpret experimental data and to establish atomic level reaction mechanisms.

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