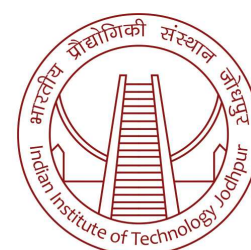


Theoretical Investigations of Unimolecular and Bimolecular Reaction Dynamics in Gas Phase

A Thesis submitted by
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in partial fulfillment of the requirements for the award of the degree of
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Reaction dynamics is concerned with atomic level changes that occur as a function of time in the molecule(s) during a chemical transformation. In this thesis, detailed theoretical investigations of the potential energy surface and the dynamics of different unimolecular and bimolecular reactions have been reported. These reactions play important role in combustion chemistry, astrophysics, and atmospheric chemistry. Simulation results were compared with experimental results, wherever possible, and provided adequate interpretation of these reactions at atomic level. The first reaction reported was the $\text{H}_3^+ + \text{CO}$ bimolecular reaction for a range of collision energies. This is one of the important reactions occurring in the interstellar media, and the simulations were performed to model a recently reported velocity map imaging study. The product isomer ratios obtained from the present simulations at low collision energies are in contrast with the experimental predictions but are in agreement with previously theoretical studies. Internal energy and scattering angle distributions were in qualitative agreement with the experimental work. Scattering angle distributions were peaked at low values, indicating primarily forward scattering at all energies except for the lowest E_{rel} . This pointed toward the operation of a stripping type mechanism which was verified by visualization of the trajectories. At the lowest E_{rel} , interesting dynamical features including a roaming mechanism were observed which led to the broad scattering angle distribution. The $\text{HCO}^+ \rightleftharpoons \text{HOC}^+$ isomerization was observed in a small fraction of trajectories at high collision energies but did not play a significant role in determining the branching ratios. It is important to note that the reaction considered here is a proton transfer reaction which implies quantum effects might be playing a role in determining the rate constants and branching ratios.

Classical chemical dynamics simulations of gas phase unimolecular reaction of γ -ketohydroperoxide are reported. The results of the simulations were compared with previously reported automated reaction discovery methods. Homolytic scissions were found to be dominant and the Korcek reaction of KHP was not observed in these high energy simulations. Trajectory lifetime distribution calculations showed non-statistical nature of the KHP unimolecular dissociation. Finally, thermal dissociation chemistry of thiophene in the gas phase was presented. Thiophene and its derivatives are present in shale oil and their removal from the fuel is a challenging process. The results of the simulations were compared with previous reported experimental and theoretical results. At high temperature C-S scissions with concomitant H-migration from C-atom to S-atom were found to be dominant initial dissociation pathway. Further, previously unknown direct dissociation of the five membered ring to form acetylene was reported. More detailed studies are needed to completely understand the thermal decomposition mechanisms of thiophene. In summary, the work presented in the thesis manifested the importance of performing chemical dynamics simulations to establish atomic level mechanisms and to correctly interpret experimental spectra. Further, such atomic level mechanistic studies are essential to develop mode selective chemistry and for controlling chemical reactions using external parameters.

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