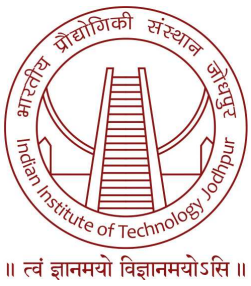
Theoretical Investigations of Unimolecular and Bimolecular Reaction Dynamics in Gas Phase

A Thesis submitted by
Erum Gull Naz

in partial fulfillment of the requirements for the award of the degree of
Doctor of Philosophy



Indian Institute of Technology Jodhpur
Department of Chemistry
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Declaration

I hereby declare that the work presented in this Thesis titled "*Theoretical Investigations of Unimolecular and Bimolecular Reaction Dynamics in Gas Phase*" submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Manikandan Paranjothy. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.

Erum Gull Naz
P14CHM001

Certificate

This is to certify that the thesis titled "*Theoretical Investigations of Unimolecular and Bimolecular Reaction Dynamics in Gas Phase*", submitted by Erum Gull Naz (P14CHM001) to the Indian Institute of Technology Jodhpur for the award of the degree of *Doctor of Philosophy*, is a bonafide record of the research work done by her under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Dr. Manikandan Paranjothy
Ph.D.Thesis Supervisor

Abstract

For decades, classical trajectory simulations have been used to determine reaction mechanisms, energy flow pathways, product branching ratio, etc. Though atoms and molecules are quantum mechanical in nature, classical mechanics is used because of the inherent computational complexities associated with full quantum dynamics calculations. In a classical trajectory simulation, Newtons's or Hamilton's equations of motion are time evolved using an appropriately selected set of initial coordinates and momenta. The time propagated coordinates and momenta are used to compute final properties of the system. A crucial aspect of trajectory integrations is selecting an appropriate potential energy surface. Conventionally, this is done with model potentials (classical force fields) and such calculations are fast but limited by accuracy. With the advancements in parallel computing techniques and sophisticated algorithms, it is possible to compute the required potentials and gradients (for trajectory integration) from a suitable electronic structure theory. Such an *on-the-fly* approach known as *direct dynamics* - is quite popular today and has led to identification of new mechanisms and pathways. Combining this method with electronic structure calculations, few unimolecular and bimolecular reactions were modeled in the present work. Selected reactions are of interest in combustion and interstellar chemistry.

The first reaction investigated was the bimolecular collision dynamics of H_3^+ + CO in the gas phase. The bimolecular reaction of H_3^+ + CO is one of the cornerstone chemical processes in the interstellar media. The products of this reaction are either formyl (HCO^+) or isoformyl (HOC^+) cation along with H_2 molecule. These are barrier-less proton transfer and exoergic processes which results in the two isomers via ion-dipole complex formation. The reaction products are known to initiate the formation of important organic molecules in the interstellar media. Several experimental and theoretical investigations of the reaction probing structure and energetics, reaction mechanism, product branching ratios and $HCO^+ \rightleftharpoons HOC^+$ isomerization have been reported. Ionic products of this reaction initiate different reaction networks in the interstellar media and their relative abundance in the space is a crucial quantity of interest. Direct dynamics simulations of H_3^+ + CO bimolecular reaction were performed using density functional PBE0/aug-cc-pVDZ level of theory to model a recently reported velocity imaging experimental studies of the same reaction. Reaction mechanisms, branching ratios, product energy and scattering angle distributions were computed from the trajectory data. Results are in qualitative agreement with experiments and detailed atomic level mechanisms are presented.

The second reaction studied was the unimolecular dissociation of γ-ketohydroperoxide (KHP). γ-ketohydroperoxide [(3-hydroperoxy)propanal] is an important reagent in synthetic chemistry. KHP is considered to be the primary source of radicals in low temperature combustion. Automated reaction discovery methods were utilized previously to study the unimolecular decomposition pathways of KHP. In the present work, direct chemical dynamics simulations at the B3LYP/6-31+G* level of theory were performed to model the unimolecular decomposition of KHP identifying important dissociation pathways. Simulations were carried out at three different total energies mimicking thermal reaction conditions. Three dissociation channels among the previously reported pathways were identified to be important. Korcek decomposition, which was proposed earlier as a source of carbonyl compounds from thermal decomposition of KHP, was not observed in the present high-temperature simulations. However, trajectories showed the formation of carbonyl compounds such as aldehydes via other pathways. Further, Rice-Ramsperger-Kassel-Marcus (RRKM) rate constants were computed and compared with the trajectory data.

Thermal decomposition of thiophene, to understand the initial dissociation steps, were modeled at the B3LYP/6-31+G* level of theory. Thiophene and its derivatives are present in the asphaltenes contained in oil shale and play an important role in the combustion reactions of alternative fuels. Electronic structure theory and experimental studies investigating the decomposition mechanisms of thiophene have been reported. In the present work, direct dynamics simulations were used to study the atomic level reaction mechanisms of gas phase pyrolysis of thiophene.

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Erum Gull Naz

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List of Symbols

Å	Angstrom
fs	femstosecond
ps	picosecond
kcal/mol	kilo calorie per mole
eV	electronvolt
ρ	Electron probability density
ψ	Molecular wave function
ψ_{el}	Electronic wavefunction
$\vec{r}$	Electronic coordinates
$\vec{R}$	Nuclear coordinates
Z	Atomic number of nucleus
$\hat{H}$	Hamiltonian operator
V	Potential energy of the system
T	Kinetic energy of the system
q	Position of a particle
p	Momenta of a particle
rc	Reaction coordinate
ν	Normal mode vibrational frequency
k	Force constant
μ	Reduced mass of the molecule
t	Time
m	Mass
F	Force
Δt	Integration timestep

k(E)	RRKM rate constant
E_{tot}	Total energy
E_{int}	Internal energy
E_{rot}	Rotational energy
E_{vib}	Vibrational energy
E_{rel}	Relative energy
b	Collision Impact parameter
σ_r	Collision cross section
v	Relative velocity
$P_r(b)$	Reaction probability
$P(\theta)$	Scattering angle distribution
f_t	Fractions of trajectories
k_B	Boltzmann constant
h	Planck's constant
T	Temperature
H	Hydrogen
C	Carbon
O	Oxygen
S	Sulphur

List of Abbreviations

BOMD	Born-Oppenheimer Molecular Dynamics
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
CBS	Complete Basis Set
CC	Coupled Cluster
CCSD(T)	Coupled Cluster Single-Double and perturbative Triple
CPMD	Car-Parrinello molecular dynamics
DFT	Density Functional Theory
HF	Hartree-Fock
IM	Intermediate
IRC	Intrinsic Reaction Coordinate
IVR	Intramolecular Vibrational energy Redistribution
KHP	Ketohydroperoxide
MCTDH	Multi-configuration time-dependent Hartree
MP2	Møller-Plesset Perturbation theory of second-order
MM	Molecular Mechanics
NWChem	NorthWest Chemistry
PBE0	Perdew-Burke-Ernzerhof-0
PE	Potential Energy
PES	Potential Energy Surface
QM	Quantum Mechanics
RRKM	Rice-Ramsperger-Kassel-Marcus
TS	Transition State
TST	Transition State Theory
ZPE	Zero Point Energy