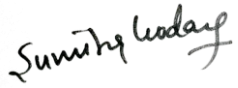
Declaration

I hereby declare that the work presented in this thesis titled *Unimolecular Reaction Dynamics: Mechanisms and Pathways via Chemical Dynamics Simulations* 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.



Sumitra Godara
P15CY007

Certificate

This is to certify that the thesis titled *Unimolecular Reaction Dynamics: Mechanisms and Pathways via Chemical Dynamics Simulations*, submitted by *Sumitra Godara (P15CY007)* 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

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List of Figures

Figure	*Title*	*page*
2.1	Flowchart of a classical trajectory simulation.	13
3.1	Equilibrium geometry of 3-oxetanone molecule and the two considered thermal decomposition pathways forming ketene + formaldehyde and ethylene oxide + carbon monoxide.	15
3.2	Optimized geometries at B3LYP/6-31G*, bond angle values are in degree (°) and bond lengths in angstroms (Å).	17
3.3	Potential energy profile of 3-oxetanone dissociation pathways computed at the B3LYP/6-31G* level of theory. The numbers in bracket are energies in kcal/mol relative to the reactant 3-oxetanone molecule. The corresponding optimized geometries are also shown.	18
3.4	Total energy as a function of time for a few sample classical trajectories. First, second, and third columns correspond to E_{tot} = 150, 200, and 300 kcal/mol, respectively. Trajectory outcomes (reaction products) are shown inside the plots. In all plots, x-axes ranges are same.	19
3.5	Potential energy profiles for (a) 3-oxetanone dissociating to CH_2OCH_2 + CO (b) isomerization of CH_2OCH_2 to ethylene oxide (c) dissociation of CH_2OCH_2 to HCHO + CH_2 and (d) ketene dissociation to CH_2 + CO. The numbers in brackets are energies in kcal/mol, relative to the corresponding reactants.	21
3.6	Snapshots of trajectories showing dissociation of 3-oxetanone to (a) $HCHO + CH_2CO \longrightarrow HCHO + CH_2 + CO$ (b) $CO + CH_2OCH_2 \longrightarrow CO + c{-}C_2H_4O \longrightarrow CO + CH_3CHO$ and (c) $CO + CH_2OCH_2 \longrightarrow CO + CH_2 + HCHO$.	21
3.7	(a) Snapshots of a typical trajectory showing dissociation of 3-oxetanone to CO and CH_2OCH_2 which isomerizes to ethylene oxide (b) $C_1{-}C_2$ distance (in Å) (c) $\angle C_1{-}O{-}C_2$ angle (in degree) as a function of time. Isomerization of CH_2OCH_2 to ethylene oxide happens around 1700 fs.	23
3.8	Optimized geometries of two isomers of ethylene oxide at B3LYP/6-31G* level	24
3.9	Optimized geometries at B3LYP/6-31G*, bond angle values are in degree (°) and bond lengths in angstroms (Å).	25
3.10	Snapshots of a typical trajectory showing dissociation of (a) $c{-}C_3H_4O_2 \longrightarrow H_2 + c{-}COCH_2CO \longrightarrow H_2 + CO + CH_2CO \longrightarrow H_2 + 2\,CO + CH_2$ (b) $c{-}C_3H_4O_2 \longrightarrow CH_3COCHO \longrightarrow CH_3 + CO + CHO$ (c) $c{-}C_3H_4O_2 \longrightarrow CH_2 + CHOCHO \longrightarrow CH_2 + CO + HCHO$ (d) $c{-}C_3H_4O_2 \longrightarrow CO + CH_2CHOH \longrightarrow CO + H_2O + C_2H_2$	26
3.11	Fraction of trajectories f_T as a function of E_{tot} showing (a) CO elimination via primary dissociation of 3-oxetanone (red), secondary decomposition of reaction products (green), and the total amount of trajectories eliminating CO (black) (b) the branching of 3-oxetanone dissociation products into various different pathways.	27
3.12	RRKM theory rate constants k_{RRKM} as a function of energy for the dissociation pathways of 3-oxetanone.	28
4.1	Potential energy profiles of dissociation pathways of halons computed using density functional PBE0/6-31G* level of theory. Energies given are relative to that of respective reactants and are without zero point energy corrections.	37
4.2	Intrinsic reaction coordinate (IRC) data for the concerted elimination of X_2 from CF_2X_2 (X=Cl,Br) computed using PBE0/6-31G* theory. Energies are in units of kcal/mol.	38

4.3 Snapshots of $CF_2Cl_2 \longrightarrow CF_2 + Cl_2$ trajectories dissociating via (a) isomerization and (b) roaming pathway. (c) shows C−Cl(1) and C−Cl(2) bond distances (in Å) for the isomerization (red) and roaming (blue) trajectories. The numbers present inside each frame is time in fs. 40

4.4 Snapshots of $CF_2Br_2 \longrightarrow CF_2 + Br_2$ trajectories dissociating via (a) concerted (b) isomerization and (c) roaming pathway. Number inside each frame is time in fs at which the snapshot was taken. (d) shows C−Br(1) and C−Br(2) bond distances (in Å) for the concerted (black), isomerization (red), and roaming (blue) trajectories. Distributions of time gaps (in fs) between the two C−Br bond cleavages dissociating via isomerization (black) and the concerted (red) pathway are shown in (e). 40

4.5 Snapshots of a $CHBr_3$ trajectory forming (a) $Br_2 + CHBr$ and (b) $HBr + CBr_2$ products. (c) shows C−Br(1) and C−Br(2) distances for the trajectory given in (a). (d) shows C−Br distance in x-axis and C−H distance in y-axis for the trajectory shown in (b). The bond distances are given in units of Å. 42

4.6 Snapshots of CH_2BrCl trajectories forming $HBr + CHCl$ via (a) concerted and (b) radical recombination pathway. Corresponding time evolved C−Br (x-axis) and C−H (y-axis) distances (in Å) are given in (c) and (d). 43

4.7 Snapshots of trajectories showing $CH_2BrCl \longrightarrow HCl + CHBr$ reaction via (a) concerted and (b) radical recombinations. (c) and (d) show C−Cl distance in x-axis and C−H distance in y-axis in units of Å. 43

4.8 Snapshots of trajectories showing (a) $CF_2Cl_2 \longrightarrow Cl + CF_2Cl$ radical dissociation (b) $CF_2Br_2 \longrightarrow CFBr + BrF$ reaction via isomerization (c) $CF_2Br_2 \longrightarrow Br + CF_2Br$ radical dissociation (d) $CHBr_3 \longrightarrow Br + CHBr_2$ radical dissociation (e) $CHBr_3 \longrightarrow HBr + CBr_2$ via concerted mechanism (f) $CH_2BrCl \longrightarrow Cl + CH_2Br$ via isomerization and (g) $CH_2BrCl \longrightarrow Br + CH_2Cl$ radical dissociation. Number inside each frame is time in fs at which the snapshot was taken. 44

5.1 Dissociation energy profiles of $RC(O)N_3$ (R = CH_3 and F) computed using B3LYP/6-31+G* level of electronic structure theory. Energies are given in kcal/mol units and zero point energy not corrected. 51

5.2 Optimized geometries of the stationary points on the $CH_3C(O)N_3$ potential energy surface 52

5.3 Optimized geometries of the stationary points on the $FC(O)N_3$ potential energy surface 53

5.4 Total energy as a function of time for a few sample classical trajectories. In all plots, x-axes ranges are same, y-axes show total energy in units of kcal/mol. 54

5.5 Numbering system used for discussion purposes in the text. 54

5.6 Density plots (a), (b), and (c) show time evolved N3-N4 (x-axes) and C2-N3 (y-axes) bond distances (in Å) for $CH_3C(O)N_3$ dissociation. (a) shows data from E_{tot} = 90 kcal/mol simulation, (b) and (c) show data from 120 kcal/mol simulation. Red, and Blue colors correspond to minimum and maximum density respectively. 55

5.7 (a) shows time evolved N3-N4 and C2-N3 bond distances (in Å) for $CH_3C(O)N_3$ dissociation for a few sample trajectories. Red circles correspond to a concerted trajectory and blue triangles correspond to a stepwise trajectory resulting in the CH_3NCO final product. The green squares correspond to a stepwise trajectory existing as nitrene when the calculation was stopped. The black thick line in this plot is the IRC data for the concerted pathway. (b) shows lifetimes τ (in fs) of the intermediate nitrene species calculated from the trajectories. 56

5.8 Snapshots of few example trajectories, (a) concerted $CH_3C(O)N_3$ dissociation; (b) stepwise $CH_3C(O)N_3$ dissociation; (c) concerted $FC(O)N_3$ dissociation followed by $FNCO \longleftrightarrow FC(O)N$ isomerization; (d) $FC(O)N_3$ stepwise dissociation followed by $FNCO \longrightarrow FC(O)N$ isomerization. The numbers inside each frame is time in fs at which the snapshot was taken. 57

5.9 Time evolved N3-N4 and F1-N3 bond distances (in Å) computed from the $FC(O)N_3$ trajectories are shown in density plots (a), (b), (d), and (e). Distributions of lifetimes τ (in fs) of the intermediate nitrene species are shown in (c) and (f). Top panels show data from the low energy (E_{tot} = 90 kcal/mol) simulation and the bottom panels show results of high energy (120 kcal/mol) simulation. Red, and Blue colors correspond to minimum and maximum density respectively. 58

5.10 Time evolved N3-N4 and F1-N3 bond distances (in Å) of the $FC(O)N_3$ system, for a concerted trajectory (red circles), stepwise trajectory (blue triangles), and a concerted trajectory forming the nitrene intermediate (green squares). The black thick line in this plot is the IRC data for the concerted pathway. Distributions of lifetimes τ (in fs) of the intermediate nitrene species are shown in (b). 59

List of Tables

Table	*Title*	*page*
3.1	Energies of stationary points on the 3-oxetanone dissociation pathways shown in Figure 3.1. Numbers are in units of kcal/mol and are relative to the reactant energy at a given level of theory.	17
3.2	Overall trajectory events following excitation of the 3-oxetanone molecule	20
3.3	Various different dissociation pathways observed for the 3-oxetanone molecule	22
3.4	Minor pathways observed in the dissociation of 3-oxetanone	25
4.1	Stationary point energies of CF_2Cl_2 dissociation profile computed using different levels of theory. The energies are in kcal/mol and relative to the reactant molecule.	33
4.2	Stationary point energies of CF_2Br_2 dissociation profile computed using different levels of theory. The energies are in kcal/mol and relative to the reactant molecule.	33
4.3	Stationary point energies of $CHBr_3$ dissociation profile computed using different levels of theory. The energies are in kcal/mol and relative to the reactant molecule.	34
4.4	Stationary point energies of CH_2BrCl dissociation profile computed using different levels of theory. The energies are in kcal/mol and relative to the reactant molecule.	35
4.5	Comparison of stationary point energies (in kcal/mol) on the dissociation energy profiles of halons computed using PBE0/6-31G* and CCSD(T)//MP2/aug-cc-pVTZ level of theories. Energies given are relative to respective reactants and zero point energy corrected.	36
4.6	Summary of trajectory events of CF_2Cl_2 and CF_2Br_2 dissociation.	39
4.7	Fractions of radical and molecular products (in percentage) produced in the unimolecular decompositions of halons.	45
5.1	Comparison of stationary point energies (in kcal/mol) on the dissociation energy profiles of $RC(O)N_3$ (R = CH_3 and F) computed using different methods with 6-31+G* basis set. Energies given are relative to the respective syn conformer without zero-point energy corrections.	51

List of Symbols

Symbol	*Description*
E_{el}	Electronic energy
E_{rot}	Rotational energy
E_o	Ground state energy
E_{tot}	Total energy
$G(E^{\ddagger})$	Sum of the states for active degree of freedom in the trasnsition state
$\hat{H}$	Hamiltonian operator
$\hat{H}_{el}$	Electronic Hamiltonian operator
$\Psi(\vec{r}, \vec{R})$	Wave function
$\Psi_{el}(\vec{r}; \vec{R})$	Electronic wavefunction
$\chi(\vec{R})$	Nuclear wavefunction
m_e	Mass of electron
m_α	Mass of nuclei
k_{RRKM}	RRKM rate constant
P	Probability
$P(\tau)$	Lifetime distribution
p_i	Momenta
q_i	Position
ρ_o	Ground state electron density
ρ_{tr}	Trial electron density
τ	Lifetime
$\hat{T}_e$	Electron kinetic energy
$\hat{T}_N$	Nuclear kinetic energy
$U(\vec{R})$	Potential energy
$\hat{V}_{ee}$	Electron-electron repulsion energy operator
$\hat{V}_{eN}$	Electron nuclei attraction energy operator
$\hat{V}_{NN}$	Nuclear-nuclear repulsion energy operator

List of Abbreviations

Abbreviation	*Full form*
AIMD	Ab-initio Molecular Dynamics
B3LYP	Becke, 3-parameter, Lee–Yang–Parr
BO	Born-Oppenheimer
BOA	Born-Oppenheimer Approximation
BOMD	Born-Oppenheimer Molecular Dynamics
CC	Coupled Cluster
c-$C_3H_4O_2$	3-oxetanone
CCSD(T)	Coupled Cluster Single Double (Triple)
CF_2Br_2	Dichlorodibromomethane (Halon 1202)
CF_2Cl_2	Dichlorodifluoromethane (Freon-12)
CFCs	Chlorofluorocarbons
CH_2BrCl	Bromochloromethane
CH_2CO	Ketene
$CH_3C(O)N_3$	Acetyl azide
$CHBr_3$	Bromoform
CI	Configuration Interaction
CO	Carbon monoxide
CP	Car Parrinello
DFT	Density Functional Theory
ESCs	Electronic Structure Calculations
$FC(O)N_3$	Fluorocarbonyl azide
Halons	Halomethanes
IRC	Intrinsic Reaction Coordinate
IVR	Intramolecular Vibrational energy Redistribution
K.E.	Kinetic Energy
LEPS	London-Eyring-Polanyi-Sato
MAD	Mean absolute deviation
MD	Molecular Dynamics
MM	Molecular Mechanics
MP2	Second-order Moller-Plesset Perturbation
NWChem	NorthWest Computational Chemistry
P.E.	Potential Energy
PBE	Perdew–Burke-Ernzerhof (PBE)
PES	Potential Energy Surface
QM	Quantum Mechanics
RRKM	Rice-Ramsperger-Kassel-Marcus
TS	Transition State
ZPE	Zero Point Energy