THEORETICAL AND EXPERIMENTAL CHARACTERIZATION OF DICYCLOPENTADIENE REACTIVITY

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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December 2015

Major Subject: Safety Engineering

ABSTRACT

Reactive chemical hazards have been a significant concern in the chemical process industries. Reactive chemicals have caused many catastrophic disasters in industries that deal with the storage, handling or manufacturing chemicals which resulted in loss of lives and property. In a report by U.S Chemical Safety and Accident Investigation Board about 167 incidents from 1980 to 2001 is attributed to reactive chemical hazards. About 35% of the incidents were due to thermal runaway reactions.

One significant reactive compound that has seldom been studied is dicyclopentadiene despite its extensive use. Dicyclopentadiene is an important cyclic olefin, obtained from naphtha or crude feedstock and used industrially for manufacturing specialty polymers, pigments, and as a starting material for high density fuels. Dicyclopentadiene was involved in a catastrophic incident in the Netherlands which resulted in about 3 casualties and huge environmental incidents. This incident was attributed to a thermal runaway which led to explosion of the reactor which destroyed the whole facility.

In this work the thermal stability of dicyclopentadiene system is studied under various conditions using both theoretical and experimental techniques. Theoretically, computational quantum chemistry is used to study the thermodynamics of some of the elementary reaction mechanisms. The reaction energies of various dicyclopentadiene reaction pathways are estimated and the “onset” temperature of a possible runaway is calculated using established correlation. Experimentally, the Reactive Systems

Screening Tool (RSST) is used to experimentally study the runaway of dicyclopentadiene. The onset temperature, self-heat rate and the temperature ramps were determined under the presence of different solvent systems and the effect of the systems on the runaway is studied. The energy of the exotherm is calculated from experimental analysis of the RSST, under various conditions.

DEDICA TION

To my Family, for everything…

ACKNOWLEDGEMENTS

My journey here at the graduate school has been a tough but an exciting time. I would like to thank Dr. Zhengdong Cheng for giving me the opportunity to work in diverse fields of research and for giving me useful critiques on my ideas which helped me in my research. Dr. Sam Mannan inspired me with his deep knowledge and leadership in process safety and I want to thank him for giving me the opportunity to work at the center, his encouragement helped me in choosing the topic of my study. I want to thank Dr. David Bergbreiter for taking time to serve in my committee. I would also like to thank Dr. Maria Papadaki and Dr. Simon Waldram for spending their valuable time with me, helping me design experiments and for discussing my results. Dr. Lisa Perez has been an inspirational figure and I would like to thank her for teaching me computational chemistry and for the time spent in endless discussions on interpreting the results and other questions and ideas that I had with her. I would also like to express my gratitude to all the professors under whom I had the opportunity to learn at A&M.

I would also like to thank all my friends, both here and back home, and my roommates for all the good times that we spent together during my time here and those endless conversations which helped me get through the regular grind. Special thanks to Valerie Green, Alanna Scheinerman and Towanna Arnold for helping me at various stages of my program here at A&M.

I also want to extend my gratitude to the Mary Kay O'Connor Process Safety Center, which provided me access to RSST calorimetry apparatus and the Texas A&M Supercomputing Center for providing computing time. I'd also like to thank Laboratory for Molecular Simulations for providing the code for running the molecular simulations which was undertaken in this work.

Finally, I would not be here without the support of my family. My regular conversations with Appa, Amma, Athi, Paati and Mathangi helped me get through tough times. Everything I am, I owe to them and words are not enough to either express my gratitude or thank them, so I'm not going to try.

NOMENCLATURE

DCPD	Dicyclopentadiene
CPD	Cyclopentadiene
TCPD	Tricyclopentadiene
GC	Gas Chromatography
ROMP	Ring Opening Metathesis Polymerization
RSST	Reaction Systems Screening Tool
AM1	Austin Model 1
MP2	Møller-Plesset second order perturbation theory
DFT	Density Functional Theory

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CHAPTER I

INTRODUCTION

Process Industries use chemical reactions on day to day basis to manufacture commodities. One of the main concerns of process industries is to prevent accidents and manufacture safely. One of the important challenges for the industries has been to appropriately assess potential reactive hazards. In a report by United States Chemical Safety and Hazard Investigation Board (CSB) there were 167 reported reactive chemical incidents from January 1980 to June 2001, which resulted in 108 causalities in total and an average of 6 injuries per year in that period.[1] Out of that 35% of the reported incidents were attributed to thermal runaway reactions.[1]

Thermal runaway is a term used to describe the scenario wherein the reaction goes out of control when the heat released by the reaction exceeds the heat removed from the reactor by cooling media or the ambient surrounding. Thermal runaway reactions are common in batch and semi batch reactors. In a study by Barton and Nolan[2] which reported over 189 incidents due to runaway reactions, 64 was from facilities manufacturing polymers. The main reason is attributed to the lack of knowledge of kinetics, human interventions, presence of a variety of reactions taking place in the single batch reactor[3] etc.

Despite many studies, reports and awareness created to identify the possible hazards, industrial accidents continue to take place. It is therefore essential that active measures for identification of possible chemical hazards be undertaken in the very early

stages of process development wherein there is ample time to evaluate, design protective cooling systems, possible safety interlocks and sometimes even eliminate the hazards by evaluating alternative processes or chemicals. From a point of view of process safety engineering, a detailed knowledge of a chemical reaction mechanism or the behavior of the particular substance at abnormal conditions can lead to proposal of robust solutions. The careful study of chemical reactants under process and abnormal conditions are necessary while performing scale up studies by gradually increasing the scale of chemicals used.

In a publication by Center for Chemical Process Safety[3], providing some screening methodology for identifying reactive chemical hazards six general classes of chemical hazards were designated as possible high risk cases. These are

- Pyrophoric materials
- Reactions involving Peroxide formation
- Reactions involving chemicals which react violently with water
- Reactions involving strong oxidizers
- Self-reactive chemicals including polymerization, decomposition, reactions involving rearrangement
- Reactions/mixtures involving potentially incompatible materials

These classes of chemicals are particularly hazardous due to their propensity for undergoing exothermic reactions, releasing gases, reactions with air etc.

1.1 Background

Dicyclopentadiene is a colorless to cloudy white camphor like solid at room temperature, having a distinct pungent odor. It is soluble in most of the organic solvents like heptane, isobutanol, benzene, toluene etc.

The polymerization of Dicyclopentadiene is accomplished by mainly 2 routes, chemically catalyzed or by thermal polymerization. There are many methods/process conditions used to polymerize DCPD. The main catalytic system used are transition metals with complexed organic compounds generally known as Grubbs Catalyst. But many earlier processes relied on transition metal salts such as tungsten chloride (WCl_4). After the invention of Grubbs' Catalyst, Ring Opening Metathesis Polymerization (ROMP) is one of the main process by which dicyclopentadiene is polymerized. ROMP produces linear polymers whose density, average molecular weight whose properties can be tuned precisely depending on the properties needed. DCPD also has 2 active sites for ROMP (shown in Figure 1), which means the amount of crosslinking can also be tuned to increase the temperature or mechanical resistance.[4] The reaction is usually carried out in the liquid phase using Grubbs Catalyst at temperatures about 100-175°C with thermosetting of polymers carried out at 80-120°C. According to the patent disclosed[5] thermal polymerization with organic sulfur compounds a temperature of 240-340°C for making specialty resins, adhesives etc.

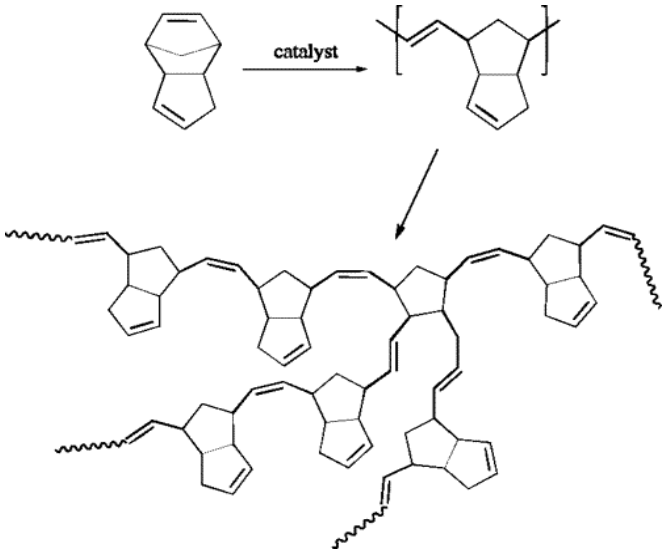

Figure 1 Schematic of Ring Opening Metathesis Polymerization of Dicyclopentadiene (adapted from Davidson et al.[6])

1.2 Physical Properties of Dicyclopentadiene

Dicyclopentadiene has 2 isomers *endo* and *exo* (shown in Figure 2) . The *endo* isomer has been used in this work and is available commonly. The following properties were taken from the SDS[7] is summarized in Table 1.

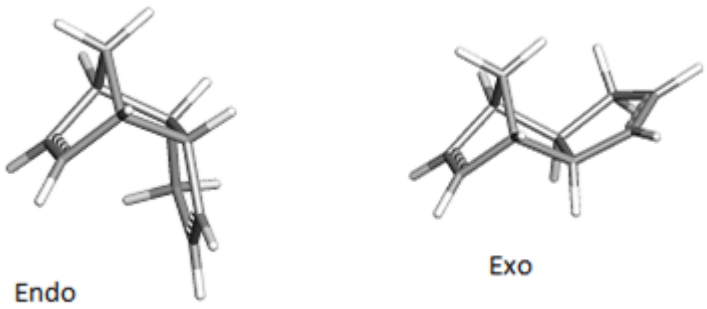

Figure 2 Isomers of Dicyclopentadiene

Table 1 Physical Properties of *endo*-Dicyclopentadiene[7-8]

Molecular Weight	132.02 g/mol
Boiling Point	170°C
Melting Point	32-34°C
Flash Point	32°C
Density	0.986 g/mL
Lower Explosive Limit	1% (V)
Upper Explosive Limit	10% (V)
Physical appearance	Colorless and camphor like solid
Odor	Unpleasant and sharp

Additionally the compound is hazardous to transport and store due to its flammability. The National Fire Protection Association classifies it as Type-III and it can form flammable vapors on exposure to ambient conditions. It has also been shown to be explosive at temperatures above 85°C.

1.3 Previous Research on Dicyclopentadiene

Previous studies on dicyclopentadiene are mainly focused on the possibility of making novel polymers via ring opening metathesis polymerization[8] or its isomerization to *exo* to manufacture high volumetric density fuel called *exo*-tetrahydrodicyclopentadiene commonly known as JP-10[9]. Few papers which focused on the manufacture of tricyclopentadiene which is also used as a high volumetric density fuel used in making efficient fuels in cases where the tank volume is constrained reported its exothermic behavior qualitatively[10]. In a work on Ring opening metathesis polymerization of DCPD by Mariana et al.[11] it was reported that the heat of polymerization was very high. They showed the feasibility of using a zone heating of DCPD from polymerization which typically requires temperatures in excess of 206°C which was corroborated with the experiment.

Studies on kinetics by Herndon et al.[12] concluded that at temperatures above 170°C the dicyclopentadiene reverts to cyclopentadiene rather than isomerization. Herndon et al.[12] also showed that the isomerization of *endo* to *exo* isomers goes via cyclopentadiene rather than just a concerted one step mechanism. They also showed

that Diels-Alder reaction of Dicyclopentadiene with itself to form a tetramer cannot take place.

There have been only few papers published with its thermal behavior at higher temperatures. Ahmed and Lavin[13] conducted a calorimetric study of Dicyclopentadiene. They used DSC and APTAC to study the thermal behavior of DCPD at temperature ranges from 30-500°C and studied the runaway of DCPD. They conducted GPC and GC to show the evolution of trimers from DCPD and that the higher oligomers that evolve from Diels-Alder reactions. Using Gas Chromatography (GC) they showed that at high temperatures DCPD olgiomers decompose to methane and benzene. Based on the GC results, an empirical reaction kinetic scheme was proposed, even though they report the pressure data from the experiments could not be fit into a theoretical vapor-liquid equilibrium data available from the open literature.

Many studies also showed the formation of non-condensable gases at higher temperatures which is a concern during polymerization. Burcat et al.[14] studied the exothermic decomposition of dicyclopentadiene at 500°C using a shock tube and proposed that benzene and methane were the most stable compounds obtained at that temperature range. Palmova et al.[15] studied the reaction behavior of dicyclopentadiene in a reactor and proposed an empirical VLE data fitted to reaction products that was observed in experiments conducted. They showed that the tricyclopentadiene production dominates rather than the production of free-radical intermediates at temperature ranges of 300°C. They also concluded that higher oligomers and thermal cracking reactions dominates at higher temperatures.

CHAPTER II

METHODOLOGY FOR CHARACTERIZING REACTIVITY

2.1 Background

Computational chemistry refers to the use of mathematical models to calculate important chemical properties of compounds. Theoretically, the thermodynamic and kinetic properties which are important to evaluate chemical reactions can be calculated *in silico*. Thermodynamic information such as enthalpies, energies, Gibbs free energy can be obtained for molecules by calculating the most stable configuration of the molecular structure. The kinetics of reaction pathways such as activation energy can be calculated by performing transition state calculations. Both the thermodynamic and kinetic properties can be modelled using Electronic Structure theory. Many software packages are developed like GAMESS[16], Schrodinger, Gaussian 09[17] are well developed and optimized for the gas phase molecular structures.

2.2 Overview of Electronic Structure Theory

Electronic Structure Theory calculates the energies of chemical structures based on fundamental theories based on Quantum Physics. Electronic Structure Theory allows for *in silico* characterization of molecules and even study mechanisms, transient species which may be impossible to obtain from experiments.

The most basic equation used to calculate the electronic energies is Schrodinger Equation:

$$H\Psi = E\Psi$$

where H is Hamiltonian operator, Ψ is the wave function and E is the energy.

The Hamiltonian of a system can be described in many ways. The three main classes to describe Hamiltonian in the Electronic Structure Theory are *ab initio*, Density Functional and semi-empirical methods. *Ab initio* methods construct the Hamiltonian from first principles and using just the fundamental physical constants. Density Functional Theory constructs the Hamiltonian by describing an approximate functional which maps the energy of the system to the electronic density.

The Hamiltonian operator can be divided into the kinetic energy and potential energy parts for the molecule by invoking the Born-Oppenheimer approximation. Born-Oppenheimer approximation separates the nuclear and electronic wave function into 2 separate parts. This means the Hamiltonian for a molecule can be approximated as

$$H = -\sum_{i=1}^{electrons} \frac{\Delta^2}{2} - \sum_{i=1}^{nuclei}\sum_{j=1}^{electrons} \frac{Z_i}{r_{ij}} + \sum_{i=1}^{nuclei}\sum_{j<1}^{electrons} \frac{1}{r_{ij}} + V_{NN}$$

The first term refers to the kinetic energy of the electrons only. The second term refers to the electrostatic attraction between electrons and nuclei which can be calculated exactly using Columbic equation. The third term refers to the electron – electron repulsion within the molecular system. The last term refers to the external potential which is solved by the Born-Oppenheimer approximation to refer to the

electronic energy of the system provided the nuclei is fixed. This is also referred to as fixed core approximation.

2.2.1 Hartree-Fock Theory

Hartree-Fock (HF) theory is an *ab initio* theory meaning that the energy of the molecular system by purely physical theories. The wave function of very simple systems can be calculated exactly, but for polyatomic systems the wave function can only be approximately calculated. HF calculates the ground state energy by approximating the electron –electron repulsion of the molecular system by replacing it with an average field experienced by a single electron due to the presence of other electrons in the system. The system also approximates the wave function with spin orbitals and minimizes the energy of the system with respect to the spin orbitals. The Molecular orbitals are assumed to be linear combination of the atomic orbitals. To describe the approximate orbitals mathematical functions called basis sets are used. Basis sets can impose restrictions such as Pauli's exclusion principle which demands that the wave function be anti-symmetric when the spin of the electron or the spatial coordinates of a set of electrons are changed.

Hartree-Fock theory also obeys the variational principle of quantum mechanics which state that the energy calculated by the approximate Hamiltonian is the upper bound of the true energy ($E_{HF} \geq E_0$). But a disadvantage of Hartree-Fock method is that the electron correlation is not included due to the mean field approximation. Explicit electron-electron repulsion is important to include in the Hamiltonian and the

mean field approximation is not a good approximation. Though electron correlation is not important to include in the qualitative results, it is important to include in cases where quantitative results are required.

2.2.2 Moller-Plesset Perturbation Theory

Moller-Plesset Perturbation Theory is one of the methods used to improve upon the results of Hartree-Fock by explicitly including electron correlation[18]. Moller-Plesset Perturbation works on a n-electron system and adds a second order perturbation term on the Hartree-Fock, thereby approximating the effect of correlation. It is therefore known as Moller –Plesset second order perturbation (MP2[19]). The explicit addition of electron correlation improves the result from Hartree-Fock tremendously. The theory presented can be applied to create a third order perturbation (MP3[20]) and fourth order perturbation (MP4[21]). It is therefore become known as MPn theory. The problem with higher order perturbation is the computational cost associated with the methods. The fourth order perturbation (MP4[21]) is the highest perturbation order used commonly as the fifth order perturbation is prohibitively expensive and the accuracy of the methods doesn't improve to match the computational cost.

2.2.3 Coupled Cluster Theory

Coupled Cluster Theory which tremendously improves on the accuracy of ab initio methods by expanding the wave functions by using a combination of many determinants[22]. The cost of the accuracy comes at the price that the calculations are

computationally very expensive, not just in CPU time, but in I/O, memory and disk space. There are various ways to expand the wave function based on the number of electronic excitations to account for electronic correlation. Coupled Cluster wave function is expanded as a Taylor's series to include the electron correlation. Coupled Cluster methods are often referred to as the "Gold-Standard" and are the best methods to quantitatively calculate the thermodynamic energies and enthalpies. Coupled Cluster methods are not variational, but are size extensive.

If a single electron is excited it calculates the effect of that excitation on the ground state energy corrected for that type of correlation. The most commonly used is single and double excitations called CCSD[22]. The number of triples possible in a molecular system is very high compared to single and double excitations and calculating the energies of all possible triplets is computationally impossible, so triples are more commonly added as a perturbative correction to account for an approximate number of triplet excitations[23] and given as a correction known as CCSD (T). Coupled Cluster calculations give the most accurate quantitative results for most chemical systems compared to other levels of theories. The application of the theory is limited to small systems due to the very expensive nature of the theory.

2.2.4 Density Functional Theory

Density Functional Theory (DFT) is an approximation to solve the Schrodinger's equation that is fundamentally different from ab initio. DFT uses electronic density instead of wave function. In a groundbreaking paper by Hohneberg

and Kohn[24] it was mathematically proven that energy of the system can be uniquely determined by the electron density of the system ρ(r). This theorem meant that the computationally expensive electron correlation can be applied, easily without any perturbation or additional corrections. Approximate functionals can be developed easily from empirical data. This approach has been used successfully by Becke.[25], Truhlar.et al.[26] DFTs have better functionals now with more specialized functionals being created to accurately calculate specific properties such as reaction energy, activation energies, kinetic parameters for reactions etc. Density Functional Theory offers the best combination of accuracy to the computing complexity of all the methods discussed here.

Density Functional Theory is now one of the most cited and most researched fields in Theoretical Chemistry. DFT can be used to calculate the thermodynamic properties from getting the energy of system from applying the functional. The exchange and correlation functionals are developed separately. Some of the popular exchange correlations include Becke's 3 paramter correlation functional[25], exchange functional of Perdew, Burke and Ernzerhof[27] etc. Some of the popular correlation are the Lee-Yang-Parr[28] correlation functional, correlation functional of Perdew[27] etc.

In an important paper by Becke[29], it has been shown that mixing Hartree-Fock exchange with pure DFTs improves the accuracy of the calculated energies. This class of DFTs are known as hybrid DFTs. Hybrid DFTs have been shown to work better for systems involving large systems and by mixing the exchange, errors arising from the self-interaction terms can be avoided.

2.3 Experimental Approaches

2.3.1 Calorimetric Techniques

There are various ways to characterize the reactivity of chemicals and evaluate the thermal properties. Controlled heating of a substance while simultaneously observing physical and pressure changes can be helpful in determining its properties under various temperature ranges. An especially popular and efficient method is use of calorimetry techniques. The energy released by a particular reaction, the energy content of a chemical compound, and its behavior at various physical conditions can all be analyzed in a laboratory setting and the data can be extremely useful in prescreening potential hazards.

Screening calorimeters are used to test very small amounts (100mg-10g) in a very rapid and can measure exothermic events. Some of the popular screening calorimeters are Differential Scanning Calorimeter (DSC), Reactive Systems Screening Tool (RSST). Adiabatic calorimeters such as Automatic Pressure Tracking Adiabatic Calorimeter (APTAC), Accelerating Rate Calorimeter (ARC) are used to characterize the reactivity in detail. Usually adiabatic calorimetry equipment is more expensive, takes more time to perform a single experiment. In this work, RSST is used to characterize the reactivity of Dicyclopentadiene.

2.3.2 Reactive Systems Screening Tool

RSST is a screening calorimeter developed by Fauske and Associates to rapidly test small amounts of chemical compounds. The schematic is shown in Figure 3. The calorimeter is non-adiabatic calorimeter which operates on a small power heater to compensate for the heat losses and doubles up as a heat source to raise the temperature of the substance to be tested.[30] The testing vessel is a small spherical open mouth glass cell of about 10mL. The calorimeter has a very low phi-factor[31] (about 1.04), it can be used to dose chemicals which heating to simulate a reactor and can evaluate effects of two-phase flows. It can also be used to evaluate vent sizing of emergency pressure relief systems.

The underlying principle of RSST is that the heat loss from the sample can be compensated by an external heating source during an exothermic process. RSST applies a constant heat ramp at a desired temperature range. The constant temperature ramp can be adjusted such that different heating rate can be programmed at different desired temperature ranges.

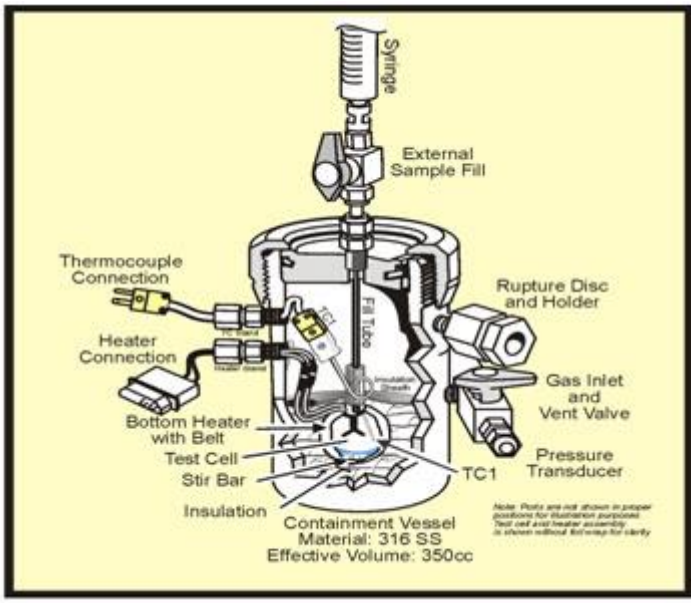

Figure 3 Schematic of RSST (adapted from Fauske[30])

2.3.3 Standard Operating Procedure

A pre-run test was conducted every time before the sample was loaded to test. The containment vessel was examined to check for any contaminants or foreign particles. The heater and the thermocouple are examined for proper functionality. The resistance of the heater was measured and the thermocouple was calibrated. Then the sample cell is loaded into the containment vessel and pressurized with nitrogen at 250 psig to mitigate sample losses. The sample is then heated in a preset heat ramp. The experimental shutdown criteria can be setup to turn off the heater and safely shut down the equipment when the temperature or pressure reaches a preset value.

Thermal Inertia is a factor introduced to correct the sample cell, to extend the results from small samples to extend to the adiabatic reactors. The thermal inertia of the test is defined as the ratio of the heat capacity of the sample and container to the heat capacity of the sample.

In RSST, the heat lost by the sample cell, is compensated by the external heater and since a small portion of it is used to heat the test cell, some portion of the heat is lost resulting in a lower maximum temperature achieved and maximum self-heat rate of the test.

The phi-factor is calculated as

$$\emptyset = 1 + \frac{m_c * C_{p\,c}}{m_s * C_{p\,s}}$$

where m stands for mass, C_p stands for the heat capacity and the subscripts c and s stands for cell and the sample.

The calorimetric data provides the temperature ramps, pressure ramps. To calculate the heat of the reaction, the approach of Townsend and Tou[32] for the n-th order reaction is used. The heat of the reaction, $\Delta H_{reaction}$ from the temperature ramps as follows,

$$\Delta H_{reaction} = \frac{m * C_p * \Delta T_{adiabatic}}{n_{reaction}}$$

where $\Delta T_{adiabatic}$ is the adiabatic temperature increase which is correction to the temperature difference from the onset to the maximum temperature rise.

$$\Delta T_{adiabatic} = \emptyset * (T_f - T_o)$$

The onset temperature is defined from the time when the self-heat rate of the sample starts to increase exponentially, indicating a sharp exothermic excursion event.

C_p is the heat capacity of the sample and $n_{reaction}$ is the moles of the reactant in the sample. The heat capacity of the reactant was 45.05 cal/mol K from NIST[33] and Yaws' handbook[34].

To calculate the Activation energy, the calorimetric data is fit into a n^{th} order reaction scheme according to the model by Townsend and Tou[32]. This model is applied to a single reactant, assuming that the reaction is pseudo 1^{st} order which was found in the literature[12, 15, 35] and constant volume, adiabatic system. The equation can be written as

$$k = \frac{dT}{dt}\frac{1}{T_f - T}$$

$$\log k = \log A - \frac{E_a}{RT}$$

where k is the first order reaction constant, A is the frequency factor, E_a is activation energy and R is the universal gas constant.

CHAPTER III

THEORETICAL ANALYSIS OF DICYCLOPENTADIENE REACTIVITY

3.1 Introduction

Dicyclopentadiene reactivity is a seldom studied problem in the literature. There has been little information regarding the possible Diels-Alder reactions of DCPD. Molecular simulations can be successfully applied in cases where there is little information for predicting possible reactive hazards. Molecular simulations form one of the trusted estimation methods to screen molecular compounds and estimate the thermodynamics and kinetics of a particular reactions pathway.

Dicyclopentadiene is one example of a common compound which is believed to be stable, but whose propensity to undergo a wide variety of reactions makes it a hazardous substance. Cyclopentadiene, the simplest unit is obtained by distilling off dicyclopentadiene at 170ºC.

Cyclopentadiene has been subjected to many computational studies. Houk et al.[36], the dimerization of cyclopentadiene to dicyclopentadiene was benchmarked by Guner et al.[37] as a part of a set of pericyclic reactions to benchmark new theoretical methods.

Dicyclopentadiene has recently been computationally studied by Jamroz et al.[38] who showed that of 14 theoretically possible conformers the [2+4] cycloadduct of dicyclopentadiene are the most favorable ones followed by [4+4] cycloadducts. There were little to no theoretical work in the estimation of thermochemical properties of the dicyclopentadiene using quantum chemical methods.

Reaction equilibrium work by Palmova et al.[15] who used theoretical and experimental works showed that the dicyclopentadiene does form tricyclopentadiene and other oligomers are temperature ranges of 300-800ºC using simulated distillation column corroborated with experimental data from 25-200ºC.

Cyclopentadiene is also an important reagent used in pharmaceutical and other applications wherein DCPD is cracked *in situ*. One such application of *in situ* cracking is used by Pfizer in manufacturing of varenicline a smoking cessation drug.[39] Cyclopentadiene is a highly reactive chemical that has only been studied recently. Cyclopentadiene is stored at -80°C or as a very dilute solution in isobutanol or other alcohols. Cyclopentadiene is prepared by heating the stable dicyclopentadiene but is not advised to store in large quantities. At temperatures greater than 0°C it starts to dimerize exothermically often explosively to *endo*-dicyclopentadiene.

Ende et al.[40] studied the thermal properties of CPD using a Vent sizing package (VSP) and Differential Scanning Calorimetry (DSC) from temperatures of -60°C. CPD and to some extent DCPD was studied and they recommended studying alternate pathways to CPD rather than storing CPD at -80°C. The process description is given below.

CPD also undergoes decomposition and reacts with oxygen to form peroxides. There is little to no information on peroxide formation of CPD peroxide formation. Peroxides are especially unstable and are used as an initiator for polymerizations. The reactions of CPD with oxygen is especially a concern in poly-DCPD reactors which

can cause the polymerization to go out of control and can initiate other free radical reactions in the reactor. Cyclopentadiene peroxide is also known to be an explosive.[41]

3.2 Computational Details

For the calculations of the reaction pathways, different levels of theories were used in this work. Particularly the semi-empirical AM1[42], *ab initio* MP2[18] and Density functional M06-2X[43] , PBEPBE[27] were used. For all calculations the 6-311++G(d,p)[44] basis set was used for the initial geometric optimization of the molecules. Frequency calculations was performed on the same molecule using the same basis set to calculate the thermodynamic partition functions.

3.3 Results and Discussions

3.3.1 Dimerization of Cyclopentadiene

The dimerization of cyclopentadiene has been studied experimentally. Most of the literature agrees that the equilibrium of the dimerization proceeds to the right from temperatures above 10°C.[45] At room temperatures the product composition almost solely is endo-dicyclopentadiene. But at temperatures above 120°C the dicyclopentadiene cracks backs into cyclopentadiene. The retro Diels-Alder reaction has been shown to have a concerted mechanism. The concerted mechanism suggests that the cyclopentadiene dimerizes directly via a formation of a transition state.

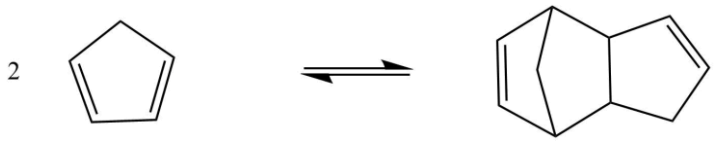

Figure 4 Dimerization of Cyclopentadiene

The results obtained from the calculations for the Diels-Alder dimerization of cyclopentadiene (Figure 4) have shown below in Table 2.

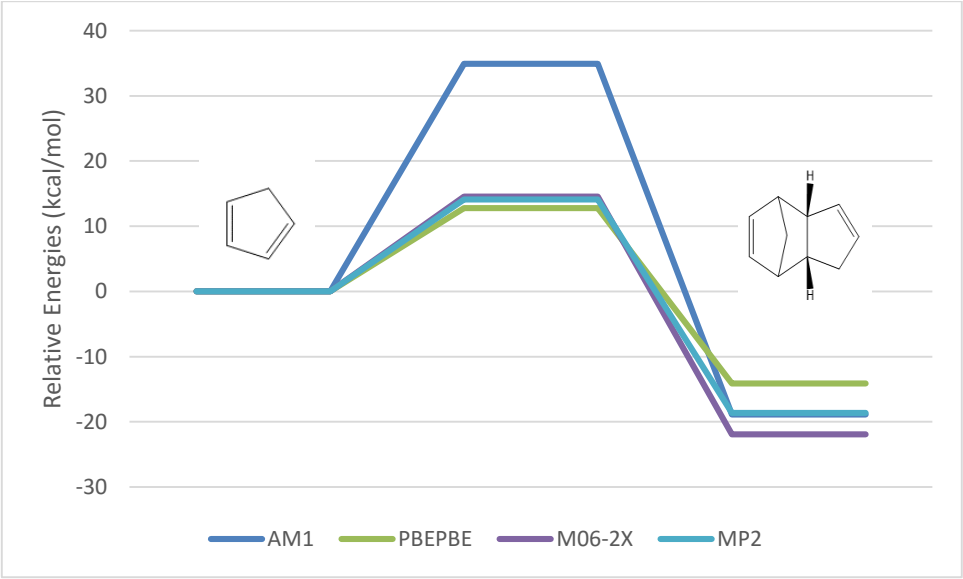

Figure 5 Potential Energy Surface for Dimerization of Cyclopentadiene to *endo*-Dicyclopentadiene

The reaction enthalpies and free energies of the reaction of dimerization is summarized in Table 2.

Table 2 Enthalpies (ΔH_r) and Free Energies (ΔG_r) of Dimerization of Cyclopentadiene and Dicyclopentadiene Reaction Calculated (in kcal/mol)

AM1 (kcal/mol)		M06-2X (kcal/mol)		PBEPBE (kcal/mol)		MP2 (kcal/mol)	
ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
- 18.90	-3.55	- 21.91	- 6.72	-14.10	- 2.16	-18.63	-3.65

As shown in Figure 5, the activation energy of the reaction calculated is between 14-21 kcal/mol and the heat of the reaction can be estimated at -18.9 to -21.1 kcal/mol. These results are consistent with the computational study of Guner et al.[37] and experimental study by Turnbull et al.[45]

The dominant pathways for dimerization of cyclopentadiene proceeds via a concerted mechanism to overwhelmingly to *endo* isomer due to both kinetic barrier and thermodynamics of the pathway being favored. Previous experiments by Herndon et al.[12] also agrees with this result, wherein the *endo* isomer was overwhelmingly the major product.

3.3.2 Diels-Alder Reaction of Cyclopentadiene and Dicyclopentadiene

The Diels-Alder reaction of Dicyclopentadiene and Cyclopentadiene has been shown to occur at temperature range from 120-400°C and is found to be exothermic with potential to runaway.[13] In the study by Ahmed and Lavin[13], trimers made up 40% of the products with higher oligomers and the reactants making up the rest by using GPLC and GC at temperature range of 200°C.

There have been studies on the Diels-Alder reaction of cyclopentadiene and dicyclopentadiene by Li et al.[10a] and the study supported a concerted mechanism consisting of a transition state which leads to formation of the trimer. Theoretically, there are 8 possible isomers that can arise from the Diels- Alder reaction between DCPD and CPD[10a]. Since only the *endo* isomer of DCPD is used as the starting material, the reaction pathways that arise from endo isomers are investigated to the thermodynamics of the reaction pathways and products.

The calculation results are presented in Table 3. In a study by Liu et al.[46] on hydrogenation of DCPD, it has been observed that the norbornene ring is more reactive than the Cyclopentene ring. This has also been corroborated by studies in polymerization of DCPD[47] and experimental studies involving the preparation of TCPD by Zhang et al.[48] The results show that the activation energy for the cycloaddition of CPD in norbornene ring is clearly lower than the cycloaddition at the Cyclopentene ring. Moreover the heat of the reaction calculated indicates that the addition via the norbornene site is thermodynamically stable. The Diels-Alder reaction pathways between *endo*- DCPD and cyclopentadiene considered in this study is shown in Figure 6.

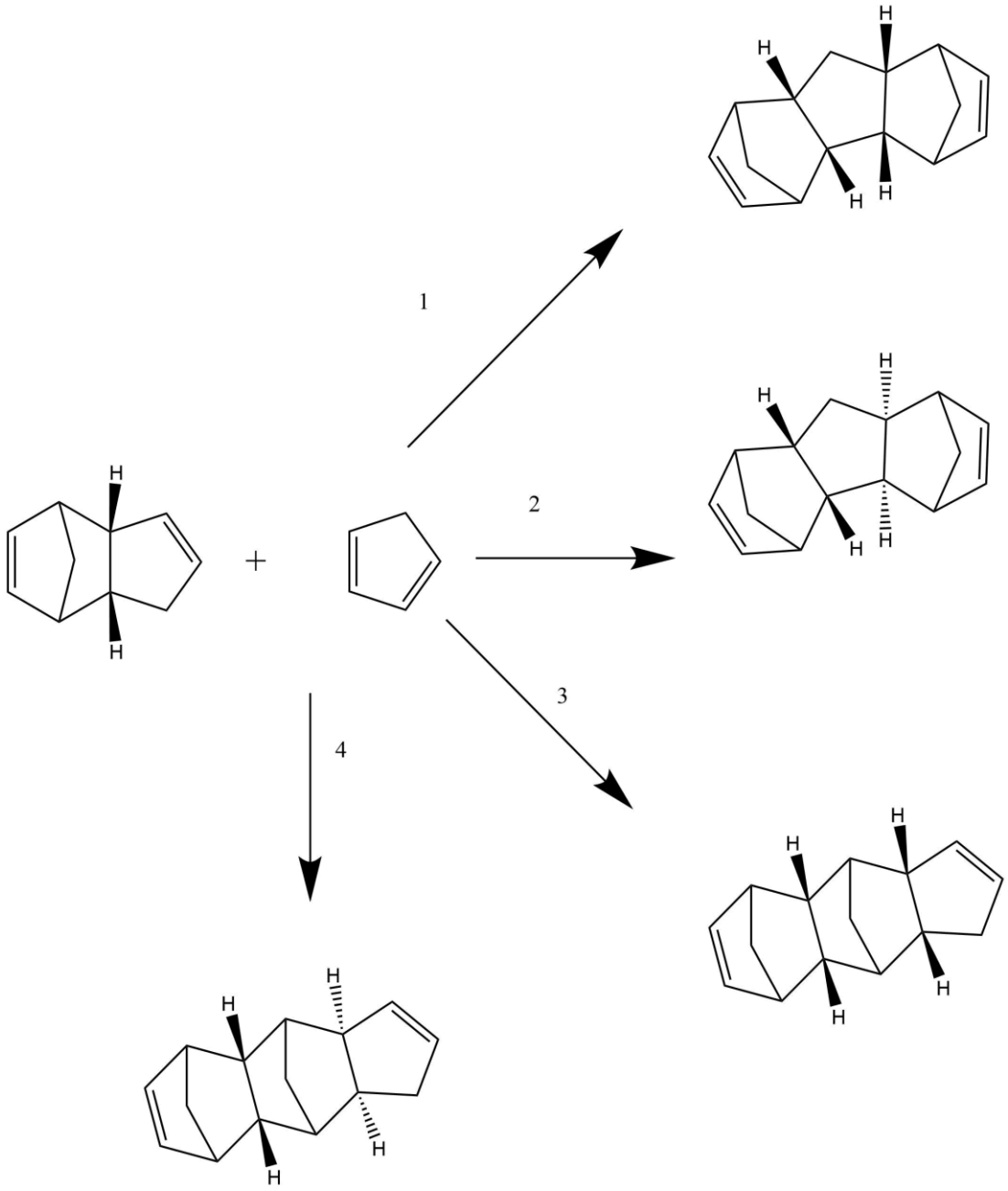

Figure 6 Diels-Alder Reaction between Cyclopentadiene and *endo* Dicyclopentadiene

Table 3 Enthalpies (ΔH_r) and Free Energies (ΔG_r) of Diels- Alder Reaction between Cyclopentadiene and Dicyclopentadiene Reaction calculated (in kcal/mol)

Reactions	AM1		M06-2X		PBEPBE	
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
1	-21.52	-3.48	-22.93	-7.69	-15.46	-1.58
2	-20.55	-5.16	-23.85	-8.81	-16.42	-0.49
3	-21.52	-5.76	-23.71	-20.71	-19.82	-4.47
4	-16.26	-5.65	-22.74	-22.68	-20.40	-5.17

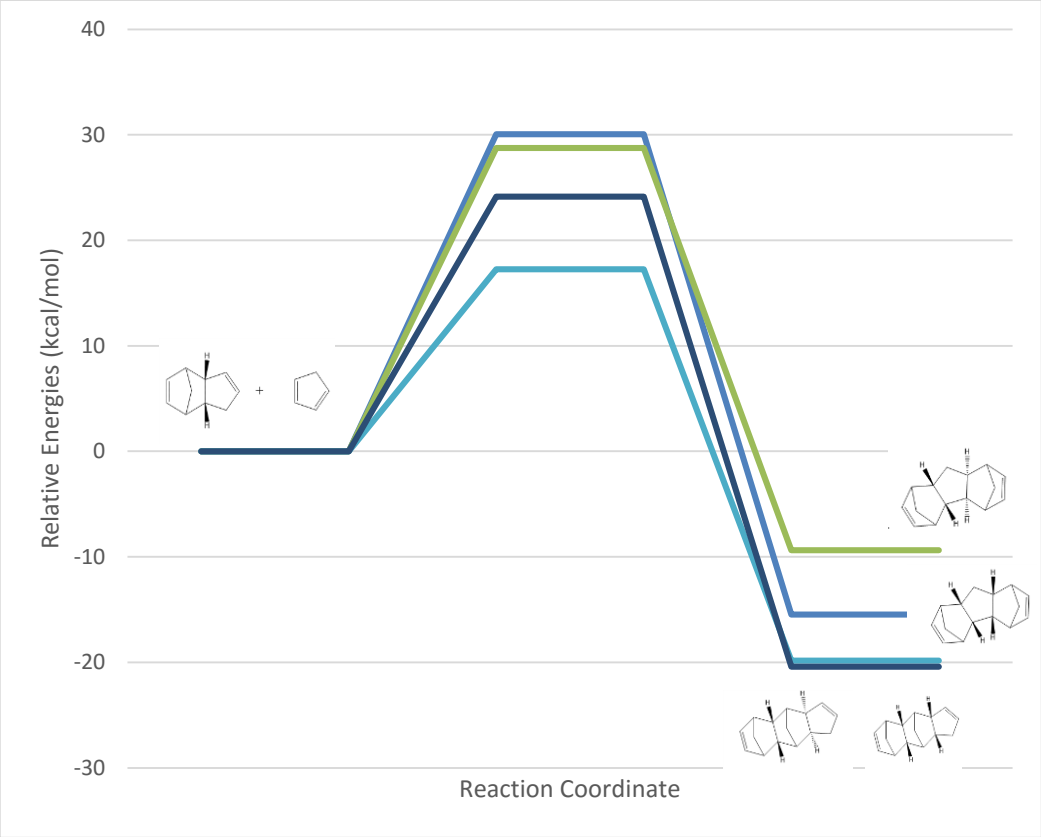

Figure 7 Potential Energy Surface of Cyclopentadiene and Dicyclopentadiene Reaction at PBEPBE Level

The potential energy surface of the reaction pathways is shown in Figure 7. At the PBEPBE level of theory, the reactions 3 and 4 are dominant and expected to give the Norbornene type adducts. This has been verified in an experimental study by Zhang et al.[48] where in using GC, they found that the product from the reaction 3 is found in the reaction mixture 6.4 times the product from reaction 4. Transition state calculations

at PBEPBE level revealed that the activation energy the major products are 17.25 kcal/mol and 24.13 kcal/mol.

3.3.3 Peroxide Formation of Cyclopentadiene

Peroxide formation in Cyclopentadiene and Dicyclopentadiene is a spontaneous process. Singlet oxygen addition to unsaturated hydrocarbons to form peroxides and hydroperoxides. The classification of some compounds to peroxide forming compounds (PFC), is especially dangerous because of their inherently unstable peroxide linkage. Cyclopentadiene peroxide is dangerous because it can explode due to mechanical shocks, pressure changes and presence of certain chemical reagents.[41] It also can imitate a variety of radical chain reactions and can initiate the polymerization of Dicyclopentadiene. The 1, 4 cycloaddition of dienes results in peroxides and dihydrogen peroxides.

There are little to no study in mechanism of peroxide formation. There are 2 different mechanisms suggested for cycloaddition, a biradical mechanism has been suggested or a concerted mechanism is possible. The biradical mechanism is when the oxygen attacks the pi bond of cyclopentadiene or Dicyclopentadiene ring and results in oxygen forming a bicyclo-ring in the process. This ring has further been shown to polymerize spontaneously or can initiate polymerization of DCPD.

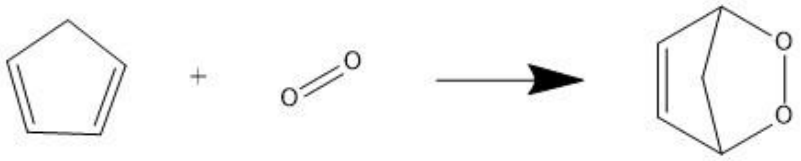

Figure 8 Proposed Reaction Pathway of Cyclopentadiene Oxidation

Table 4 Enthalpies (ΔH_r) and Free Energies (ΔG_r) of Oxidation of Cyclopentadiene Reaction Calculated (in kcal/mol)

Reaction	B3LYP		M06-2X		MP2		PBEPBE	
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
1	-18.58	- 9.51	-18.09	-8.52	-18.09	-10.43	-16.89	-11.27
2	-42.59	-20.67	-33.13	-30.21	-51.22	-47.11	-30.19	-20.19

The results from the molecular simulations of the reaction (Figure 8) are tabulated in Table 4. According to the results, the radical addition is exothermic and favored compared to the concerted mechanism. The radical mechanism suggests that the exothermic event is much more favored than the oligomerization to trimers. The radical formation involves oxygen attached to one of the terminal carbon forming a cyclic peroxide. It can also be interpreted from the results that the peroxide formation reactions have lower activation barrier and is thermodynamically more favorable than

other oligomerization reactions and maybe the dominant pathway. The enthalpy of the reaction is estimated from -33.13 kcal/mol using M06-2X level of theory. The reactivity of CPD is more hazardous in presence of any free radical generator, oxygen and high temperature because of the energy that can potentially be from oxidation than other reactions discussed before.

3.3.4 Prediction of Onset Temperatures from Theoretical Values

Molecular simulations are an important tool to provide very reliable estimations for reactivity hazards. One important parameter that is of interest to industries is the "onset" temperature. "Onset" temperature is the temperature above which the heat generated from the sample under investigation is more than what can be removed from the system. "Onset" temperature serves as a guide for making decisions on safe storage and process conditions required for the sample under consideration. An estimate of the "onset" temperatures can be obtained from the value of enthalpy estimation from the calculations or other decomposition mechanisms.

One way to predict the reactivity hazards from molecular simulations is by constructing a quantitative structure property relationship (QSPR) of similar systems with some experimental data. This was the process undertaken by Saraf et al.[49] wherein a QSPR study was conducted on nitro compounds and other reactive compounds and an equation was proposed to predict the "onset" temperature of the compounds from a test set of 19 organic nitro compounds.

Based on the equation proposed by Saraf et al.[49] we tried to determine the "onset" temperatures for the Diels-Alder reaction of oligomerization of DCPD using the data from our calculations presented in Table 3. The results for the calculations are tabulated in Table 5.

Table 5 Predicted "Onset" Temperature of DCPD and CPD Reaction

Reactants	Predicted Onset Temperatures
1	281.42 ± 18.34
2	263.88 ± 12.44
3	258.79 ± 15.55
4	243.49 ± 17.83

These values are not conservative calculations and must be used with caution. The authors showed that the equation works well for the organo-nitro compounds, but a thorough QSPR study must be conducted using the available data for dienes or other similar compounds.

3.3 Conclusions

Molecular simulations were used to explore the various elementary Diels-Alder reactions of CPD and DCPD. Using the techniques, the most probable reaction pathways are examined and quantitatively the thermodynamic quantities of the dimerization, trimerization and oxidation reactions are calculated. All of the reactions are exothermic to a large extent and the oxidation reaction is particularly hazardous due to the high exothermicity and the relative ease with which the oxidation is possible at normal reaction conditions. The propensity of the peroxides to form free radicals thereby initiating further exothermic polymerization and oligomerization reactions makes it concern. These calculations help in the fundamental understanding of the hazards in these elementary reactions and could possibly be used to formulate strategies for safer storage and reaction conditions.

CHAPTER IV

EXPERIMENTAL CHARACTERIZATION OF DICYCLOPENTADIENE

4.1 Introduction

Dicyclopentadiene is hazardous to due to its sensitivity to heat which makes it even more challenging. Dicyclopentadiene is classified as Type-II flammable substance.[7] Due to the proprietary information of various manufactures using DCPD in their resins and other products, the process conditions in which they are used remain unknown in the open literature. To conduct a reactivity assessment the study must include both the standard operation and abnormal process condition. The study of substance under abnormal conditions can also lead to protective measures such as estimation of reactor pressure rating needed, possible fire protection technology needed, sizing the pressure relief valves and safety interlocks to prevent addition or to conduct a safe release of the chemical reactants.

Calorimetry can help in not only determining the safe operation, but can help in stud of the abnormal and worst case scenarios. Some of the important information like onset temperature, maximum temperature, temperature rise rate, self-heat rate, adiabatic temperature rise, maximum pressure possible, maximum pressure rise rate and the evolution of any non-condensable gases at various process pressures can be safely studied.

4.2 Experimental Details

4.2.1 Chemicals

All experimental materials were obtained from Sigma-Aldrich. Dicyclopentadiene (CAS: 77-73-6) was used as received. The purity according to the assay was 95%. To study the effect solvent on thermal stability, 2 solvents were used namely isobutanol (CAS: 78-83-1) and heptane (CAS: 142-82-5). All of the solvents were used to create a 50% solution (by mass).

4.2.2 Operation Mode

i. During the testing the sample is loaded in a new glass test cell and the heater belt is attached to it.

ii. The heater coil and the thermocouple are tested using a multi meter to measure the resistance. The thermocouple is also tested for proper functioning.

iii. The containment vessel is flushed with nitrogen before the sample is loaded and then pressurized at 300 psi after the sample is loaded.

iv. The temperature ramp was set at 2°C/min till the sample reached 150°C. Then it was reduced to 0.5°C/min for the rest of the experiment.

v. The shutdown criteria is set as follows, if any of the criteria is met the heater belt turns off while the data is saved

    a. Maximum temperature - 400°C

    b. Maximum Pressure – 400 psi

    c. Time period – 800 min

4.3 Results and Discussions

4.3.1 Runaway Behavior of Dicyclopentadiene

The temperature profiles, self-heat rate, pressure and pressure rise has been shown below for dicyclopentadiene without any solvents.

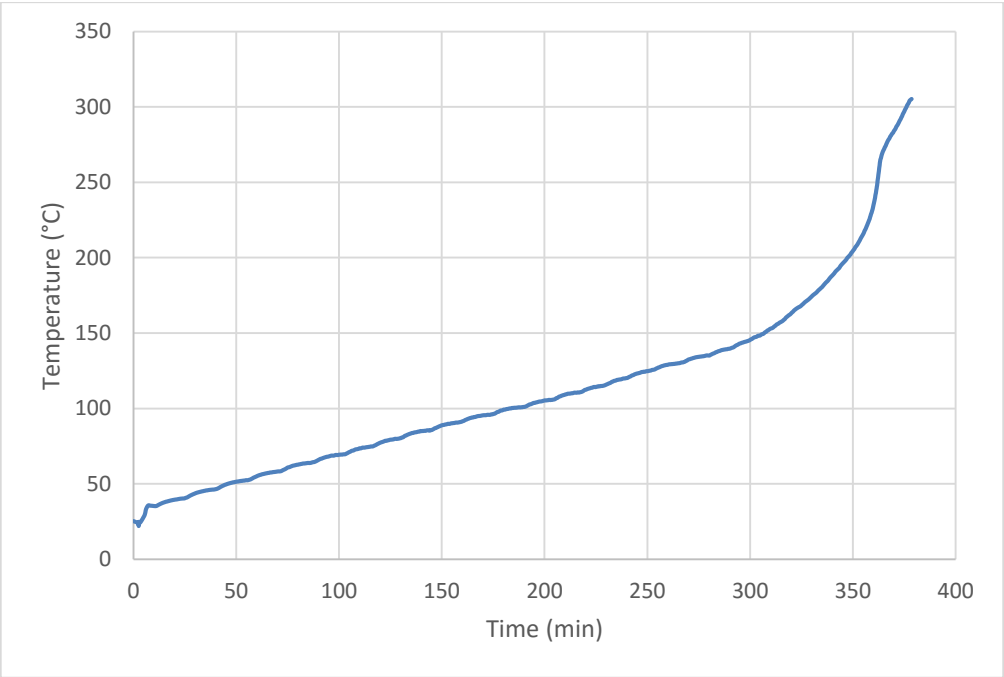

Figure 9 Temperature Profile of Dicyclopentadiene

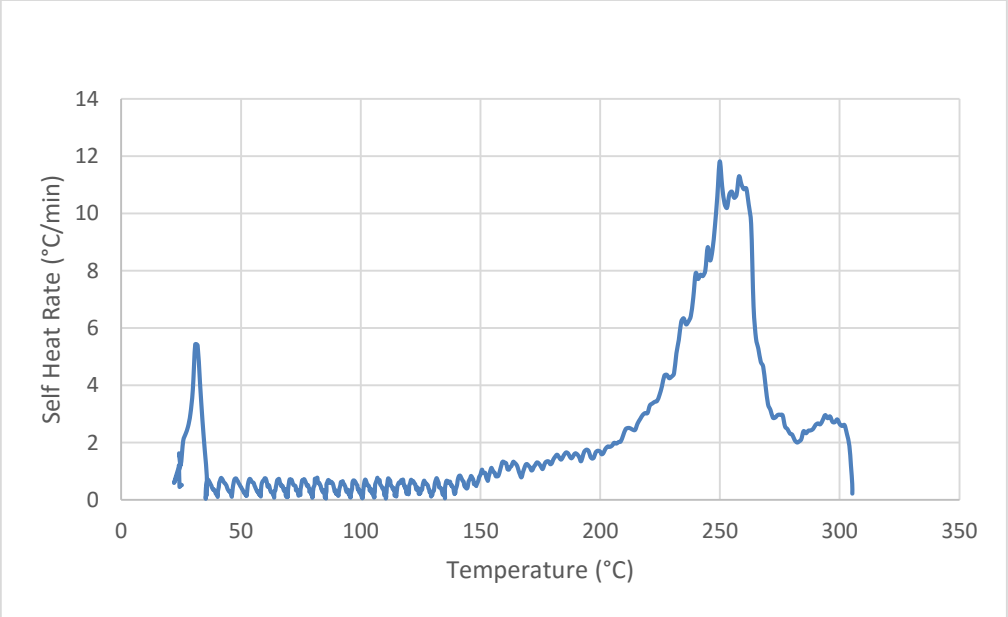

Figure 10 Self Heat Rate of Dicyclopentadiene

In this work, the “onset" temperature is obtained from the self-heat profile. The onset is determined from the point where the self-heat rate starts increasing exponentially with respect to the temperature. For the pure DCPD, the experimental results are tabulated below. The pressure increase is not as drastic as the temperature increase during the runaway. The reaction also did not seem to produce measurable amounts of non-condensable gases.

The “onset” temperature of the system was determined by the interception of the linear fit of the base heat ramp and the exponential fit from the data when the self-heat rate of the system increases consistently from the base ramp rate of 0.5°C/min.

The error of the onset temperature was determined from the propagation of errors from the fit parameters of the exponential curve.

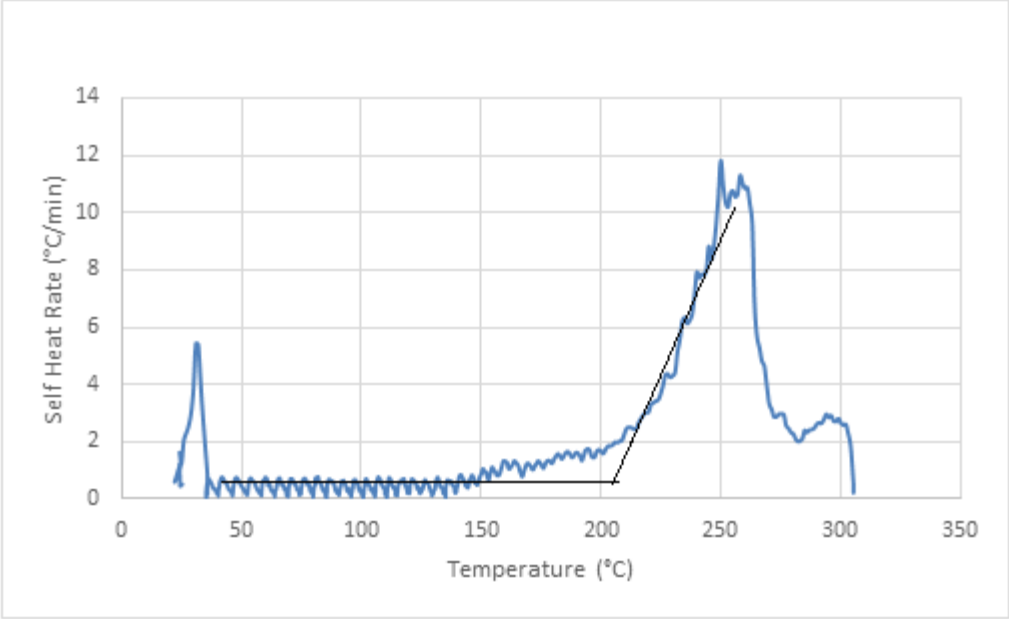

Figure 11 Experimental Determination of "Onset" Temperature for DCPD

The fit parameters were of the form

$$S = a_1 T + b_1$$

$$S = a_2 T + b_2$$

where S denotes the Self-Heat Rate and T denotes the Temperature

The error propagation was done as the 95% Confidence interval of the fit parameters

$$(a_1 \pm \Delta a_1)T + (b_1 \pm \Delta b_1) = (a_2 \pm \Delta a_2)\, T \pm (b_2 \pm \Delta b_2)$$

$$T = \frac{(b_2 - b_1) \pm (\Delta b_1 + \Delta b_2)}{(a_1 - a_2) \pm (\Delta a_1 + \Delta a_2)} = \frac{B \pm \Delta B}{A \pm \Delta A}$$

$$T \pm \Delta T = (\frac{B}{A}) \pm (\frac{\Delta A}{A} + \frac{\Delta B}{B})$$

Table 6 Experimental Data of Dicyclopentadiene Using RSST

Mass (g)	T_{onset} (°C)	$(\frac{dT}{dt})max$ (°C/min)	T_{max} (°C)	ΔH_{rxn} (kcal/mol)	ø	E_a (kcal/mol)	R^2
2.04 ± 0.01	202 ± 5.44	11.82 ± 5	305 ± 5	-18.86 ± 3.6	1.08 ± 0.01	38.4 ± 2.8	0.86

The plots of the DCPD data was fitted for the calorimetric data obtained from calculating the log k vs log $\frac{1}{T}$ and the data was fitted to a linear function and the regression coefficient obtained ranged from $R^2 = 0.86$, indicating that the assumption was valid for this system.

The thermal behavior of dicyclopentadiene has not been studied using the RSST in the literature. The temperature profiles, self-heat rate, pressure and pressure rise has been shown below. The first exothermic event detected by the RSST occurs around the 180°C and the major exothermic event occurs at around 200°C and lasts till the sample temperature reaches 340°C. This agrees well with DSC scans by Ende et al.[40] wherein they observed that the "onset" temperature of the DCPD sample was around 190°C and lasted till 384°C. The exothermic enthalpy was calculated to -21.34 kcal/mol. They also observed a smaller exotherm from 108°C to 143°C which was not observed in the RSST test.

There was also a formation of black glass like deposit which could not be dissolved in acetone, heptane or ethanol. This was suspected to be a higher order oligomer which was also found in the case of Ahmed et al.[13] The reaction order was assumed to be a pseudo 1st order according to previous experimental research[13, 40] and it was also found to be true in this case. A linear fit was obtained when the calculated 1st order reaction constant was plotted against the reciprocal of the temperature.

4.3.2 Effect of Solvents on Dicyclopentadiene Runaway

Certain industrial applications of DCPD involves its use in solution form.[50] Even in the case of Nevcin Polymers, the DCPD was charged with a solvent. To study the possible solvent effects, a 50% solution by mass of DCPD with isobutanol and heptane was prepared and studied to understand its effects on onset temperature and its thermal behavior.

In case of heptane a more severe self-heat rate (Figure 12 and Figure 13) was noticed and the exotherm "onset" occurred at a considerably lower temperature. Again, there was negligible amount of non-condensable gases formed and the residue from the test cell was an oily dark brown liquid which dissolved in common organic solvents. We believe this to be higher oligomers of DCPD and other polymeric compounds. The results are tabulated in Table 7.

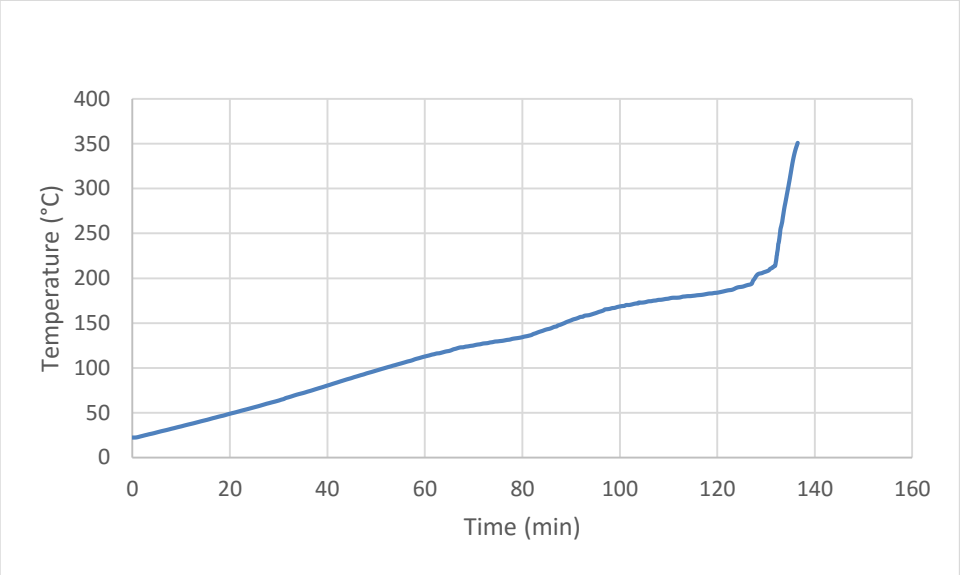

Figure 12 Temperature Profile of DCPD/Heptane Solution

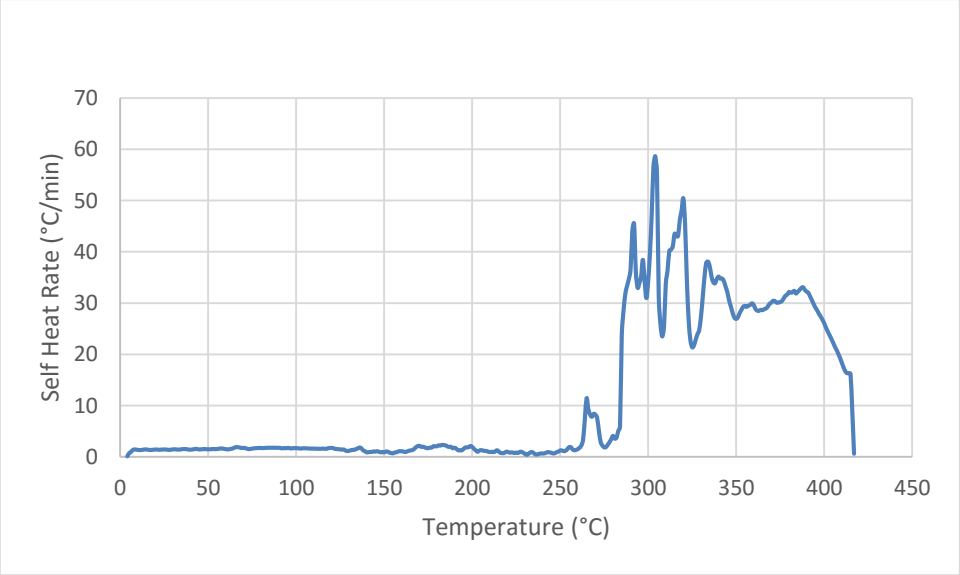

Figure 13 Self Heat Rate of DCPD/Heptane Solution

Table 7 Experimental Data of DCPD/Heptane Solution

Mass (g)	T_{onset} (°C)	$(\frac{dT}{dt})max$ (°C/min)	T_{max} (°C)	ΔH_{rxn} (kcal/mol)	ø	E_a (kcal/mol)	R^2
3.8 ± 0.01	258 ± 5.43	56.63 ± 5	417 ± 5	-26.38 ± 3.6	1.12 ± 0.04	24 ± 3.6	0.89

In case of isobutanol, the reaction is more exothermic than in case of pure DCPD. The "onset" temperature of the mixture is increased from about 202°C to about 258°C (Figure 14), and the self-heat rate increased dramatically (Figure 15). The severity of the exotherm is theoretically affected by solvent choice due to the fact that the specific transition state complex of isomers are more stable in more polar solvents and plays a role in determining the major product, thereby affecting the reaction enthalpy. The other experimental details are tabulated in Table 8.

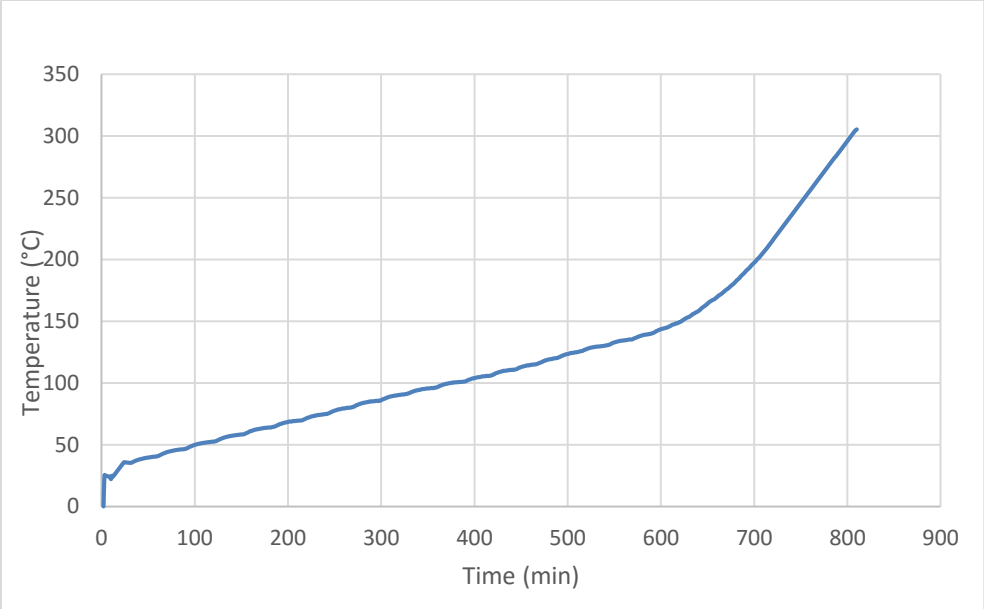

Figure 14 Temperature Profile of DCPD/Isobutanol Solution

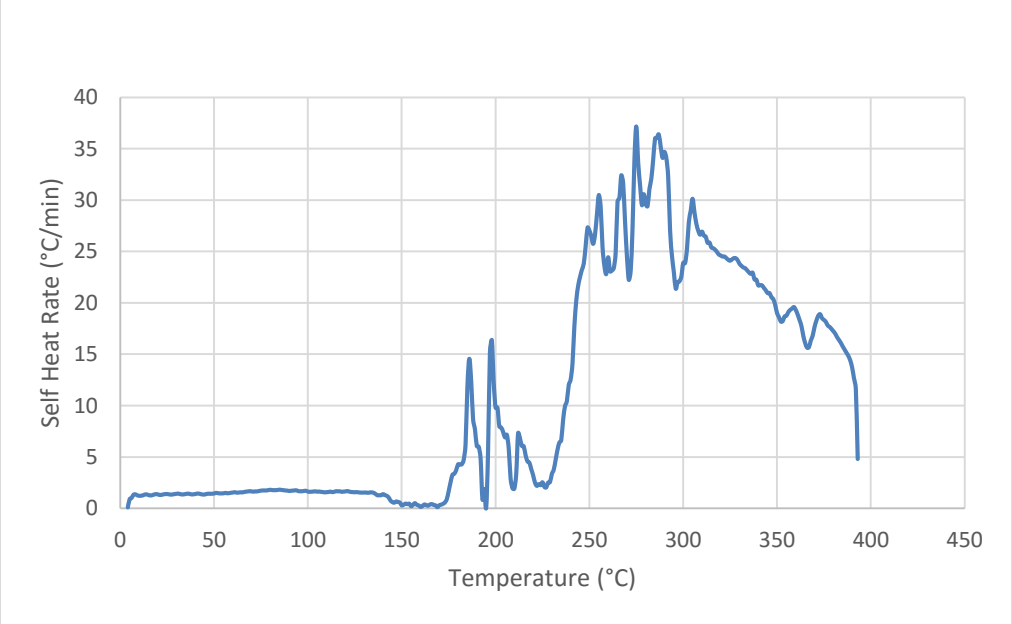

Figure 15 Self Heat Rate of DCPD/Isobutanol Solution

Table 8 Experimental Data of DCPD/Isobutanol System

Mass (g)	T_{onset} (°C)	$(\frac{dT}{dt})max$ (°C/min)	T_{max} (°C)	ΔH_{rxn} (kcal/mol)	ø	E_a (kcal/mol)	R^2
4.74 ± 0.01	176 ± 6.07	37.17 ± 5	500 ± 5	-16.43 ± 3.6	1.12 ± 0.04	26.26 ± 3.8	0.904

Solvent choice is an important parameter for study in Diels-Alder system and the change of another parameter namely, the ø-factor due to the choice of solvents needs to be studied. In our tests the change of ø-factor due to changing the solvents does not seem to have a significant effect on the enthalpy of the reaction. The use of solvents led to a dark brown oily substance most likely a lower oligomer being formed at the end of the experimental run. There was no glassy polymer and the oily substance dissolved in acetone and heptane. This system needs to be studied more in detail to examine the conditions responsible in formation of the glassy substance vis-à-vis an oily liquid.

4.4 Conclusions

In this work, Dicyclopentadiene has been studied using RSST to study its runaway reaction both in pure and solution form. The main reaction pathway is oligomerization and there is little to no non-condensable gas generated from reaction.

The RSST was used to determine the onset temperature, pressure, maximum temperature, maximum pressure and estimating the thermodynamics (namely the heat of reaction) and the kinetics of the process from the experiments.

Solvent systems in the experiments were selected to represent the industrial preparations. In case of isobutanol, the onset temperature of slightly decreased from 202°C to 176°C and in case of Heptane, the onset of the system significantly increased from 202°C to 263°C. In case of the self-heat rate, heptane significantly has a larger max self-heat rate than isobutanol and also has a larger heat of reaction. This may be due to the fact that heptane also undergoes decomposition and may not be effective at the conditions at which the experiment is carried out.

The determination of "onset" temperature is carried out from experimental runs determine the temperature at which the self-heat rate was greater than the base heat ramp rate of 0.5°C/min and is highly dependent on the equipment used to measure the onset. Adiabatic tests may be needed to get a more precise reaction thermodynamics and kinetics.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

With the demand of metathesis polymerization of cheap dienes in demand due to its availability, DCPD polymerization will be in high demand especially with more specialized catalytic systems available. This work is intended to advance the reactive hazards associated with DCPD and CPD. Both theoretical and experimental methods were used to characterize the elementary reactions associated with reactive hazards, solvent systems were used.

The experiments were conducted using a screening tool RSST and the heat of the reaction, self-heat rate, temperature ramp were obtained and analyzed. Theoretical methods were used to understand the primary reaction pathways, reaction mechanisms and the thermochemistry of the reactions.

This work will be useful to industries that use and store Dicyclopentadiene. The various strategies for safeguarding against potentially dangerous thermal runaway of dicyclopentadiene. The reaction mechanisms that are discussed here using quantum chemical methods can help in designing novel protection systems or can help in designing control systems which can help in safe shutdown of the reactor in case the critical concentration or can provide an estimate on the reaction heat that can be expected from the system.

Future improvements can be used to extend the accuracy of this study. Detailed adiabatic calorimetric techniques must be used to track the reaction energy and measure the "onset" temperature better. Also, more detailed studies are needed to identify whether solvent systems can provide possible protections against runaway system of DCPD using detailed methods.

In theoretical methods, a full kinetic model must be developed which fits well with the experiments. The next logical system is to study the ROMP of DCPD which is highly exothermic and has the propensity to run away. The choice of catalyst systems also contribute to the thermal excursions in the DCPD, and more thorough study needs to be done. To predict the reactive hazards from molecular information, a QSPR study is to be conducted with similar diene systems to improve the theoretical screening criteria.

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