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Ab Initio Quantum Chemical Studies on Neutral-Radical Reactions of Ethynyl (C2H) and Cyano (CN) with Unsaturated Hydrocarbons

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

AB INITIO QUANTUM CHEMICAL STUDIES ON NEUTRAL-RADICAL REACTIONS OF ETHYNYL (C_2H) AND CYANO (CN) WITH UNSATURATED HYDROCARBONS

A dissertation in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY
by
Adeel Jamal

2012

To: Dean Kenneth Furton
College of Arts and Sciences

This dissertation, written by Adeel Jamal and entitled Ab Initio Quantum Chemical Studies on Neutral-Radical Reactions of Ethynyl (C_2H) and Cyano (CN) with Unsaturated Hydrocarbons, having been approved in respect to style and intellectual content, is referred to you for judgment. We have read this dissertation and recommend that it be approved.

Jeffrey Joens

David Chatfield

Yong Cai

John Zweibel

Alexander Mebel, Major Professor

Date of Defense: November 2, 2012

The dissertation by Adeel Jamal is approved.

Dean Kenneth Furton
College of Arts and Sciences

Dean Lakshmi N. Reddi
University Graduate School

Florida International University, 2012

DEDICATION

This work is dedicated to the three women in my life; my mother, Farida Jamal, my sister, Rabiya Jamal, and my grandmother, Zubaida Jamal. They were encouraging when times were good and supportive when times were tough. I strive to excel in life because they strived in excelling me in life.

And in loving memory of my late father, Mohammed Jamal, and my late brother, Umer Jamal.

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Last, but certainly not least, my family and friends for sticking through all these years and being supportive. I couldn’t have done this without your love and compassion To Reby Valdi, who has been by my side during much of my graduate studies. A big consideration goes out to my colleagues during my graduate studies, especially Alexander Lander and Armando Pardillo. Our conversations could never get dull as long as we have science to discuss. Nash Naviwala, for being a brother and an uncle. He always believed I can accomplish anything as long as I pursue it. And finally, Jeff West

and Marcelo Delgado, for being brothers from another mother, and often times reflections of myself from a parallel universe.

Also, to every person and experience that I have encountered, good or bad, for making me who I am today.

ABSTRACT OF THE DISSERTATION

AB INITIO QUANTUM CHEMICAL STUDIES ON NEUTRAL-RADICAL REACTIONS OF ETHYNYL (C_2H) AND CYANO (CN) WITH UNSATURATED HYDROCARBONS

by

Adeel Jamal

Florida International University, 2012

Miami, Florida

Professor Alexander Mebel, Major Professor

An *Ab Initio*/RRKM study of the reaction mechanism and product branching ratios of neutral-radical ethynyl (C_2H) and cyano (CN) radical species with unsaturated hydrocarbons is performed. The reactions studied apply to cold conditions such as planetary atmospheres including Titan, the Interstellar Medium (ISM), icy bodies and molecular clouds. The reactions of C_2H and CN additions to gaseous unsaturated hydrocarbons are an active area of study. NASA's Cassini/Huygens mission found a high concentration of C_2H and CN from photolysis of ethyne (C_2H_2) and hydrogen cyanide (HCN), respectively, in the organic haze layers of the atmosphere of Titan. The reactions involved in the atmospheric chemistry of Titan lead to a vast array of larger, more complex intermediates and products and may also serve as a chemical model of Earth's primordial atmospheric conditions. The C_2H and CN additions are rapid and exothermic, and often occur barrierlessly to various carbon sites of unsaturated hydrocarbons. The reaction mechanism is proposed on the basis of the resulting potential energy surface (PES) that includes all the possible intermediates and transition states that can occur, and all the products that lie on the surface. The B3LYP/6-311g(d,p) level of theory is employed to determine optimized electronic structures, moments of inertia, vibrational frequencies, and zero-point energy. They are followed by single point higher-level CCSD(T)/cc-vtz calculations, including extrapolations to complete basis sets (CBS) of the reactants and products. A microcanonical RRKM study predicts single-collision (zero-pressure limit) rate constants of all reaction paths on the potential energy surface, which is then used to compute the branching ratios of the products that result. These theoretical calculations are conducted either jointly or in parallel to experimental work to elucidate the chemical composition of Titan's atmosphere, the ISM, and cold celestial bodies.

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1. INTRODUCTION

The neutral-radical reactions of unsaturated hydrocarbons with radicals has been an active area of research in astrochemistry, since it involves studies of gas-phased constituents of planetary atmospheres, the Intersteller Medium (ISM), and icy bodies such as comets. The neutral free radicals are generated through photodissociation processes from irradiation directly from the sun or deflections from neighboring planetary bodies. Being free radicals, they are highly reactive and react readily in addition-type reactions with any molecular species they encounter. The radical addition can occur to several possible sites on an unsaturated hydrocarbon, yielding a vast amount of larger, more complex products that can result.[23-35, 55-64] The products are generated either immediately upon the radical addition to the unsaturated hydrocarbon or through various isomerization steps including cyclizations, followed by an atom or polyatomic group loss.

The neutral-radical reactions of unsaturated hydrocarbons in the atmosphere of Titan, Saturn's biggest moon, is an active topic since NASA's Cassini/Hyugens mission in 2004.[3-28] Titan has atmospheric conditions and constituents similar to what is considered to of early Earth. It also has a hydrocarbon-rich haze layer analogous to Earth's ozone layer. Understanding the reactions involved, starting from those of simple free radicals with unsaturated hydrocarbons that produce larger, more complex products, is paramount in understanding the vast and rich chemistry found on Earth, both living and nonliving. One of the simplest unsaturated hydrocarbon free radical is ethynyl radical, C_2H ($X^2\Sigma^+$), while the simplest nitrogen-bearing unsaturated free radical is cyano radical, CN ($X^2\Sigma^+$), ultimately produced from photochemical reactions initiating from methane (CH_4) and nitrogen (N_2), the second and first most abundant atmospheric constituent of Titan, respectively.[5-20]

This *ab initio* quantum chemistry study of neutral-radical reactions with unsaturated hydrocarbons consists of two fundamental parts. The first is an investigation of the reaction mechanism, derived from quantum chemical calculations of the ethynyl or cyano addition reaction to the unsaturated hydrocarbon. From this, the full potential energy surface is constructed, which includes all of the individual reaction species and steps, including the intermediates that exist from isomerizations and the barriers that must be overcome through a transition state. Highly accurate electronic energies, optimized electronic structures, moments of inertia, and vibrational frequencies are calculated. The second fundamental part is a quantitative kinetic treatment of the forward and reverse individual reaction steps. Once the reaction rates are known, the product distribution or branching ratios can be determined through steady-state calculations, giving the relative yield of the products. The reactions studied are either coupled either jointly or in parallel with experiments to determine the reaction mechanisms and product branching ratios of the atmospheric constituents of Titan.

1.1 Titan's Chemistry

In 1997, the Cassini/Huygens spacecraft was launched as a joint collaborative mission from the National Aeuronatical Space Administration (NASA), European Space Agency (ESA), and Italian Space Agency (ASI). The mission was aimed at studying the planetary bodies of the outer solar system, including Saturn and its many natural satellites, or moons, such as Titan.[87] The spacecraft contained the Cassini orbiter, used for fly-by studies of Saturn, its rings, and its many moons, and the Huygens probe, aimed specifically for studying Titan's atmosphere and surface. It contained several on-board spectrometers and imaging instruments, including a gas chromatograph to separate constituents, mass spectrometer to analyze the mass and defragmenting patterns of the constituents, and a pyrolyzer to analyze aerosols. In mid 2004, the spacecraft finally reached Saturn, and at the end of 2004, the Huygens probe separated from the orbiter and entered Titan's atmosphere where it descended and landed in the beginning of 2005. Along its descent, it analyzed the atmospheric constituents at various altitudes.

The atmospheric chemistry of Titan has been an active area of research from the Hyugens findings. Many astrochemists and planetary scientists consider it to be a planetary scale laboratory and analogous to pre-biotic Earth. The rich chemistry found on Titan is analogous to a frozen pre-biotic Earth and is a model for the complex chemistry including that of life found on Earth.[87] It is the second largest moon in our solar system and its volume is larger then the planet Mercury. Titan is the only planetary body besides Earth that has a thick atmosphere of 1.5 atm, liquid bodies on its surface, and an organic hydrocarbon haze layer analogous to the Earth's ozone layer. Like Earth, its atmosphere is very dense mainly nitrogen based, and contains hydrocarbons to a lesser extent. Of these, methane is the prevalent atmospheric constituent. Methane is so abundant that it condenses out and forms into methane clouds that rain liquid methane, which eventually forms methane lakes and rivers in its higher altitude polar caps; these lakes and rivers also contain significant amounts of ethane. The trace constituents include molecular clouds of many small unsaturated hydrocarbons. Nitrogen accounts for 98.4% of the atmospheric constituent, while methane accounts for 1.4% and the remainder 0.2% are unsaturated hydrocarbons. The simplest of these unsaturated hydrocarbons is acetylene (C_2H_2), while hydrogen cyanide (HCN) is the simplest unsaturated N-containing hydrocarbon.[5-19]

The opaque haze layer is rich in hydrocarbons and shields Titan from the constant bombardment of ultraviolet rays and charged particles coming from the Sun and deflections from Saturn's magnetic poles, thus acting like a pre-biotic ozone layer.[3-28] It is these ultraviolet rays and charged particles that initiate chemical reactions, such as photolysis of the simplest unsaturated hydrocarbons and N-bearing hydrocarbons such as acetylene and hydrogen cyanide, respectively.

1.2 Photochemical Models

The photochemical models are important because they start from the simplest atmospheric constituents, and are developed to describe most of the atmospheric species and processes that result through photochemistry from the Sun, giving rise to atmospheric free radicals from simple photodissociation reactions. It is these atmospheric free radicals that react with other stable gas-phased species, such as unsaturated hydrocarbons, that this work aims to study. Starting from methane, the most abundant hydrocarbon of Titan, several photochemical reactions must take place to eventually produce ethynyl radical, the simplest unsaturated free radical.[18] Figure 1.2a illustrates all of the photochemical reaction models starting with methane.

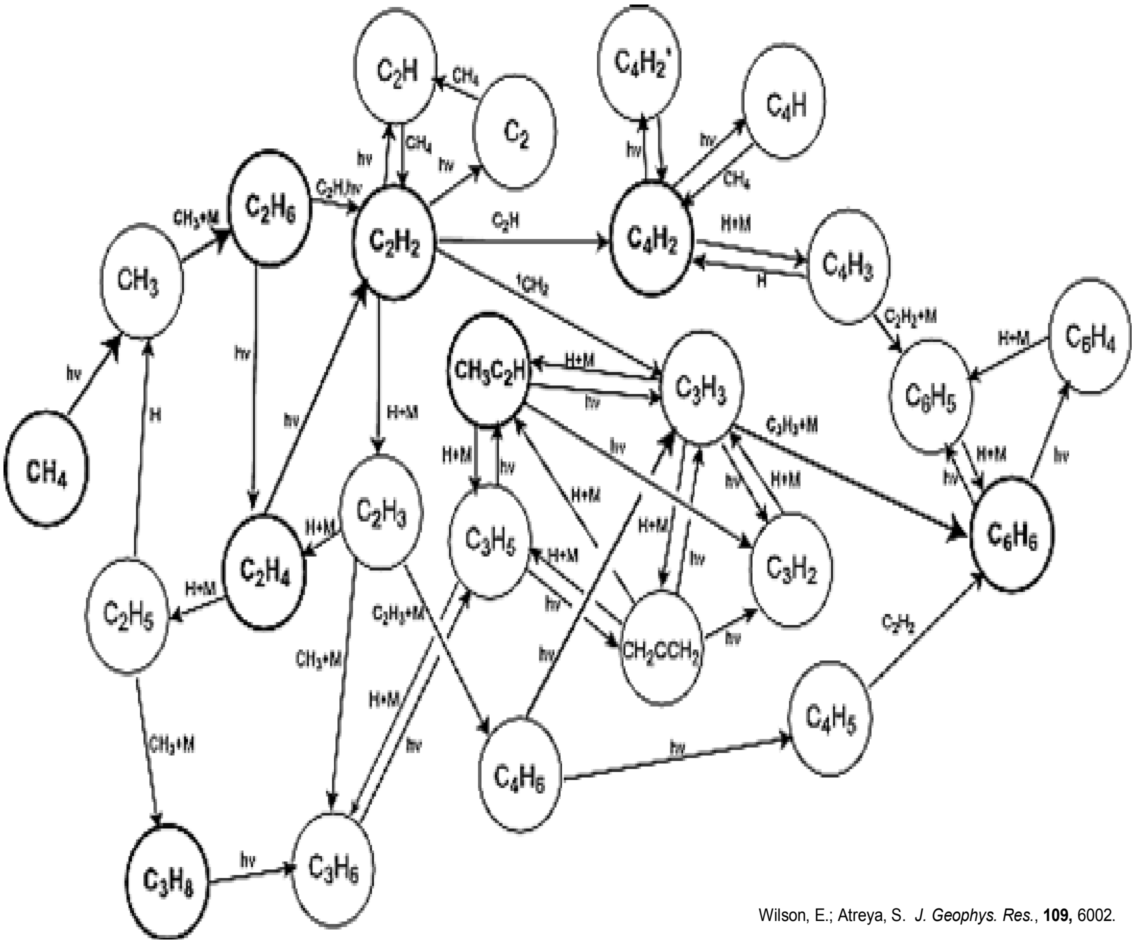

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Figure 1.2a. A photochemical model starting with methane that shows the formation of ethynyl radical.

First, methane photodissociates to form methyl radical by the following reaction:

$$CH_4 \rightarrow CH_3 + H$$

Methyl radical, being the simplest free radical, combines with another methyl radical to produce ethane, C_2H_6. Ethane can then lose one or two H_2 molecules through photodissosication processes and collisions with a third-body, respectively, to produce ethane (C_2H_4) and acetlylene (C_2H_2), respectively. Acetylene can further photodissociate to produce ethynyl radical + H:

$$C_2H_2 \rightarrow C_2H + H$$

Alternatively, ethynyl radical can be produced from gas-phased C_2 reaction with an H atom:

$$C_2 + H \rightarrow C_2H$$

Cyano radical formation occurs through similar photochemical reactions, starting with the most abundant atmospheric constituent, nitrogen gas (N_2). Here, the nitrogen molecule splits into two nitrogen atoms, which reacts with atmospheric methyl radical and/or ethynyl radical to form H_2CN. Aftter an H-loss, the stable hydrogen cyanide (HCN) forms. Hydrogen cyanide photodissociates into cyano radical by the following reaction:

$$HCN \rightarrow CN + H$$

Alternatively, two equivalents of cyano radical can be generated by the photochemical cleavage of cyanogen (C_2N_2). Cyanogen is formed by a self-recombination reaction of HC_2N.

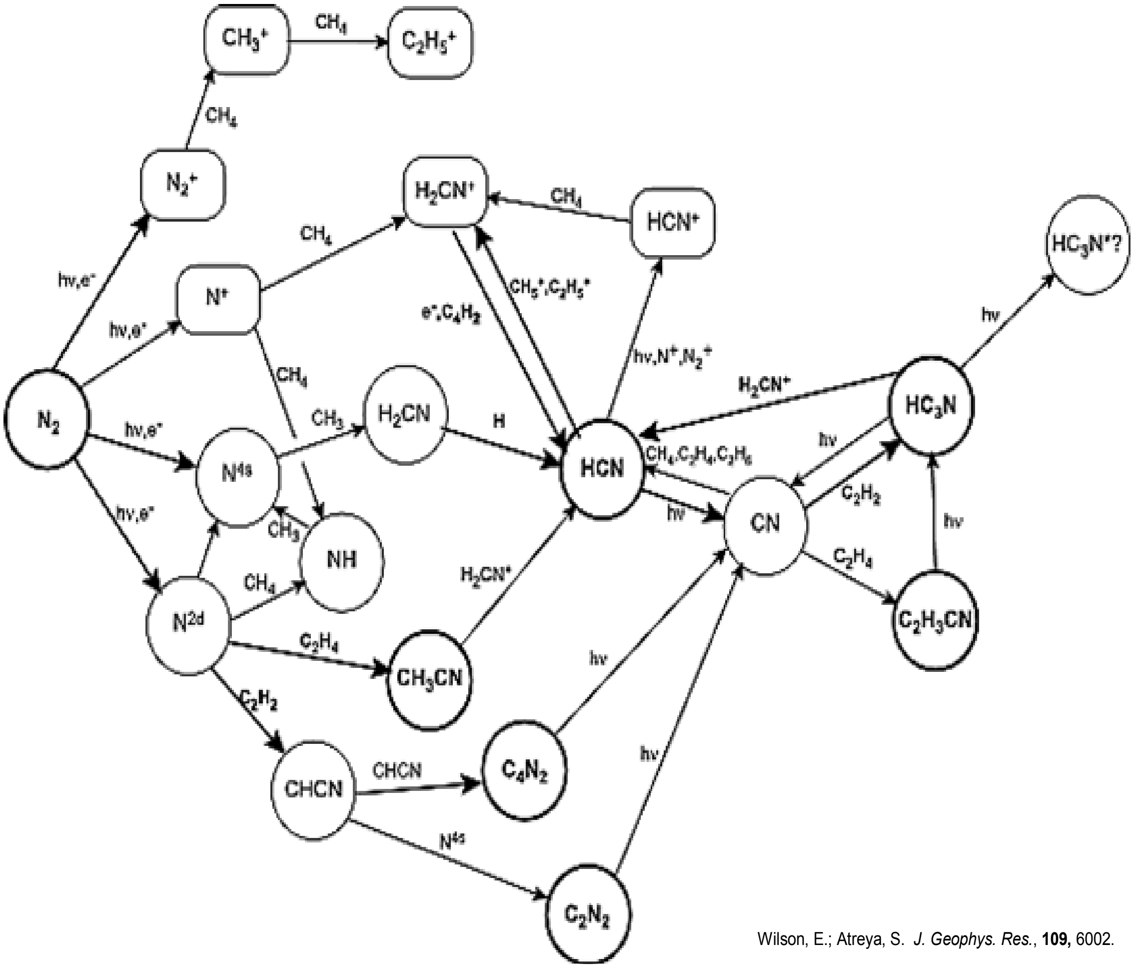

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Figure 1.2b. A photochemical model starting with nitrogen that shows the formation of cyano radical.

1.3 Ethynyl and Cyano Radicals

My work will address the hypothesis that the ethynyl radical can efficiently react with unsaturated hydrocarbons and these reactions prefer a C_2H-for-H reaction mechanism, which causes a two carbon-unit growth, while competing with the C_2H-for-CH_3 reaction mechanism, which causes a CH_2-unit growth. For the former reaction mechanism, ethynyl radical associates barrierlessly to the unsaturated hydrocarbon in either the terminal carbon or one of the central carbons of the unsaturated hydrocarbon, causing a growth of the unsaturated hydrocarbon moiety by two carbon units and one hydrogen. Then, any number of different H-losses (via the C_2H-for-H reaction mechanism) can occur, leading to a product that is larger by two carbon units. The latter reaction mechanism adds ethynyl radical to the unsaturated hydrocarbon barrierlessly as well, however, a CH_3-loss occurs (opposite to an H-loss), which results in a product that is one carbon larger, yet three hydrogen atom deficient. These products can form either instantly upon ethynyl radical addition to the unsaturated hydrocarbon, or after various isomerization steps (that may include cyclization/decyclization processes). For the case of cyano radical reaction mechanisms with unsaturated hydrocarbons, the CN-for-H reaction mechanism competes with the CN-for-CH_3 reaction mechanism in a similar fashion to the ethynyl radical addition mechanisms. The overall reaction scheme for the C_2H-for-H and C_2H-for-CH_3 mechanism to an unsaturated hydrocarbon of the form C_xH_y can be summarized as:

$$C_2H + C_xH_y \rightarrow C_{x+2}H_{y+1} \rightarrow C_{x+2}H_y + H$$

$$C_2H + C_xH_y \rightarrow C_{x+2}H_{y+1} \rightarrow C_{x+1}H_{y-2} + CH_3$$

Here, both the first and second equations depict a potential energy surface of $C_{x+2}H_{y+1}$ which arose from the addition of an ethynyl radical to one of many sites of the C_xH_y unsaturated hydrocarbon. Then, any number of isomerization steps can occur, followed by either a loss of an H, giving a $C_{x+2}H_y$ product as shown in the first equation, or a loss of CH_3, giving a $C_{x+1}H_{y-2}$ product as shown in the second equation. Similarly, for the case of cyano radical addition, the overall reaction scheme for the CN-for-H and CN-for-CH_3 mechanism to an unsaturated hydrocarbon of the form C_xH_y can be summarized as:

$$CN + C_xH_y \rightarrow C_{x+1}H_yN \rightarrow C_{x+1}H_yN + H$$

$$CN + C_xH_y \rightarrow C_{x+1}H_yN \rightarrow C_xH_{y-3}N + CH_3$$

Both of the equations show a $C_{x+1}H_yN$ potential energy surface from the addition of a cyano radical to a C_xH_y unsaturated hydrocarbon. Isomerization steps can occur in the $C_{x+1}H_yN$ PES as well, which eventually leads either to a $C_{x+1}H_yN$ or $C_xH_{y-3}N$ product from H-loss or CH_3-loss, respectively.

Our second hypothesis addresses the overall products that result between the two isoelectronic radicals, ethynyl and cyano radical; the products of these two reactions should be isoelectronically equivalent, where the CH moiety of ethynyl radical is replaced by the N moiety of cyano radical. For instance, reactions of ethynyl radical and cyano radical with a specific unsaturated hydrocarbon should result in an isoelectronic equivalent product.

2. BACKGROUND

In this chapter, a survey of previously studied reactions of ethynyl radical and cyano radical with unsaturated hydrocarbons will be addressed, both from an experimental and a theoretical stand-point. This chapter is divided into two fundamental parts, one addressing astrochemical observations and the other describing previous *ab initio* studies that included these astronomical species and therefore are useful to be incorporated into astrochemical models. Overall, it is important to compare the reactions studied in this work to those that have been previously studied for the sake of consistency and the inclusion of novel systems that produce important planetary and intergalactic constituents. These constituents include polyenes (unsaturated hydrocarbons with one or more double bonds), polyynes (unsaturated hydrocarbons with more than one triple bonds), polyenynes (unsaturated hydrocarbons with one or more double bonds and one or more triple bonds), cyclic structures including aromatics, and polycyclic structures including polycyclic aromatic hydrocarbons (PAHs). Their nitrogen-bearing counterparts includes cyanopolyenes, cyanopolyynes, N-containing cyclic structures including N-containing aromatics, and N-containing PAHs (N-PAHs).

2.1 Astrochemical Observations

Of the over 150 different molecular species detected in the interstellar and circumstellar media, approximately 50 contain 6 or more atoms.[111] Polyynes and cyanopolyynes have been implicated in the astrochemical evolution of the interstellar medium such as of cold molecular clouds such as TMC-1, the planetary nebula CRL 618, and the circumstellar envelope of the carbon star IRC+10216.[112] In cold molecular clouds, all cyanopolyynes up to HC_6N have been detected.[112] Diacetylene $H\text{-}(C\equiv C)_2\text{–}H$ and triacetylene $H\text{-}(C\equiv C)_3\text{–}H$ have been monitored toward CRL 618.

Polycyclic aromatic hydrocarbons (PAHs) and related species such as (de)hydrogenated, ionized, and substituted PAHs are presumed to be ubiquitous in the interstellar medium (ISM). Today, PAH-like species account for up to 30% of the cosmic carbon, they have been implicated in the chemical evolution of the interstellar medium, and provide critical nucleation sites for the formation of carbonaceous dust particles.[103] They are thought to play an important role in astrobiology. Formation of PAH has been modeled in carbon-rich circumstellar envelopes. They have been also linked to the unidentified infrared (UIR) emission bands observed in the range of 3-14 μm (3300-700 cm^{-1})[i] and to the diffuse interstellar bands (DIBs), discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the near-infrared (1.2 μm). Although significant works have been dedicated to the observation of PAHs and their aromatic building blocks in the interstellar medium, only benzene was proposed to exist in the protoplanetary nebula CRL-618.[103]

The remainder of this section will focus on atmospheric constituents that have been either already been observed on Titan, or could possibly form from reactions with ethynyl or cyano radical and unsaturated hydrocarbons. The simplest members of the polyacetylene and cyanopolyyne families that have been observed in the gas phase on Titan is diacetylene and cyanoacetylene.[112] Dicyanodiacetylene is suggested to exist as a solid on Titan. The cyanoacetylene molecule is known to be formed in the Miller–Urey experiment, an experiment which presumably mimics the chemical processing of the atmosphere of early Earth.[113] Since the C_2H addition is highly exothermic and takes place without a barrier, with the final dissociation products lying lower in energy than the initial reactants, the reactions of the ethynyl and cyano radical with unsaturated hydrocarbons are fast even at very low temperatures and hence can drive the growth of complex hydrocarbon molecules under low-temperature conditions.[83-90] Detections via Gas Chromatograph-Mass Spectrometer (GC-MS) aboard the Huygens probe and recent photochemical models based on the vertical temperature profile derived by the Huygens Atmospheric Structure Instrument (HASI) suggest Titan lakes to consist of about 76-79% ethane, 7-8% propane, 5-10% methane, 2-3% hydrogen cyanide, and less then 1% of butane, butane, and acetylene.[107] A large fraction of the major unsaturated species C_2H_2, C_2H_4, HCN, and HC_3N with mixing ratios of about 3×10^{-6}, 10^{-7}, 10^{-8}, respectively, reside in Titan's atmosphere between 150 and 500 km before they condense near the tropopause. Titan's haze layer, located in the mesosphere, is a hub of rich organic molecules.[108] It contains aerosols that span to the troposphere, and contain key compounds such as benzene, the simplest aromatic, thought to be the starting point towards PAH formation. Laavas et. al.[114] modeled the formation of aerosol through the growth of PAHs. In their simulations, benzene produced in the thermosphere reacts with radical species and grows to form larger aromatic structures. The large abundance of benzene that is observed in Titan's thermosphere by Vuitton[115] and co-workers, the discovery of heavy ions of several hundred amu's by Coates and co-workers[116] and neutral molecules up to 91 amu observed by Vuitton[115] and co-workers in the upper atmosphere, as well as PAHs with two or three rings detected above 950 km by Crary and co-workers with the Cassini/CAPS-IBS sensor,[117] all strongly support the formation of aerosols at much higher altitudes in Titan's atmosphere than previous thought prior to the Cassini mission. Aside from aromatics and PAHs, a whole array of straight chain and branched hydrocarbons and nitrogen bearing hydrocarbons exist. The next section covers the evolution and fate of these hydrocarbons. Methane plays an important role in the thermal structure of the atmosphere through the greenhouse effect caused by CH_4–N_2 collisions as reported by Lorenz and co-workers[118], and through the anti-greenhouse effect due to the formation of the haze via photolysis. Titan's methane cycle may be analogous to the hydrological cycle on Earth. Retrieving the methane vertical profile provides information regarding the relative degree of methane condensation and CH_4–N_2 saturation, and the recycling of gaseous methane via surface–atmosphere interactions.

2.2 Previous Ab Initio Studies

Extensive crossed-beam and *ab initio* work exists in the literature that involves either carbon (C) or dicarbon (C_2) atom reactions with unsaturated hydrocarbons. They start from the simplest unsaturated hydrocarbon, ethene, and continue with an increase in the carbon chain length to systems as big as six carbons, such as benzene (C_6H_6). However, the focus of this section will be towards reactions that involve C_2H, since this is the simplest hydrocarbon bearing two carbons. Furthermore, it is one of the main reactants of this work. Noteworthy is an emerging research area with other radical reactants simpler then C_2H, which include CH_3, CH_2, and CH. This sudy, however, will focus on C_2H and CN.

Since C_2H arises from acetylene (C_2H_2) as discussed in the last chapter, a natural starting point is C_2H additions to the simplest unsaturated hydrocarbon, ethyne. Le et. al.[83] showed this reaction forms diacetylene (C_4H_2) almost exclusively. Ethene (C_2H_4)[28,29] is similar to acetylene but bears a double bond instead of a triple bond, and consequently two more hydrogens. C_2H additions to ethene has been performed by Bouwman and co-workers[102] and showed exclusive formation of vinylacetylene (C_4H_4). Next in the series of reactions involving C_2H would be to increase the carbon chain length to allene and methylacetylene (C_3H_4). This reaction is studied in this work and its results are given in the successive chapters.[86] Having one less degree of unsaturation from C_3H_4 leads to propene (C_3H_6).[54,102] Reactions of C_2H with propene (C_3H_6) have also been studied by Bouwman and co-workers[102], who found 85 ± 10% vinylacetylene (C_4H_4) to form via CH_3-loss and the remainder being C_5H_6 isomers of mainly 4-penta-1-yne via H-loss. Next up the hierarchy of carbon chain length brings us to four carbons. The simplest four carbon system is diacetylene (C_4H_2). Landera and co-workers[30,56] studied C_2H + diacetylene, which almost exclusively forms triacetylene (C_6H_2). For C_4H_4, several isomers exist. They are vinylacetylene, butatriene (cumulene), and cyclobutadiene. Zhang et. al.[103] studied C_2H additions to vinylacetylene, and showed its implications of leading to PAHs by the formation of ortho-benyzyne (C_6H_4). Reactions of C_2H with butatriene and cyclobutadiene have not been reported in the literature. For the reactions of C_2H with C_4H_6, this work encompasses all of the reactions involved with the C_4H_6 isomers, including 1,3-butadiene,[112] 1,2-butadiene,[97] 1-butyne, and 2-butyne.[89] Their results are given in successive chapters. Finally, the last class of compounds with four carbons are of the C_4H_8 isomers 1- and 2-butene. Reactions of C_2H with these isomers has not been reported in the literature. Similarly, there has been no reported studies of C_2H with any unsaturated hydrocarbons with five carbons (i.e. C_5H_4, C_5H_8, etc.). For the case of six carbons, although C_2H additions to systems such as benzyne (C_6H_4) has not been reported, extensive work has been conducted towards C_6H_6 since key compounds such as benzene bear the C_6H_6 molecular formula. For instance, Jones et. al.[104] studied the formation of phenylacetylene (C_8H_6) from C_2H additions to benzene. Although there isn't any studies on seven carbon systems such as toluene (C_7H_8), C_2H additions to styrene (C_8H_8)[84] has shown to produce substituted naphthalene ($C_{10}H_9$ and $C_{12}H_9$) at low temperatures relevant to Titan. Reactions of larger unsaturated hydrocarbons with ethynyl radical is an active area of research, however, most of their applications are towards combustion chemistry since addition to a PAH ring usually involves a barrier. Here, the C_2H is generated from acetylene flames and often involves other radicals such as phenyl radical (C_6H_5).

Our focus will now divert to reactions involving the isoelectronic equivalent to C_2H, namely CN. Again, starting from the simplest unsaturated hydrocarbon, acetylene (C_2H_2), Huang and co-workers[105] showed CN addition to C_2H_2 yields about 85% of cyanoacetylene (HC_3N). Balucani and co-workers[106] studied CN additions to a whole host of unsaturated hydrocarbons, including ethylene (C_2H_4), allene and methylacetylene (C_3H_4), and benzene (C_6H_6). CN additions to diacetylene (C_4H_2)[99], a long with the C_4H_6 isomers of 1,2-butadiene, 1-butyne, and 2-butyne is covered in this work, and is presented in the successive chapters.

3. COMPUTATIONAL METHODS

The reaction mechanism of a radical reactant species with an unsaturated hydrocarbon is determined by the potential energy surface (PES) of the radical bonded onto a site on the unsaturated hydrocarbon. The reaction begins with initial adducts or intermediates that are usually exothermic, based upon the addition site on the unsaturated hydrocarbon. The radical additions can occur on either the terminal carbon(s), any one of the center carbon(s), or the sp^2- or the sp-hybridized bonds of the unsaturated hydrocarbon.[55-64] For some radicals, these additions may occur barrierlessly in cold conditions such as interstellar media, planetary and icy bodies, resulting to a plethora of individual reaction steps that leads to products. The situation is different in the hot conditions of combustion flame, where the radical additions occurring with a barrier are also possible and the entrance barrier height often dictates the reaction paths and products. After the formation of the initial adduct, several isomerization steps can occur, including 1,2-, 1,3-, 1,4- and 1,5-hydrogen shifts, cyclization and decycyclization processes, shift of moieties, etc. All of the isomerization reaction barriers compete with product forming reaction barriers in each individual step. These product forming reaction barriers may lead to a hydrogen H-loss, a methyl CH_3-loss, an ethyl C_2H_5-loss, and/or a vinyl C_2H_3-loss products. Noteworthy that based on the initial adduct that forms (i.e. which carbon of the unsaturated hydrocarbon the radical species initially bonds to), a certain product will form. Therefore, it is important to address the energetically favorable paths to product forming based upon the initial adduct that forms.

The structures of all of the reactants, products, intermediates, and transition states studied were calculated in this study using density functional theory employing the Becke, three-parameter, Lee-Yang-Parr (B3LYP) hybrid-functional.[42] The basis functions used with the B3LYP functional is the Pople-type split-valence 6-311g(d,p) basis set, which includes six primitives for the core functions and a valence triple-ζ basis for the valence functions.[43] The basis set also includes polarization functions of d for carbon and p for hydrogens. Optimized geometries in Cartesian coordinates, moments of inertia, vibrational frequencies, and zero-point energy (ZPE) were obtained using the B3LYP/6-311g(d,p) level of theory. The optimized structure was used for single-point energy calculations at a higher level of quantum chemistry, usually at the coupled cluster with singles, double, and perturbed triple excitation level of theory (CCSD(T)). This level of theory is considered the "gold standard" in the computational chemistry community. Dunning's correlation-consistent polarized triple zeta (cc-pVTZ) basis set was used with the CCSD(T) calculations.[44-48] The CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ were assigned cardinal number 2, 3, and 4, respectively, and substituted into the following formula[48]:

$$E_{\mathrm{tot}}(x) = E_{\mathrm{tot}}(\infty) + B\mathrm{e}^{-C}$$

where x is the cardinal number of the basis set (2, 3, and 4) and $E_{\mathrm{tot}}(\infty)$ is the CCSD(T)/CBS total energy. Basis set extrapolations to the infinite, or complete basis set (CBS) limit was done for the reactants and all of the products by also calculating the coupled cluster energy at the double-zeta basis set (CCSD(T)/cc-pVDZ) and quadruplezeta-basis set (CCSD(T)/cc-pVQZ) levels of theory. It should be noted that the T1 diagnostic values in CCSD(T) calculations were within 0.01-0.02 for all species on the PES indicating that their wave functions do not exhibit a strong multi-reference character and thus the CCSD(T) approach should be reliable for energy evaluation. We expect that our CCSD(T)/CBS + ZPE(B3LYP/6-311G**) relative energies should be accurate within 1-2 kcal/mol.[56-64]

Single-collision (zero-pressure limit) microcanonical rate constants for each reaction step were calculated using the Rice-Ramsperger-Kassel-Marcus (RRKM) theory.[51-53] This theory is an *ab initio* quantum mechanical variation of transition state theory (TST) and uses the calculated energies, individual reaction steps, and vibrational frequencies to calculate forward and reverse rate constants as functions of the internal energy, $k(E)$. According to RRKM theory, the rate constant $k(E)$ at an internal energy E for a unimolecular reaction $A^* \rightarrow A^\# \rightarrow P$ can be expressed as[56-60]:

$$k(E) = \frac{\sigma W^\#(\mathrm{E} - \mathrm{E}^\#)}{h\rho(E)}$$

where σ is the reaction path degeneracy, h is the Plank constant, $W^\#(E-E^\#)$ denotes the total number of states for the transition state (activated complex) $A^\#$ with a barrier $E^\#$, $\rho(E)$ represents the density of states of the energized reactant molecule A^*, and P is the products.

The following sections provide a more in-depth description and derivations of the theories involved in these calculations.

3.1. Molecular Orbital Theory

Quantum Mechanics (QM) is the foundation of *ab initio* quantum chemistry. It describes the phenomenon that occurs at the atomic and subatomic level, which includes electrons and nuclei, in contrast to Classical Mechanics (CM) which describes processes at the macroscopic level from condensed phases to planetary motion. The heart of quantum mechanics lies in the operator-expectation value approach, which is generally stated as:

$$\hat{O}\Psi = O\Psi$$

Here, the operator $\hat{O}$ operates on a wave function Ψ is equal to the product of the observable O and the wave function. The observable O is a scalar property of the system that results from a particular operator. When this equation holds true, the wave function Ψ is considered an eigenfunction and the observable O is considered an eigenvalue. However, a more practical representation is the Schrödinger equation[90], which succinctly states:

$$\hat{H}\Psi = E\Psi$$

Here the $\hat{H}$ is the Hamiltonian operator describing the wave function and E is the total energy of the system. This is the common form found as a starting point in many quantum mechanical formalisms. For an electronic time-independent implementation of the Hamiltonian, it is described as[91,92]:

$$\hat{\mathrm{H}} = -\sum_{i}\frac{\hbar^{2}}{2m_{e}}\nabla_{i}^{2} - \sum_{k}\frac{\hbar^{2}}{2m_{k}}\nabla_{k}^{2} - \sum_{i}\sum_{k}\frac{e^{2}Z_{k}}{r_{ik}}\nabla_{i}^{2} + \sum_{i<j}\frac{e^{e}}{r_{ij}} + \sum_{k<l}\frac{e^{e}Z_{k}Z_{l}}{r_{il}}$$

where $\hbar = \frac{h}{2\pi}$ and $\nabla_{i}^{2} = \frac{\partial^{2}}{\partial x_{i}^{2}} + \frac{\partial^{2}}{\partial y_{i}^{2}} + \frac{\partial^{2}}{\partial z_{i}^{2}}$. The Hamiltonian consists of two fundamental parts, the first two terms relate to the kinetic energy of the electrons and nuclei, respectively, while the last three terms describe the potential energy of the subatomic particles: the interactions of the electron with the nuclei, the electron-electron repulsions, and the nuclei-nuclei repulsions, respectively.

3.1.1. Variational Principle

If we assign an arbitrary function, Φ, which is an eigenfunction for the Shrödinger equation, and since we defined the set of orthonormal wave functions Ψ_i to be complete, the function Φ must be some linear combination of the Ψ_i as shown below:

$$\Phi = \sum_{i}\mathrm{c}_{\mathrm{i}}\Psi_{i}$$

An exact solution of the Schrödinger equation for any atomic or molecular system with more then one electrons cannot be achieved. However, approximate solutions can be found using the variational principle.[91,92] In the set of all E_i there must be a lowest energy value corresponding to the ground state, E_0. By combining equations, it follows that:

$$\int \Phi H \Phi \partial r - E_o \int \Phi^2 \partial r = \sum_i c_i^2 (E_i - E_o)$$

Assuming the coefficients c_i and E_i-E_o are real positive numbers, we get:

$$\frac{\int \Phi H \Phi \partial r}{\int \Phi^2 \partial r} \geq E_o$$

When Φ is normalized, we get the variational principles result of: $\int \Phi H \Phi \partial r \geq E_o$. The variational principle provides a mathematical way to find the Schrödinger equation solutions through minimization of a function, here $\int \Phi H \Phi \partial r$. The equation resulting from such minimaztion process is called a secular equation and its form and complexity depends on the form of the chosen wavefunction Φ.

3.1.2. Born Oppenheimer Approximation

The nuclei of molecular systems are moving much more slowly than the electrons. It is convenient to compute the electronic energies for fixed nuclear positions by decoupling it from electronic motion. Correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a constant for a given geometry. The electronic Schrödinger equation becomes the Born-Oppenheimer approximation[91,92]:

$$(H_{\mathrm{el}} + V_{\mathrm{N}})\Psi_{\mathrm{el}}(\mathrm{q_i};\mathrm{q_k}) = E_{\mathrm{el}}\Psi_{\mathrm{el}}(\mathrm{q_i};\mathrm{q_k})$$

The Born-Oppenheimer has very profound consequences including the concept of a potential energy surface (PES), the surface defined by E_{el} over all possible nuclear coordinates. This further includes the concepts of equilibrium and transition state geometries, since these are defined as critical points on the PES.

3.1.3. Self-Consistent Field Method

In the Born-Oppenheimer approximation, the separable Hamiltonian does not include the electron-electron repulsion term, which is tedious since it depends not on one electron but on all possible simultaneous pair wise interactions. In 1928, the English physicist Douglas Hartree developed the self-consistent field (SCF) method to overcome this hurdle. In the first SCF process, one guesses the wave function Ψ for all of the occupied molecular orbitals and uses these to construct the necessary one-electron operators h.[91,92] Solution of each one-electron Schrödinger equation provides a new set of wave function Ψ, presumably different (and more accurate) then the initial guess. Then, recursively, one uses this new wave function Ψ to construct an even more accurate wave function Ψ. At some point, the difference between a newly determined set and the immediately preceding set is below some threshold criterion, and the final set of Ψ is referred to as the ‘converged’ SCF orbitals. In constructing antisymetric wave functions, a Slater determinant is used where the sign changes when two rows or columns are interchanged. The Slater determinant can be expressed as:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} = \begin{vmatrix} \chi_1 & \chi_2 & \cdots & \chi_N \end{vmatrix},$$

3.2. Ab Initio Quantum Chemistry

Ab initio methods, latin for “from the beginning” methods are so called because they do not make references to any empirical parameters, and thus construct a solution from first principles. They include Hartree Fock (HF) theory, Coupled Cluster (CC) theory, and even density functional theory (DFT).[91-93]

3.2.1. Hartree-Fock Theory

Hartree-Fock (HF) theory makes an assumption that each electron sees all of the others as an average field by neglecting electron correlation and consisting of only of the exchange integral. The HF molecular orbitals consist of Slater Determinant wave functions that include the exchange effects of the electrons. Solving the secular equation, which originates from the variational principle, determines the orbital coefficients, which is used in the HF SCF method.[91-93] Vladimir Fock proposed an extension to Hartree’s

SCF method to include Slater-determinant wave functions. Similar to Hartree product orbitals, the Hartree-Fock molecular orbitals can be individually determined as eigenfunctions of a set of one-electron operators, but the interaction of each electron with the static field of all other electrons includes exchange effects on the Coulomb repulsion. The one-electron Fock operator is defined for each electron i[91-93]:

$$fi = \frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{r_{ik}} + V_i^{HF}\{j\}$$

Just as in the Hartree method, the HF method follows a SCF procedure: first we guess the orbital coefficients and then we iterate to convergence. From a practical standpoint, HF theory had some very challenging technical problems to early computational chemists, such as the choice of a basis set. The MO-LCAO (Molecular Orbitals as Linear Combonations of Atomic Orbitals) approach using hydrogenic orbitals is attractive but this basis set requires numerical solution of the tedious four-index integrals, with each index spanning over the total number of basis functions, creating a quartic scaling behavior which is ultimately the bottleneck in HF calculations.

A great deal of work has been towards developing mathematical and computational techniques to reach the HF limit, which is to solve the HF equations with the equivalent of an infinite basis set. If the HF limit is achieved, then the energy error associated with the HF approximation for a given system, the electron correlation energy E_{corr} can be determined as $E_{corr} = E - E_{HF}$.

3.2.2. Coupled Cluster Theory

To overcome the electron correlation energy problem for molecular systems, several theories were developed for applications to many-body systems. They are often considered post-Hartree-Fock ab initio quantum chemistry methods, and have become a commonplace to modern computational chemistry. One such theory is coupled cluster (CC) theory, where the full-configuration interaction (CI) wave function can be described as[91-93]:

$$\Psi = e^{\check{T}}\Psi_{HF}$$

where the CC operator is: $\check{T} = \check{T}_1 + \check{T}_2 + \check{T}_3 + \ldots \check{T}_n$ and $\check{T}_1$ is the operator of all single excitations, $\check{T}_2$ is the operator of all double excitations and so forth. Taking into consideration the structure of $\check{T}$ the exponential operator $e^{\check{T}}$ may be expanded into Taylor series:

$$\Psi_{CCD} = e^{\check{T}}\Psi_{HF} = (1 + \check{T} + \check{T}^2/2! + \ldots)\Psi_{HF} = (1 + \check{T}_1 + \check{T}_2 + \check{T}_1^2/2 + \check{T}_1\check{T}_2 + \check{T}_2^2/2 + \ldots)\Psi_{HF}$$

here, CCD implies the double-excitation operator. The first two terms define the CI method, while the remaining terms involve excitation operators. This ensures size consistency since the square of $\check{T}_2$ generates quartet excitations, and so on. Therefore, it is important to observe T_1 values for reliability. After determining the cluster amplitude, the coupled cluster energy becomes:

$$<\Psi_{HF} \mid H \mid e^{\check{T}}\Psi_{HF}> = E_{CC}$$

Single excitations are included in CC calculations, to obtain CCSD energies. One can also use perturbation theory to evaluate the contribution of triple excitations CCSD(T). Here, the single and double excitations are included fully while the triple excitation is solved non-iteratively. The coupled-cluster method described above is also known as the single-reference (SR) coupled-cluster method because the exponential ansatz involves only one reference function. For single-reference calculations, it is considered the “gold standard” when there is no significant multireference character in the wave function. A measure of the multireference character T_1 diagnostic should be below 0.02.

$$T_1 = \frac{\sqrt{\sum_{i}^{occ}\sum_{a}^{vir}(t_i^a)^2}}{n}$$

The standard generalizations of the SR-CC method are the multi-reference (MR) approaches: state-universal coupled cluster (also known as Hilbert space coupled cluster), valence-universal coupled cluster. A T_1 value greater then 0.02 is indicative of multireference character, in which an active space level of theory will deem suitable.

3.3. Basis Set

An arbitrary wave function Ψ function can be represented by a combination of more convenient functions called a basis set. Other then the simplest system, the hydrogen atom, H, the Schrödinger equation cannot be solved exactly because of the absence of the electron-electron repulsion term. Therefore, one needs to apply an approximation to solve the system of interest and constructing wave functions.[91-93] Molecules consist of atoms with electrons that share molecular orbitals, so Molecular Orbital (MO) theory describes the spread of electrons across these atomic orbitals. Hence the Linear Combination of Atomic Orbitals (LCAO) consists of the MO that encompasses this span. The basis is the set of mathematical functions, or basis functions, from which the wave function is constructed.

Each MO in HF theory is expressed as a linear combination of basis functions, the coefficients from which are determined from the iterative solution of HF SCF equations. The full HF wave function is expressed as a Slater determinant formed from the individual occupied MOs. In principle, the HF limit is achieved by use of an infinite basis set, however, in practice, one cannot make use of an infinite basis set. A more in-depth description and examples of basis sets can be found in the following sections.

3.3.1. Gaussian Type Functions

Historically, the use of atomic orbitals was in the form of Slater Type Orbitals (STO), which closely resemble hydrogenic orbitals. However, there is no solution for the two-electron integrals needed with the use of STO. In 1950, Samuel Francis Boys suggested normalizing the STOs which uses polar coordinates [94]:

$$\varphi\ (r,\theta,\varphi;\varsigma,n,l,m) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}\, r^{n-1} e^{-\varsigma r} Y_l^m(\theta,\varphi\ )$$

into a more convenient Gaussian Type Orbitals (GTO), which basically turns the e^{-r} term to e^{-r^2} and uses Cartesian coordinates:

$$\varphi\ (x,y,z;\alpha,i,j,k) = \left(\frac{2a}{\pi}\right)^{3/4}\left[\frac{(8a)^{i+j+k}\, i!\, j!\, k!}{(2i)!(2j)!(2k)!}\right] x^i y^j z^k\, e^{-a(x^2+y^2+z^2)}$$

Here, the term in the exponent is squared so that the product of the Gaussian "primitives" (original Gaussian equations) is another Gaussian. The downfall of this is the loss of accuracy, but the use of more Gaussian equations compensates for the accuracy.

When a basis function is defined as a linear combination of Gaussians, it is considered as a ‘contracted’ basis function or individual Gaussians ‘primitives’. The degree of contraction, M, is the total number of primitives used to make all of the contracted functions.

In 1969, John Pople and coworkers successfully determined optimal coefficients and exponents for contracted GTOs, which can be used in place of STOs for solving the two electron integrals. Here, they used the Slater-Type Orbital approximated by M Gaussians, or STO-MG.[43] The STO-3G basis set has only one basis function defined for each type of core or valence orbital, and is known as a ‘single-ζ’ or minimal basis. One way to increase the flexibility of a basis set is to de-contract it. This is done by taking the STO-3G basis set, and instead of contracting each basis function as a linear combination of three Gaussians, we could construct two basis functions for each AO, the first being a contraction of the first two primitive Gaussians and the second the normalized third primitive. Since we would have to evaluate all the same individual integrals as before, the basis set would not double, rather the size of our secular equation would increase. A basis set with two functions for each AO – 'double-ζ' basis. We could de-contract further and treat each primitive as a new basis function, known as a 'triple-ζ' basis, and we could then decide to add more functions indefinitely creating higher and higher multiple-ζ basis sets. This brings the basis set closer to the HF limit.

3.3.2 Split-Valence Functions

Valence orbitals can vary. Atoms bonded to significantly more electronegative elements take on partial positive charge from loss of valence electrons. Therefore, it is more beneficial to have flexibility in the valence basis functions than in the core. This sprouts the development of split-valence basis sets, where the core orbitals continue to be represented by a contracted single basis function but valence orbitals are split into arbitrarily many functions. The most widely used split-valence basis sets include 3-21G, 6-31G, 6-311G. The first number indicates the number of primitives used in the contracted core functions. The numbers after the hyphen indicate the number of primitives used in the valence functions, if there are two numbers, it is a valence-double-ζ basis, if there are three numbers, it is a valence- triple-ζ basis.[43]

3.3.3. Polarization Functions

Atomic orbitals are centered about the atom's nucleus, so they can be accurately represented with s functions, p functions, etc. Molecular orbitals are spanned about several atomic nuclei, therefore it is necessary for them to be more flexible. This means that although atomic orbitals are good approximations, a better approximation is to acknowledge and account for the fact that sometimes molecular orbitals, such as those of hydrogen, share qualities of s and p-type orbitals, while p-block elements such as carbon, nitrogen, and oxygen share qualities of p and d-type orbitals, and not necessarily have characteristics of only one or the other.[91-93] This is especially true when atoms are brought close to one another, and their charge distribution causes a polarization effect. The use of an additional quantum number of higher angular momentum than the valence orbitals provides the necessary flexibility for these shared characteristics, and is known as polarization functions. The nomenclature consists of "(d)" (or "*") for the d-type GTOs, and "(p,d)" (or "**") for both p and d-type GTOs.

3.3.4. Diffuse Functions

In the case of anions or excited states, certain regions of the wavefunction become increasingly important. As the nuclear separation increases, the energy of the system decreases. The small exponents used in this "tail region" of the wave function are characterized by diffuse functions. Molecular complexes involving transition metals also are sensitive to diffuse functions. The nomenclature consists of "+" for the p-orbitals, and

"++" for both s and p-orbitals. Particularly for the calculations of acidities and electron affinities, diffuse functions are absolutely required. They have found more practical usage in condensed phased systems. This study, however, will focus on gas phased atmospheric reactions.

3.3.5. Correlation-Consistent Functions

Correlation-consistent basis sets of Dunning includes double-zeta or cc-pVDZ, triple-zeta or cc-pVTZ, quarternary-zeta or cc-pVQZ, and quintet-zeta or cc-pV5Z. Their exponents and contraction coefficients are variationally optimized not only for HF calculations, as in Pople-type split-valence basis sets developed earlier, but also including electron correlation.[47-48]

3.4 Density Functional Theory

The Hamiltonian depends only on the positions, atomic numbers of the nuclei, and the total number of electrons. A useful physical observable would be the electron density ρ, because integrated over all space, it gives the total number of electrons. Therefore, it is convenient to consider the electron cloud as a cluster oppose to individual electron movement:

$$N = \int \rho(r)\, \partial r$$

Thus, given a known density, one could form a Hamiltonian operator, solve the Schrödinger equation, and determine the wave functions and energy eigenvalues. The motivation towards DFT was to avoid using the Schrodinger equation, so the energy must be determined directly from density. By using the density over wave functions, it is much more cost-effective.[40-43]

Since electrons interact with one another and with an external potential such as charges and position of nuclei, the Hohenberg-Kohn theorem states that the Hamiltonian operator can be determined from the ground state density. Similar to the variational approach, by choosing different densities and wave functions, one can find lower energies.

3.4.1. Kohn-Sham Self-Consistent Field Method

Kohn and Sham treated a system with interacting electrons as a system with non-interacting electrons and calculate the ground-state density. The energy of the system can be expressed as[95]:

$$E\,[\rho(r)] = T_{ni}\,[\rho(r)] + V_{ne}\,[\rho(r)] + V_{ee}\,[\rho(r)] + \Delta T\,[\rho(r) + \Delta V_{ee}\,[\rho(r)]$$

where T_{ni} is kinetic energy of non-interacting electrons, V_{ne} is the potential of nuclear-electron interaction, V_{ee} is the potential of the electron-electron repulsion, ΔT is the correction to the kinetic energy deriving from the interacting nature of the electrons, and ΔV_{ee} is the corrections to the electron-electron repulsion energy. It is convenient to couple ΔT and ΔV_{ee} into the exchange correlation energy E_{xc}. DFT, by optimizing a density, is exact, unlike HF, which optimizes a wave function, is an approximation and becomes exact towards a limit. The only thing necessary is E_{xc} as a function of ρ. This is stated as:

$$E_{xc}\,[\rho(r)] = \int \rho(r)\varepsilon_{xc}[\rho(r)]\, dr$$

where ε_{xc} is the energy density. In the Kohn-Sham SCF method, the main difference from HF SCF is the use of Kohn-Sham secular equation and orbitals. Local density approximation (LDA)) developed to describe a uniform electronic gas was originally used to indicate any DFT method where the value of ε_{xc} at some position r could be computed exclusively from the value of ρ at that position. LDA approach has limitations and appeared to be inaccurate for chemical system where electron density is far from uniform.

3.4.1. Hybrid Functionals

One way to improve the correlation potential is to make it depend not only on the local value of the density, but on the extent to which the density is locally changing. This introduces the idea of generalized gradient approximation (GGA). Most gradient-corrected functionals are constructed by adding a correction term to the LDA functional. The commonly used GGA functional is the Becke (B) functional, which has correct asymptotic behavior at long range for the energy density and incorporates a single empirical parameter the value of which is optimized by fitting to the exactly known exchange energies of the six noble gas atoms He-Rn. The inclusion of correlation functionals makes GGA functionals very robust. For instance, the LYP functional (named after Lee, Yang, and Parr) does not correct the LDA expression but computes the full correlation energy. LYP is the only functional that provides an exact cancellation of the self-interaction error in one-electron system. The methods which incorporate HF and DFT exchange are called hybrid DFT methods. A hybrid exchange-correlation functional is usually constructed as a linear combination of the Hartree-Fock exact exchange functional, E_x^{HF} and any number of exchange and correlation explicit density functionals. Another useful method is to combine the exchange-correlation functional with the exact exchange that can be obtained from Hartree-Fock calculations[91-93]:

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_x^{HF}$$

The B3LYP exchange-correlation functional can then be expressed as[41-42]:

$$E_x^{B3LYP} = E_x^{LDA} + a_o(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} + E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

3.5 Statistical Theory of Reaction Rates

The potential energy surface (PES) along with *ab initio* calculations of electronic structure, energies and vibrational frequencies are used in microcannonical Rice–Ramsperger–Kassel–Marcus (RRKM) calculations to determine individual reaction steps and product branching ratios of unimolecular single-collision reactions. RRKM theory, a commonly used variation of transition state theory (TST) proposed by Rudolph Marcus in 1952, uses a quantum chemical approach in which zero-point energies have been taken into account.[49-53] TST was introduced by Henry Erying in 1935, and later reformulated by Rice and Ramsperger in 1927 and Kassel in 1928 into RRK theory. The steps to RRKM formalism on unimolecular reaction rates starts with Transition State Theory, Lindemann-Hinshelwood Theory, RRK theory, and eventually RRKM theory. The latter of which has become a common-place in theoretical chemical kinetics. Reaction dynamics is also necessary to consider but not included in this study.

3.5.1. Transition State Theory

Before the development of transition state theory (TST), the Arrhenius rate law was widely used to determine energies for the reaction barrier. The Arrhenius rate law is given by:

$$\mathrm{k} = \mathrm{A}\,e^{(-\frac{Ea}{RT})}.$$

The Arrhenius equation derives from empirical observations and ignores any reaction mechanisms that play a role. The only thing needed is the activation energy E_a and the temperature T. TST is a semi-empirical method that is successful in calculating the standard enthalpy of activation ($\Delta^{\ddagger}H^{*}$), the standard entropy of activation ($\Delta^{\ddagger}S*$), and the standard Gibbs energy of activation ($\Delta^{\ddagger}G*$) for a particular reaction if its rate constant has been experimentally determined. It assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes, or saddle points on the PES. The activated complexes can convert into products which allow collision theory to calculate the rate of this conversion. In early 1900, Max Trautz and William Lewis studied the rate of the reaction using collision theory, which treats molecules as hard spheres, based on the kinetic theory of gases. Some forrmalisms involve the Maxwell-Boltzman distribution law to obtain the following equation for the rate constant of the forward reaction.[49-53, 65, 91-93]. Much of these formalisms start with the basic Maxwell-Boltzman distribution law stated as:

$$\mathrm{k}_1 = \frac{k_b T}{h}\left(1 - e^{\left(\frac{-hv}{k_b T}\right)}\right) e^{\left(\frac{-E\Theta}{-RT}\right)}$$

where E^{Θ} is the dissociation energy at absolute zero, k_B is the Boltzmann constant, h is the Planck constant, T is thermodynamic temperature, v is vibrational frequency of the bond. This expression is very important since it is the first time that the factor $k_B T/h$, which is a critical component of TST, has appeared in a rate equation.

3.5.2. Lindemann-Hinshelwood Theory

A gas-phased unimolecular reaction is a pseudo first-order reaction because it requires a second-body M such as a gas bath.[63] The overall reaction steps of a bimolecular reaction is given by:

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_1} \mathrm{P}$$

where A is the reactant, A^* is an activated complex, P is the product. Then, after steady-state approximation, the concentration for A^* is:

$$[\mathrm{A}^*] = \frac{k_1[A][M]}{k_{-1}[M]+k_2}$$

and the overall rate is[63]:

$$\frac{d[P]}{dT} = k_2[A^*] = \frac{k_1 k_2[A][M]}{k_{-1}[M]+k_2} = k_{eff}[A]$$

At high pressures, collisional deactivation of A^* is more likely than unimolecular reaction, k_{eff} reduces to $\frac{k_1 k_2}{k_{-1}}$, which makes the reaction a true first-order. Hinshelwood included the internal modes of A by having s equivalent simple harmonic oscillators of frequency n and using statistical methods to determine the probability of the molecule being collisionally activated to a reactive state. The fraction of molecules in state v is given by the Boltzman distribution:

$$\frac{n_v}{N} = \frac{g_v e^{\frac{-vhv}{kt}}}{q}$$

where

$$\mathrm{q} = \left(\frac{1}{1 - e^{\frac{-hv}{kT}}}\right)^3 \qquad \text{and} \qquad \mathrm{g_v} = \frac{(v + s - 1)!}{v!(s-1)!}$$

After integrating over all energies with a rate equation that involves the density of states between E and E + *d*E, we obtain:

$$\mathrm{k_1} = \frac{Z}{(s-1)!}\left(\frac{E_o}{kT}\right)^{s-1} e^{\frac{-E_o}{kT}}$$

3.5.3. RRK Theory

RRK theory starts with an additional step that includes the activated complex $A^{\ddagger}$ which the excited molecule A^* converts into. The Lindemann reaction becomes:

$$A^* \rightarrow^{k_{2a}} A^{\#} \rightarrow^{k_*} P$$

Since $k_{2a} << k^{\#}$, we obtain $k_{2a} = k^{\#} \frac{[A^{\#}]}{[A^{*}]}$. Through considerations to quantum states, energy levels, an harmonic and anharmonic frequencies, RRK define k_2 as:

$$k_2(E) = k^{\#} (1 - \frac{E_o}{E})^{s-1}$$

3.5.4. RRKM Formalism

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the non-fixed component E^*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction. The various terms of the rate expression are now evaluated using statistical mechanics. The thermal rate constant is obtained by integrating E over E_o to ∞:

$$k = \int_{Eo}^{\infty} \frac{k_2(E) \partial k_1(E)[M]}{k_{-1}[M] + k_2(E)}$$

RRKM theory has a pseudo equilibrium A^* and $A^{\#}$, but not between A^* and A. However, at high pressures A^* and A are also in equilibrium. In the high pressure limit, RRKM theory reduces to transition state theory. Transition state theory assumes that the activated complex $A^{\#}$ is in thermal equilibrium with the reactants. This then leads to the kinetic expression as a function of internal energy $k(E)$ used in this study:

$$k(E) = \frac{\sigma W^{\#}(\mathrm{E}-\mathrm{E}^{\#})}{h\rho(E)}$$

3.5.5. Master Equation Methods

To solve a multiple-well system with the rate law as a function of energy *k(E),* contrary to a function of temperature and/or pressure *k(p,T)*, master-equations must be used to describe the time-evolution of a system that can be modeled as being in exactly one of countable number of states at any given time, and where switching between states is treated probabilistically. The equations are usually a set of differential equations for the variation over time of the probabilities that the system occupies at each different states. The most primitive form of the master equation can be written as

$$\frac{\partial n_i(t)}{\partial t} = \sum_j (p_{ij} n_j(t) - p_{ji} n_i(t))$$

where $n_i(t)$ is the probability of finding the system (molecule) in state i at time t and p_{ij} is the probability per unit time of a transition from state j to state i. This equation is also sometimes called the Pauli master equation, after Wolfgang Pauli derived an equation of the same form in 1928 using the Schrödinger equation describing the time evolution of a many-body system. Generally the transition probabilities are of only two types, reactive and collisional.

In the Car-Parrinello (CP) approach to *ab initio* MD for example, the electronic structure is described using the Kohn-Sham formulation of the density functional theory, and the Kohn-Sham orbitals are expanded in a plane wave basis. The CP approach usually employs periodic boundary conditions, plane wave basis sets, and density functional theory. The expansion coefficients are treated as a set of fictitious dynamical variables that are propagated adiabatically with respect to the nuclei, so that, at each time step, they describe the instantaneous ground state Born-Oppenheimer surface.

4. C_2H RADICAL REACTIONS

Ethynyl radical ·C≡CH can add to an unsaturated hydrocarbon by the carbon bearing the unpaired electron ·C, resulting in CH being at the terminal. However, a more energetically unfavorable addition can occur by the CH of ethynyl radical, resulting in a terminal acetylenic carbon atom with an unpaired electron ·C. From hereon, only the addition which results in a terminal CH will be considered in determining the energetically favorable reaction steps in forming a product.

There are two common forms of gas-phased C_3H_4, one being allene CH_2CCH_2 bearing two π-bonds, and the other as methylacetylene CH_3CCH bearing a triple bond. Allene and methylacetylene have been observed in combustion reactions and in planetary atmospheres and are included in kinetic models of these systems. Allene has one more carbon then the simplest alkene, ethylene C_2H_4, which lies in a linear fashion. Methylacetylene is the simplest substituted alkyne and has a net one carbon and two hydrogen's more then the simplest alkyne, acetylene C_2H_2.

The C_4H_6 molecule has four main isomers, 1,3-butadiene, 1,2-butadiene, 1-butyne, and 2-butyne. The first two are alkenes bearing two π-bonds in various locations on the carbon chain, while the last two are alkynes bearing a triple-bond in various locations. Namely, 1,3-butadiene has a repeating double-single bond moiety, while 1,2-butadiene has both double bonds consecutively, similar to a methyl substituted allene. The 1-butyne and 2-butyne isomers have a triple bond lying in the terminal and central carbons, respectively. This gives 1-butyne one of two addition sites while 2-butyne has only one due to symmetry.

4.1. C_2H + Allene

Ethynyl radical addition to allene (CH_2CCH_2) can occur on the terminal allylic sp^2-hybridized carbon forming a linear initial adduct, on the π-bond between the terminal carbon and the central carbon forming a 3-membered cyclic initial adduct, or the central double sp^2-hybridized carbon. Due to symmetry, only these additions can occur. The C_2H reactions with allene can consist of one of three possible reaction routes:

$$C_2H + CH_2{=}C{=}CH_2 \rightarrow C_5H_5 \rightarrow C_5H_4 + H$$

$$C_2H + CH_2{=}C{=}CH_2 \rightarrow C_5H_5 \rightarrow C_4H_2 + CH_3$$

$$C_2H + CH_2{=}C{=}CH_2 \rightarrow C_5H_5 \rightarrow C_3H_3 + C_2H_2$$

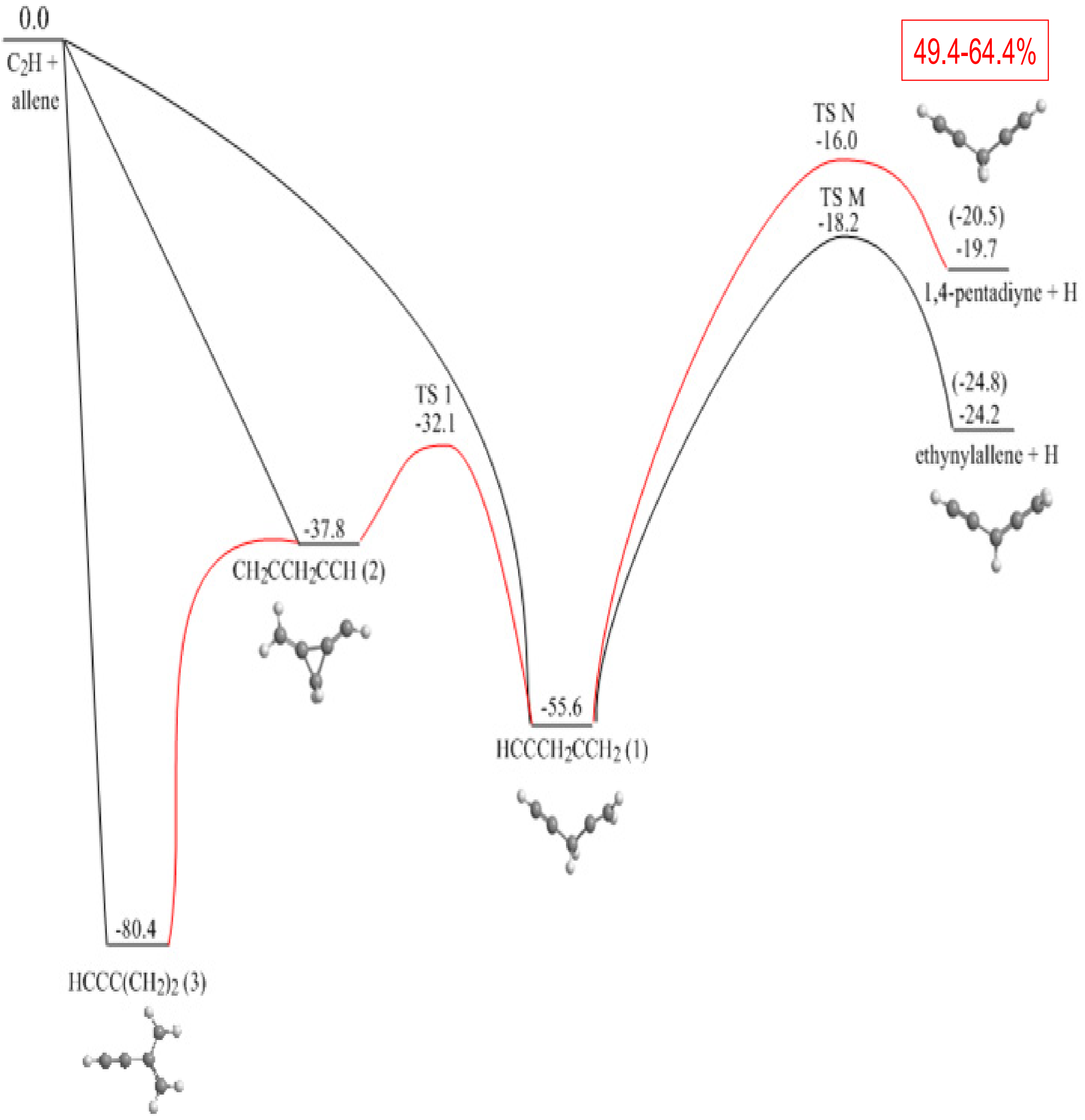
The first reaction consists of an H-loss process producing C_5H_4 products, the middle reaction consists of a CH_3-loss process producing C_4H_2 products such as diacetylene, and the third reaction consists of isothermal fragmentation leading to C_3H_3 and C_2H_2.

4.1.1. Reaction Mechanism

We first consider the reaction mechanism of the ethynyl radical with allene. The calculated potential energy diagram for this system together with the optimized structures of various intermediates and products is illustrated in Figure 4.1a.

C_2H can add to one of the terminal carbon atoms of CH_2CCH_2 to form the initial adduct (1), $HCCCH_2CCH_2$, to a double C=C bond to produce a three-member-ring intermediate (2), or to the central C to give structure (3), $HCCC(CH_2)_2$. The C_2H addition is highly exothermic, with the C_5H_5 isomers (1), (2), and (3) residing 55.6, 37.8, and 80.4 kcal/mol lower in energy than the initial reactants, respectively. We were not able to locate any transition state connecting the intermediates (1)-(3) with $C_2H + CH_2CCH_2$. All attempts to optimize a saddle point in the entrance channel converged to the separated reactants indicating that no barrier exists for the C_2H addition to allene. This is common for the reactions of ethynyl radicals with unsaturated hydrocarbons, as supported both by theoretical calculations for a variety of systems, including $C_2H + C_2H_2$,[28,29] $C_2H + C_2H_4$,[55,56] $C_2H + C_4H_2$,[30] $C_2H + C_6H_6$,[57,58] and by experimentally measured reaction rate constants, which are fast even at very low temperatures and exhibit no apparent activation energies.[59] The question which of the three adducts is preferably formed at the initial reaction step remains open. Different downhill trajectories can in principle lead from the reactants to any of the (1)-(3) isomers and dynamics calculations would be required to address this issue, which is beyond the scope of the present study. We will see however that the product branching ratios are practically independent of relative initial concentrations of the initial adducts.

The primary C_5H_5 isomers (1)-(3) can rearrange to each other relatively easily because barriers for their mutual rearrangements are much lower as compared to those for all other isomerization or dissociation processes involving (1)-(3) and the corresponding transition states lie below the $C_2H + CH_2CCH_2$ reactants. For instance, (1) transforms to (2) by C_2H shift (three-member-ring closure) via a barrier of 23.5 kcal/mol at TS 1 residing 32.1 kcal/mol lower in energy than C_2H + CH_2CCH_2. The transition state TS 2 connecting (2) and (3) was located at the B3LYP/6-311G** level, at which the ring opening barrier (including ZPE) is 3.6 kcal/mol.



Jamal, A.; Mebel, A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2606.

Figure 4.1a. Potential Energy map of the terminal and central addition of ethynyl radical to allene. Most energetically favorable routes are given.

However, at the CCSD(T)/cc-pVTZ level, the transition state energy is lower than that of (2) indicating that the cyclic intermediate is likely to be only a metastable structure and TS 1 connects (1) directly to (3), which is the most thermodynamically favorable initial adduct.

Now we consider possible fates of the intermediate (1). $HCCCH_2CCH_2$ (1) can lose hydrogen atoms from the central or terminal CH_2 groups to produce ethynylallene $HC{\equiv}C\text{-}CH{=}C{=}CH_2$ (18) and 1,4-pentadiyne $HC{\equiv}C\text{-}CH_2\text{-}C{\equiv}CH$ (20) via transition states TS M and TS N, respectively. The overall reaction energies to form the C_5H_4 products (18) and (20) from $C_2H + CH_2CCH_2$ are calculated to be -24.2 (-24.8) and -19.7 (-20.5) kcal/mol, respectively at the CCSD(T)/cc-pVTZ (CCSD(T)/CBS) levels with ZPE corrections included (see Figure 4.1b). The reaction energy to produce ethynylallene is very close to the value obtained by Stahl et al. at the B3LYP/6-311+G** level (-24.5 kcal/mol), but for 1,4-pentadiyne the deviation of the DFT result (-15.6 kcal/mol) from our supposedly more accurate value is significant. The barriers at TSs M and N are 37.4 and 39.6 kcal/mol, respectively. Relative energies of these transition states with respect to C_2H + allene are computed to be -18.2 (-19.2) kcal/mol for TS M and -16.0 (-17.3) kcal/mol for TS N, which corresponds to exit barriers (or H addition barriers to ethynylallene and 1,4-pentadiyne) of 6.0 (5.6) and 3.7 (3.2) kcal/mol at the CCSD(T)/cc-pVTZ (CCSD(T)/CBS) levels of theory. Because of their critical importance in determining the branching ratios of (18) and (20), geometries of TS M and TS N were additionally re-optimized using the QCISD/6-311G** approach. The QCISD geometries appeared to be very similar to the B3LYP optimized structures, with the only exception being the length of the breaking C-H bond, which is 0.04-0.05 Å shorter at the QCISD level as compared to the value obtained at B3LYP. Nevertheless, the CCSD(T)/CBS//QCISD/6-311G** and CCSD(T)/CBS//B3LYP/6-311G** energies of the transition states agree within 0.1 kcal/mol, indicating that the barrier heights are not sensitive to the choice of the geometry optimization method, QCISD or B3LYP.

The products (18) and (20) can also be formed from (1) via less favorable two-step routes. For instance, 1,2-H shift from the central CH_2 group in (1) to the cumulenic carbon leads to isomer (5), $HCCCHCHCH_2$, 85.4 kcal/mol below the reactants, after clearing a barrier of 39.7 kcal/mol at TS 4. (5) in turn can lose the hydrogen atom displaced in the previous step and produce ethynylallene with an exit barrier of 3.8 kcal/mol (TS D). Alternatively, 1,2-H migration from the terminal CH_2 group in (1) gives intermediate (4), $HCCCH_2CHCH$ (-53.3 kcal/mol). The barrier for this process occurring via TS 3 is higher, 48.1 kcal/mol. The shifted H atom in (4) can be eliminated at the following reaction step leading to the formation of 1,4-pentadiyne (2) via an exit barrier of 6.2 kcal/mol.

Another possible isomerization route for (1) involves 1,2-H shift from the central CH_2 to the neighboring acetylenic C atom producing structure (16), $HCCHCHCCH_2$ (-56.2 kcal/mol), via a 37.6 kcal/mol barrier at TS 5. One can see that, in terms of the barrier heights, several rearrangement/dissociation channels of (1) can be competitive.

Now we return to the intermediate (5) and consider its isomerization pathways. 1,5-H shift from the terminal CH_2 group to the opposite end of the molecule leads to the isomer (16) via a barrier of 60.6 kcal/mol (TS 22); this barrier is 4.4 kcal/mol lower than that for the H elimination via TS D. H elimination from the CH_3 group produces ethynylallene (18) via TS F with a barrier of 39.6 kcal/mol (an exit barrier of 3.1

kcal/mol). Splitting an H atom from the central CH group in (6) gives a product indicated in the figures. Moskaleva and Lin[41] have carefully investigated this segment of the C_5H_5 PES using chemically accurate G2M(RCC,MP2) and CASPT2 calculations and so we can rely on their results in our discussion here. They located three different conformers of the $CHCHCHCCH_2$ isomer, cis carbon chain – cis HCCH ((16) in the present paper and **3a** in their work), cis carbon chain – trans HCCH (**3b**), and trans carbon chain – trans HCCH (**3c**) – see Figure 4.1b.

methyldiacetylene product $HCCCCCH_3$ (21) via a lower barrier of 37.4 kcal/mol at TS E. Methyldiacetylene is the most stable C_5H_4 isomer found in the present work (and according to our previous detailed exploration of the C_5H_4 PES[ii]), as $HCCCCCH_3$ + H lie 30.1 (30.2) kcal/mol below the initial reactants according to the CCSD(T)/cc-pVTZ (CCSD(T)/CBS) calculations. This means that the exit barrier at TS E is 6.7 kcal/mol. Alternatively to the H elimination pathways, (6) can be subjected to further isomerization by hydrogen migrations. For instance, 1,2-H shift from the central CH group to the bare C atom next to the CH_3 end of the molecule forms isomer (7), $HCCCCHCH_3$ (-68.1 kcal/mol), via a 44.4 kcal/mol barrier (TS 10). 1,2-H migration from the same CH group but in the opposite direction produces intermediate (8), $HCCHCCCH_3$ (-59.6 kcal/mol), via a slightly lower barrier of 43.3 kcal/mol. Finally, (6) can undergo a three-member ring closure to form a cyclic intermediate (10) (-39.6 kcal/mol) with a much smaller barrier of 27.9 kcal/mol at TS 20. We will see in the next Section that (10) can be one of initial adducts in the ethynyl + methylacetylene reaction. The $HCCCCHCH_3$ structure (7) can lose the H atom from the vicinal CH group leading to methyldiacetylene (21) via TS G overcoming a 42.0 kcal/mol barrier (exit barrier of 4.0 kcal/mol).

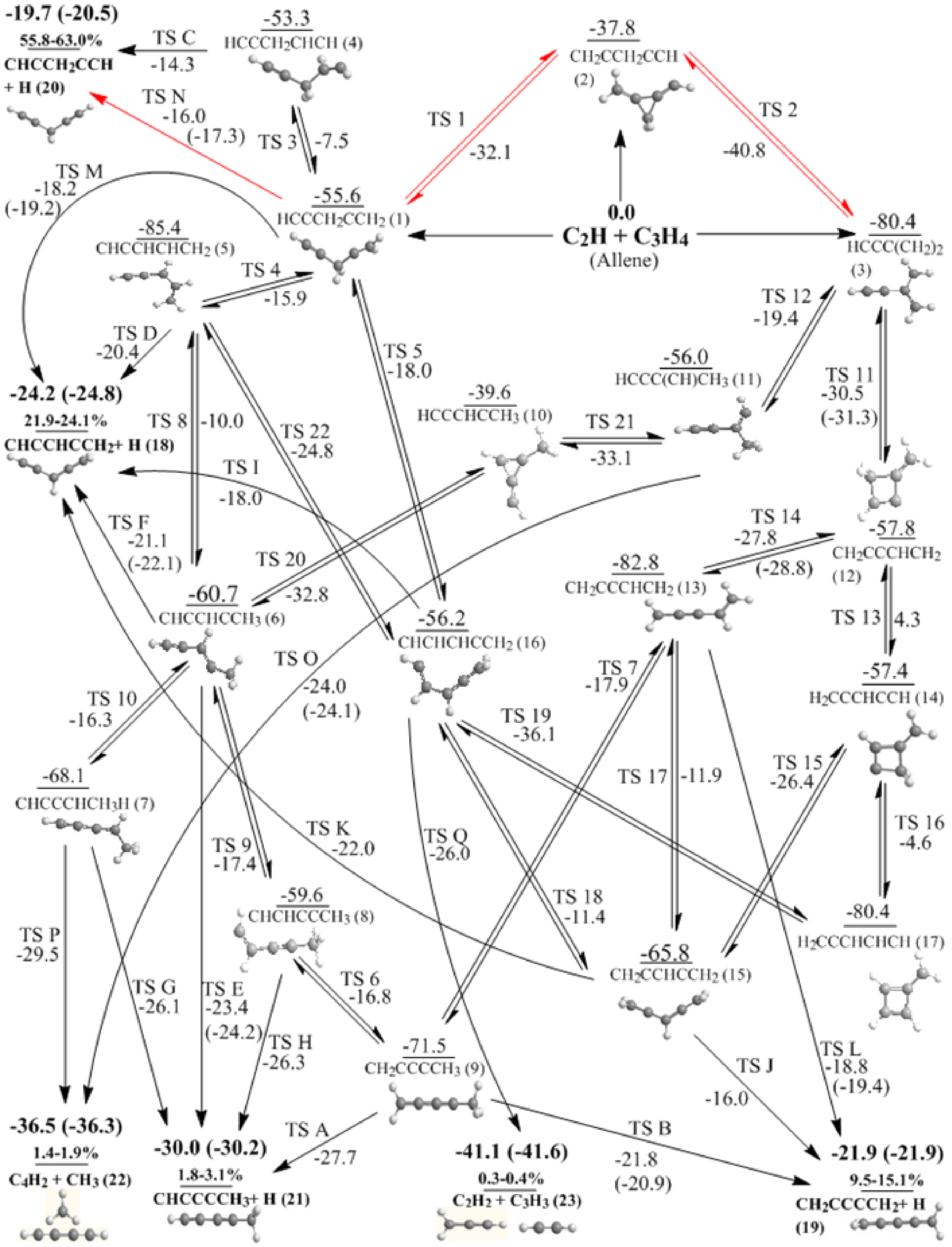


Figure 4.1b. Potential energy diagram for the C_2H + CH_2CCH_2 (allene) reaction. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products). Calculated product branching ratios (in %) are also shown

Meanwhile, (7) can also serve as a precursor for the C_4H_2 (diacetylene) + CH_3 (methyl radical) products (22), which are 36.5 (36.3) more exothermic than the C_2H + CH_2CCH_2 reactants at the CCSD(T)/-cc-pVTZ (CCSD(T)/CBS) levels. C_4H_2 + CH_3 are produced from (7) by elimination of the CH_3 group occurring via TS P with a barrier of 38.6 kcal/mol and the exit barrier of 7.0 kcal/mol. The isomer (8) can also split the H atom from the vicinal CH group producing methyldiacetylene via TS H overcoming a 33.3 kcal/mol barrier (exit barrier of 3.8 kcal/mol). Otherwise, migration of the same hydrogen to the CH end gives another intermediate (9), CH_2CCCCH_3 (-71.5 kcal/mol), over a higher barrier of 42.8 kcal/mol (TS 6). There are two possible H elimination routes from (9): H loss from the CH_2 end gives the most stable C_5H_4 methyldiacetylene product (21) via TS A with a barrier of 43.8 kcal/mol (exit barrier of 2.4 kcal/mol), whereas a hydrogen atom splitting from the CH_3 group produce a fourth feasible C_5H_4 product, D_{2d}-symmetric pentatetraene CH_2CCCCH_2 (19). The overall exothermicity of the C_2H + CH_2CCH_2 → CH_2CCCCH_2 + H reaction, which can be considered as a formal extension of the cumulene chain by a C_2 unit, is calculated to be 21.9 kcal/mol. Interestingly, the H elimination from the CH_3 group in (9) takes place via a very late TS B, with the C-H distance for the breaking bond of 5.225 Å. The corresponding exit barrier at the B3LYP/6-311G** level with ZPE is only 0.1 kcal/mol and it practically disappears at the CCSD(T)/cc-pVTZ level, indicating that the reverse H addition to a terminal CH_2 group of pentatetraene is barrierless and actually occurs without a distinct transition state.

The $CHCHCHCCH_2$ intermediate (16), which can be produced from (1) or (5), deserves a special attention because it represents a pivotal structure connecting the region of the C_5H_5 surface accessed by the C_2H + C_3H_4 reaction with the most stable C_5H_5

isomer, cyclopentadienyl radical. All three conformations have very close energies within 2 kcal/mol and are separated from each other by rotational barriers of 2-5 kcal/mol. Therefore, mutual isomerizations between the three structures should be much faster than any other process involving them and for kinetics consideration they can be regarded as a single isomer. (16) (or **3a**) can undergo a five member ring closure via a barrier of 17.0 kcal/mol to form a cyclic –CH-CH-CH-CH_2-C– intermediate **2**, which is then subjected to 1,2-H shift from CH_2 to the bare carbon producing cyclopentadienyl **1** over a 32.8 kcal/mol barrier. At the G2M(RCC,MP2) level, cyclopentadienyl is 58.9 kcal/mol more stable than $CHCHCHCCH_2$ (16) and our CCSD(T)/cc-pVTZ calculations give a very similar energy difference of 59.0 kcal/mol. The cyclopentadienyl radical lies 115.2 kcal/mol lower in energy than C_2H + CH_2CCH_2 and represents the deepest well on the C_5H_5 PES, which can be achieved from the reactants via intermediates (1) and (16). The formation of cyclopentadienyl from ethynyl radical and C_3H_4 is therefore quite feasible and at high-pressure conditions this c-C_5H_5 radical can be stabilized by collisions and thus become an important reaction product. However, at single-collision conditions of crossed molecular beams experiments or in low-pressure (< 1 mbar) Titan's stratosphere, such collisional stabilization would not occur and chemically activated c-C_5H_5 produced in the C_2H + C_3H_4 reaction would have to dissipate its energy through fragmentation. A direct H loss from c-C_5H_5 to produce c-C_5H_4 is highly unfavorable as the strength of the C-H bond in cyclopentadienyl was earlier evaluated as 113.7 kcal/mol.[iii] This result puts the c-C_5H_4 + H products only 1.4 kcal/mol below the initial C_2H + CH_2CCH_2 reactants, much higher than all other reaction products considered here. Therefore, it will be much more facile for the energized cyclopentadienyl to undergo the 1,2-H shift and ring opening resulting in the chain isomer (16) and then decompose via some of more favorable routes.

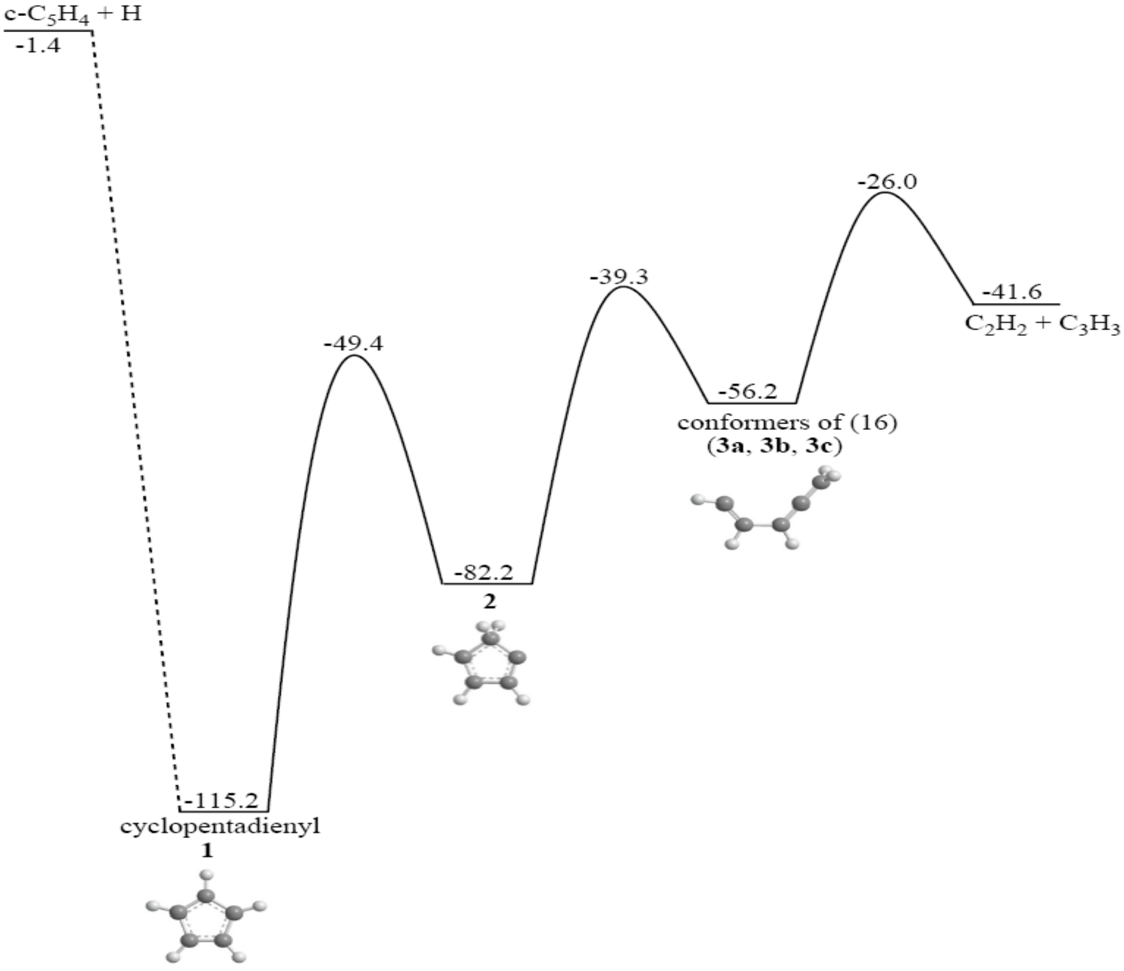


Figure 4.2c. Composite potential energy diagram for the reaction channels connecting intermediate (16) with the cyclopentadienyl radical and the C_2H_2 + C_3H_3 products based on the results of the present calculations and the data from refs.

If the collisional stabilization of c-C_5H_5 does not occur, it only serves as a kinetic dead end on the surface, which should not affect relative product yields.

Intermediate (16) can split an H atom from the middle CH group and produce ethynylallene (18) via TS I overcoming a barrier of 38.2 kcal mol (exit barrier of 6.2

kcal/mol). However, another dissociation channel is significantly more favorable energetically. A cleavage of the central CH-CH bond produces C_2H_2 (acetylene) + C_3H_3 (propargyl), the most thermodynamically stable reaction products residing 41.1 (41.6) kcal/mol below the initial reactants at the CCSD(T)/cc-pVTZ (CCSD(T)/CBS) levels of theory. This fragmentation takes place with a barrier of 30.2 kcal/mol relative to (16) via TS Q, which actually connects the products with another $CHCHCHCCH_2$ conformer 3c. The barrier for the reverse C_2H_2 + C_3H_3 reaction computed presently at CCSD(T)/cc-pVTZ + ZPE is 15.2 kcal/mol, is in close agreement with the G2M(RCC,MP2) value of 15.0 kcal/mol reported by Moskaleva and Lin.[41] Another possibility for (16) is to be subjected to 1,2-H shift to the terminal CH group giving a chain isomer (15), $CH_2CCHCCH_2$ (-65.8 kcal/mol relative to the reactants) via TS 18 and over a barrier of 44.8 kcal/mol. Next, (15) can lose a hydrogen atom from a terminal CH_2 group producing ethynylallene via TS K (barrier 43.8 kcal/mol, exit barrier 2.2 kcal/mol) or from the central CH moiety with formation of pentatetraene (19) through TS J (barrier 49.8 kcal/mol, exit barrier 5.9 kcal/mol). The remaining isomerization pathway for (16) is a four-member ring closure to a cyclic –(CH_2)C-CH-CH-CH– structure (17) (-80.4 kcal/mol) via a barrier of 20.1 kcal/mol at TS 19.

Now we can return to the fate of another initial C_2H + CH_2CCH_2 reaction adduct (3). The energetically most preferable pathway for its rearrangement is (3) → TS 2 → (2) → TS 1 → (1) with the barrier of 48.3 kcal/mol at TS 1 if we do not regard (2) as a local minimum. Otherwise, (3) can undergo a four-member ring closure to (12), –(CH_2)C-C-CH-CH_2– (-57.8 kcal/mol), via a somewhat higher barrier of 49.9 kcal/mol (TS 11). The four-member ring in (12) can then re-open along the (CH_2)C-CH_2 bond giving rise to another chain intermediate (13), $CH_2CCCHCH_2$ (-82.8 kcal/mol) overcoming a 30.0 kcal/mol barrier at TS 14. The structure (13) can dissociate to pentatetraene (19) either directly by the H loss from the vicinal CH group via TS L (barrier 64.0 kcal/mol, exit barrier 3.1 kcal/mol) or by two-step routes starting with 1,2-H migrations from the CH group to neighboring CH_2 or bare carbon atom and completed by H eliminations: (13) → TS 7 → (9) → TS B → (19) or (13) → TS 17 → (15) → TS J → (19). The H shift barriers here are rather high, 64.9 and 70.9 kcal/mol, respectively. Alternatively, the (13) → TS 7 → (9) → TS A → (21) pathway leads from (13) to the most stable C_5H_4 methyldiacetylene product. The four-member cyclic isomer (12) can be subjected to H migrations instead of the ring opening, but this reaction channel is energetically unfavorable. For instance, the H shift from CH to the H-less carbon in the ring produces (14), $–(CH_2)C\text{-}CH\text{-}C\text{-}CH_2–$ (-57.8 kcal/mol), via TS 13 and a 62.1 kcal/mol barrier. Noteworthy, TS 13 is the only transition state found in the present reaction scheme, which has its relative energy above the initial reactants (4.3 kcal/mol). In the unlikely event if the intermediate (14) is formed, it can either ring-open to (15) via TS 15 over a barrier of 31.0 kcal/mol or undergo one more 1,2-H shift from CH_2 to the bare C atom in the ring (TS 16, barrier 52.8 kcal/mol) to form the most stable four-member ring structure (17). It should be mentioned that both (15) and (17) can be produced by more competitive reaction channels passing through the intermediate (16).

Another isomerization pathway initiating from (3) involves 1,3-H migration between the two CH_2 group making one of them CH and the other CH_3 in the isomer (11). The latter resides 56.0 kcal/mol below the reactants and can be produced as an initial adduct in the CH_2 + CH_3CCH reaction. The 1,3-H shift barrier in (3) located at TS

12 is computed to be 61.0 kcal/mol, so that this is the least favorable rearrangement of (3). (11) serves a precursor for the C_4H_2 + CH_3 products, which can be formed from it by elimination of the methyl group via TS O (barrier 32.0 kcal/mol, exit barrier 12.5 kcal/mol). Alternatively, a three-member ring closure in (11) gives the cyclic structure (10) via TS 21 and a 22.9 kcal/mol barrier. We already know that (10) is connected with (6) by TS 20, and so other reaction channels can be accessed from the initial adduct (3) via the intermediates (11), (10), and (6) as well as via (12), (13), (15), and (16) or (12), (13), and (9).

The complete reaction scheme (Fig. 4.1b) is rather complex and intertwined, but at this stage we can at least summarize the most energetically preferable pathways leading to various products and specify their kinetic bottlenecks – the critical transition states with the highest relative energy with respect to the initial reactants:

C_2H + CH_2CCH_2 → [(3) →] (1) → TS M → ethynylallene + H (18)

(TS M, -18.2 kcal/mol)

→ [(3) →] (1) → TS N → 1,4-pentadiyne + H (20)

(TS N, -16.0 kcal/mol)

→ [(3) →] (1) → TS 4 → (5) → TS D → 1,4-pentadiyne + H (20)

(TS 4, -15.9 kcal/mol)

→ [(1) →] (3) → TS 11 → (12) → TS 14 → (13) → TS L →
pentatetraene + H (19) (TS L, -18.8 kcal/mol)

→ [(1) →] (3) → TS 11 → (12) → TS 14 → (13) → TS 7 → (9) →

TS B → pentatetraene + H (19) (TS 7, -17.9 kcal/mol)

→ [(1) →] (3) → TS 11 → (12) → TS 14 → (13) → TS 7 → (9) →

TS A → methyldiacetylene + H (21) (TS 7, -17.9 kcal/mol)

→ [(1) →] (3) → TS 12 → (11) → TS 21 → (10) → TS 20 → (6) →

TS 10 → (7) → TS G → methyldiacetylene + H (21) (TS 10, -16.3 kcal/mol)

→ [(1) →] (3) → TS 12 → (11) → TS O → C_4H_2 + CH_3 (22)

(TS 12, -19.4 kcal/mol)

→ [(1) →] (3) → TS 12 → (11) → TS 21 → (10) → TS 20 → (6) →

TS 10 → (7) → TS P → C_4H_2 + CH_3 (22) (TS 10, -16.3 kcal/mol)

→ [(3) →] (1) → TS 5 → (16) → TS Q → C_2H_2 + C_3H_3

(TS 5, -18.0 kcal/mol)

→ [(3) →] (1) → TS 4 → (5) → TS 22 → (16) → TS Q →

C_2H_2 + C_3H_3 (TS 4, -15.9 kcal/mol)

One can see that in principle all the product channels can be competitive, however, the consideration only in terms of the bottleneck transition states is over-simplistic.

4.1.2. Product Branching Ratios

Rate constants for individual reaction steps on the C_5H_5 PES were calculated using RRKM theory for collision energies ranging from 0 to 5.3 kcal/mol (the value used in the most recent crossed molecular beams experiments by Kaiser's group[39]) and are tabulated in Table A2 of the Appendix. Product branching ratios computed at various E_{col} are collected in Table A2 of the Appendix. The calculations indicate that 1,4-pentadiyne (20), pentatetraene (19), and ethynylallene (18) should be the most important reaction products with the branching ratio of 37/35/20 at zero collision energy and 48/25/21 at 5.3 kcal/mol. The other products give only minor contributions, about 4% for C_4H_2 + CH_3, 2-3% for methyldiacetylene, and virtually zero for acetylene + propargyl radical. The outcome is practically independent of the choice of the initial adduct in the C_2H + CH_2CCH_2 reaction, (1), (2), or (3), and therefore the reaction dynamics in the entrance channel is not expected to notably affect the relative product yields. This result owes to the fact that the isomerization barriers between the initial adducts are significantly lower than those for their other rearrangements and so the equilibration between (1), (2), and (3) occurs on a faster scale than their dissociation.

Let us now compare the present theoretical results with the available experimental measurements. Goulay et al. reported the relative yields of 45-30% 1,4-pentadiyne, 35-45% ethynylallene, and 20-25% methyldiacetylene.[35] Whereas the theory and experiment agree that 1,4-pentadiyne and ethynylallene should be the major products, the calculations underestimate the relative yield of methyldiacetylene and overestimate that of pentatetraene, which was not detected by Goulay et al. It is possible that, because the pathway on the C_5H_5 PES from (1)-(3) to $CHCCCCH_3$ is multi-step and is hindered by higher barriers, the observation of the methyldiacetylene product by Goulay et al. may be due to secondary collisions of the primary C_5H_4 products with hydrogen atoms in the slow flow reactor.

Table 4.1. Product branching ratios in the C_2H + CH_2CCH_2 (allene) reaction calculated for different collision energies and with various C_5H_5 initial adducts (1)-(3).

E_{col}, kcal/mol	Initial adduct	Product Branching Ratios (%)					
		ethynylallene (18)	pentatetraene (19)	1,4-pentadiyne (20)	methyldiacetylene (21)	C_4H_2 + CH_3 (22)	C_2H_2 + C_3H_3 (23)
0.0	(1)	19.9	24.2	49.4	4.0	2.2	0.2
	(2)						
	(3)	19.5	25.3	48.4	4.2	2.3	0.2
1.0	(1)	19.9	22.8	51.2	3.7	2.2	0.2
	(2)						
	(3)	19.4	24.1	50.0	3.9	2.3	0.2
2.0	(1)	19.8	21.4	53.0	3.4	2.2	0.2
	(2)						
	(3)	19.4	22.8	51.7	3.6	2.3	0.2
3.0	(1)	19.8	20.1	54.7	3.1	2.1	0.2
	(2)						
	(3)	19.3	21.6	53.2	3.4	2.3	0.2
4.0	(1)	19.7	18.8	56.3	2.8	2.1	0.2
	(2)						
	(3)	19.2	20.5	54.7	3.1	2.3	0.2
5.26	(1)	19.7	17.3	58.2	2.5	2.1	0.2
	(2)						
	(3)	19.1	19.2	56.4	2.8	2.3	0.2

For instance, the pathway from pentatetraene to methyldiacetylene, CH_2CCCCH_2 + H (19) → TS B → (9) → TS A → $CHCCCCH_3$ + H (21), is rather straightforward, exothermic by ~8 kcal/mol, can occur practically without a barrier, and therefore can contribute to the formation of methyldiacetylene. The fast secondary reaction of pentatetraene with H might also be responsible for the non-observation of pentatetraene in experiment. However, given that the rate constants of the primary (C_2H + CH_2CCH_2) and secondary (CH_2CCCCH_2 + H) reactions are close to each other since both of them are barrierless, the initial C_2H concentration in experiment should be comparable to the initial C_3H_4 concentration for the secondary reaction to influence the product distribution in a major way. This does not appear to be the case; a rough estimate of the C_2H concentration, based on the absorption cross section of the CF_3CCH precursor and the experimental laser intensity, gives $\sim 10^{13}$ cm^{-3}, about a factor of 50 lower than the C_3H_4 concentration, 5.1×10^{14} cm^{-3}.[39] Thus, although the H atom reaction could transfer substantial population from pentatetraene to methyldiacetylene, it seems unlikely that it could erase a 35% contribution of pentatetraene, especially as pentatetraene is the C_5H_4 isomer with the lowest ionization energy (8.67 eV) and hence easiest to see in a time-dependent photoionization efficiency spectrum, but no evidence of its formation was observed. The disagreement between theory and experiment concerning the yield of pentatetraene may be due to deviations from the statistical behavior of the reaction system; dynamics factors should favor the direct production of 1,4-pentadiyne and ethynylallene from the initial adduct (1) rather than the multistep route to pentatetraene.

Nevertheless, the hypothesis that methyldiacetylene is a secondary reaction product is supported by the fact that no evidence of methyldiacetylene was observed in the crossed molecular beams experiments under single collision conditions. Kaiser and coworkers[39] have concluded that ethynylallene is the major product of the C_2H + CH_2CCH_2 reaction, with 1,4-pentadiyne possibly contributing up to 20%. Their conclusion is mostly based on the analysis of the reaction energetics, i.e., on the comparison experimental reaction exothermicity derived from the high-energy cut-off of translational energy distribution with the product exothermicities computed at the B3LYP level of theory. For instance, the experimental reaction energy was deduced as -22.2 ± 3.6 kcal/mol, which compares more favorably with the B3LYP computed energy to produce ethynylallene (-24.4 kcal/mol) than with that to form 1,4-pentadiyne (-15.8 kcal/mol).[34] Although the present more reliable CCSD(T)/CBS calculations do not significantly alter the reaction energy for the formation of ethynylallene (-24.8 kacl/mol), they give a notably different result for 1,4-pentadiyne (-20.5 kcal/mol). The reaction energy to produce pentatetraene is -21.9 kcal/mol and therefore the computed reaction exothermicities are within the error limits of the experimental measurements for the three C_5H_4 isomers, ethynylallene, 1,4-pentadiyne, and pentatetraene, and we can conclude that the formation of these three products is consistent with the translational energy distribution observed in the crossed molecular beams experiments. The CCSD(T)/CBS calculated energy to produce methyldiacetylene (-30.2 kcal/mol) is close to the previous B3LYP value (-29.6 kcal/mol) and hence the formation of a significant amount of this product is indeed inconsistent with the experimental observations. Our computed branching ratio for methyldiacetylene, only 2-3%, corroborates the conclusion of Kaiser's group that the contribution of this product is insignificant at least under single-collision conditions. In addition, the present theoretical result that the dominant reaction products should be 1,4-pentadiyne and ethynylallene is consistent with the fact that no H atom loss was observed in the reaction of C_2H with D_4-allene;[39] if these products are formed via the most favorable reaction route, i.e., directly from the adduct (1), only D elimination can be observed. On the other hand, the most favorable pathway to pentatetraene, (3) → TS 11 → (12) → TS 14 → (13) → TS L → (19), should lead, in the case of the C_2H + CD_2CCD_2 reaction, to the CD_2CCCCD_2 + H products via H elimination at the last step, which is contradictory to the experimental finding. The comparison with experiment also indicates that the calculated branching ratio for 1,4-pentadiyne is somewhat overestimated, whereas that for ethynylallene is underestimated. We now try to understand a possible origin of this discrepancy. The dominant pathways leading to these products are (1) → TS N → (18) and (1) → TS M → (20), respectively. The barrier at TS N is 2.2 kcal/mol higher than that at TS M, however, the rate constant for the (1) → (18) reaction step appears to be faster than for (1) → (20). This is a consequence of the fact that TS N is a significantly looser transition state (with the three lowest vibrational frequencies of 47, 135, and 228 cm^{-1}) as compared to TS M (137, 224, and 299 cm^{-1}) and hence TS N has a higher number of states than TS M in the range of internal energies considered here. However, the treatment of the lowest 47 cm^{-1} frequency in TS N as a harmonic oscillator may introduce certain inaccuracy in the calculations of its number of states and therefore of the rate constant for (1) → (18). Moreover, B3LYP values for low frequencies are often uncertain and dependent on the basis set size. Systematic calculations of vibrational frequencies in the C_5H_5 system at a higher theoretical level, such as QCISD or CCSD(T), and the RRKM treatment taking into account anharmonic effects are rather expensive and cumbersome and we leave them beyond the scope of the present paper.

4.2. C_2H + Methylacetylene

Ethynyl radical addition to methylacetylene (CH_3CCH) can occur to the terminal acetylenic sp-hybridized carbon forming a linear initial adduct, to the triple-bond forming a 3-membered cyclic initial adduct, or to the central acetylenic sp-hybridized carbon forming a branched initial adduct. The overall reaction for the H-loss, CH_3-loss, and decomposition is the following, respectively:

$$C_2H + CH_3\text{-}C{\equiv}CH \rightarrow C_5H_5 \rightarrow C_5H_4 + H$$

$$C_2H + CH_3\text{-}C{\equiv}CH \rightarrow C_5H_5 \rightarrow C_4H_2 + CH_3$$

$$C_2H + CH_3\text{-}C{\equiv}CH \rightarrow C_5H_5 \rightarrow C_3H_3 + C_2H_2$$

4.2.1. Reaction Mechanism

The potential energy diagram for the C_2H + CH_3CCH reaction is shown in Figure 4.2a. Note that for consistency all relative energies in Fig. 4.2a are still given with respect to C_2H + CH_2CCH_2 and the 'zero' energy level lies at -1.0 kcal/mol, because at the present level of theory methylacetlene is computed to be 1.0 kcal/mol more stable than allene. Similarly to the allene reaction, C_2H can add to methylacetylene without barrier to form three different initial adducts. The additions to the acetylenic carbons connected to H and CH_3 give isomers (6), $HCCCHCCH_3$, and (11), $HCCC(CH)CH_3$, respectively, and the addition to the triple C≡C bond produces the cyclic intermediate (10). The calculated exothermicities of the initial reaction steps are 59.7, 55.0, and 38.6 kcal/mol for (6), (11), and (10), respectively. Again, dynamics calculations would be required to determine which of the three additions is preferable, but the barriers separating the three entrance isomers from each other are lower than those for their other isomerzation or dissociation processes. In particular, (6) can ring-close to (10) via a barrier of 27.9 kcal/mol at TS 20 and (10) can in turn ring-open to (11) overcoming a 6.5 kcal/mol barrier (TS 21). The three-member ring intermediate (10) is kinetically more stable than the cyclic adduct (2) produced in the ethynyl + allene reaction because (10) is separated from (6) and (11) by

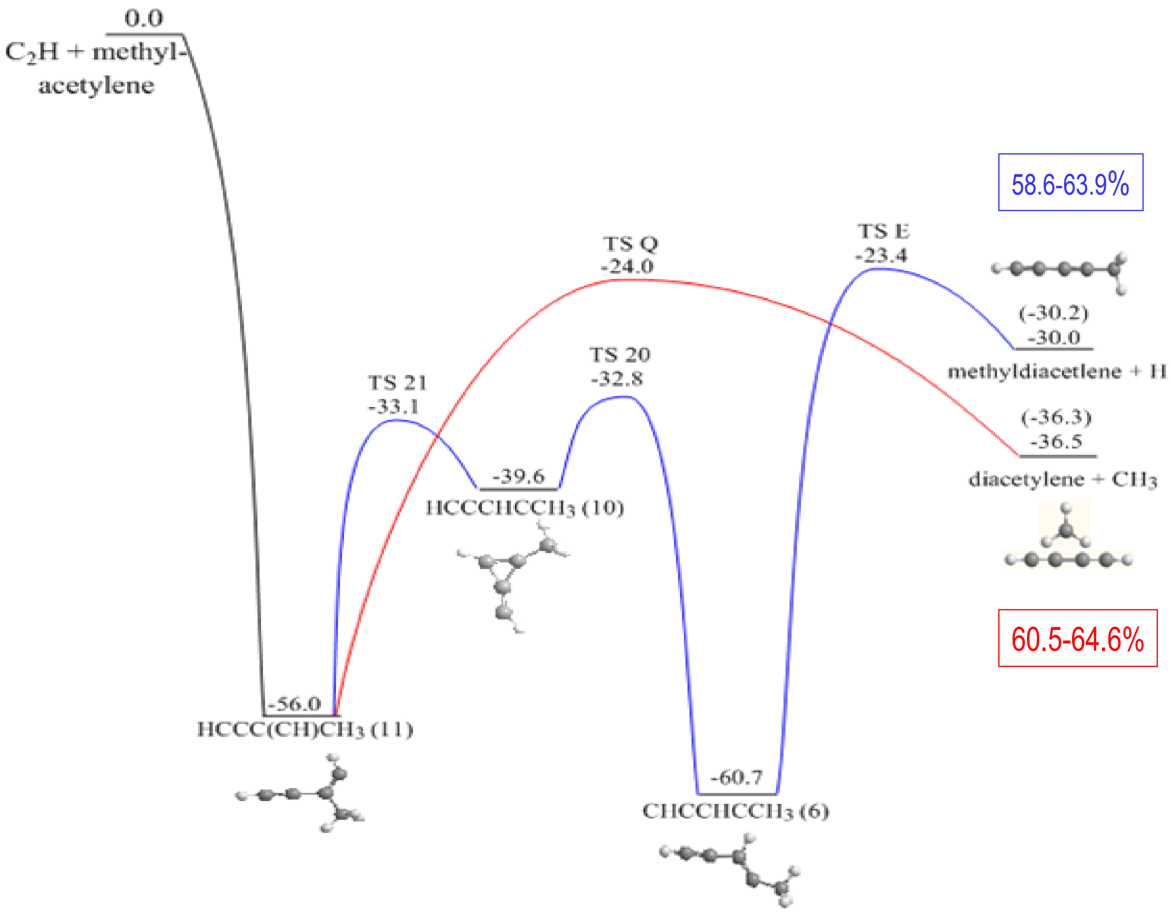


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Figure 4.2a. Potential Energy diagram of the terminal and central addition of ethynyl radical to methylacetylene.

the barriers of 6-7 kcal/mol, whereas (2) is at best a metastable structure. The intermediate (6) can directly decompose by H elimination to two C_5H_4 isomers. The third, C_5H_4 isomer, pentatetraene (19), can be produced in the three-step mechanism

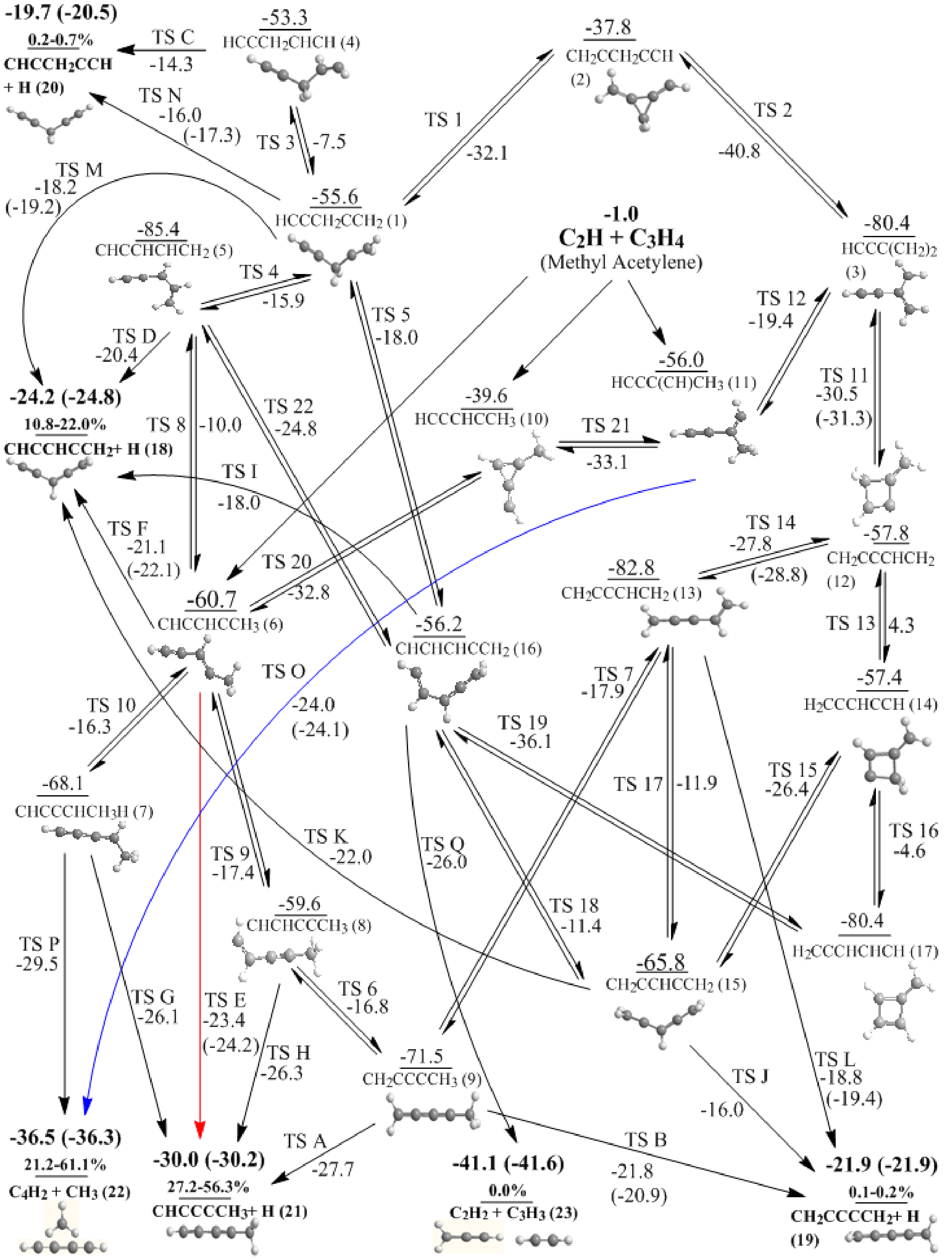


Figure 4.2b. Potential energy diagram for the C_2H + CH_3CCH (methylacetylene) reaction. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products). Calculated product branching ratios (in %) are also shown.

Which starts with (6) → TS 9 → (8) → TS 6 → (9) → TS B → (19). The pathways leading to the fourth C_5H_4 isomer 1,4-pentadiyne (19) either have to go through TS 8 with a high barrier of 50.7 kcal/mol relative to (6) or involve numerous steps (for example, via the intermediates (10), (11), (3), (2), and (1)). The formation of diacetylene + methyl can achieved in two steps, H migration to produce (7) via a barrier of 44.4 kcal/mol followed by CH_3 elimination.

On the other hand, another initial reaction adduct (11) is a more feasible precursor for the production of diacetylene because the CH_3 loss can occur directly from (11) via a relatively low barrier of 32.0 kcal/mol. Actually, besides the isomerization pathway from (11) to (6) via (10), the elimination of CH_3 is the most energetically favorable channel for the evolution of (11). Otherwise, this intermediate can rearrange to (3) by the 1,3-H shift via TS 12 and a barrier of 36.6 kcal/mol and then enter the rearrangement pathways of (3) described in the previous Section.

Here is a summary of the most energetically favorable pathways of the ethynyl + methylacetylene reaction resulting in the various products:

C_2H + CH_3CCH → (6) → TS E → methyldiacetylene + H (21) (TS E, -22.4 kcal/mol)

→ (6) → TS F → ethynylallene + H (18) (TS F, -20.1 kcal/mol)

→ (16) → TS O → C_4H_2 + CH_3 (22) (TS O, -23.0 kcal/mol)

→ (6) → TS 10 → (7) → TS P → C_4H_2 + CH_3 (22)

(TS 10, -15.3 kcal/mol)

→ (6) → TS 10 → (7) → TS G → methyldiacetylene + H (21)

(TS 10, -15.3 kcal/mol)

→ (6) → TS 9 → (8) → TS H → methyldiacetylene + H (21)

(TS 9, -16.4 kcal/mol)

→ (6) → TS 9 → (8) → TS 6 → (9) → TS A →
methyldiacetylene + H (21) (TS 6, -15.8 kcal/mol)

→ (6) → TS 9 → (8) → TS 6 → (9) → TS B → pentatetraene + H (19)

(TS 6, -15.8 kcal/mol)

→ (16) → TS 12 → (3) → TS 2 → (2) → TS 1 → (1) → TS N →
1,4-pentadiyne (20) (TS N, -15.0 kcal/mol)

→ (16) → TS 12 → (3) → TS 2 → (2) → TS 1 → (1) → TS 5 → (16)
→ TS Q → C_2H_2 + C_3H_3 (23) (TS 5, -17.0 kcal/mol)

This list is not complete as the C_2H + CH_3CCH reaction can eventually access the same C_5H_5 isomers as the reaction with allene and the other pathways described in the previous section may follow. Again, we can see that a prediction of product branching ratios would not be possible without kinetics calculations.

4.2.2. Product Branching Ratios

Calculated branching ratios for the reaction of C_2H with methylacetylene are presented in Table A2 of the Appendix. In this case, the results appeared to be sensitive to the choice of the initial reaction adduct, (6), (10), or (11), and hence to the dynamics in the entrance reaction channel. Methyldiacetylene and diacetylene + methyl appear to be the major reaction products, with ethynylallene contributing in the range of 3-7%, whereas 1,4-pentadiyne, pentatetraene, and $C_2H_2 + C_3H_3$ have negligibly small branching ratios. The relative yield of $C_4H_2 + CH_3$ is calculated to be in the range of 38-62% at zero collision energy and to slightly change to 31-66% at E_{col} = 5.3 kcal/mol. The largest amount of diacetylene + methyl is produced with (11) being the initial adduct, while the smallest amount of these products is formed if the initial adduct is (6). This result can be understood in terms of the corresponding reaction pathways on the PES.

Table 4.2. Product branching ratios in the $C_2H + CH_3CCH$ (methylacetylene) reaction calculated for different collision energies and with various C_5H_5 initial adducts (6), (10), and (11)

E_{col}, kcal/mol	Initial adduct	Product Branching Ratios (%)					
		ethynylallene (18)	pentatetraene (19)	1,4-pentadiyne (20)	methyl-diacetylene (21)	$C_4H_2 + CH_3$ (22)	$C_2H_2 + C_3H_3$ (23)
0.0	(6)	8.0	0.0	0.0	60.5	31.4	0.0
	(10)	6.4	0.0	0.0	48.5	44.9	0.0
	(11)	4.8	0.0	0.1	36.4	58.6	0.0
1.0	(6)	8.2	0.0	0.0	61.3	30.3	0.0
	(10)	6.5	0.0	0.0	48.4	44.9	0.0
	(11)	4.8	0.0	0.1	35.4	59.6	0.0
2.0	(6)	8.4	0.0	0.0	62.1	29.3	0.0
	(10)	6.6	0.0	0.0	48.4	44.9	0.0
	(11)	4.7	0.0	0.1	34.5	60.6	0.0
3.0	(6)	8.7	0.0	0.0	62.9	28.3	0.0
	(10)	6.7	0.0	0.0	48.3	44.9	0.0
	(11)	4.6	0.0	0.1	33.5	61.6	0.0
4.0	(6)	8.9	0.0	0.0	63.7	27.3	0.0
	(10)	6.7	0.0	0.1	48.2	44.9	0.0
	(11)	4.6	0.0	0.1	32.6	62.6	0.0
5.26	(6)	9.1	0.1	0.0	64.6	26.1	0.0
	(10)	6.8	0.1	0.1	48.1	44.9	0.0
	(11)	4.5	0.1	0.2	31.4	63.9	0.0

For instance, $C_4H_2 + CH_3$ can be formed by direct methyl loss from (11) and the barrier for this process at TS O is 9 kcal/mol higher than that for the isomerization of (11) to another initial adduct (10) via TS 21. The rate constant for the (11) → $C_4H_2 + CH_3$ step is only a factor of ~3 lower than that for (11) → (10) and, as a result, a full equilibration between all three possible initial adducts is not achieved before isomer (11) decomposes. On the contrary to diacetylene + methyl, the production of methyldiacetylene + H is favored by the formation of the initial adduct (6) in the entrance reaction channel. (6) can directly lose a hydrogen atom to give methyldiacetylene and, as a consequence, the relative yield of the latter is 55-61% if the reaction starts from (6), but only 30-34% when the initial adduct is (11).

The computed product branching ratios are in good agreement with the experimental results by Goulay et al.[35] (50-70% diacetylene, 43-24% methyldiacetylene, and 10-5% ethynylallene) and with the 80-90% / 20-10% ratio measured by Kaiser and coworkers[33] for the C_5H_4 products.

4.3. C_2H + 1,3-Butadiene

The C_4H_6 isomer of 1,3-butadiene consists of two π-bonds in alternating double-double-single double bond configuration. This makes 1,3-butadiene attractive for being the seed to benzene, the aromatic cyclic compound at the cornerstone of many-body structure and systems. 1,3-butadiene can have ethynyl radical additions to the terminal or central allylic carbons only due to symmetry, forming a linear and branched initial adduct, respectively. The major reaction scheme expected is the H-loss process from the C_6H_7 PES:

$$C_2H + CH_2{=}CH{=}CH{=}CH_2 \rightarrow C_6H_7 \rightarrow C_6H_6 + H$$

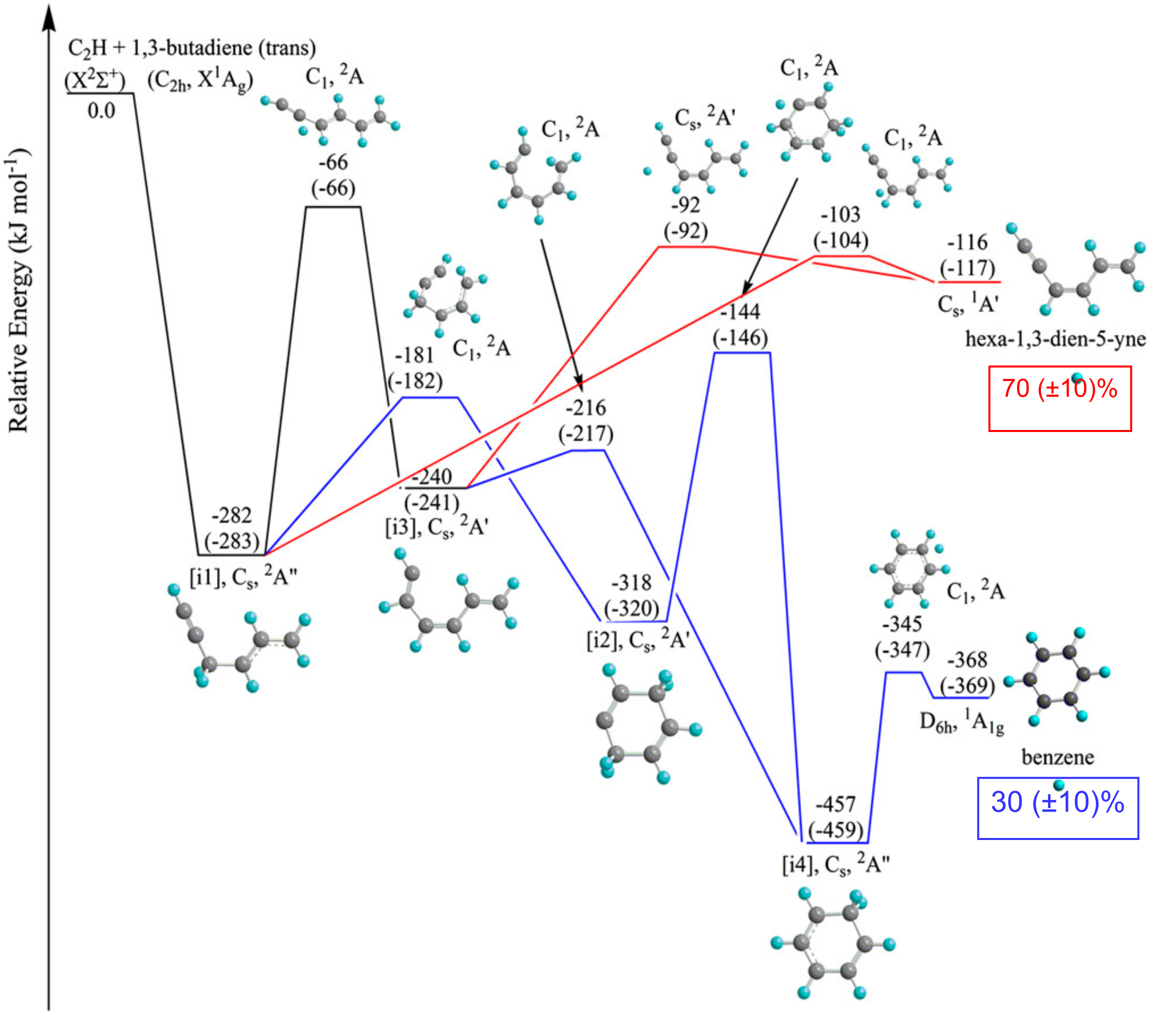
here, C_6H_6 can be a linear product or the cyclic benzene, as described below.

4.3.1. Reaction Mechanism

Our electronic structure calculations were conducted at an adequate level of theory to predict relative energies of all local minima, transition states, and products of the reactions of the ethynyl and D1-ethynyl radical with 1,3-butdiene to an accuracy of about 5 kJmol^{-1} ([iv]) (Figure 4.3a). The calculations depict that the reaction has no entrance barrier. An initial addition of the ethynylic radical center to one of the terminal carbon atoms of the 1,3-butadiene molecule leads to an acyclic reaction intermediate [i1], which is stabilized by 282 kJmol^{-1} with respect to the reactants.

This collision complex can undergo unimolecular decomposition by emitting a hydrogen atom via a tight exit transitions state forming an acyclic C_6H_6 isomer: 1,3-hexadien-5-yne. The overall reaction was computed to be exoergic by 116 kJmol^{-1}. Alternatively, intermediate [i1] can isomerize to the cyclic structure [i4].

A comparison of the height of transition states involved in the initial steps of the reaction sequence [i1] → [i2] → [i4] versus [i1] → [i3] → [i4] suggests that [i1] preferentially undergoes ring closure followed by hydrogen migration. Our statistical calculations support this conclusion and we find that over a range of collision energies from 0 kJmol^{-1} to 50 kJmol^{-1}, a large fraction near 99 % of [i1] reaches the hydrogenated benzene molecule [i4] via [i2]. Once formed, the cyclic intermediate [i4] emits a hydrogen atom via a tight exit transition state located 13 kJmol^{-1} above the separated products forming the aromatic benzene molecule.



Jones, B.; Zhang, F.; Kaiser, R.; Jamal, A.; Mebel, A.; Cordiner, M.; Charnley, S. *Proc. Nat. Acad. Sci.* **2011**, *108,* 452-457.

Figure 4.3a. Potential energy surface (PES) for the reaction of ground state ethynyl radicals [$C_2D(X^2\Sigma^+)$] with 1,3-butadiene [$CH_2CHCHCH_2(X^1A_g)$]. Relative energies are given in units of kJ mol^{-1}. Energies in parenthesis refer to the energetics of the reaction with the D1-ethynyl radicals. Also indicated are electronic wave functions and point groups of the reactants, intermediates, and transition states. Optimized Cartesian coordinates for all structures are given in Table A3 of the Appendix.

4.3.2. Product Branching Ratios

It is also important to discuss the branching ratios of the two isomers formed. This is crucial, if we transfer our findings to real, interstellar environments. Note that the crossed molecular beam experiment was conducted at a collision energy of ~ 45 kJmol^{-1}. The temperature equivalent of this collision energy of about 5,400 K is significantly higher than the average translational temperature in cold molecular clouds (10 K); it is however comparable with temperatures in the circumstellar envelopes of carbon-rich stars close to the photosphere holding up to a few 1,000 K[v]. Our computations suggest that this is the case. At the limit of zero pressure and zero collision energy, which resembles conditions on cold molecular clouds, about 40 % of the products are benzene. As the collision energy rises to 45 kJmol^{-1}, this fraction drops monotonically to about 20%. This can be rationalized in terms of the reduced lifetime (which is still higher than its rotational period) of the initial addition intermediate [i1] and hence less favorable cyclization step to [i2] versus a decomposition to form the acyclic isomer. In our experiment, we find benzene fractions of about 30 ± 10 %, in good agreement with the computational predictions. Finally, we would like to address briefly a competing reaction pathway at elevated collision energies and temperatures: the hydrogen abstraction forming acetylene and resonantly stabilized n-C_4H_5 radicals. Here, the direct hydrogen abstraction from the terminal and central carbon atoms of 1,3-butadiene involve barriers of about 4 and 7 kJmol^{-1}. Hence, in low temperature interstellar clouds, these pathways are closed, but might be relevant in interstellar environments of elevated temperatures.

4.4. C_2H + 1,2-Butadiene

The C_4H_6 isomer of 1,2-butadiene can be thought of as a methyl substituted allene. So, similar to the C_2H + allene reaction, ethynyl radical additions can occur to the terminal or central carbon in one of the following reaction schemes:

$$C_2H + CH_2{=}C{=}CHCH_3 \rightarrow C_6H_7 \rightarrow C_6H_6 + H$$

$$C_2H + CH_2{=}C{=}CHCH_3 \rightarrow C_6H_7 \rightarrow C_5H_4 + CH_3$$

$$C_2H + CH_2{=}C{=}CHCH_3 \rightarrow C_6H_7 \rightarrow C_4H_2 + C_2H_5$$

These may form various C_6H_7 intermediates and transition states via initial C_2H addition to 1,2-butadiene followed by H migrations and cyclization/decyclization processes. These intermediates can eventually decompose leading to different isomers of the C_6H_6, C_5H_4, or C_4H_2 products via H, CH_3, or C_2H_5 loss channels, respectively. Here, we present the results of *ab initio* calculations of the PES followed by RRKM computations of individual reaction rate constants and product branching ratios with the goal to understand the reaction mechanism and to predict the reaction outcome under single-collision conditions.

4.4.1 Reaction Mechanism

Our consideration of the reaction mechanism is based on *ab initio* calculations of the C_6H_7 PES. It should be noted that we targeted all possible C_6H_7 intermediates and transition states that connect them, but here we present only most favorable channels related to the C_2H + 1,2-butadiene reaction. Ethynyl radical can attack various sites in 1,2-butadiene. In particular, C_2H additions can occur to the terminal CH_2 carbon (designated C1) resulting in a linear initial adduct, and to the central carbon atoms including the second allenic carbon C2 or the third sp^2-hybridized carbon C3, producing branched initial adducts. Furthermore, C_2H additions can take place to one of the two C=C double bonds, one between C1 and C2, and the other between C2 and C3, forming three-membered cyclic intermediates. The overall potential energy maps for the terminal and central C_2H additions are depicted in Figures 4.4b and 4.4c, respectively. All relative energies of the intermediates and transition states shown on the maps and discussed hereafter are calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory. For the reactants, C_2H + 1,2-butadiene, and all of the products the values given in parentheses show CCSD(T)/CBS extrapolated results. We will see that product branching ratios depend on the initial adduct that forms, and so we first address the results separately for each initial ethynyl radical addition channel, before summarizing the general picture. Figure 4.4b and Figure 4.4c has the full potential energy map of the terminal and central addition, respectively.

Terminal addition to C1:

The potential energy diagram for the most important channels following terminal addition of ethynyl radical to 1,2-butadiene is depicted in Figure 4.4a. This barrierless addition to the C1 sp^2-carbon of $H_2C=C=CHCH_3$ results in the initial intermediate INT 1 and is exothermic by 57.0 kcal/mol. Several products can be formed directly from INT 1, including penta-1,4-diyne by CH_3-loss on the opposite terminal of INT 1 via TS 22 and a barrier of 35.4 kcal/mol as well as hexa-3,4-diene-1-yne and hexa-1,4-diyne by H eliminations via TSs 10 and 13 via barriers of 38.1 and 38.3 kcal/mol, respectively. The products, penta-1,4-diyne + CH_3, hexa-3,4-diene-1-yne + H, and hexa-1,4-diyne + H, were found to be exothermic relative to the reactants by 31.2, 25.4, and 23.8 kcal/mol, respectively, at the CCSD(T)/CBS level of theory. Alternatively to the direct fragmentation, INT 1 can undergo several (de)cyclization and/or H migration steps leading to other intermediates on the C_6H_7 surface and decompose after that. In particular, another favorable C_6H_6 product, 2-ethynyl-1,3-butadiene, exothermic by 39.1 kcal/mol, can be formed through a sequence of three reaction steps. These include ring closure, ring opening, and an H-loss processes on the following overall pathway, C_2H + 1,2-butadiene → INT 1 → INT 18 → INT 7 → 2-ethynyl-1,3-butadiene. INT 1 rearranges to the 3-membered-ring adduct INT 18 with a barrier of 24.2 kcal/mol via TS 49. This occurs by a cyclization of the added ethynyl moiety towards the C1=C2 bond of 1,2-butadiene, where the reverse process leading back to INT 1 has a barrier of 14.0 kcal/mol. Notably, INT 18 serves as the initial adduct of the central addition to the C=C bond between C1 and C2 and resides 46.8 kcal/mol below the C_2H + 1,2-butadiene reactants. INT 18 can further ring-open to produce the branched adduct INT 7, which lies 81.4 kcal/mol below the reactants. This decyclization process occurs with a low barrier of 2.1 kcal/mol via TS 50, whereas the reverse process leading back to INT 18 has a barrier of 36.7 kcal/mol. INT 7 is also the initial adduct of the central C_2H addition to the C2 atom in 1,2-butadiene. Finally, INT 7 can exhibit an H-loss from the CH_3 terminal leading to the 2-ethynyl-1,3-butadiene product with a barrier of 46.6 kcal/mol via TS

Channels include 1,3-H shift in INT1 leading to INT3 via a barrier of 40.3 kcal/mol, with subsequent dissociation of INT 3 by H elimination to hexa-1,3-diene-5-yne or hexa-4,5-diene-1-yne with barriers of 45.0 and 61.3 kcal/mol, respectively, 1,2-H shift from INT 1 to INT 5 via a barrier of 38.8 kcal/mol with two possible:

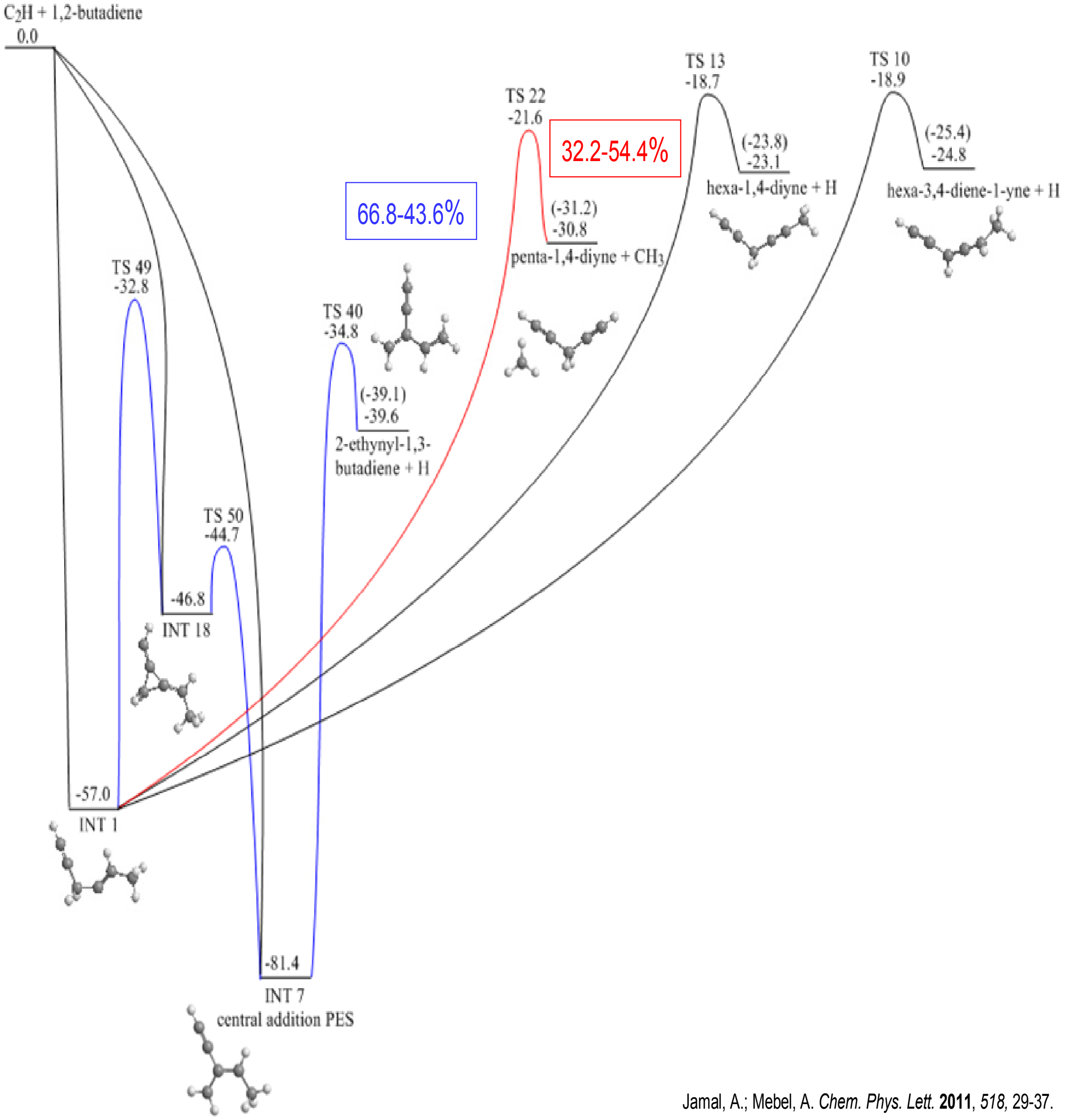


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Figure 4.4a. Composite potential energy diagram of terminal addition with the most favorable product formation channels.

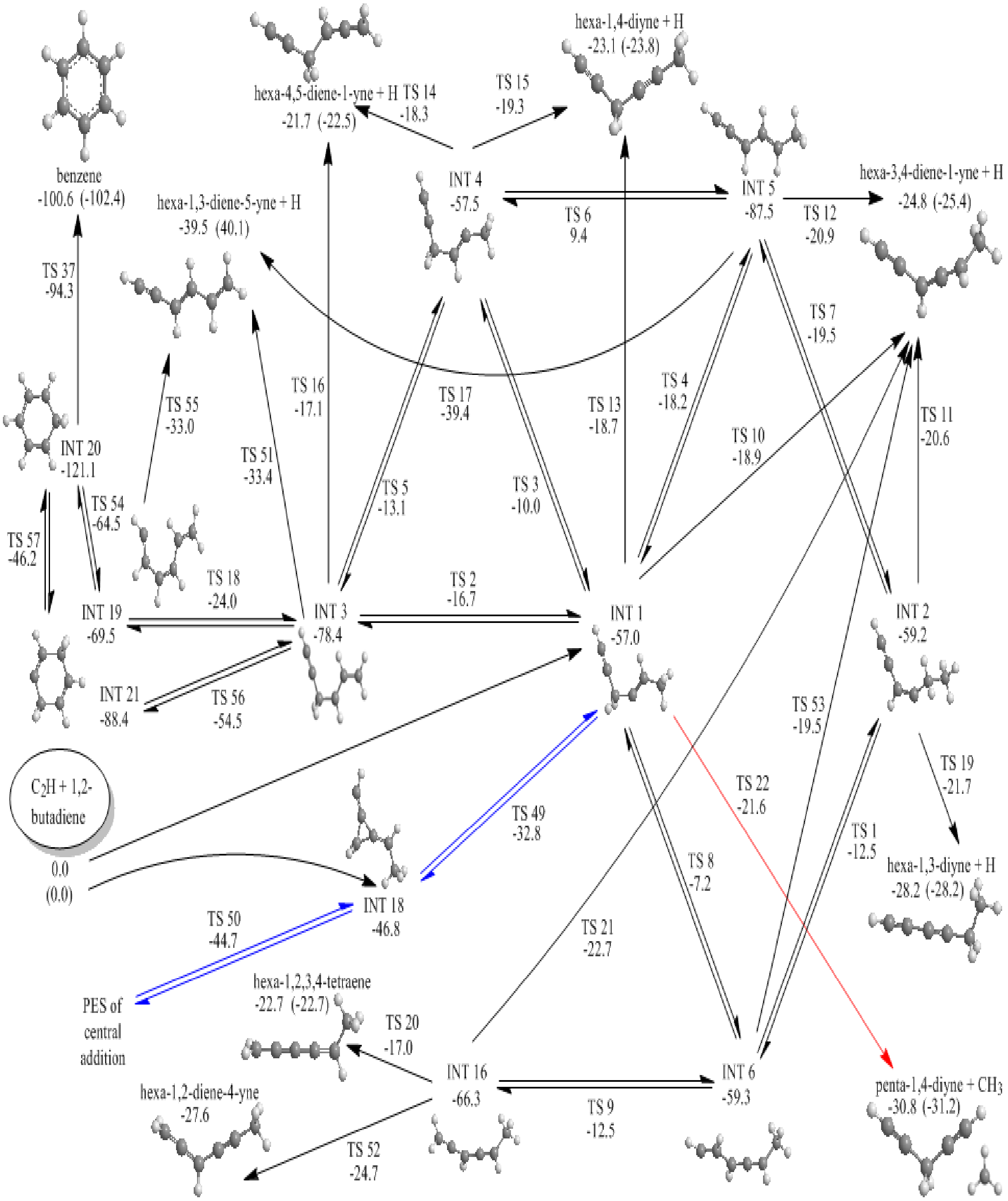

Figure 4.4b. Potential energy diagram map for the C_2H + 1,2-butadiene reaction of terminal addition forming INT 1 and central addition of the C1=C2 bond forming INT 18. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

A pathway leading to the formation of the aromatic benzene molecule is also worth mentioning. The intermediate INT 3 can cyclize to INT X via a barrier of 23.9 kcal/mol, which then undergoes an H shift to the hydrogen-less C atom in the ring followed by H elimination from the remaining CH_2 group producing the most stable C_6H_6 isomer benzene, 102.4 kcal/mol lower in energy than the C_2H + 1,2-butadiene reactants. Since INT 3 is the initial adduct in the C_2H + 1,3-butadiene reaction, this channel has been described in detail in our previous work.

For C_2H + 1,2-butadiene, this path is not likely to be accessed because the INT 1 → INT 3 rearrangement has a higher barrier than that for the CH_3 loss in INT 1 producing penta-1,4-diyne as well as those on the INT 1 → INT 18 → INT 7 → 2-ethynyl-1,3-butadiene pathway and for the H losses leading to hexa-3,4-diene-1-yne and hexa-1,4-diyne. Figure 4.4a depicts the PES of the terminal addition with the most favorable pathways and products.

Central addition to C2:

The potential energy diagram for the central addition of ethynyl radical to the C2 carbon of 1,2-butadiene is depicted in Figure 4.4d. This barrierless addition results in INT 7 and is exothermic by 81.4 kcal/mol relative to the products. The only significant product that can be formed directly from INT 7 is 2-ethynyl-1,3-butadiene, via an H loss and a barrier of 46.6 kcal/mol, with the overall C_2H + 1,2-butadiene → INT 7 → 2-ethynyl-1,3-butadiene + H reaction being 39.1 kcal/mol exothermic. Alternatively, INT 7 can isomerize to INT 1 via INT 18 by migration of the C_2H moiety over the C1=C2 bond, with highest barrier of 48.6 kcal/mol relative to INT 7.

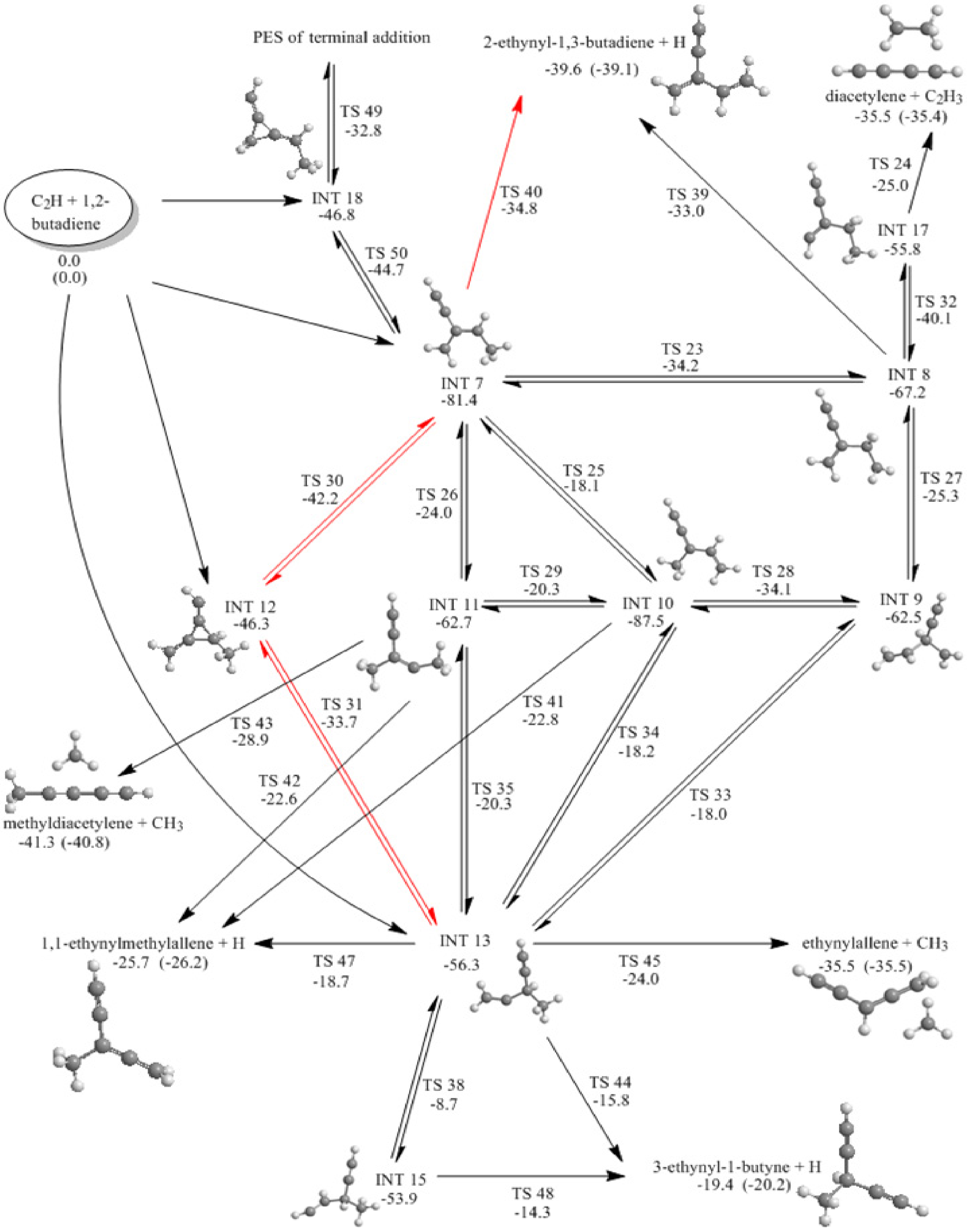

Figure 4.4c. Potential energy diagram map for the C_2H + 1,2-butadiene reaction of central additions forming INT 7 and INT 13, and central addition to the C1=C2 bond and C2=C3 bond forming INT 18 and INT 12, respectively. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

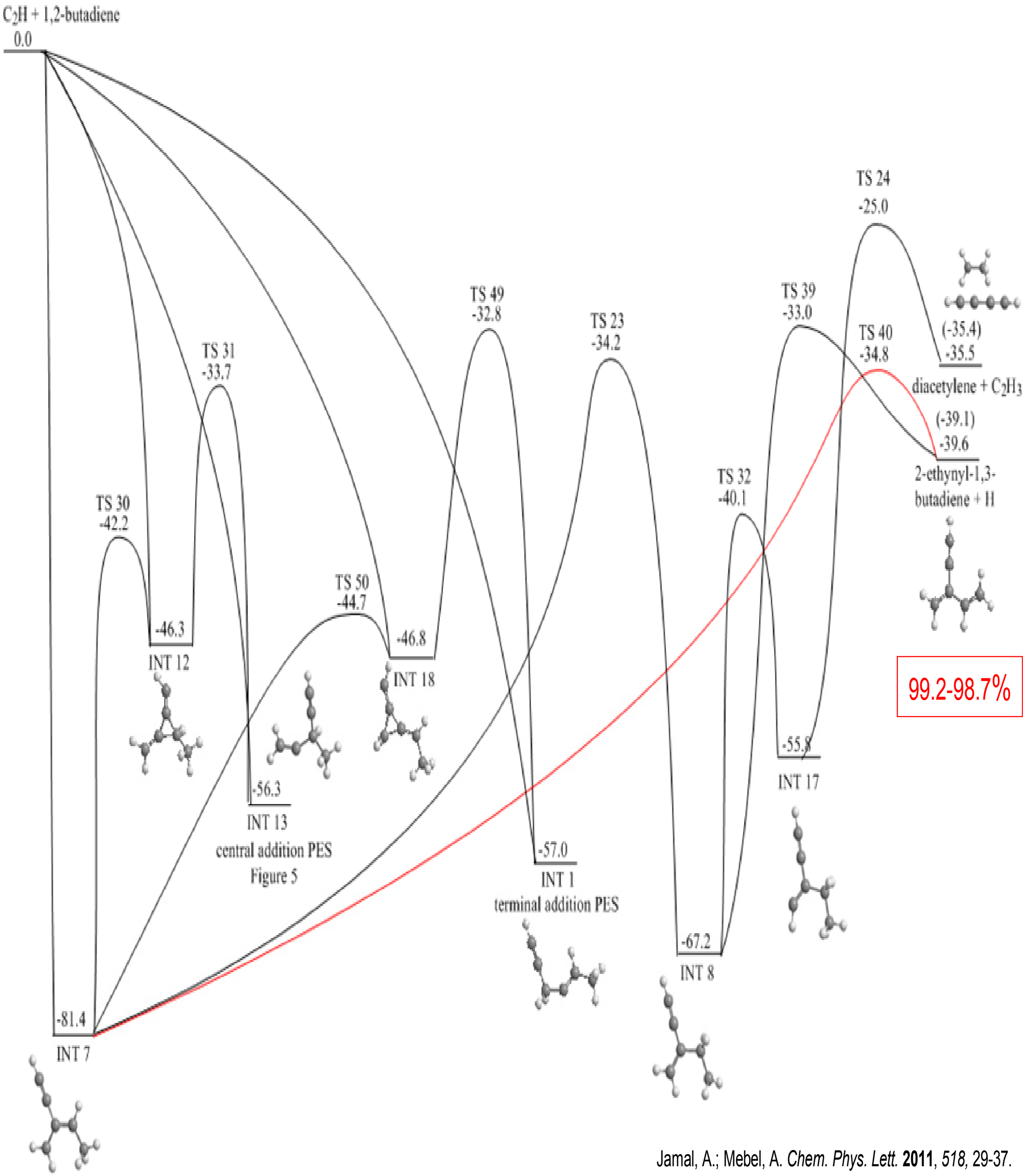

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Figure 4.4d. Composite potential energy diagram of central addition to C2 of 1,2-butadiene with the most favorable product formation channels.

This pathway connects INT 7 with the area of the surface accessed by the terminal C_2H addition to C1 and described in the previous section. The C_2H group can also migrate over C2=C3 resulting in INT 13 via a cyclic intermediate INT 12, with the critical transition state lying 47.7 kcal/mol above INT 7. INT 13 is the initial adduct for the central addition to C3 and we consider its possible transformations in the next section. The other reaction channels from INT 7 shown in Figure 4.4d are less likely to compete.

Those worth mentioning include INT 7 → TS 23 (1,2-H shift) → INT 8 → TS 39 (H loss) → 2-ethynyl-1,3-butadiene, with a critical barrier of 48.4 kcal/mol with respect to INT 7; INT 7 → TS 23 (1,2-H shift) → INT 8 → TS 32 (1,4-H shift) → TS 24 (C_2H_5 loss) → diacetylene + ethyl radical, with the highest barrier of 56.4 relatively INT 7, and INT 7 → TS 26 (1,3-H shift) → INT 11 → TS 43 (CH_3 loss) → methyldiacetylene + CH_3, where the highest in energy transition state resides 57.4 kcal/mol above INT 7. Figure 4.4d depicts the PES of the central addition to C2 with the most favorable pathways and products.

Central addition to C3:

The potential energy diagram of the central addition of ethynyl radical to the C3 carbon of 1,2-butadiene is illustrated in Figure 4.4e. In this case, the barrierless addition produces INT 13 and is 56.3 kcal/mol exothermic. From INT 13, ethynylallene can be formed by the CH_3 loss with a barrier of 32.3 kcal/mol via TS 45. Ethynylallene + CH_3 are 35.5 kcal/mol exothermic with respect to the reactants. However, a more probable dissociation mechanism of INT 13 involves its initial isomerization to INT 7 (via INT 12) followed by an H loss leading to 2-ethynyl-1,3-butadiene, C_2H + 1,2-butadiene → INT 13 → INT 12 → INT 7 → 2-ethynyl-1,3-butadiene. The highest barrier on this pathway (relative to INT 13) is found for the first step, with the corresponding transition state TS

31 residing only 22.6 kcal/mol above INT 13. The H loss channels from INT 13 producing 3-ethynyl-1,2-butadiene and 3-ethynyl-1-butyne exhibit prohibitively high barriers of 37.6 and 40.5 kcal/mol, respectively (Fig. 4.4c) and are unlikely to contribute.

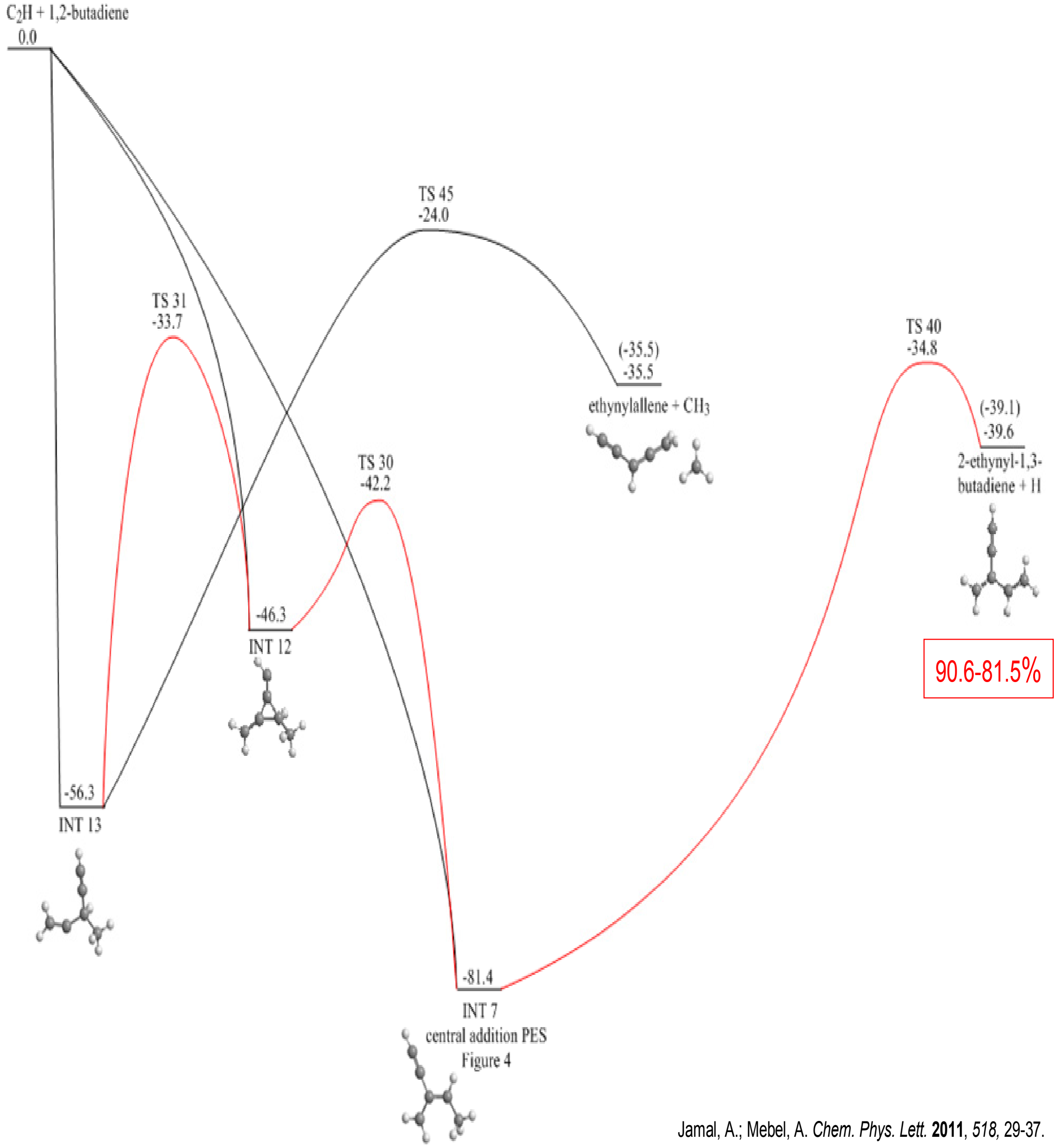

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Figure 4.4e. Composite potential energy diagram of central addition to C3 of 1,2-butadiene with the most favorable product formation channels.

Central additions to the C1=C2 and C2=C3 bonds:

This barrierless C_2H addition to C1=C2 results in the 3-membered cyclic intermediate INT 18 and is exothermic by 46.8 kcal/mol. This intermediate cannot directly decompose and would rather decyclize to INT 7 or INT 1 via 2.1 and 14.0 kcal/mol barriers, and enter the areas of the PES accessed by the ethynyl additions to C2 and C1, respectively, described in the previous sections. Clearly, the rearrangement to INT 7 is preferable and therefore, the 2-ethynyl-1,3-butadiene + H products are expected to be dominante. The ethynyl addition to C2=C3 is also predicted to occur without a barrier and to form INT 12, 46.3 kcal/mol below C_2H + 1,2-butadiene. INT 12 can ring-open to INT 7 or INT 13 overcoming respective barriers of 4.1 and 12.6 kcal/mol. As for INT 18, the isomerization of INT 12 to INT 7 is more favorable and thus we can expect the 2-ethynyl-1,3-butadiene + H products to dominate following the C_2H addition to C2=C3. Figures 4.4d and 4.4e includes the PES of the central addition to the C1=C2 bond and C2=C3 bonds, respectively, along with the most favorable pathways and products.

4.4.2. Product Branching Ratios

In this section, we move from the qualitative discussion of the reaction mechanism to a quantitative consideration of product branching ratios obtained from kinetic calculations based on RRKM rate constants. All of the rate constants for every channel are given in Table A5 of the Appendix. The calculations were carried out at collision energies of 0-7 kcal/mol assuming any one of the adducts, INT 1, INT 7, INT

12, INT 13, and INT 18, are the only initial intermediates that form. The results are also given in Table A5 of the Appendix. We then considered 20% concentrations of each initial adduct to give an insight of the formation of products when equal probabilities of any of the initial adducts are considered. The results of this equal probability product branching ratios are given in Table A6 of the Appendix.

For the case of terminal addition leading to the formation of INT 1, the two major products is the H-loss product of 2-ethynyl-1,3-butadiene + H and the CH_3-loss product of penta-1,4-diyne + CH_3. The statistical producing branching ratio at 0 kcal collision energy is 66.8% and 32.2%, respectively. The trend of increasing collision energy is a decrease on the formation of 2-ethynyl-1,3-butadiene + H and an increase on the formation of penta-1,4-diyne + CH_3. At 7 kcal collision energy, the formation of 2-ethynyl-1,3-butadiene + H drops to 43.6% while the formation of penta-1,4-diyne + CH_3 increases to 54.4%.

For the case of central addition to C2 leading to the formation of INT 7, central addition of C2=C3 leading to the formation of INT 12, and central addition to C1=C2 leading to the formation of INT 18, the major product is 2-ethynyl-1,3-butadiene + H. For the collision energies in the range of 0-7 kcal, the formation of 2-ethynyl-1,3-butadiene + H shows a decreasing trend. With the formation of INT 7, the statistical branching ratio of 2-ethynyl-1,3-butadiene + H is 99.2% to 98.7% in this collision energy range. The formation of INT 12 leads to branching ratios of 2-ethynyl-1,3-butadiene + H of 98.9% to 97.8% in this collision energy range. Finally, the formation of INT 18 has branching ratios of 98.5% to 96.8% for the 2-ethynyl-1,3-butadiene + H product.

The central addition to C3 leading to the formation of INT 13 also has 2-ethynyl-1,3-butadiene + H as a major product, however, a minor product is worth mentioning. In the 0-7 kcal collision energy range, 2-ethynyl-1,3-butadiene + H shows a branching ratio of 90.6% to 81.5%. The minor product observed in this range is the CH_3-loss product of ethynylallene + CH_3, having a branching ratio of 8.2% to 15.4%.

Finally, with 20% initial concentrations of each initial adduct of INT 1, INT 7, INT 12, INT 13, and INT 18, the 2 major products observed were the H-loss product of 2-ethynyl-1,3-butadiene + H and the CH_3-loss product of penta-1,4-diyne + CH_3. This was done to simulate an equal probability of initial adduct formation so the overall general trend of the statistical product branching ratios can be observed. Similar to the situation of terminal addition to INT 1, the 2-ethynyl-1,3-butadiene + H showed a decrease in the 0-7 kcal collision energy range, while penta-1,4-diyne + CH_3 showed an increase. The product branching ratio of 2-ethynyl-1,3-butadiene + H went from 66.8% to 43.6% in the 0-7 kcal collision energy range. The product branching ratio of penta-1,4-diyne + CH_3 went from 32.2% to 54.4% in the 0-7 kcal collision energy range.

4.5. C_2H + 1-Butyne

The C_4H_6 isomer of 1-butyne ($CHCCH_2CH_3$) is similar in moiety to the C_3H_4 isomer methylacetylene. Here, the methyl group in methylacetylene is replaced by an ethyl group, or ethylacetlyene. Similar to ethynyl radical additions to methylacetylene, terminal addition of ethynyl radical can occur to the sp-hybridized carbon forming a linear initial adduct, the triple bond forming a 3-membered cyclic initial adduct, or to the central acetylenic sp-hybridized carbon forming a branched initial adduct.

$$C_2H + HC{\equiv}CCH_2CH_3 \rightarrow C_6H_7 \rightarrow C_6H_6 + H$$

$$C_2H + HC{\equiv}CCH_2CH_3 \rightarrow C_6H_7 \rightarrow C_5H_4 + CH_3$$

$$C_2H + HC{\equiv}C\ CH_2CH_3 \rightarrow C_6H_7 \rightarrow C_4H_2 + C_2H_5$$

The C_2H + 1-butyne reaction has been studied experimentally by Soorkia et al.[100] The authors have measured rate constants in a pulsed Laval nozzle apparatus over the temperature range of 74-295 K and found the reaction to be fast, with nearly temperature-independent rate coefficients of $\sim 2.5\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, close to the collision limit. They also analyzed the reaction products by means of multiplexed photoionization mass spectrometry coupled to the tunable vacuum ultraviolet synchrotron radiation. Although benzene was not detected, somewhat unexpectedly, the authors observed less stable cyclic C_6H_6 isomers, fulvene ($18\pm5\%$) and dimethylenecyclobut-1-ene (DMCB, $32\pm8\%$). The other identified C_6H_6 products included 2-ethynyl-1,3-butadiene ($8\pm5\%$), 3,4-hexadiene-1-yne ($28\pm8\%$), and 1,3-hexadiyne ($14\pm5\%$). The C_5H_4 + CH_3 product channel was also found, with the linear C_5H_4 isomers ethynylallene and methyldiacetylene observed in a 4:1 ratio. The formation of the C_4H_2 + C_2H_5 products was recognized to be thermodynamically feasible, but could not be detected owing to experimental limitations. The authors suggested the reaction mechanism, which included isomerization pathways followed by dissociation to all observed reaction products, however, these pathways were not verified by theoretical calculations of the potential energy surface (PES).

4.5.1. Reaction Mechanism

We start our consideration with a survey of the reaction mechanism based on ab initio calculated potential energy diagrams for various reaction channels. It should be noted that in our systematic calculations we targeted all possible C_6H_7 isomers and transition states connecting them, but here we present only the most favorable channels related to the C_2H + $CHCCH_2CH_3$/CH_3CCCH_3 reactions as well as the pathways suggested by Soorkia et al.[100] to explain the experimentally observed reaction products. 1-Butyne possesses one triple C≡C bond and no double bonds and hence, C_2H addition can occur to either of the two acetylenic carbon atoms, terminal C^1 or central C^2, or to the triple bond itself. On the other hand, ethynyl addition to highly-symmetric 2-butyne can proceed to one of the middle carbon atoms or to the central triple C≡C bond.

Terminal C_2H addition to 1-butyne:

The potential energy diagram of the reaction pathway initiated by the terminal C_2H addition is illustrated in Figure 4.5a. One can see that this addition takes place without a barrier and produces the initial adduct INT A with exothermicity of 60.2 kcal/mol, as calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level. Note that this energy gain is similar to those for C_2H additions to acetylene (58.5 kcal/mol, G2M(MP2))[29] and for the terminal addition to diacetylene (63.9 kcal/mol, CCSD(T)/cc-pVTZ).[30] The most energetically favorable dissociation channel of INT A is elimination of the CH_3 group from the opposite end of the molecule producing a C_5H_4 isomer ethynylallene. The barrier for the CH_3 loss is 32.7 kcal/mol relative to INT

A and the overall exothermicity of the C_2H + 1-butyne → ethynylallene + CH_3 reaction is 36.7 (36.9) kcal/mol at the CCSD(T)/cc-pVTZ (CCSD(T)/CBS) levels, with the reverse barrier for CH_3 addition to the CH_2 terminal of ethynylallene of 9.2 kcal/mol. INT A can also lose H atoms from two different positions. H elimination from the CH_2 group gives 3,4-hexadiene-1-yne via a barrier of 37.3 kcal/mol and the products reside 29.4 kcal/mol below the initial reactants. Alternatively, INT A can split an H atom from the attacked carbon forming 1,3-hexadiyne (26.6 kcal/mol lower in energy than C_2H + 1-butyne) via a slightly higher barrier of 38.4 kcal/mol. The other two H eliminations are not likely to compete as they would produce unfavorable diradical or carbene C_6H_6 isomers $CHCCHCCH_2CH_2$ or $CCCHCCH_2CH_3$. The initial adduct can also isomerize by the 1,3-H shift from the CH_3 group leading to the $CHCCHCHCH_2CH_2$ intermediate INT B, which is 8.4 kcal/mol more stable than INT A. The H migration barrier is calculated to be 38.7 kcal/mol, slightly higher than those for the H eliminations. In turn, INT B can eliminate a hydrogen atom from the vicinal CH_2 group producing 1,3-hexadiene-5-yne via a barrier of 33.7 kcal/mol. The calculated exothermicity of the C_2H + 1-butyne → 1,3-hexadiene-5-yne reaction is 41.3 kcal/mol at the CCSD(T)/CBS level. Finally, INT A can undergo a two-step C_2H migration over the neighboring C=C bond producing a branched intermediate INT 1 (57.6 kcal/mol below the reactants) via a three-member ring intermediate INT C-T. The barriers for the isomerization of INT C-T back to INT A and forward to INT 1 are rather low, 6.8 and 6.3 kcal/mol, respectively. Note that both INT C-T and INT 1 can be produced directly from the reactants by barrierless C_2H additions to the C≡C bond and the C2 carbon of 1-butyne, respectively. No other competitive pathways starting from INT A were found.

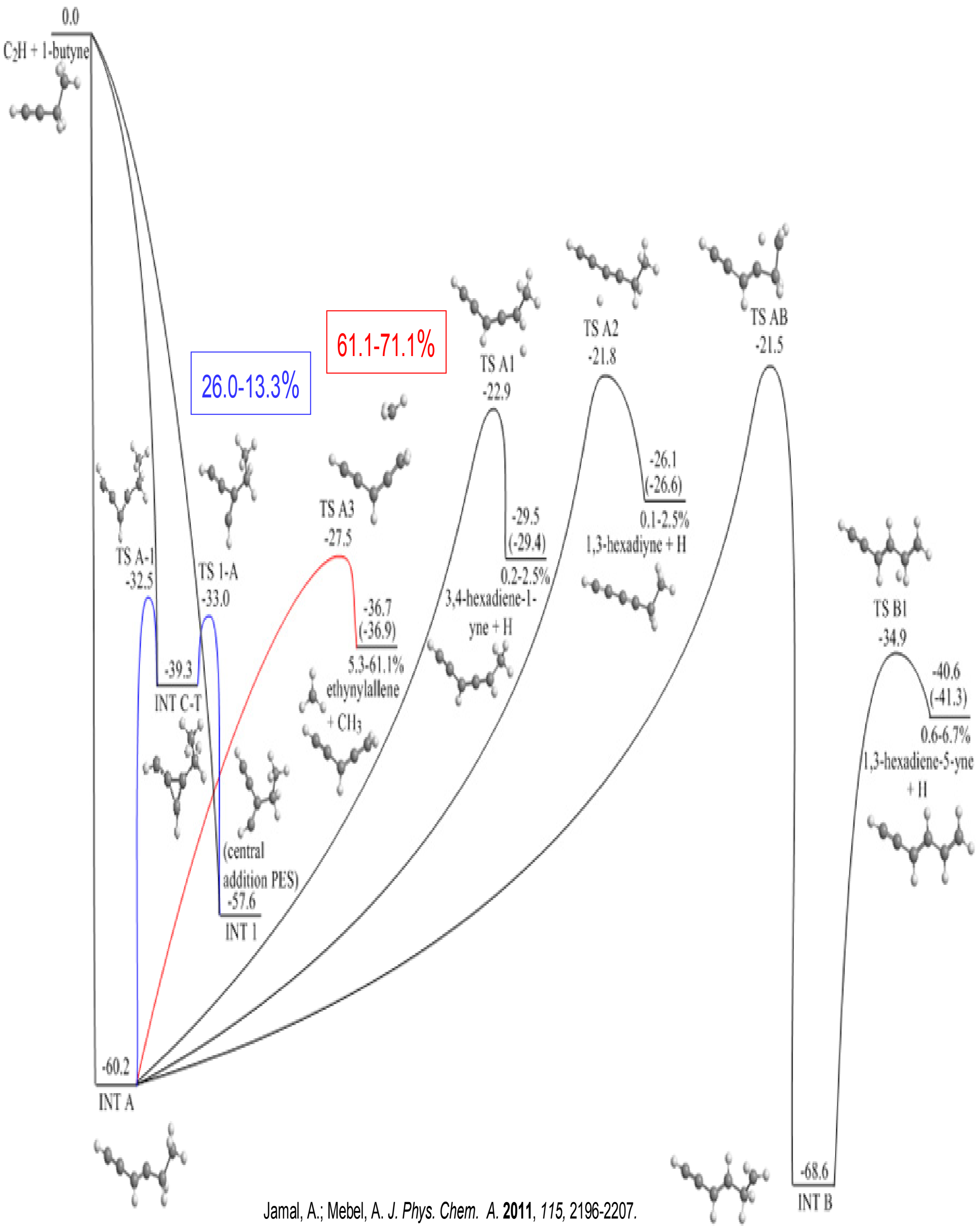

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Figure 4.5a. Potential energy diagram for the terminal C_2H addition to 1-butyne. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

Central C_2H addition to 1-butyne:

Reaction channels originating from the intermediate INT 1, which can be produced as an initial adduct of the central addition, are illustrated in Figure 4.5b. The only plausible fragmentation pathway of INT 1 is elimination of the C_2H_5 group to form diacetylene. The corresponding barrier for the C-C bond cleavage via TS 1x is 32.0 kcal/mol and the C_4H_2 + C_2H_5 products are exothermic by 36.6 kcal/mol relative to the initial reactants. Neither CH_3 nor H eliminations from INT 1 can be competitive as they would lead to higher-energy carbene or diradical products. Otherwise, INT 1 can be subjected to H migrations followed by various rearrangements and dissociations. For instance, a 1,4-H shift from the CH_3 group to CH occurring via TS 1-4 with a relatively low barrier of 16.2 kcal/mol produces another branched intermediate INT 4 (68.6 kcal/mol below the reactants). The latter can lose a hydrogen atom from the vicinal CH_2 group forming 2-ethynyl-1,3-butadiene via a 34.3 kcal/mol barrier. The overall exothermicity of the C_2H + 1-butyne → 2-ethynyl-1,3-butadiene reaction is 40.3 kcal/mol. A 1,3-H shift from the vicinal CH_2 group in INT 1 gives INT 2, which is 25.0 and 14.0 kcal/mol more stable than INT 1 and INT 4, respectively. However, the barrier for the 1,3-H migration, 35.3 kcal/mol, is much higher than that for the 1,4-H shift. A more feasible path from INT 1 to INT 2 is two-step, INT 1 → INT 4 followed by 1,2-H migration from CH_2 to CH_2 in INT 4. The highest in energy transition state along the INT 1 → INT 4 → INT 2 path, TS 2-4, lies 22.5 kcal/mol higher in energy than INT 1. INT 2 can lose a hydrogen atom from the CH_3 group producing 2-ethynyl-1,3-butadiene via TS2x located 37.0 kcal/mol below the reactants. Alternatively, another 1,3-H shift from vicinal CH to CH_2 in INT 2 gives rise to INT 3.

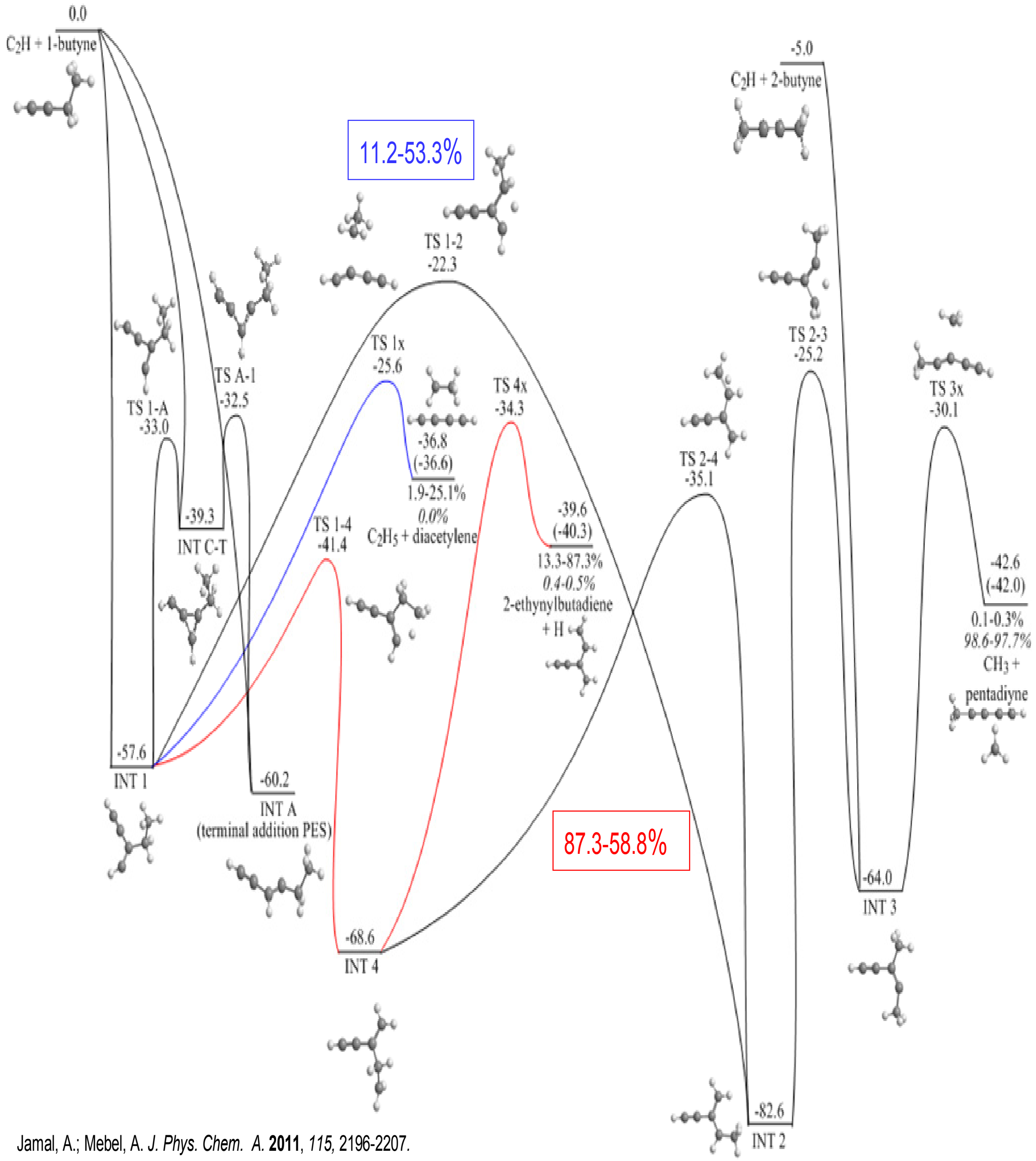

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Figure 4.5b. Potential energy diagram for the central C_2H addition to 1-butyne. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

Two dissociation channels of INT 3 are feasible, elimination of the vicinal CH_3 group producing methyldiacetylene via a barrier of 33.9 kcal/mol and a hydrogen atom loss from terminal CH_3 forming 1,1-ethynylmethylallene (3-methyl-1,2-pentadiene-4-yne) with a barrier of 40.1 kcal/mol. The overall exothermicities of the methyldiacetylene + CH_3 and 1,1-ethynylmethylallene + H channels of the C_2H + 1-butyne reaction are computed to be 42.0 and 27.4 kcal/mol, respectively. At this point, we can summarize the most important reaction pathways leading to acyclic products and originating from the initial adduct INT 1 formed as a result of central C_2H addition to 1-butyne: INT 1 → C_4H_2 + C_2H_5 (the highest in energy transition state TS 1x, -25.6 kcal/mol relative to C_2H + 1-butyne, the barrier relative to INT 1 – 32.0 kcal/mol), INT 1 → INT 4 → 2-ethynyl-1,3-butadiene (TS 4x, -34.3 kcal/mol, 23.3 kcal/mol), INT 1 → INT 4 → INT 2 → 2-ethynyl-1,3-butadiene (TS 2-4, -35.1 kcal/mol, 22.5 kcal/mol), INT 1 → INT 4 → INT 2 → INT 3 → methyldiacetylene + CH_3 (TS 2-3, -25.2, 32.4 kcal/mol), and INT 1 → INT 4 → INT 2 → INT 3 → 1,1-ethynylmethylallene + H (TS 3x2, -23.9, 33.7 kcal/mol). Note that since the INT 1 → INT C-T → INT A isomerization features the highest in energy transition state at -32.5 kcal/mol relative to C_2H + 1-butyne (25.1 kcal/mol above INT 1), the aforementioned dissociation channels have to compete with the C_2H shift and hence with the dissociation pathways of INT A described in the previous Section.

Next, we consider reaction pathways involving ring closures and leading to the formation of cyclic C_6H_6 products, fulvene and DMCB, illustrated in Figure 4.4c. INT 4 can easily undergo cyclization into a five-member ring isomer INT 5, which resides 82.4 kcal/mol below the reactants, overcoming a low barrier of 2.3 kcal/mol at TS 4-5. However, INT 5 has two adjacent CH_2 groups and one bare C atom in the ring and therefore cannot serve as an immediate precursor of fulvene. Soorkia et al.[93] suggested that a 1,3-H shift from CH_2 to the hydrogen-less carbon atom in the ring can produce a fulvene precursor.

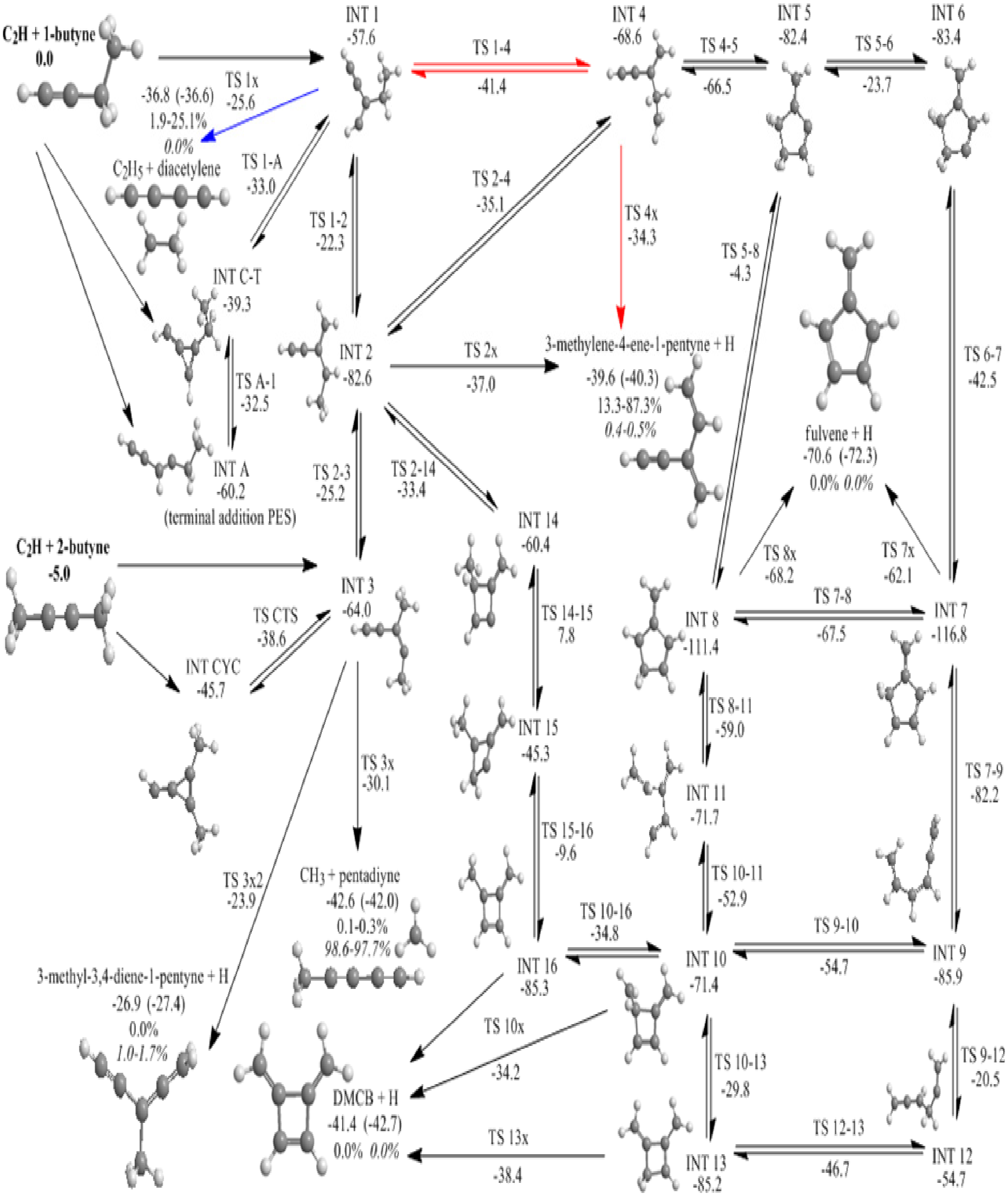


Figure 4.5c. Potential energy map of the C_2H + 1-butyne reaction including channels leading to the formation of fulvene and DMCB.

Our calculations show that this hydrogen shift can occur via TS 5-8 to form INT 8, but the corresponding barrier is very high, 78.1 kcal/mol, with the transition state lying only 4.3 kcal/mol lower in energy than the reactants. This makes the INT 5 → INT 8 rearrangement highly unlikely. Alternatively, the 1,3-H shift can be replaced by a series of 1,2-H migrations. At the first step, a hydrogen atom migrates from the CH group in the ring to the neighboring bare carbon to produce INT 6. The barrier for this process is 58.7 kcal/mol, almost 20 kcal/mol lower than that for the 1,3-H shift. Then, a second 1,2-H shift can occur from a CH_2 group in the ring to the adjacent C atom, which lost its hydrogen at the previous step. This results in the formation of INT 7 via TS 6-7, residing 116.8 and 42.5 kcal/mol below the C_2H + 1-butyne reactants, respectively. INT 7 possesses only one CH_2 group in the ring, in *ortho* position with respect to the out-of-ring CH_2 moiety, and can directly decompose to fulvene by splitting an H atom from the ring's CH_2 group. The H loss takes place via TS 7x lying 62.1 kcal/mol lower in energy than the reactants. The reverse H addition barrier to fulvene to form INT 7 is calculated to be 8.5 kcal/mol at the CCSD(T)/cc-pVTZ + ZPE level and the overall exothermicity of the C_2H + 1-butyne → fulvene + H reaction is 70.6 and 72.3 kcal/mol according to the CCST(T)/cc-pVTZ and CCSD(T)/CBS calculations including ZPE corrections. INT 7 can isomerize to INT 8 by yet another 1,2-hydrogen shift from CH_2 to CH in the ring via TS 7-8 lying at -67.5 kcal/mol below the reactants. INT 8 has the ring CH_2 group in a *meta* position and is 5.4 kcal/mol less stable than INT 7, 111.4 kcal/mol lower in energy compared to C_2H + 1-butyne. INT 8 can lose an H atom from the ring's CH_2 group to form fulvene via TS 8x, which lies 6.1 kcal/mol lower in energy than TS 7x. Thus, the H addition barrier to the *meta* C atom in fulvene to produce INT 8 is only 2.4 kcal/mol, making this process preferable as compared to the *ortho* H addition forming INT 7. In terms of the energetics, the most favorable pathway from the reactants to fulvene is the following: C_2H + 1-butyne → INT 1 → INT 4 → INT 5 → INT 6 → INT 7 → INT 8 → fulvene + H, with the highest in energy transition state TS 5-6 residing 23.7 kcal/mol below the reactants or 33.9 kcal/mol above INT 1. One can see that in terms of the height of the critical barrier this pathway is comparable with the channels leading to C_4H_2 + C_2H_5, pentadiyne + CH_3, and 1,1-ethynylmethylallene + H, but less favorable than the channels producing 2-ethynyl-1,3-butadiene. The mechanism proposed by Soorkia et al., C_2H + 1-butyne → INT 1 → INT 4 → INT 5 → INT 8 → fulvene + H, is clearly unfavorable to the high barrier for the 1,3-H shift at TS 5-8.

Several reaction channels can lead to the formation of the four-member ring DMCB product (Fig. 4.5c). For instance, INT 2 can ring-close to a four-member ring intermediate INT 14 via TS 2-14 at -33.4 kcal/mol relative to C_2H + 1-butyne. Soorkia et al. suggested that a 1,3-H migration in INT 14 can form INT 16, which is a precursor of DMCB. However, despite a careful search we were not able to locate a saddle point corresponding to such rearrangement. Instead, we found a two-step pathway connecting INT 14 and INT 16 via another intermediate INT 15. Along this path, 1,2-H migration takes place from the $C(H)(CH_3)$ group to the neighboring CH group in the ring via a high barrier of 68.2 kcal/mol, with TS 14-15 residing 7.8 kcal/mol above the initial reactants. At the second step, an H atom shifts from the CH_2 group in the ring to the adjacent bare C atom to produce INT 16 via TS 15-16 at -9.6 kcal/mol. Finally, INT 16 can lose an H atom from the out-of-ring CH_3 to form DMCB without an exit (reverse) barrier and the overall energy of the C_2H + 1-butyne → DMCB + H reaction is -42.7 kcal/mol at the

CCSD(T)/CBS + ZPE level. One can see that the C_2H + 1-butyne → INT 1 → INT 2 → INT 14 → INT 15 → INT 16 → DMCB + H channel is not expected to be competitive. Alternative pathways producing DMCB involve five-member ring intermediates. INT 7 can ring-open to a chain intermediate INT 9 via a barrier of 34.6 kcal/mol, with TS 7-9 residing 82.2 kcal/mol below the reactants. Next, INT 9 can undergo a four-member ring closure to INT 10 overcoming a barrier of 31.2 kcal/mol. INT 10 possesses a $C(H)(CH_2)$ group in one of the ring vertices and can lose the H atom from this moiety producing DMCB via a barrier of 37.2 kcal/mol. Alternatively, the INT 10 intermediate can rearrange to INT 16 via a 36.6 kcal/mol barrier and then dissociate to DCMB + H. INT 10 can be also produced from INT 8 via a two-step process. At the first step, a ring opening along the CH_2-CH bond produces INT 11 via a 52.4 kcal/mol barrier and after that a four-member ring closes to form INT 10 overcoming a lower barrier of 18.8 kcal/mol. The third DMCB precursor is INT 13. This intermediate can be formed in one step by 1,2-H shift in INT 10 via TS 10-13 lying 29.8 kcal/mol below the reactants, or by a two-step isomerization of INT 9 involving a 1,2-hydrogen migration to form INT 12 followed by a four-member ring closure, with the corresponding transition states TS 9-12 and TS 12 -13 residing 20.5 and 46.7 kcal/mol below the initial reactants, respectively. Now we can identify the most energetically favorable pathways to DMCB as the following: C_2H + 1-butyne → INT 1 → INT 4 → INT 5 → INT 6 → INT 7 → INT 9 → INT 10 (→ INT 16) → DMCB + H and C_2H + 1-butyne → INT 1 → INT 4 → INT 5 → INT 6 → INT 7 → INT 8 → INT 11 → INT 10 (→ INT 16) → DMCB + H. Similar to the fulvene pathways, the critical transition state is TS 5-6 at -23.7 kcal/mol. However, for DMCB to be produced, the rearrangements of INT 7 and INT 8 eventually leading to

INT 10 and H elimination from INT 10 have to compete with the H losses from INT 7 and INT 8, which are clearly energetically preferable.

Interestingly, according to the calculations by Senosiain and Miller[88] at the similar QCISD(T)/CBS level of theory, who studied the C_6H_7 PES in relation to the C_4H_5 + C_2H_2 reaction, a pathway exists connecting the intermediate INT 8 with the benzene + H products. Along this pathway, INT 8 undergoes a ring opening along the (CH_2)C-CH bond, then re-closes to a six-member ring c-(CH_2CHCCH_2CHCH) structure, which in turn is subjected to 1,2-H migration from CH_2 in the ring to the bare C atom to c-($CH_2CHCHCHCHCH$), and the latter loses an H atom from CH_2 to form benzene. Using the relative energies with respect to INT 8 for various species along this pathway as reported by Senosiain and Miller,[88] we can evaluate their relative energies in context of the C_2H + 1-butyne reaction as follows: INT 8 (-111.4 kcal/mol) → five-member ring opening TS (-51.1 kcal/mol) → CH_2CCHCH_2CHCH (-53.3 kcal/mol) → six-member ring closure TS (-45.3 kcal/mol) → c-(CH_2CHCCH_2CHCH) (-87.6 kcal/mol) → 1,2-H shift TS (-46.6 kcal/mol) → c-($CH_2CHCHCHCHCH$) (-121.2 kcal/mol) → H loss TS (-94.1 kcal/mol → benzene + H (-99.7 kcal/mol).

C_2H addition to the C≡C bond in 1-butyne

Ethynyl addition to the triple C≡C bond in 1-butyne forms a three-member ring intermediate INT C-T without a barrier and with exothermicity of 39.3 kcal/mol. Whereas dissociation channels of INT C-T are not expected to be competitive as they may produce only high-lying C_6H_6 or C_5H_4 isomers, this initial adduct can easily isomerize to INT 1 or INT A overcoming relatively low barriers with the corresponding transition states at -32.5 and -33.0 kcal/mol below the reactants. After that, the reaction accesses the areas of the PES described in the previous Sections.

4.5.2. Product Branching Ratios

RRKM rate constants computed at collision energies varying from 0.0 to 7.0 kcal/mol in the reactions of C_2H with 1-butyne is given in Table A8 of the Appendix. They were used in calculations of product branching ratios, which were carried out using the kinetic scheme encompassing all considered reaction channels and taking INT 1, INT C-T, and INT A (1-butyne) or INT 3 (2-butyne) as the initial chemically activated reaction intermediates. The resulting branching ratios are collected in Tables 1 and 2 for C_2H + 1-butyne and C_2H + 2-butyne, respectively. One can see that for the reaction with 1-butyne, the outcome strongly depends on the choice of the initial adduct. If the reaction starts from INT A (terminal ethynyl addition), the major reaction product (61.7-71.7%) is expected to be ethynylallene C_5H_4 formed by a direct CH_3 loss from INT A and the relative yield of ethynylallene increases with the collision energy. Ethynylallene is followed by four C_6H_6 isomers, 2-ethynyl-1,3-butadiene (26.0-13.3%), 1,3-hexadiene-5-yne (6.7-4.1%), 3,4-hexadiene-1-yne (2.5-2.1%), and 1,3-hexadiyne (1.7-3.1%), of which the last two are produced by direct H eliminations from INT A and 1,3-hexadiene-5-yne is formed via 1,3-H migration followed by an H loss, INT A → INT B → 1,3-hexadiene-5-yne.

Table 4.5. Product branching ratios in the C_2H + 1-butyne reaction calculated for different collision energies and with various C_6H_7 initial adducts INT A, INT C-T, and INT 1.

Products	Initial Adduct	**E_{col}, kcal/mol**							
		0.0	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
C_6H_6 (isomers) + H									
2-ethynyl-1,3-butadiene	INT A	26.0	24.4	22.9	17.7	16.4	15.3	14.2	13.3
	INT C-T	57.8	56.5	55.3	42.1	40.6	39.3	37.9	36.6
	INT 1	87.3	86.5	85.6	65.0	63.4	61.8	60.3	58.8
1,3-hexadiene-5-yne	INT A	6.7	7.3	7.9	3.2	3.4	3.6	3.9	4.1
	INT C-T	3.5	3.9	4.2	1.9	2.0	2.1	2.3	2.4
	INT 1	0.6	0.6	0.7	0.6	0.7	0.7	0.8	0.8
3,4-hexadiene-1-yne	INT A	2.5	2.7	2.9	1.7	1.8	1.9	2.0	2.1
	INT C-T	1.3	1.4	1.5	1.0	1.1	1.1	1.2	1.2
	INT 1	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4
1,3-hexadiyne	INT A	1.7	1.9	2.0	2.4	2.6	2.8	2.9	3.1
	INT C-T	0.9	1.0	1.1	1.4	1.5	1.6	1.7	1.8
	INT 1	0.1	0.2	0.2	0.5	0.5	0.5	0.6	0.6
1,1-ethynylmethylallene	INT A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT C-T	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fulvene	INT A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT C-T	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB	INT A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT C-T	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_5H_4 (isomers) + CH_3									
Ethynylallene	INT A	61.1	61.7	62.2	69.7	70.4	70.9	71.3	71.7
	INT C-T	32.2	32.6	32.9	40.9	41.4	41.6	41.9	42.1
	INT 1	5.3	5.4	5.5	13.9	14.0	14.0	14.1	14.1
methyldiacetylene	INT A	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1
	INT C-T	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2
	INT 1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3
C_4H_2 + C_2H_5									
Diacetylene	INT A	1.9	2.0	2.1	5.3	5.4	5.5	5.6	5.7
	INT C-T	4.2	4.6	5.0	12.5	13.3	14.1	14.9	15.6
	INT 1	6.4	7.0	7.7	19.4	20.8	22.2	23.6	25.1

Interestingly, the critical transition state TS AB for the formation of 1,3-hexadiene-5-yne is slightly higher in energy than TS A1 and TS A2 leading to 3,4-hexadiene-1-yne and 1,3-hexadiyne, but the rate constant for the INT A → INT B step appears to be higher that those for H losses from INT A. This is mostly due to the higher symmetry factor of 3 owing to the fact that any of the CH_3 group H atoms can undergo the 1,3-shift via TS AB, as the methyl group rotation is quasi-free in INT A. 2-Ethynyl-1,3-butadiene is produced via C_2H migration over the attacked C=C bond, INT A → INT C-T → INT 1, followed by H migrations to form INT 4 and INT 2 and finally, H loss from either of these two intermediates. A noticeable amount of diacetylene + C_2H_5 (1.9-5.7%) can be also produced from INT 1 following the C_2H migration steps. When the reaction starts from the central C_2H addition (from the initial adduct INT 1), the product distribution is calculated to be quite different. 2-Ethynyl-1,3-butadiene formed via the INT 1 → INT 4 (→ INT 2) → H elimination pathway is predicted to be the most important product, with the relative yield decreasing from 87.3% to 58.8%, as E_{col} rises from 0 to 7 kcal/mol. The C_4H_2 + C_2H_5 pair produced by the direct decomposition of INT 1 is the second significant product and its contribution rises from 6.4% to 25.1% with the collision energy. The third product in the order of importance is ethynylallene + CH_3 (5.3-14.1%) and it is formed after the C_2H migration, INT 1 → INT C-T → INT A, followed by decomposition of INT A. The other C_6H_6 isomers, 1,3-hexadiene-5-yne, 3,4-hexadiene-1-yne, and 1,3-hexadiyne, which can be also produced from INT A, give only minor contributions of less than 1%. According to our calculations, regardless of the initial adduct, no cyclic fulvene and DMCB C_6H_6 isomers can be formed. If the reaction starts from C_2H addition to the triple C≡C bond in 1-butyne (INT C-T), the calculated branching ratios are in the middle between those obtained with INT A and INT 1 as the initial adducts. This result follows from the fact that INT C-T is not expected to dissociate directly and rate constants for its isomerization to INT A and INT 1 are very high and close to each other; for example, their values at zero collision energy are 1.51×10^{12} and 1.62×10^{12} s^{-1}, respectively (Table A8 of the Appendix).

Summarizing, if the C_2H + 1-butyne reaction follows a statistical behavior and the three initial adducts are created with equal probabilities, the following major products are expected to be formed: 2-ethynyl-1,3-butadiene (57% at zero collision energy and 36% at 7 kcal/mol), ethynlallene + CH_3 (33% at $E_{\rm col}$ = 0 and 43% at $E_{\rm col}$ = 7 kcal/mol), and diacetylene + C_2H_5 (4% at $E_{\rm col}$ = 0 and 15% at $E_{\rm col}$ = 7 kcal/mol). The other acyclic C_6H_6 isomers are minor products, with the order of their contributions being: 1,3-hexadiene-5-yne (3.6-2.4%) > 3,4-hexadiene-1-yne (1.3-1.2%) > 1,3-hexadiyne (0.9-1.8%). The yield of 2-ethynyl-1,3-butadiene + H and C_4H_2 + C_2H_5 may be increased by 30-23% and 2-10%, respectively, if the reaction starts exclusively from INT 1 whereas in the case of terminal C_2H addition (INT A) the yield of ethynylallene + CH_3 may rise by 28-29%.

4.6. C_2H + 2-Butyne

The C_4H_6 isomer of 2-butyne (CH_3CCCH_3) can be considered as a di-methylated acetylene. Therefore, only central addition of ethynyl radical to the acetylenic sp-hybridized carbon can occur, leading to a branched initial adduct. Addition of ethynyl radical to the triple bond can also occur, but decyclization processes are usually barrierless and lead to the central addition adduct. Due to symmetry, only one of the central sp-hybridized carbon is considered. The overall reaction scheme is the following:

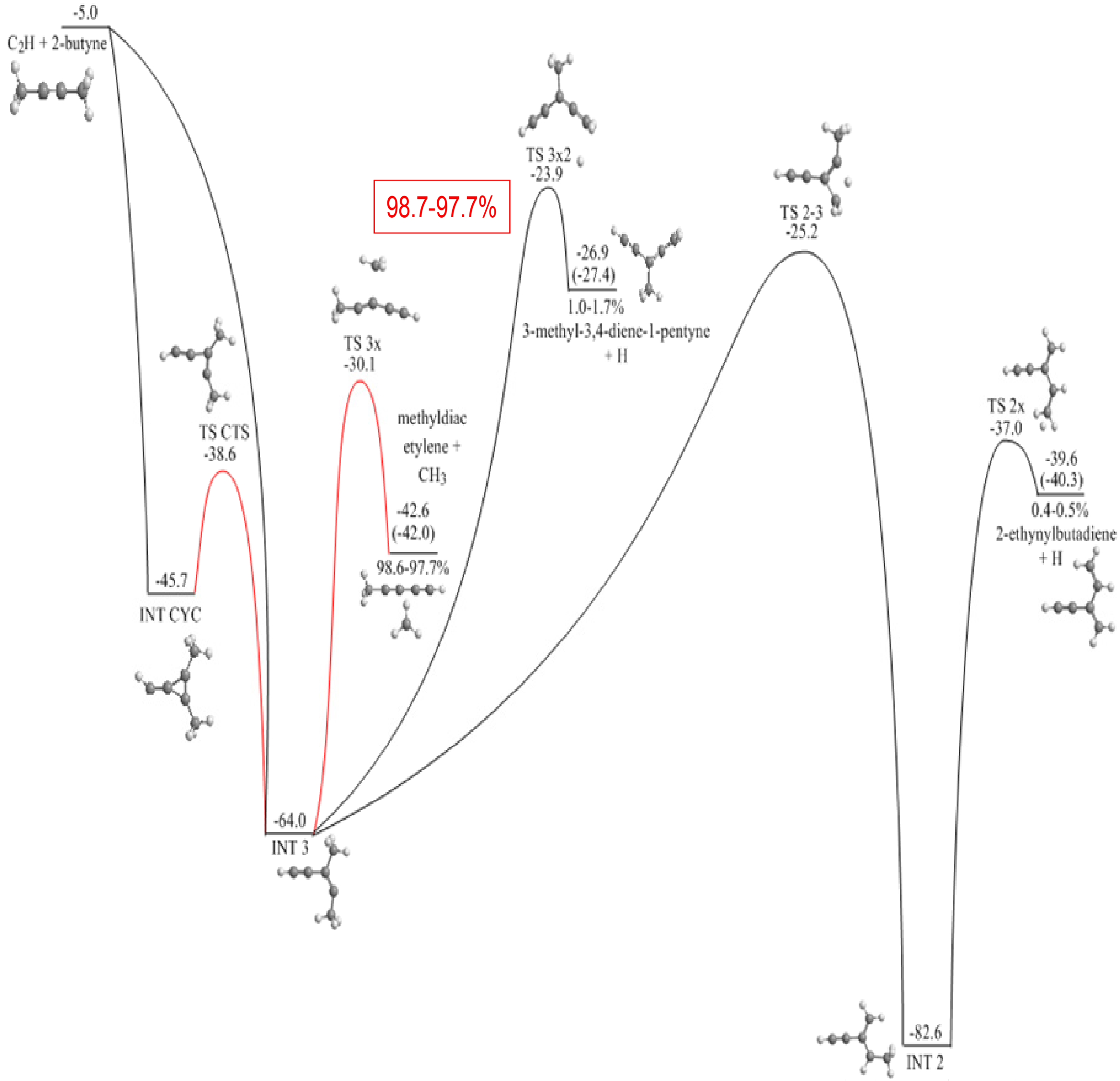
$$C_2H + CH_3C{\equiv}CCH_3 \rightarrow C_6H_7 \rightarrow C_6H_6 + H$$

$$C_2H + CH_3C{\equiv}CCH_3 \rightarrow C_6H_7 \rightarrow C_5H_4 + CH_3$$

$$C_2H + CH_3C{\equiv}CCH_3 \rightarrow C_6H_7 \rightarrow C_4H_2 + C_2H_5$$

4.6.1 Reaction Mechanism

The potential energy map shown in Fig. 4.5c also allows us to deduce the mechanism of the C_2H reaction with 2-butyne, which is shown explicitly in Figure 4.6a. 2-butyne is a highly symmetric molecule and the barrierless C_2H addition can occur to either of the two middle carbons linked by a triple bond to form the INT 3 initial adduct. The exothermicity of this addition is 59.0 kcal/mol. Next, INT 3 can either lose a hydrogen atom to form 1,1-ethynylmethylallene or CH_3 to produce methyldiacetylene via the barriers of 40.1 and 33.9 kcal/mol. The overall energies of the C_2H + 2-butyne reaction channels leading to the formation of 1,1-ethynylmethylallene + H and methyldiacetylene + CH_3 are 22.4 and 37.0 kcal/mol, respectively. Alternatively, INT 3 can isomerize to INT 2 via a 38.8 kcal/mol barrier, after which INT 2 can either decompose to 2-ethynyl-1,3-butadiene + H or pursue the other isomerization and dissociation pathways shown in Fig. 4.5c and described in the previous sections. No other reaction pathways are expected due to high barriers.



Jamal, A.; Mebel, A. *J. Phys. Chem. A.* **2011**, *115*, 2196-2207.

Figure 4.6a. Potential energy diagram for the C_2H + 2-butyne reaction. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

Barrierless C_2H addition to the C≡C bond in 2-butyne is also possible and leads to the formation of INT CYC, 40.7 kcal/mol below the reactants. However, due to symmetry, it is only sufficient to consider one entrance channel as C_2H addition can occur only on the acetylenic carbon and not the single bonded carbon.

4.6.2. Product Branching Ratios

The product distribution in the C_2H + 2-butyne reaction appears to be much simpler. Methyldiacetylene formed via the direct CH_3 loss from the initial adduct INT 3 is predicted to be the dominant product (98.6-97.7%), whereas 1,1-ethynylmethyl produced by the H loss from INT3 (1.1-1.7%) and 2-ethynyl-1,3-butadiene generated via isomerization of INT 3 to INT 2 and H elimination (0.4-0.5%) are only minor products.

Table 4.6. Product branching ratios in the C_2H + 2-butyne reaction calculated for different collision energies with INT 3 as the initial adduct.

Products	***E***							
	0.0	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
C_6H_6 (isomers) + H								
2-ethynyl-1,3-butadiene	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5
1,3-hexadiene-5-yne	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3,4-hexadiene-1-yne	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiyne	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,1-ethynylmethylallene	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
Fulvene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_5H_4 (isomers) + CH_3								
Ethynylallene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pentadiyne	98.6	98.5	98.4	98.3	98.1	98.0	97.9	97.7
C_4H_2 + C_2H_5								
Diacetylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

5. CN RADICAL REACTIONS

Cyano radical is isoelectronic to ethynyl radical, where a CH group on ethynyl has been replaced by an N atom. Cyano radical ·C≡N, similar to ethynyl radical, can add by the carbon bearing the unpaired electron ·C, resulting in the nitrogen atom at the terminal. However, a more energetically unfavorable addition can occur by the nitrogen, resulting in a terminal acetylenic carbon atom with an unpaired electron ·C. From hereon, only the addition which results in a terminal nitrogen will be considered in determining the energetically favorable reaction steps in forming a product.

5.1. CN + Diacetylene

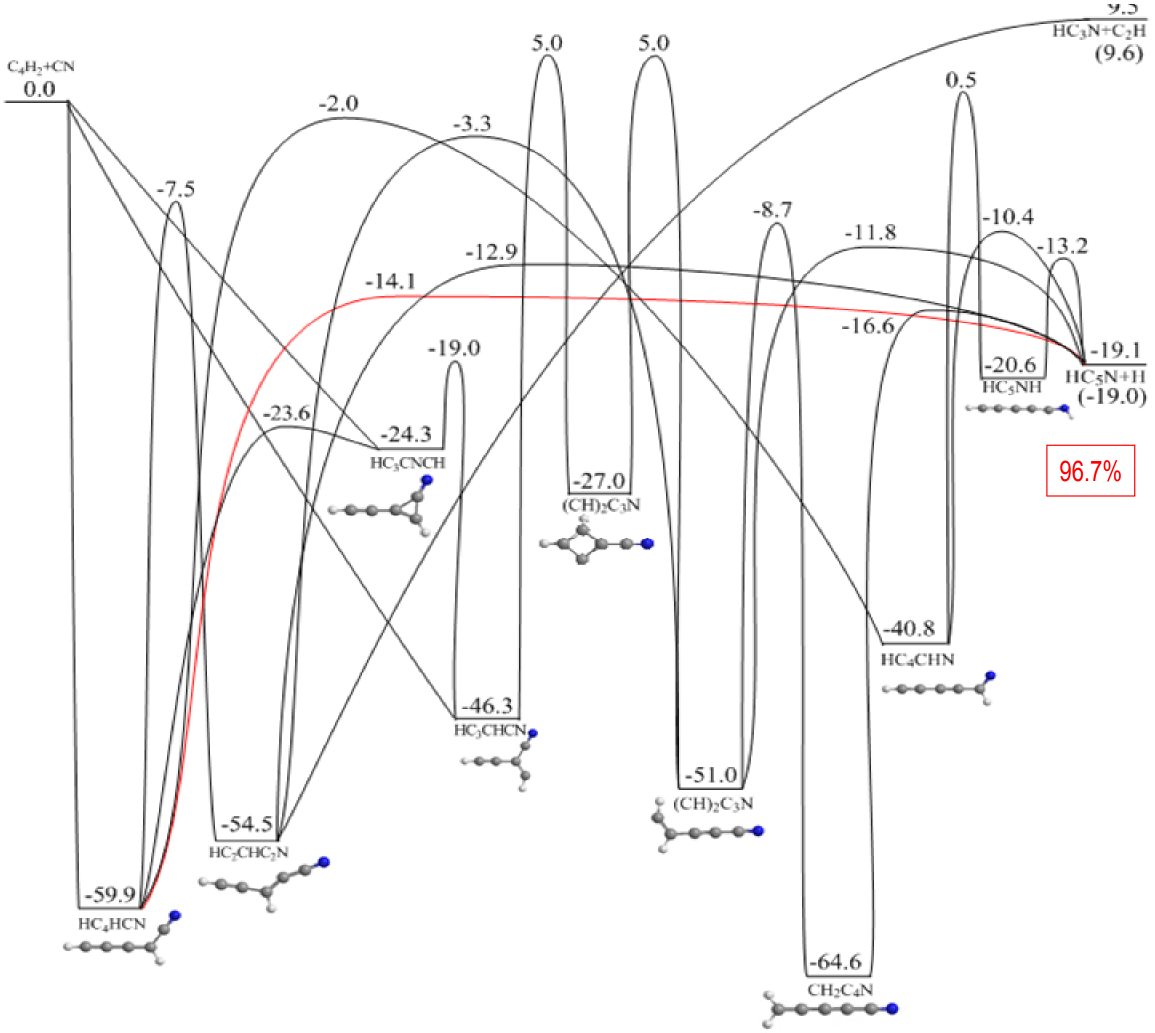
Diacetylene (C_4H_2) can be thought of as two acetylenes joined together. Therefore it contains two triple sp-bonds, and 3 possible entrance channels. The overall reaction can be summed up as an H-loss, yielding cyanodiacetylene

$$CN + C_4H_2 \rightarrow C_5H_2N \rightarrow C_5HN + H$$

The first is terminal addition of CN to the terminal carbon, forming a linear initial adduct, to the triple bond, forming a 3-membered cyclic adduct, or the first central carbon, forming an initial adduct. No other initial adducts are expected due to symmetry. Therefore, only one addition channel can be considered and all other are assumed to not play a role.

5.1.1. Reaction Mechanism

To guide the subsequent discussion of the underlying reaction mechanism and the chemical dynamics, it is useful to discuss the computed H_2C_5N surface (Fig. 5.1a). This enables us to combine the experimental with the theoretical data so that a comprehensive picture of the reaction mechanism emerges. The computations reveal the existence of two low lying closed shell HC_5N isomers: the linear, C_v symmetric cyanodiacetylene (HCCCCCN; [p1]) and isocyanodiacetylene molecules (HCCCCNC; [p2]). The cyanodiacetylene structure [p1] is lower in energy by kJ / mol 112 ± 5^{-1} compared to [p2]; this energy difference agrees nicely with a previous study computing kJ / mol 100^{-1}. Therefore, the reaction pathway to [p2] is endoergic by kJ / mol 32^{-1}. Considering our collision energy of kJ / mol 27.3^{-1}, we conclude that isomer [p2] can neither be formed in our experiments nor in low temperature extraterrestrial environments such as in planetary atmospheres and cold molecular clouds. For completeness, it should be mentioned that three more isomers exist which are energetically even less favorable: HNCCCCC [p3], CC(H)CCCN [p4], and CCCC(H)CN [p5] by 255, 209, and kJ / mol 206^{-1} compared to cyanodiacetylene, respectively. Hence, the following discussion focuses on the formation of the cyanodiacetylene molecule via the bimolecular reaction of cyano radicals with diacetylene. Three entrance channels were identified. The electron-deficient cyano radical can add without entrance barrier to the terminal carbon atom (C1), to the center carbon atom (C2), or to both C1 and C2 simultaneously. The electrophilic radical addition to the π system leads to doublet radical intermediates [1], [2], and [3], respectively. Here, isomer [1] is the lowest in energy and stabilized by kJ /



Zhang, F.; Kim, S.; Kaiser, R. Jamal, A.; Mebel, A. *J. Chem. Phys.* **2009**, *130*, 234-308.

Figure 5.1a. PES of the reaction of cyano radicals with diacetylene molecules under single collision conditions to form cyanodiacetylene in low temperature environments computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** level of theory. Relative energies are given with respect to the separated reactants in kJ / mol^{-1}. Bold numbers show relative energies of the products calculated at the CCSD(T)/CBS/B3LYP/6-311G** level. The accuracy of all energies is expected to be kJ / mol ±5^{-1}. Also shown are the structures of higher energy isomers of cyanodiacetylene. Bond angles and lengths are given in degrees and angstrom, respectively, for selected species.

mol 251^{-1} with respect to the separated reactants. The cyclic structure [2] is formally an intermediate which also can be accessed via the cyano group migration from C1 (in [1]) via [3] to the C2 atom (in [2]). All barriers involved are lower in energy than the cyano and diacetylene reactants. A C1–C2 hydrogen shift in [1] leads to a fourth H_2C_5N isomer: structure [4]. Both intermediates [1] and [4] can emit a hydrogen atom via tight exit transition states located 20 and kJ / mol 25^{-1} above the separated products, respectively. Other isomerization channels shown in Fig. 5.1a do not compete with the hydrogen loss from [1] and [4] owing to much higher barriers. For instance, consecutive 1,2-H shifts in [4] in the direction of the terminal CH group can lead to intermediates [5] and [6], whereas 1,2-hydrogen migrations in [1] toward the nitrogen atom can produce [7] and then [8]. All isomers [5]–[8] can serve as precursors for the formation of the main reaction product, cycanodiacetylene, by hydrogen elimination; however, none of them are likely to be accessed in this reaction because, at each step, the hydrogen loss barrier is significantly lower than the barrier for the hydrogen shift. Isomer [3] could rearrange to [5] via a four-member ring intermediate [9] by ring closure–ring opening processes, but the corresponding transition states reside kJ / mol 21^{-1} above the initial reactants, rendering such rearrangement uncompetitive. Note finally that the cyano versus ethynyl exchange and the hydrogen abstraction channel were found to be endoergic by 40 and kJ / mol 33^{-1}.

5.2. CN + 1,2-butadiene

The CN radical addition to 1,2-butadiene consists of similar overall reaction schemes as in the case of C_2H radical addition to 1,2-butadiene. The overall product forming schemes can be an summarized as either an H-loss, CH_3-loss, or a C_2H_5-loss, respectively:

$$CN + CH_2{=}C{=}CHCH_3 \rightarrow C_5H_6N \rightarrow C_5H_5N + H$$

$$CN + CH_2{=}C{=}CHCH_3 \rightarrow C_5H_6N \rightarrow C_4H_3N + CH_3$$

$$CN + CH_2{=}C{=}CHCH_3 \rightarrow C_5H_6N \rightarrow C_3HN + C_2H_5$$

5.2.1. Reaction Mechanism

The barrierless addition to the C^1 sp^2-carbon of 1,2-butadiene results in the initial adduct INT D1 and is exothermic by 52.0 kcal/mol relative to the reactants energy. The CH_3-loss product that can be formed directly from INT D1 via TS D1-1 and a barrier of 34.9 kcal/mol is 1-cyano-prop-3-yne. This product is exothermic by 25.8 (26.2) kcal/mol relative to the reactants. Alternatively, the H-loss product 2-cyano-1,3-butadiene can be formed through a sequence of three reaction steps. These include ring closure forming INT D2, then ring opening to form INT E1, and finally elimination of the H atom from the terminal CH_3 group of INT E1.

The overall pathway is CN + 1,2-butadiene → INT D1 → INT D2 → INT E1 → 2-cyano-1,3-butadiene + H exothermic by 30.0 (33.7) kcal/mol. This pathway begins with INT D1 rearranging to the 3-membered-ring adduct INT D2 via a barrier of 27.3 kcal/mol at TS D1-D2. This occurs by a cyclization of the added cyano moiety towards the $C^1{=}C^2$ bond of 1,2-butadiene, where the reverse process leading back to INT D1 has a barrier of 7.6 kcal/mol. However, the decyclization process of INT D2 to form INT E1 appears to occur barrierlessly, because a small barrier found at B3LYP disappears at the CCSD(T) level of theory. Thus, we can assume that INT D2 is likely to be only a

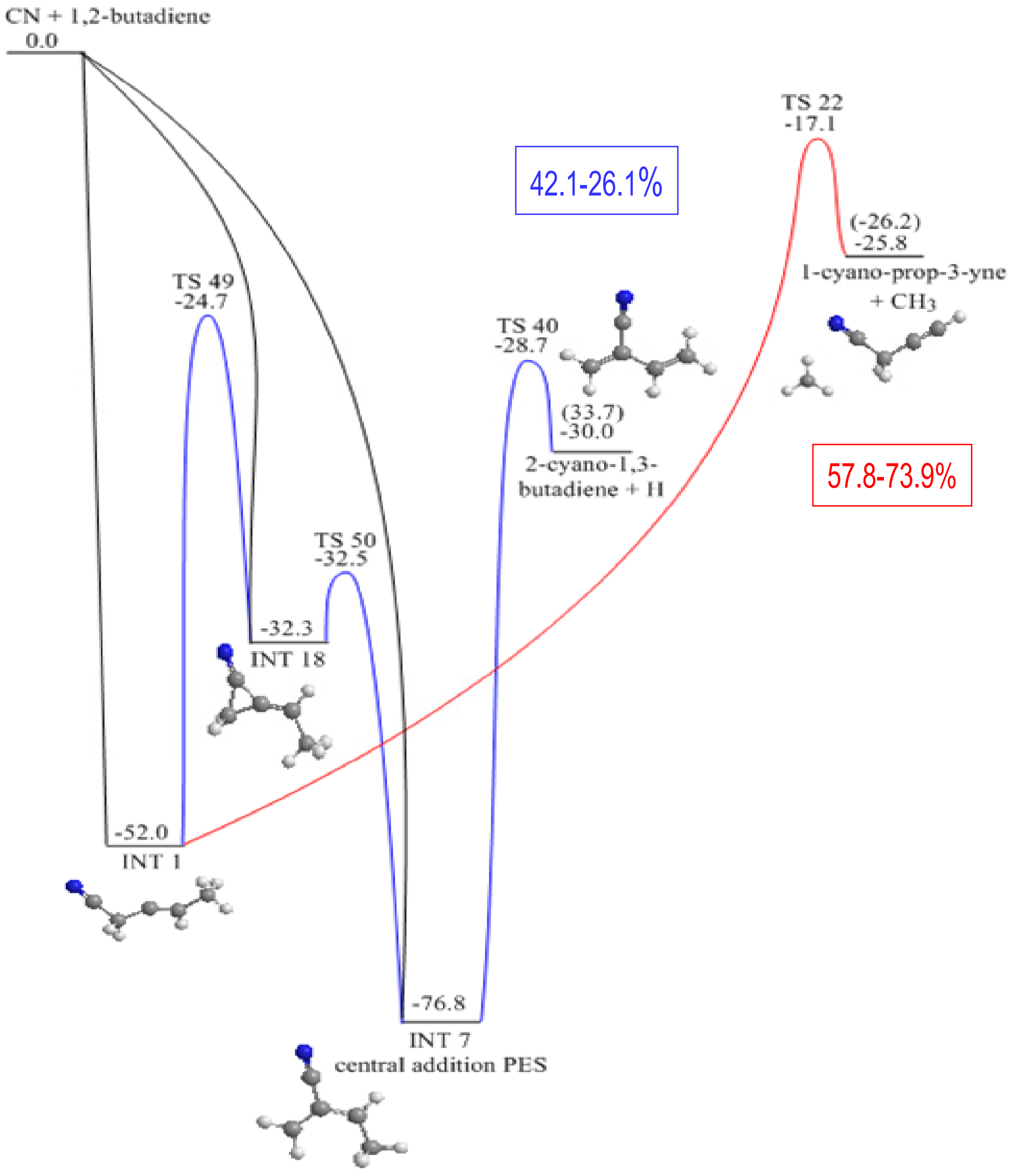


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Figure 5.2a. Potential energy diagram for the CN + 1,2-butadiene reaction pathways involving CN additions to C^1 and to the C^1=C^2 bond. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

metastable intermediate if at all a stationary point on the PES and the central CN addition to the $C^1=C^2$ bond leads directly to INT E1. Finally, INT E1 exhibits an H-loss process leading to 2-cyano-1,3-butadiene via a barrier of 48.1 kcal/mol. Reaction channels to all other intermediates that can be formed by 1,2- and 1,3-H shifts from INT D1 have high barriers and cannot compete with the most favorable pathways depicted in Fig. 5.2a.

Central CN addition to C^2:

The potential energy diagram for the central addition of CN to the C^2 carbon of 1,2-butadiene is depicted in Fig. 5.2b. This barrierless addition results in INT E1 and is exothermic by 76.8 kcal/mol relative to the reactants energy. INT E1 is identical to the INT B3 intermediate considered in Section 3.1.2. The only significant product that can be formed directly from INT E1 is 2-cyano-1,3-butadiene, through an H loss via a barrier of 48.1 kcal/mol, with the overall CN + 1,2-butadiene → 2-cyano-1,3-butadiene + H reaction being 30.0 (33.7) kcal/mol exothermic. A 1,2-H shift can occur, leading to INT E3 (the same as INT B2 in the CN + 1-butyne reaction), which also loses an H atom to form 2-cyano-1,3-butadiene. The INT E1 → INT E3 → 2-cyano-1,3-butadiene + H reaction has a critical barrier height of 34.5 kcal/mol relative to INT E3 at TS E3-1. INT E3 can also undergo a C_2H_5 loss process yielding diacetylene + ethyl radical, preceded by a 1,4-H shift to INT E4 (INT B1), however this route involves a C_2H_5-cleavage barrier of 29.6 kcal/mol at TS E4-1, which is the highest lying transition state on the PES corresponding to the central CN addition to C^2. Alternatively, INT E1 can isomerize into INT D1 via metastable INT D2 by migration of the CN moiety over the $C^1=C^2$ bond with a barrier of 52.1 kcal/mol at TS D1-D2. The CN group can also migrate over the $C^2=C^3$

bond to form INT F1 via a metastable INT E2 intermediate, which exists as a stationary structure only at the B3LYP level. The barrier separating INT E2 from INT E1 disappears at the CCSD(T) level as the corresponding TS E1-E2 becomes lower in energy than INT E2. The critical transition state on the path from INT E1 to INT F1 is TS E2-F1 and the barrier is 51.4 kcal/mol relative to INT E1.

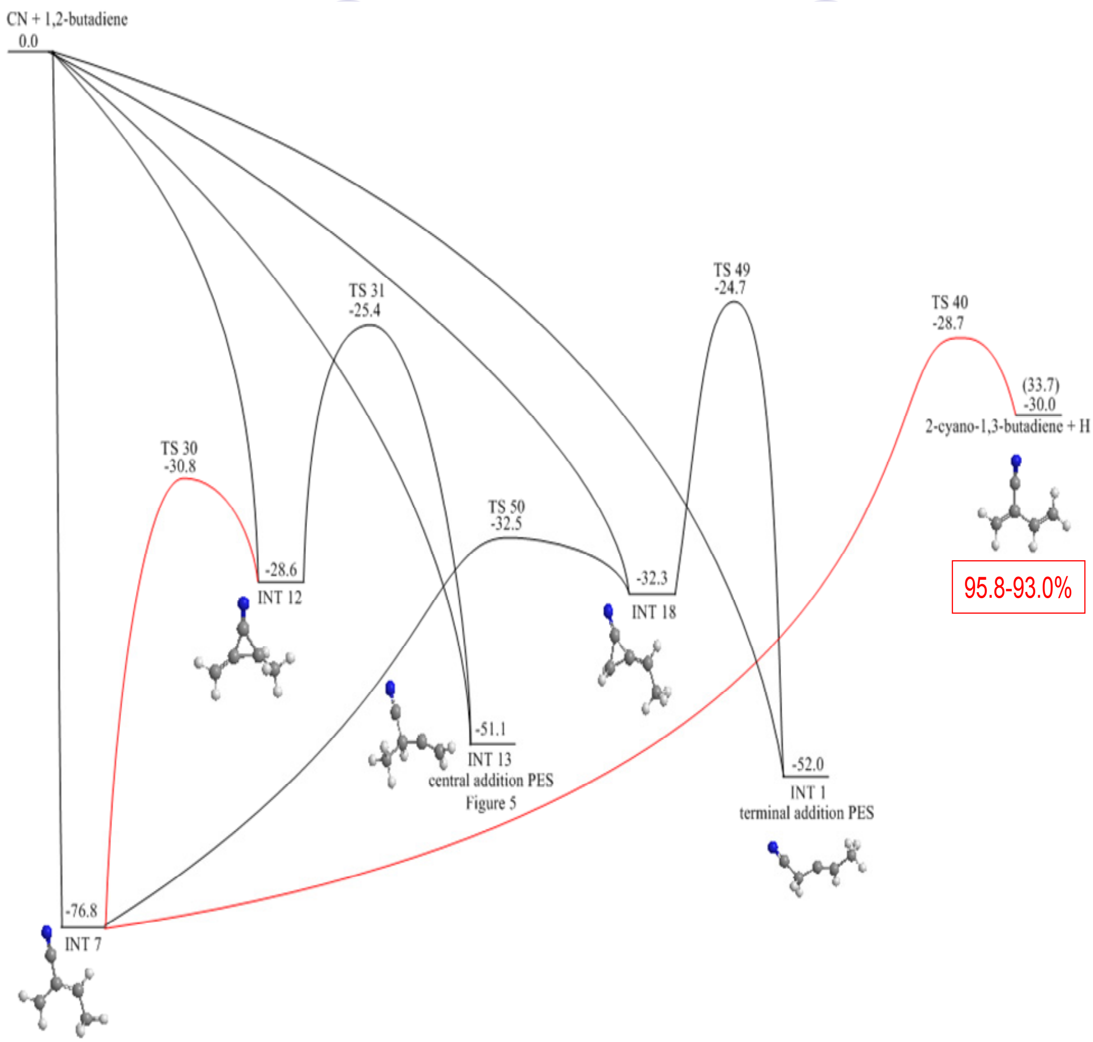

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Figure 5.2b. Potential energy diagram for the CN + 1,2-butadiene reaction pathways involving CN additions to C^2 and to the C^1=C^2 and C^2=C^3 bonds. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

The other reaction channels from INT E1 are not shown in Fig. 5.2b as they have higher barriers and are less likely to compete. One of them worthy mentioning involves a CH_3-loss process via the INT E1 (INT B3) → INT C1 → 1-cyano-prop-1-yne + CH_3 path (see Fig. 5.2b) with an overall exothermicity of 33.2 (33.0) kcal/mol relative to the CN + 1,2-butadiene reactants, but with a high 1,3-H shift barrier of 58.5 kcal/mol relative to INT E1.

Central CN addition to C^3:

The potential energy diagram of the central addition of cyano radical to the C^3 carbon of 1,2-butadiene is illustrated in Fig. 5.2c. In this case, the barrierless addition produces INT F1 and is exothermic by 51.1 kcal/mol relative to the reactants energy. From INT F1, cyanoallene can be formed by the CH_3 loss overcoming a barrier of 32.0 kcal/mol via TS F1-1. The cyanoallene + CH_3 products are 30.0 (30.1) kcal/mol exothermic with respect to the reactants.

However, a more probable dissociation mechanism of INT F1 involves its initial isomerization to INT E1 (via metastable INT E2) followed by an H loss leading to 2-cyano-1,3-butadiene, CN + 1,2-butadiene → INT F1 → INT E2 → INT E1 → 2-cyano-1,3-butadiene. The highest barrier on this pathway (relative to INT F1) is found for the first step, with the corresponding transition state TS E2-F1 residing only 25.7 kcal/mol above INT F1. Also, H loss channels from INT F1 producing 3-cyano-1,2-butadiene and 3-cyano-1-butyne exhibit prohibitively high barriers of 38.0 and 40.3 kcal/mol, respectively and are unlikely to contribute.

Central CN additions to the C^1=C^2 and C^2=C^3 bonds:

The barrierless CN addition to C^1=C^2 results in the 3-membered cyclic intermediate INT D2 and is exothermic by 32.3 kcal/mol. This intermediate cannot directly decompose and transforms into INT E1 by a barrierless decyclization process.

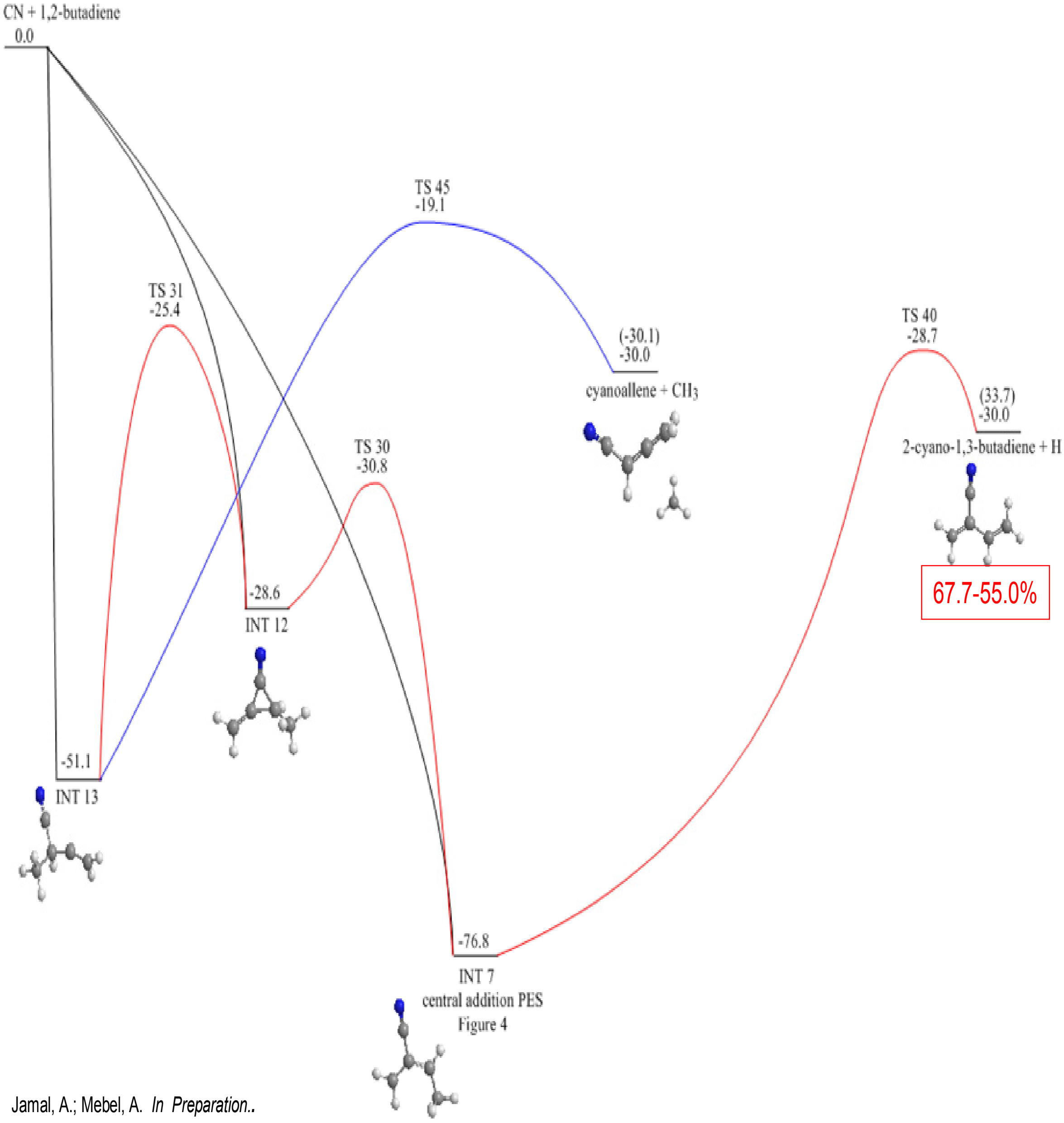

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Figure 5.2c. Potential energy diagram for the CN + 1,2-butadiene reaction pathways involving CN additions to C^3 and to the C^2=C^3 bond. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

The CN addition to C^2=C^3 is also predicted to occur without a barrier and to form INT E2, 28.6 kcal/mol below CN + 1,2-butadiene. INT E2 can ring-open to INT E1 or INT F1, however, the formation of INT E1 occurs barrierlessly while the path to INT F1 involves a 3.2 kcal/mol barrier. Since both CN additions to the C^1=C^2 and C^2=C^3 bonds result in metastable 3-membered cyclic intermediates, which decyclize to form INT E1 through barrierless ring-opening, 2-cyano-1,3-butadiene + H is expected to be the major product as described in the previous sections.

5.2.2. Product Branching Ratios

The calculations were carried out at collision energies of 0-5 kcal/mol, assuming that one of the adducts, INT D1, INT E1, and INT F1, is the only initial intermediate that forms in the entrance channel. We also considered a 1:1:1 concentrations of each initial adduct as done before for the CN + 1-butyne reaction, to give an insight of the formation of products when the three initial adducts are formed with equal probabilities. The resulting product branching ratios are collected in Table 3.

For the case of terminal addition of the cyano radical to C^1, leading to the formation of INT D1, two major products include the H-loss product 2-cyano-1,3-butadiene and the CH_3-loss product 1-cyano-prop-3-yne. The computed branching ratio for the H-loss channel at the collision energy of 0 kcal/mol is 42.1%, but it drops to 26.1% at 5 kcal/mol. This results in an increase of the branching ratio for the CH_3-loss product 1-cyano-prop-3-yne formed directly from INT D1 from 57.8% to 73.9% in the 0-5 kcal/mol collision energy range. For the case of central addition of CN to C^2 leading to the formation of INT E1, central addition to C^2=C^3 leading to INT E2, and central addition to C^1=C^2 leading to INT D2, the dominant product is 2-cyano-1,3-butadiene + H. For the collision energies in the range of 0-5 kcal/mol, the yield of 2-cyano-1,3-butadiene + H shows a decreasing trend for all aforementioned central additions. For the cyano radical addition to C^2 yielding INT E1, the 2-cyano-1,3-butadiene + H branching ratio decreases only slightly from 99.4% to 99.2%, while CN addition to the C^1=C^2 bond yielding INT D2, gives this product with the branching ratio in the 96.2-93.6% range. Finally, following CN addition to C^2=C^3 forming INT E2, 2-cyano-1,3-butadiene is produced with the branching ratio of 95.8-93.0%. Central CN addition to C^3 leading to the formation of INT F1 also has 2-cyano-1,3-butadiene + H as a major product with a

Table 5.2 Product branching ratios (%) in the CN + 1,2-butadiene reaction calculated for different collision energies and with various initial adducts INT D1, INT E1, and INT F1.

Product	Initial Adduct	0.0	1.0	2.0	3.0	4.0	5.0
1-cyano-prop-3-yne + CH_3	INT D1	57.8	61.8	65.3	68.5	71.3	73.9
	INT E1	0.4	0.4	0.5	0.5	0.5	0.5
	INT F1	0.3	0.3	0.3	0.3	0.3	0.3
	1:1:1	19.5	20.8	22.0	23.1	24.0	24.9
2-cyano-1,3-butadiene + H	INT D1	42.1	38.1	34.6	31.5	28.6	26.1
	INT E1	99.4	99.4	99.3	99.3	99.3	99.2
	INT F1	67.7	65.0	62.4	60.0	57.3	55.0
	1:1:1	69.7	67.5	65.4	63.6	61.7	60.1
cyanoallene + CH_3	INT D1	0.0	0.0	0.0	0.0	0.0	0.0
	INT E1	0.2	0.2	0.2	0.2	0.2	0.3
	INT F1	32.1	34.7	37.4	40.0	42.4	44.7
	1:1:1	10.8	11.6	12.5	13.4	14.2	15.0

decreasing branching ratio of 67.7-55.0% in the specified collision energy range. However, the CH_3-loss product cyanoallene is additionally formed in significant amounts, with the branching ratio varying from 32.1 to 44.7%.

With initial concentrations of each initial adduct INT D1, INT E1, and INT F1 set to be equal at a 1:1:1 ratio, the major product predicted by our calculations is 2-cyano-1,3-butadiene + H with the branching ratio of 80.2 to 73.4% in the 0-5 kcal/mol collision energy range. The CH_3-loss products 1-cyano-prop-3-yne and cyanoallene give relatively minor contributions of 12.5-16.3% and 7.3-10.3%, respectively.

5.3. CN + 1-Butyne

1-Butyne possesses one triple C≡C bond and CN addition can occur to either of the two acetylenic carbon atoms, terminal C^1 or central C^2, or to the triple bond itself. Similar to the C2H reactions with 1-Butyne, CN reactions with 1-Butyne are expected to have the overall reaction scheme of:

$$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_5H_5N + H$$

$$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_4H_3N + CH_3$$

$$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_3HN + C_2H_5$$

However, only the most favorable reaction pathways are described and the least likely are given, but not explained in detail.

5.3.1. Reaction Mechanism

Terminal CN addition to 1-butyne:

The potential energy diagram of the reaction route initiated by the terminal CN addition to C^1 is illustrated in Figure 5.3a. The addition takes place barrierlessly and produces the intermediate INT A1 with an exothermicity of 55.6 kcal/mol. The barrier at TS A1-1 for the CH_3-loss is 35.3 kcal/mol relative to INT A1 and the overall exothermicity of the CN + 1-butyne → cyanoallene + CH_3 reaction is 31.2 (31.3) kcal/mol at the CCSD(T)/cc-pVTZ(CBS) levels. H elimination can also occur from the CH_2 group giving 1-cyano-1,2-butadiene + H via a 39.3 kcal/mol barrier at TS A1-2 and

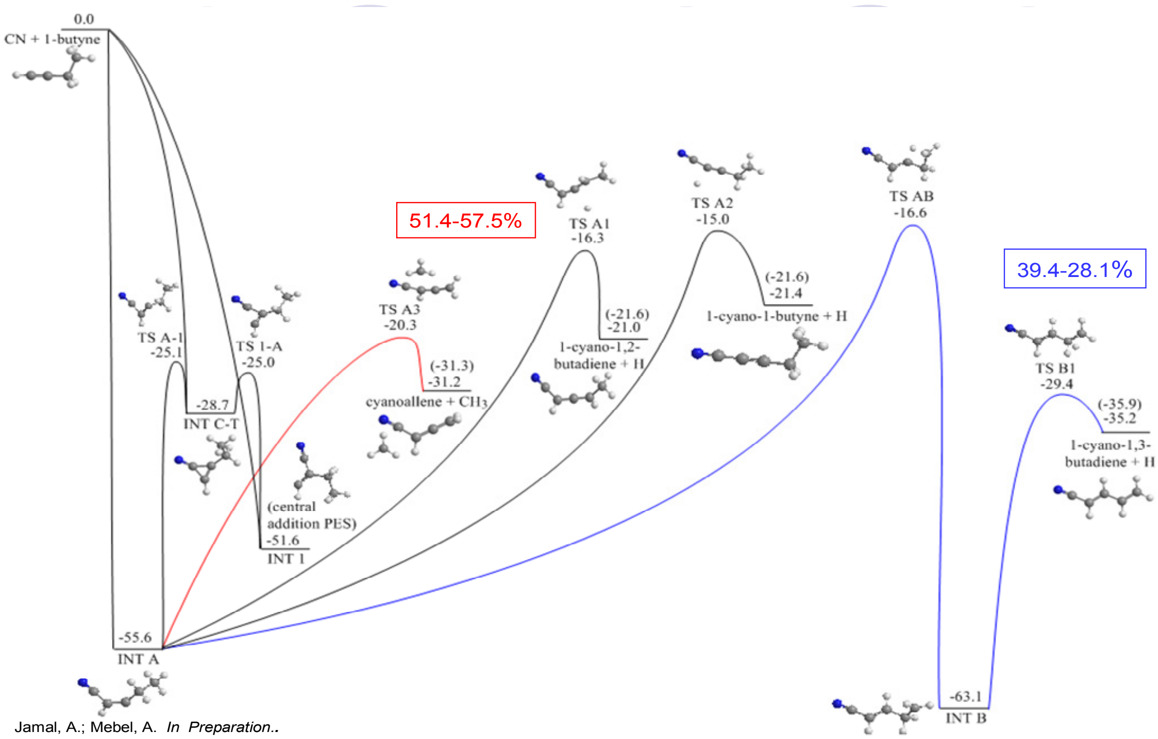

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Figure 5.3a. Potential energy diagram for the terminal CN addition to 1-butyne. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

the overall exothermicity to produce 1-cyano-1,2-butadiene + H is 21.0 (21.6) kcal/mol. Alternatively, INT A1 can lose an H atom from the terminal acetylenic carbon forming via TS A1-3 with a barrier of 40.6 kcal/mol. This CN + 1-butyne → INT A1 → TS A1-3 → 1-cyano-1-butyne + H reaction path completes at the products lying 21.4 (21.6) kcal/mol lower in energy than the reactants. The terminal H elimination from the CH_3 group in INT A1 is not likely to compete as it would produce an unfavorable diradical C_6H_5N isomer. An isomerization process involving a 1,3-H shift from the CH_3 group leads to the $NCCHCHCH_2CH_2$ intermediate INT A3, which is 7.5 kcal/mol lower in energy than INT A1. The H migration barrier at TS A1-A3 is 39.0 kcal/mol, comparable to those for H eliminations. An H elimination in INT A3 can occur from the vicinal CH_2 group producing 1-cyano-1,3-butadiene + H via a barrier at TS A3-1, residing 33.7 kcal/mol above INT A3. The calculated exothermicity of the CN + 1-butyne → 1-cyano-1,3-butadiene + H reaction is 35.2 (35.9) kcal/mol at the CCSD(T)/cc-pVTZ(CBS) levels. Finally, INT A1 can undergo a two-step CN migration over the neighboring C=C bond producing a branched intermediate INT B1, residing 51.6 kcal/mol below the reactants, via a three-member ring intermediate INT A2. The barriers for the isomerization of INT A2 back to INT A1 (via TS A1-A2) and forward to INT B1 (via TS A2-B1) are rather low, 3.6 and 3.7 kcal/mol, respectively.

Central CN addition to 1-butyne:

The potential energy diagram resulting from central addition is depicted in Figure 5.3b. This barrierless addition proceeds with cyano radical addition to the non-terminal acetylenic carbon atom C^2, resulting in INT B1 with an exothermicity of 51.6 kcal/mol relative to the reactants. The only plausible fragmentation pathway of INT B1 is elimination of the C_2H_5 group to form cyanoacetylene + C_2H_5. The barrier for the C-C bond cleavage via TS B1-1 is 32.6 kcal/mol relative to INT B1. The overall exothermicity of the CN + 1-butyne → cyanoacetylene + C_2H_5 reaction is 27.2 (27.1) kcal/mol. Neither CH_3 nor H eliminations from INT B1 will result as they would lead to higher-energy carbene or diradical products. Otherwise, INT B1 can be subjected to H

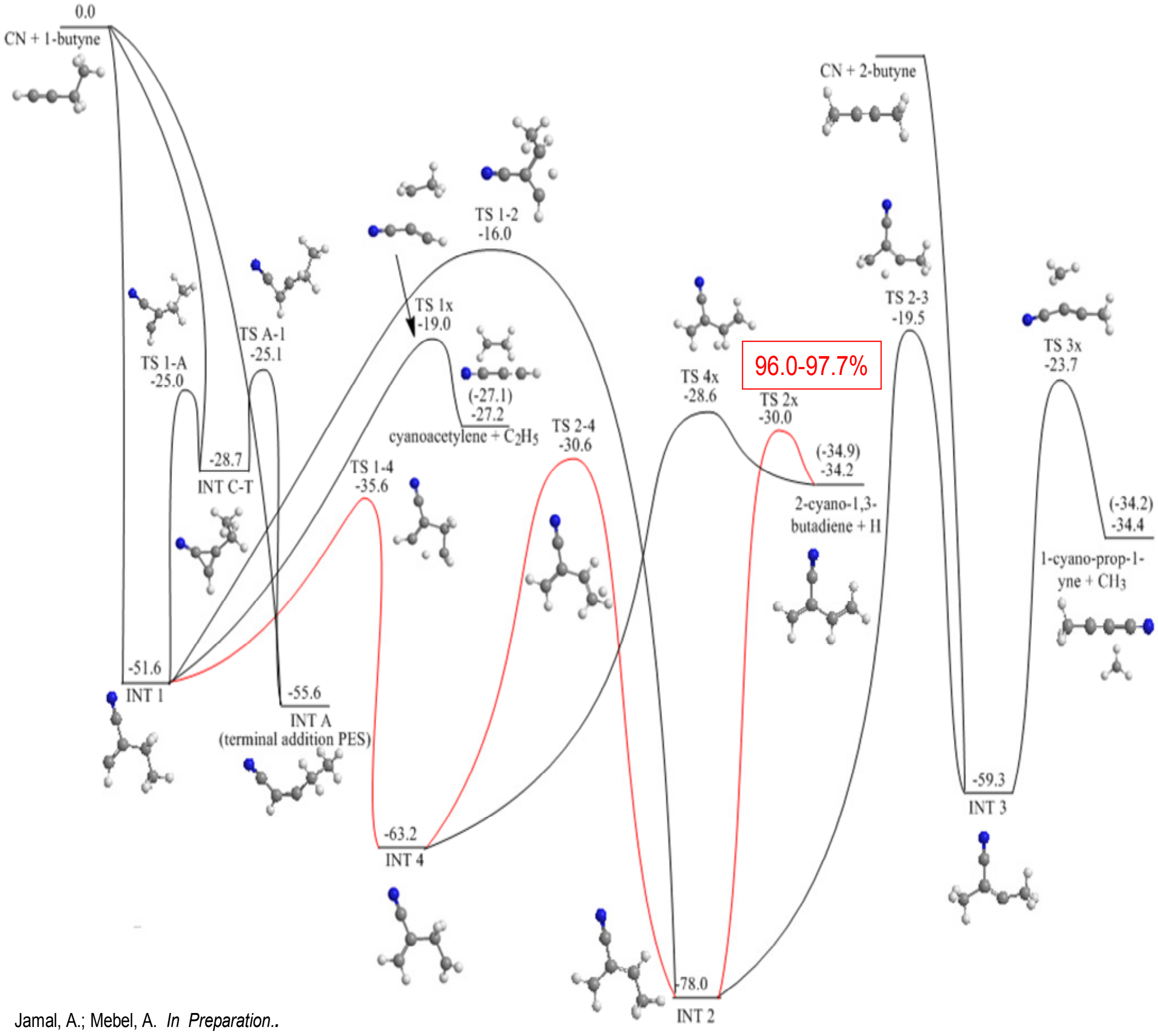

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Figure 5.2b. Potential energy diagram for the central CN addition to 1-butyne. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

migrations followed by various rearrangements and dissociations. For instance, a 1,4-H shift from the CH_3 group to CH occurring via TS B1-B2 with a relatively low barrier of 16.0 kcal/mol produces another branched intermediate INT B2, residing 63.2 kcal/mol below the reactants. Then, INT B2 can lose an H atom from the vicinal CH_2 group via TS B2-1 and a barrier of 34.6 kcal/mol relative to INT B2. The overall exothermicity of the CN + 1-butyne → 2-ethynyl-1,3-butadiene reaction is 34.2 (34.9) kcal/mol relative to the reactants. A 1,3-H shift from the vicinal CH_2 group of INT B1 gives INT B3, which is 22.4 and 14.8 kcal/mol lower in energy than INT B1 and INT B2, respectively. However, the barrier for the 1,3-H migration, 35.6 kcal/mol, is much higher than that for the 1,4-H shift. A more feasible path from INT B1 to INT B3 is two-step, INT B1 → INT B2 followed by 1,2-H migration between two neighboring CH_2 groups, INT B2 → INT B3. The highest in energy transition state along the INT B1 → INT B2 → INT B3 path, TS B2-B3, lies 21.0 kcal/mol higher in energy than INT B1. INT B3 can lose a hydrogen atom from the CH_3 group producing 2-cyano-1,3-butadiene via TS B3-1 located 30.0 kcal/mol below the reactants. As mentioned in the previous section, INT B1 can rearrange to the terminal addition adduct INT A1 via the 3-membered cyclic intermediate INT A2 via the barrier via of 26.6 kcal/mol at TS A2-B1, so that this isomerization and the subsequent dissociation channels of INT A1 may compete with the dissociation channels of INT B1 shown in Fig. 5.3a.

CN addition to the C≡C bond in 1-butyne:

Cyano radical addition to the triple C≡C bond in 1-butyne occurs barrierlessly forming the three-member ring intermediate INT A2 with an exothermicity of 28.7

kcal/mol. As discussed above, this intermediate can easily isomerize to INT B1 or INT A1 overcoming relatively low barriers. INT B1 or INT A1 would then dissociate via the pathways illustrated in Figs. 1 and 2.

5.3.2. Product Branching Ratios

The calculations were carried out assuming that the reaction starts from either the terminal addition adduct INT A1 or the central addition adduct INT B1. We then considered a 1:1 ratio of the initial concentrations of INT A1 and INT B1, to get an insight on the product branching ratios under the conditions when the initial adducts are formed in the entrance channel with equal probabilities. The computed branching ratios are presented in Table 1. For the terminal addition, the major product is cyanoallene + CH_3 yielding 51.3-57.5% of the total product yield in the 0-5 kcal/mol collision energy range. This is due to the fact that the CN + 1-butyne → cyanoallene + CH_3 product formation channel had the lowest barrier relative to the adduct INT A1 among all direct dissociation processes involving this intermediate. Meanwhile, the two-step process leading from INT A1 to INT B1 has an even lower barrier and can compete with the direct dissociation, bringing the system in the region of the PES accessed by the central CN addition. As a result of this competition, the second most abundant product is 2-cyano-1,3-butadiene + H produced from INT B1 via INT B2, with the 39.4-28.1% branching ratios in the specified range of collision energies. The overall reaction path leading to this product is CN + 1-butyne → INT A1 → INT A2 → INT B1 → INT B2 → 2-cyano-1,3-butadiene + H. The other reaction products are minor and contribute 4.2-

6.4% (1-cyano-1,2-butadiene + H), 1.4-2.5% (1-cyano-1-butyne + H), 1.1-1.7% (cyanoacetylene + C_2H_5), and 1.2-1.6% (1-cyano-1,3-butadiene + H). For central addition, the major product is 2-cyano-1,3-butadiene + H with the yield of 96.0-92.7% in the specified collision energy range. The overall reaction path for this channel is CN + 1-butyne → INT B1 → INT B2 → 2-cyano-1,3-butadiene + H. The C_2H_5 elimination channel from CN + 1-butyne → INT B1 → cyanoacetylene + C_2H_5 accounts for 2.7-5.5%, whereas the other product channels are negligible. With equal initial concentrations of INT A1 and INT B1, the results showed 2-cyano-1,3-butadiene + H formed from the central addition adduct to be the major product at 67.7-60.4% in the 0-5 kcal collision energy, whereas cyanoallene + CH_3 formed from the terminal addition adduct, exhibits the 26.3-29.5% yield. We then considered a 1:1:1 concentrations of each initial adduct to give an insight of the formation of products when the three initial adducts are formed with equal probabilities. The central addition product of 2-cyano-1,3-butadiene + H had a product branching ratio of 66.7-59.3% if any one of the initial adducts are formed.

Table 5.3. Product branching ratios (%) in the CN + 1-butyne reaction calculated for different collision energies and with various initial adducts INT A1 and INT B1.

Product	Initial Adduct	0.0	1.0	2.0	3.0	4.0	5.0
1-cyano-1,3-butadiene + H	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	1.2	1.2	1.3	1.4	1.5	1.6
	INT A2	0.7	0.7	0.8	0.8	0.9	0.9
	1:1:1	0.6	0.6	0.7	0.7	0.8	0.8
1-cyano-1,2-butadiene + H	INT B1	0.1	0.1	0.1	0.1	0.1	0.2
	INT A1	4.2	4.6	5.0	5.5	6.0	6.4
	INT A2	2.4	2.6	2.8	3.1	3.4	3.6
	1:1:1	2.2	2.4	2.6	2.9	3.2	3.4

2-cyano-1,3-butadiene + H	INT B1	96.0	95.6	94.8	94.1	93.4	92.7
	INT A1	39.4	37.1	34.3	32.2	30.1	28.1
	INT A2	64.6	62.9	61.3	59.9	58.4	57.0
	1:1:1	66.7	65.2	63.5	62.1	60.6	59.3
3-cyano-1,2-butadiene + H	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A2	0.0	0.0	0.0	0.0	0.0	0.0
	1:1:1	0.0	0.0	0.0	0.0	0.0	0.0
cyanoacetylene + C_2H_5	INT B1	2.7	3.1	3.7	4.3	4.9	5.5
	INT A1	1.1	1.2	1.3	1.5	1.6	1.7
	INT A2	1.8	2.1	2.4	2.7	3.0	3.4
	1:1:1	1.9	2.1	2.5	2.8	3.2	3.5
1-cyano-1-butyne + H	INT B1	0.1	0.1	0.1	0.1	0.1	0.1
	INT A1	2.7	3.1	3.5	3.9	4.3	4.8
	INT A2	1.5	1.7	2.0	2.2	2.4	2.7
	1:1:1	1.4	1.6	1.9	2.1	2.3	2.5
1-cyano-prop-1-yne + CH_3	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A2	0.0	0.0	0.0	0.0	0.0	0.0
	1:1:1	0.0	0.0	0.0	0.0	0.0	0.0
cyanoallene + CH_3	INT B1	1.1	1.2	1.3	1.3	1.4	1.5
	INT A1	51.3	52.8	54.4	55.5	56.5	57.5
	INT A2	29.0	30.2	30.7	31.3	31.8	32.4
	1:1:1	27.1	28.1	28.8	29.4	29.9	30.5

5.4. CN + 2-Butyne

The CN radical addition to the C_4H_6 isomer of 2-butyne has a similar overall reaction scheme to the other C_4H_6 isomers of 1,2-butadiene and 1-butyne. The overall reaction scheme can be summarized as:

$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_5H_5N + H$

$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_4H_3N + CH_3$

$CN + CH_3C{\equiv}CCH_3 \rightarrow C_5H_6N \rightarrow C_3HN + C_2H_5$

5.4.1. Reaction Mechanism

The potential energy diagram for the CN + 2-butyne reaction is shown in Fig. 5.4a. CN addition to a highly-symmetric 2-butyne molecule can proceed to one of the middle acetylenic carbon atoms or to the central triple C≡C bond. The addition of CN to either of the two middle carbons linked by a triple bond occurs without a barrier to form INT C1, with an exothermicity of 54.3 kcal/mol. Next, INT C1 can either lose a hydrogen atom (via TS C1-2) to form 3-cyano-1,2-butadiene + H or CH_3 (via TS C1-1) to form 1-cyano-prop-1-yne + CH_3 via the barriers 41.1 and 35.6 kcal/mol, respectively. The overall energies of the CN + 2-butyne → 3-cyano-1,2-butadiene + H and CN + 2-butyne → TS C1-1 → 1-cyano-prop-1-yne + CH_3 reactions are calculated to be -16.7 (-17.1) and -29.4 (-29.0) kcal/mol, respectively. Alternatively, INT C1 can isomerize into INT B3 via TS B3-C1 overcoming a 39.8 kcal/mol barrier, after which INT B3 can either decompose to 2-ethynyl-1,3-butadiene + H or pursue the other isomerization and dissociation pathways shown in Fig. 5.4a and described in the previous section. Earlier, the CN + 2-butyne reaction was studied theoretically at the B3LYP/6-311+G** level. Two conformations (*cis* and *trans*) were found for INT C1, but since their energies are close to each other and the isomerization barrier between them was calculated to be only 4.6 kcal/mol relative to the slightly (by 1.2 kcal/mol) less stable *cis* form, kinetically both conformations can be taken as the same intermediate on the surface the rate constants for their mutual isomerization are much faster than any other reaction involving INT C1.

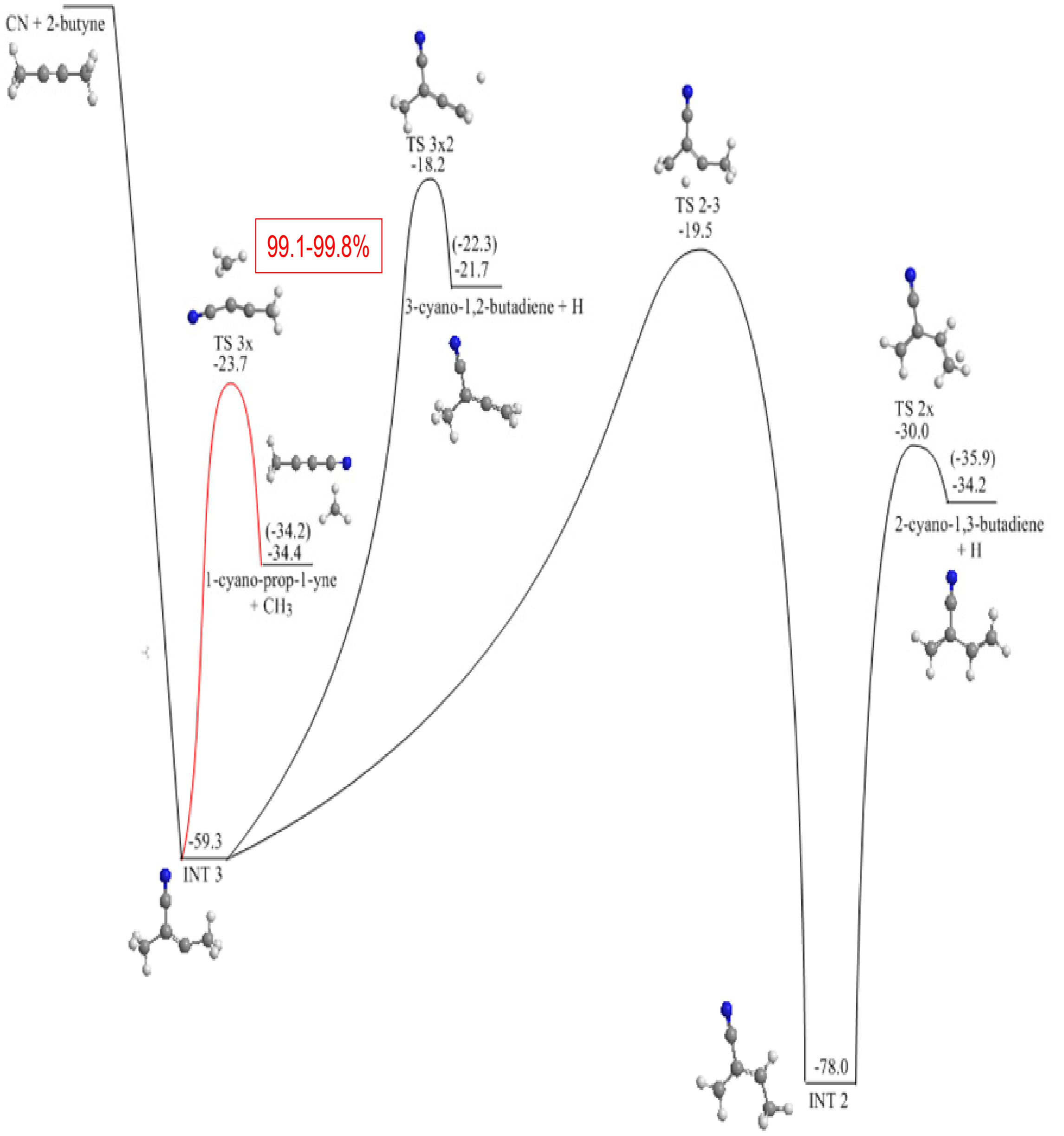

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Figure 5.4a. Potential energy diagram for the CN + 2-butyne reaction. Numbers show relative energies (in kcal/mol) of the reactants, intermediates, transition states, and products calculated at the CCSD(T)/cc-pVTZ//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level of theory and at CCSD(T)/CBS (in parentheses, for the products).

Based on this, we consider only the more stable *trans* form (INT C1) in RKKM calculations in the next section. Cyano radical addition to the triple bond forms a 3-membered ring intermediate designated as INT C2. Although a low barrier between INT C1 and INT C2 exists at the B3LYP level, at the CCSD(T) level the decyclization of INT C2 occurs barrierlessly leading INT C1. At the B3LYP/6-311+G** level, the *trans* adduct INT C1, TSs C1-2 and C1-1, and the 3-cyano-1,2-butadiene (1-cyano-1-methylallene) + H and 1-cyano-prop-1-yne + CH_3 products reside 57.5, 17.6, 25.0, 19.2, and 36.0 kcal/mol lower in energy than the initial reactants, respectively,[27] which agrees with the present CCSD(T) values shown in Fig. 3 within reasonable margins. Although the CCSD(T) relative energies are expected to be more accurate, both B3LYP and CCSD(T)/cc-pVTZ(CBS) calculated exothermicities of the 3-cyano-1,2-butadiene + H products, 19.2 and 16.7 (17.1) kcal/mol, respectively, are within the error bars of the experimental value of 21.5±4.8 kcal/mol measured in crossed molecular beams.[27]

5.4.2. Product Branching Ratios

The product distribution in the CN + 2-butyne reaction is dominated by the CH_3 loss product 1-cyano-prop-1-yne from the initial adduct INT C1, with the branching ratios in the 0-5 kcal/mol collision energy range being 99.1-98.8%. Only small amounts of the H elimination product 3-cyano-1,2-butadiene + H are formed due to high barriers at TS C1-2. Nevertheless, the H loss product, 3-cyano-1,2-butadiene (1-cyano-1-methylallene) was detected in crossed molecular beam experiments on the CN + 2-butyne reaction, where unfavorable kinematics prevented the authors from observing the CH_3 loss channel.

Table 5.4. Product branching ratios in the CN + 2-butyne reaction calculated for different collision energies with INT 3 as the initial adduct.

Product	**Collision Energy, kcal/mol**					
	0.0	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
1-cyano-prop-1-yne + CH_3	99.1	99.5	99	98.9	98.8	98.8
3-cyano-1,2-butadiene + H	0.3	0.3	0.3	0.3	0.3	0.3

6. COMPARISON WITH EXPERIMENTS

Integrating laboratory experiments to *ab initio* studies is crucial in understanding the reaction mechanism and product branching ratios of ethynyl and cyano radical additions to unsaturated hydrocarbons. Experimenters often detect product masses, and determining the isomer of these masses is key to understanding which product prevails. Furthermore, understanding the reaction mechanism involved in forming these products is key since that governs the fate of the reaction. The theoretical calculations need to be supported with laboratory findings to confirm the proposed mechanisms are indeed correct. From the ethynl and cyano radical reactions with unsaturated hydrocarbons studied, only the reactions of C_2H + C_3H_4 (both allene and methyacetylene), C_2H + 1,3-butadiene, and CN + diacetylene have been jointly investigated through crossed molecular-beam experiments by Kaiser's group at University of Hawaii. The reaction of C_2H + 1-butyne has been investigated in parallel with experiments using the Synchotron at the Advanced Light Source by Stephen Leone's group at University of California, Berkeley. The experimental findings are discussed below.

6.1 Reactions of C_2H + C_3H_4

The experimental data on product branching ratios for the C_2H + allene reaction are somewhat controversial. Goulay et al. reported the following results from their measurements of relative yields: 35-45% ethynylallene, 20-25% methyldiacetylene, and 45-30% 1,4-pentadiyne. They also concluded that diacetylene most likely was not produced in the C_2H + H_2CCCH_2 reaction and derived an upper limit of 30% for its branching fraction. On the other hand, in their new crossed molecular beams study of this reaction under single-collision conditions at a collision energy of 5.3 kcal/mol, Kaiser and coworkers[78] concluded that ethynylallene is the major product with 1,4-pentadiyne possibly contributing up to 20% and no evidence for methyldiacetylene was found. The difference in the results of the two groups for the ethynyl + allene reaction can be caused by the difference in the experimental conditions and detection methods. On one hand, in the slow flow reactor study secondary collisions may affect the reaction mechanism and the relative product yields, but on the other, the detection of the products is based on the measurements of their ionization potentials and fitting the corresponding photoionization efficiency curves, which should be more accurate than deriving the branching ratios based on a comparison of the fitted kinetic energy distribution curves of the products with theoretically computed energies of the corresponding product channels, as in the crossed beams experiments. One can also see that the results of both experiments exhibit significant error bars for the branching ratios.

Kaiser and coworkers investigated the mechanism and dynamics of the C_2H reaction with methylacetylene and its deuterated isotopomers in crossed molecular beams under single-collision conditions with a focus on the detection of C_5H_4 products. Combining their experimental results with a theoretical study of the reaction potential energy surface (PES) using a density functional theory (DFT) approach, they were able to estimate relative yields of C_5H_4 isomers as 80-90% for methyldiacetylene, CH_3-C≡C-C≡CH, and 10-20% for ethynylallene, CH_2=C=CH-C≡CH. However, the isotope-labeling technique they applied did not allow them to detect a third thermodynamically favorable

C_5H_4 isomer 1,4-pentadiyne, HC≡C-CH_2-C≡CH. Goulay et al. measured product branching ratios of the C_2H + C_3H_4 reactions in a slow flow reactor at 4 Torr and 293 K using an experimental setup combining tunable ultraviolet radiation with time-resolved mass spectrometry. They found that the reaction with methylacetylene gives 50-70% diacetylene (channel 5b) and 50-30% C_5H_4 (channel 5a), with an isomer distribution of 85-80% methyldiacetylene and 15-20% ethynylallene, which is in an agreement with the results of Kaiser's group.

6.2 Reactions of C_2H + 1,3-Butadiene

The mechanism and products of the C_2H + 1,3-butadiene reaction have been recently probed in a combined experimental (crossed molecular beams) and theoretical (ab initio/RRKM) study,[112] which demonstrated that this reaction can indeed produce benzene under single-collision conditions. According to the experimental results, the relative yield of benzene was 30±10% at the collision energy of ~45 kJ mol^{-1}, whereas 1,3-hexadien-5-yne was the second major product. RRKM calculations showed that the relative fraction of benzene is expected to increase to ~40% for very low and zero collision energies pertinent for cold interstellar clouds.

Having verified the formation of the aromatic benzene molecule under single collision conditions, we applied these findings to the 'real' interstellar medium. Most important, our studies indicate that the reaction has no entrance barriers, all barriers involved in the formation of benzene are below the energy of the separated reactants, and the overall reaction to form benzene is exoergic. These findings represent crucial prerequisite for this reaction to be important in low temperature molecular clouds. If any barrier lies above the energy of the separated reactants or if the reaction is endoergic, the low temperatures of the molecular clouds such as the Taurus Molecular Cloud (TMC-1) would typically inhibit the formation of benzene. In constructing a chemical reaction network for the gas phase formation of benzene in interstellar clouds, two input parameters are crucial: the reaction products (benzene and its acyclic isomer) and the rate constants. In our network, we implemented a rate constant of 3.0×10^{-10} cm^3s^{-1} and accounted for the branching fractions of benzene versus the 1,3-hexadien-5-yne isomer as elucidated in our present study. We recognize that Leone et al.'s data were recorded at temperatures between 104 K and 296 K. However, an analysis of ethynyl radical reactions with unsaturated hydrocarbons shows that their rate constants are almost invariant on the temperature even down to 10 K.[84] Therefore, a rate constant of 3.0×10^{-10} cm^3s^{-1} for cold interstellar clouds with benzene fractions of 40 % versus 60 % of the 1,3-hexadien-5-yne isomer presents sensible input parameter. The results of our astrochemical models for dark clouds like TMC-1 have important implications.

We would like to stress that alternative neutral-neutral reactions to form benzene in the interstellar medium have been 'borrowed' from the high temperature, combustion chemistry community and incorporated in previous interstellar chemistry models. These bimolecular processes involve, for instance, reactions of resonantly stabilized free radicals such as n-C_4H_3 and n-C_4H_5 with acetylene (C_2H_2). However, these reactions have significant entrance barriers of about 20-31 kJ / mol^{-1} ([vi]) to 23 kJ / mol^{-1} ([vii]), respectively, which cannot be overcome at molecular cloud temperatures of 10 K. Likewise, the self-recombination of the propargyl radical (C_3H_3) followed by isomerization and stabilization of the benzene intermediate via a third body collision had been discussed to form benzene in flames. However, although this reaction has no entrance barrier, third body collisions are on the order of magnitude of 10^9 years and, hence, clearly absent in interstellar clouds with typical number densities of a 10^2 – 10^4 cm^{-3} for which the time scale is much larger than the typical life time of a cold molecular cloud at 10^5 – 10^6 years. This leads to the conclusion that three body processes are unimportant in molecular clouds. Therefore, reactions which may lead to the formation of benzene under combustion relevant conditions cannot yield benzene under those low temperature and pressure conditions in cold molecular clouds. However, the newly investigated ethynyl radical mediated formation of benzene overcomes these problems, and the aromatic benzene molecule can be formed via a single collision of two neutral particles under bimolecular conditions without entrance barrier in interstellar space.

To summarize, we have presented compelling evidence that the aromatic benzene molecule – the central building block of polycyclic aromatic hydrocarbons - can be formed under single collision conditions via the gas phase reaction of ethynyl radicals with 1,3-butadiene. The formation of an aromatic, closed shell molecule via a rapid neutral – neutral reaction also presents a first step toward a systematic understanding how complex PAHs and related molecules might be formed in the interstellar medium via neutral – neutral reactions involving benzene. Electronic structure calculations predicted that the phenylacetylene molecule (C_6H_5CCH), synthesized from exoergic, barrier-less reactions of benzene with the ethynyl radical can even react with a second ethynyl radical to form 1,2-diethynylbenzene ($C_6H_4(C_2H)_2$) plus a hydrogen atom. The reaction of 1,2-diethynylbenzene with a third ethynyl radical in turn produces an intermediate, which isomerizes via ring closure and emits atomic hydrogen to yield a dehydrogenated, aromatic and bicyclic naphthalene core. Therefore, neutral – neutral reactions of aromatic molecules such as benzene and naphthalene with ethynyl radicals could present a versatile, hitherto overlooked reaction class to yield complex, PAH (like) structures via ring expansions at temperatures as low at 10 K as present in cold molecular clouds.

6.3 Reactions of C_2H + 1-Butyne

The experimental measurements of relative product yields in the C_2H + 1-butyne reaction by Soorkia et al.[93] showed that both the C_6H_6 + H and C_5H_4 + CH_3 products are formed, whereas the C_4H_2 + C_2H_5 product was not ruled out but could not be observed due to experimental limitations. For C_5H_4 + CH_3, they detected ethynylallene and methyldiacetylene in a 4:1 ratio and concluded that the latter most likely to be formed in a secondary reaction of isomerizarion of the former, providing that ethynyl has sufficient internal energy. This observation is an agreement with our calculation results showing that ethynylallene is the dominant C_5H_4 isomer produced in the reaction. Meanwhile, since the calculated highest barrier on the isomerization pathway from ethynylallene to methyldiacetylene is ~69 kcal/mol relative to the former,[100] the unimolecular rearrangement seems to be unlikely. In our view, a more plausible explanation for the observation of a small amount of methyldiacetylene would be an H atom assisted isomerization of ethynylallene, i.e., H addition to the CH_2 group to form $CH_3CCHCCH$ via a barrier of 2.7 kcal/mol followed by the H loss from the vicinal CH group via a transition state residing 0.6 kcal/mol higher in energy than the initial ethynylallene + H reactants, as follows from our recent calculations of the C_5H_5 PES.[89] This would require secondary collisions of the C_5H_4 and H primary products, which might be possible in the experimental flow tube at 4 Torr.

A significant qualitative disagreement is however found for the C_6H_6 isomeric product distribution. Soorkia et al.[100] detected cyclic DMCB and fulvene as the most significant C_6H_6 products and, among the acyclic isomers, the order of the measured branching ratios was 3,4-hexadiene-1-yne > 1,3-hexadiyne > 2-ethynyl-1,3-butadiene. In our calculations, none of the cyclic isomers are formed and 2-ethynyl-1,3-butadiene is the major acyclic product, with minor contributions from 1,3-hexadiene-5-yne, 3,4-hexadiene-1-yne, and 1,3-hexadiyne. How to explain the discrepancy between theory and experiment? One can argue that the experimental conditions of the room temperature (295 K) and 4 Torr (5.33 mbar) pressure are not exactly compatible with the single-collision (E_{col} = 0-7 kcal/mol) conditions assumed in our kinetic calculations. The collision energies used in the calculations cover the kinetic energy range typical for 295 K, but the nonzero pressure in the experiment implies a possibility of collisional stabilization of C_6H_7 intermediates and also secondary reactions in the system. Multichannel-multiwell RRKM/Master Equation (RRKM-ME) calculations would be required to evaluate the product distribution at the experimental conditions. However, the recent RRKM-ME study by Woon[54] for a slightly larger $C_2H + C_6H_6$ system showed that collisional stabilization of the energized radical intermediates was appreciable only at higher pressures. For instance, the yield of the stabilized intermediates was found to exceed 50% at 300 K only at pressures above 117.9 mbar and to be negligibly small at 5 mbar at room temperature. In addition, the collisional stabilization of the C_6H_7 species is not expected to enhance the yield of the cyclic fulvene and DMCB products because the pathways leading to them involve numerous isomerization steps, which would become even less probable if the C_6H_7 intermediates are collisionally stabilized.

Meanwhile, there exists a secondary reaction that can lead to the formation of fulvene as the dominant product. It starts with the H addition to 2-ethynyl-1,3-butadiene to produce INT 11 via a barrier of 6.2 kcal/mol with the exothermicity of 32.1 kcal/mol (see Fig. 4.5c). Next, INT 11 ring closes to INT 8 via a TS 8-11 residing 19.4 kcal/mol below the H + 2-ethynyl-1,3-butadiene reactants and then INT 8 can eliminate an H atom to form fulvene overcoming a barrier at TS 8x lying 28.6 kcal/mol lower in energy than the reactants. Overall, the H + 2-ethynyl-1,3-butadiene → INT 11 → INT 8 → fulvene + H reaction is 32.0 kcal/mol exothermic. However, two conditions are required for the secondary reaction to influence the product distribution in a major way: first, the rate constants of the primary (C_2H + 1-butyne) and the secondary (H + 2-ethynyl-1,3-butadiene) should be close to each other and second, the initial C_2H concentration in experiment should be comparable to the initial 1-butyne concentration. At thermal conditions at 295 K, the H + 2-ethynyl-1,3-butadiene reaction occurring via a relatively high 6.2 kcal/mol barrier is expected to be much slower than the barrierless C_2H addition to 1-butyne; moreover, H additions to 2-ethynyl-1,3-butadiene producing INT 2 and INT 4 exhibit lower barriers and hence are more competitive than the H addition leading to INT 11. On the other hand, 2-ethynyl-1,3-butadiene produced in the C_2H + 1-butyne reaction may have an internal vibrational energy content of up to ~40 kcal/mol (at zero collision energy), which may render it much more reactive towards the H addition, if this product is not fully thermalized. In this view, a possibility of a fast H + 2-ethynyl-1,3-

butadiene → INT 11 reaction may not be completely excluded. A rough estimate of the C_2H concentration, based on the absorption cross section of the CF_3CCH precursor and the experimental laser intensity,[35, 100] gives at most $\sim 10^{13}$ cm^{-3}, a factor of 50 lower than the 1-butyne concentration, 5.0×10^{14} cm^{-3}. All this indicates that the secondary H + 2-ethynyl-1,3-butadiene encounters are not likely to affect the relative product yield significantly, but may account for the formation of a small amount of fulvene. It is highly improbable that DMCB can be formed from INT 11, because the highest barrier on the INT 11 → INT 10 → DMCB + H pathway, 37.5 kcal/mol relative to INT 11 at TS 10x, is 24.8 kcal/mol higher than that on the INT 11 → INT 8 → fulvene + H pathway, at TS 8-11. Using a simplified steady-state treatment, the rate constants to form fulvene and DMCB from INT 11 are $\frac{k_{8-H}k_{11-8}}{k_{8-11}+k_{8-H}}$ and $\frac{k_{10-H}k_{11-10}}{k_{10-11}+k_{10-H}}$, respectively. Using the individual rate constants computed at zero collision energies (Table A2 of the Appendix), these rate constants are calculated as 5.55×10^{10} and 3.35×10^{7} s^{-1}, i.e., the formation of fulvene is preferable by a factor of more than 10^3. Thus, the experimental observation of DMCB cannot be attributed to the secondary H + 2-ethynyl-1,3-butadiene reaction.

A secondary reaction of CH_3 with ethynylallene may also lead to the formation of fulvene. As illustrated in Figure 4.5c, the methyl radical can add to a hydrogen-less carbon atom in ethynylallene overcoming a barrier of ~12 kcal/mol to form INT 17. Next, INT 17 can either dissociate to propyne + C_3H_3 or ring close to INT 18 via barriers of 28.4 and 15.6 kcal/mol, respectively. In turn, INT 18 can be subjected to 1,2-H migration in the ring to produce a very stable intermediate INT 19, which is a precursor of fulvene. INT 19 can lose a hydrogen atom from the out-of-ring CH_3 group without an exit barrier giving rise to fulvene + H. However, the ethynylallene + CH_3 reaction is expected to be slow at the experimental temperature of 295 K due to its high entrance barrier. Moreover, the barrier to form INT 17 from the ethynylallene and CH_3 reactants is about 3 kcal/mol higher than that to produce INT A (Fig. 5.4c) and hence the reaction path leading to fulvene would be less competitive.

Can inaccuracies in our calculations be a source of the disagreement with experiment? Relative energies of various transition states computed at the CCSD(T)/cc-pVTZ level are expected to have error bars of ±2 kcal/mol. In order to verify whether such errors could affect the relative yield of fulvene, we decreased the critical barrier on the pathway leading to fulvene (at TS 5-6) by 2 kcal/mol, while increasing the highest barriers on the pathways leading to the acyclic C_6H_6 isomers, ethynylallene + CH_3, and diacetylene + C_2H_5 also by 2 kcal/mol. Using these adjusted energetics, we repeated the RRKM calculations of the rate constants and first-order kinetics calculations of the branching ratios. The results showed that still virtually no fulvene can be produced. In general, the ±2 kcal/mol variations in the energies of the critical transition states may significantly affect the ratio of the 2-ethynyl-1,3-butadiene + H, ethynylallene + CH_3, and diacetylene + C_2H_5 products, which are already sensitive with respect to the choice of the initial adduct. For the C_6H_6 isomers, the relative yields can be affected for the minor products, 3,4-hexadiene-1-yne, 1,3-hexadiyne, and 1,3-hexadiene-5-yne, because the critical transition states on their formation pathways lie within a 1.4 kcal/mol range. However, the conclusion that 2-ethynyl-1,3-butadiene is the major C_6H_6 isomer to be produced is not expected to change because the critical barrier for its formation is at least 10 kcal/mol lower than those for the other C_6H_6 species. Deviations from the statistical

(RRKM) behavior may enhance direct dissociation of the initial adducts, especially the cleavage of the bonds nearest to the carbon atom attacked by C_2H. In this case, an increase of branching ratios may be expected for 1,3-hexadiyne + H (from INT A) and diacetylene + C_2H_5 (from INT 1). Thus, neither the inaccuracies in the energetic parameters nor possible deficiency of the statistical approach to the calculations of branching ratios can explain the observations of fulvene and DMCB as major C_6H_6 products.

Soorkia et al.[100] evaluated branching ratios of various C_6H_6 isomers based on the fit of the experimental photoionization efficiency (PIE) curve in terms of individual contributions of these isomers. The authors utilized experimental PIE curves for some of the C_6H_6 isomers and, apparently, theoretically simulated curves for others. Such theoretical simulations require the knowledge of the adiabatic ionization energies (AIEs), ionization Franck-Condon factors and the vibrational temperature of these molecules. The vertical and adiabatic ionization energies for the C_6H_6 isomers, which may be produced in the C_2H + 1-butyne/2-butyne reactions, calculated in the present work at the CCSD(T)/CBS//B3LYP/6-311G** level of theory (with ZPE(B3LYP/6-311G**) included for the AIEs) are collected in Table 3. One can see that the agreement of our results with the literature data is rather close. Also, it is apparent that the AIEs of four C_6H_6 isomers, 1,3-hexadiene-5-yne, DMCB, 2-ethynyl-1,3-butadiene, and 3,4-hexadiene-1-yne, lie within a relatively narrow range of 8.66-9.02 eV, which complicates their assignment based on the PIE curves. Could 2-ethynyl-1,3-butadiene (AIE = 8.99 eV), which is the major C_6H_6 product according to our calculations (>90% among the C_6H_6 species), be incorrectly assigned to DMCB (AIE = 8.79 eV)? Since AIE for the former is

0.2 eV higher than that for the latter, this would be possible if a significant amount of

Table 6.3. Calculated vertical and adiabatic ionization energies (eV) of various C_6H_6 isomers produced in the reaction of C_2H with 1- and 2-butynes in comparison with the literature data.

Isomers	CCSD(T)/CBS//B3LYP		Literature (adiabatic)	
	vertical	adiabatic	CBS-QB3[a]	exp.
Fulvene	8.64	8.40	8.40	8.36[b]
1,3-hexadiene-5-yne	8.83	8.66	8.63	9.2[c,d]
DMCB	9.01	8.79	8.75	8.80[b]
2-ethynyl-1,3-butadiene	9.16	8.99	8.95	
3,4-hexadiene-1-yne	9.27	9.02	8.99	
1,3-hexadiyne	9.60	9.39	9.37	9.41[c]
1,1-ethynylmethylallene	9.62	8.89		

[a]From Ref. 43. [b]From Ref. 62. [c]From Ref. 63. [d]Electron impact value minus 0.3 eV as reported in Ref. 63.

vibrationally excited 2-ethynyl-1,3-butadiene is present in the flow tube reactor when it is subjected to the ionizing VUV synchrotron radiation. 2-Ethynyl-1,3-butadiene is formed in the C_2H + 1-butyne reaction with the exothermicity of ~40 kcal/mol (~1.7 eV). Some fraction of this released energy goes to the kinetic energy of the C_6H_6 + H dissociation products. However, it is plausible that a part of the energy remains in the form of the internal vibrational energy of 2-ethynyl-1,3-butadiene resulting in a reduction of its ionization energy. Soorkia et al. apparently used in their fit individual PIE curves measured or simulated at 300 K, which is close to the experimental temperature. If the 2-ethynyl-1,3-butadiene product does not have sufficient time to completely thermalize before it is ionized under the experimental conditions, it may have an internal vibrational energy distribution different from that typical for the room temperature, further complicating the fit of the measured PIE curve. Our hypothesis therefore is that the experimental observation of a rise in the ionization intensity around 8.8 eV assigned to DMCB may be in fact due to vibrationally excited 2-ethynyl-1,3-butadiene.

6.4 Reactions of CN + Diacetylene

The combination of the crossed molecular beams data and the electronic structure calculations provides a comprehensive picture of the underlying reaction mechanism. First of all, let us consider the energetics of the reaction. The experimentally derived reaction energy of kJ mol -87 ± 15^{-1} agrees very well with the computed data to form the cyanodiacetylene isomer [p1] plus a hydrogen atom kJ / mol (-79 ± 5^{-1}). Based on these energetical constraints, the isocyanodiacetylene isomer [p2] cannot be formed since this reaction would be too endoergic. Consequently, the cyanodiacetylene molecule is the sole molecular product of the bimolecular gas phase reaction of cyano radicals with diacetylene in our experiment, in hydrocarbon-rich atmospheres of planets and their satellites, and in the interstellar medium. We would like to propose the following reaction mechanism to form this important molecule. Dictated by a barrierless addition with its unpaired electron at the carbon atom, the cyano radical adds to the carbon-carbon triple bond of the diacetylene molecule leading to the H_2C_5N intermediates [1], [2], and/or [3]. The barrierless addition suggests that large impact parameters dominate the formation of the reaction intermediate. This likely results in a preferential formation of [1] via addition to the terminal (C1) carbon atom of the diacetylene molecule. The indirect nature of this process was verified by the CM angular distribution and flux contour map which depict flux over the complete angular range. Also, the fraction of available energy channeling into the translational degrees of freedom of the reaction products of 30(±5%) suggested indirect scattering dynamics via reaction intermediate(s). What is the fate of these reaction intermediates? The structure of the cyclic intermediate [2] cannot lead within one step to the cyanodiacetylene reaction product. The calculations suggest that [2] isomerizes via ring opening to [1] and/or [3]. Considering the inherent barriers to rearrangement of 23 and kJ / mol 3^{-1}, it is likely that [2] rearranges preferentially to intermediate [1]. Intermediate [3] itself can either fragment back to the initial reactants or isomerize to [2] which in turn yields [1]. Since the barrierless entry channel is far above the barriers to rearrangement from the intermediates, the hydrogen atom might migrate fairly freely in the intermediates involved. Nevertheless, all initial reaction intermediates yield eventually isomer [1]. The latter can either undergo a hydrogen migration to form [4] or decomposes via hydrogen elimination. This process involves a tight exit barrier and a transition state located kJ / mol 20^{-1} above the final products. The tight nature of an exit transition state is also supported by the distribution maximum of the CM translational energy distribution peaking at about kJ / mol 20^{-1}. Therefore, both the electronic structure calculations and the experiments support the existence of a tight exit transition state. In other words, the reversed reaction of an addition of a hydrogen atom to a carbon-carbon triple bond of a closed shell molecule involves an entrance barrier. The magnitude of this barrier is close to the one of kJ / mol 18^{-1} documented in the addition of a hydrogen atom to acetylene forming the vinyl radical. For completeness, it should be mentioned that [4] could also decompose to the cyanodiacetylene product. However, [4] can only be formed via hydrogen shift from [1]. Considering the barriers involved in the hydrogen migration from [1] versus the unimolecular decomposition of [1] to cyanodiacetylene plus a hydrogen atom, we expect that [1] fragments preferentially to cyanodiacetylene. Our statistical calculations confirm this deduction. 96.7% of cyanodiacetylene was found to be formed via unimolecular decomposition of intermediate [1].

7. CONCLUSIONS

An *ab initio* study of PES of involving ethynyl and cyano radicals with unsaturated hydrocarbons was conducted. This allowed the reaction mechanism to be determined, and the parameters of the PES were used in RRKM theory eventually determine the branching ratios of the products.[55-64] The unsaturated hydrocarbons include diacetylene (C_4H_2),[99] C_3H_4 isomers allene and methylacetylene,[86] and C_4H_6 isomers 1,3-butadiene,[112] 1,2-butadiene,[97] 1-butyne, and 2-butyne.[89] The parameters obtained from the *ab initio* calculations includes optimized electronic structure, moments of inertia, vibrational frequencies, and zero-point energy at the hybrid-functional B3LYP/6-311g(d,p) level of theory. They were followed by single-point calculations at the CCSD(T)/cc-pVTZ level of theory, with CBS extrapolations of the reactants and products. The unimolecular single-collision rate constant was calculated for all forward and reverses individual reaction steps using the RRKM theory, which after steady-state calculations gave the product branching ratios. This work aimed to study the H-loss reaction mechanisms versus the CH_3-loss reaction mechanisms. When ethynyl radical or cyano radical reacted with an unsaturated hydrocarbon, either an H-loss product occured, or a CH_3-loss product occurred when there was a methyl group on the unsaturated hydrocarbon. The following sections summarize the H-loss reaction mechanisms and the CH_3-loss reaction mechanisms when a methyl group existed in the potential energy surface.

The first hypothesis of the C_2H-for-H reaction mechanism is preferable over the C_2H-for-CH_3 reaction mechanism (or H-loss is preferred over CH_3-loss) holds true for most cases. However, the opposite case where the C_2H-for-CH_3 reaction mechanism is preferable is pronounced in certain reactions discussed below, especially ones that contain methyl groups on the unsaturated hydrocarbon. The same situation occurs when using cyano radicals instead of ethynyl radical, where CN-for-H is preferable for most cases, and CN-for-CH_3 is strongly pronounced only under specific conditions.

The second hypothesis that substituting cyano radical for ethynyl radical produces isoelectronic equivalent products holds true for the cases studied. A survey of these reactions and commentary in this trend is also given below.

7.1 H-loss vs CH_3-loss Reaction Channels

H-loss channels are the most common reaction paths since there are several hydrogen atoms that can be lost. Therefore, the amount of products one observes in a full PES should be mainly H-loss products. Unsaturted hydrocarbons that do not contain a methyl group exhibit only H-loss products. Even when there exists a methyl group on the unsaturated hydrocarbon, as in the case of C_2H/CN + 1-butyne, there is four possible H-loss products and only one CH_3-loss product, yet this CH_3-loss channel that forms ethynylallene is the prelevant product. For the case of C_2H + allene[86], the C_2H-for-H is the dominant mechanism for both terminal and central addition, giving 1,4-pentadiyne after the initial adduct forms. This can be explained by the absence of a methyl group, allowing only H-loss products to occur. The opposite is true for the case of C_2H + methylacetylene, which contains a terminal methyl group. Terminal addition of ethnyl radical gives arise to the H-loss product methyldiacetylene. Here, a CH_3-loss cannot occur since it would lead to a highly unfavorable acetylenic radical. However, through central addition of ethynyl radical to the middle carbon, the C_2H-for-CH_3 reaction mechanism is favorable,

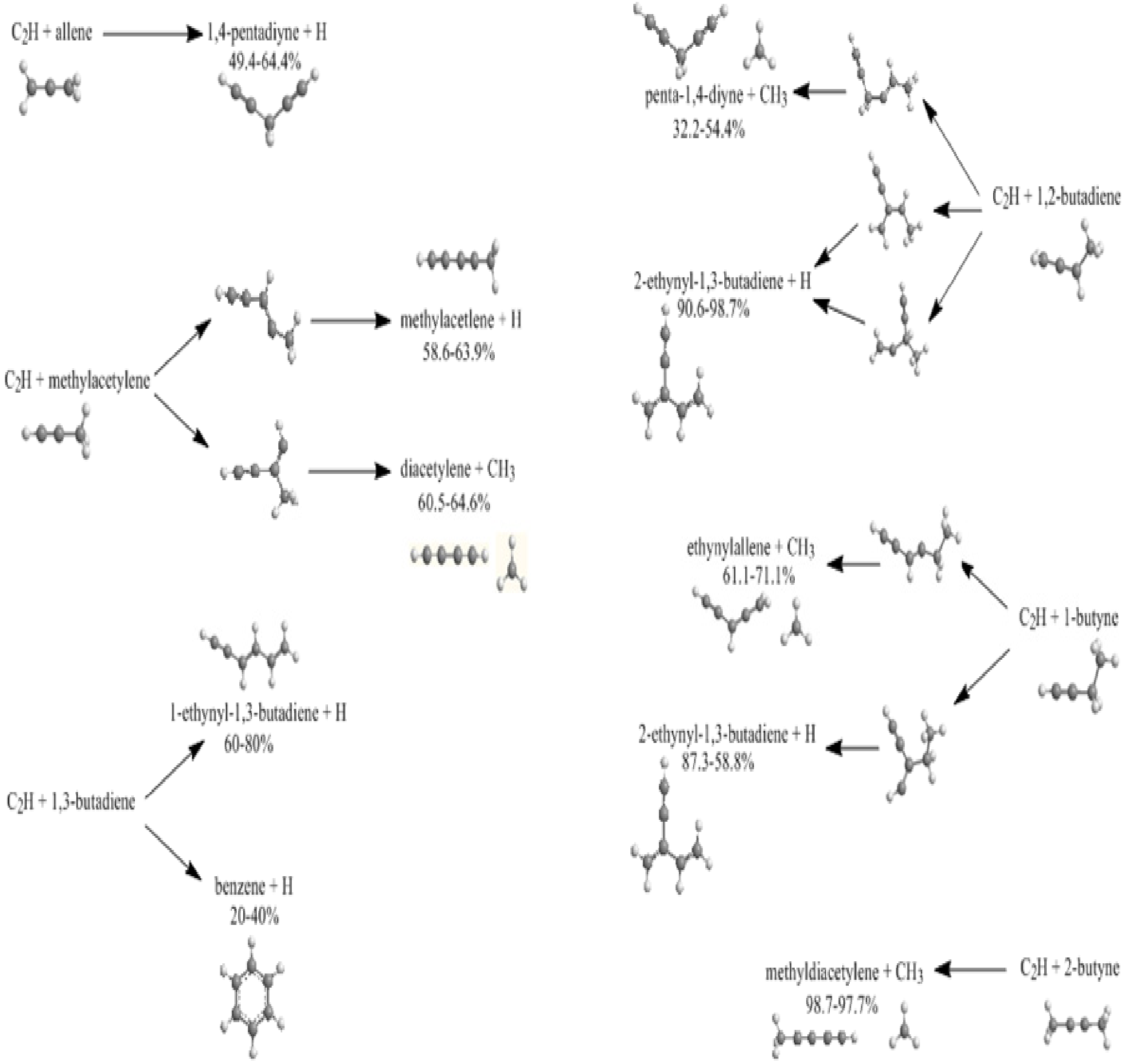

Figure 7.1a. Overall reactants and products from ethnyl radical additions to unsaturated hydrocarbons studied in this work. Both terminal and central addition are given, where applicable. Given percentage is product branching ratios using RRKM theory.

giving rise to diacetylene + CH_3. Here, the methyl group is not terminal, but branched, allowing its cleavage to occur with a low barrier after the initial adduct forms.

Noteworthy is that only CH3-loss can occur, H-loss would produce a diradical species. The reaction of CN + C_3H_4 was not studied in this work.

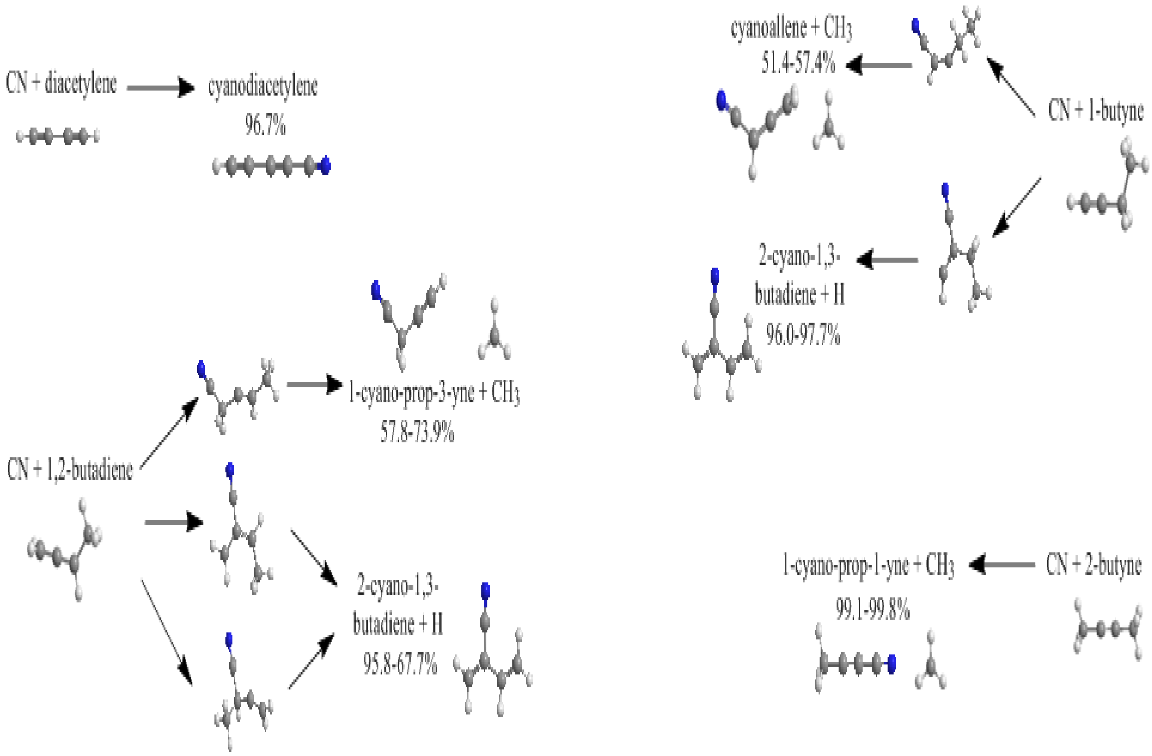

Figure 7.1b. Overall reactants and products from cyano radical additions to unsaturated hydrocarbons studied in this work. Both terminal and central addition are given, where applicable. Given percentage is product branching ratios using RRKM theory.

For the case of C_2H + 1,3-butadiene[112], only C_2H-for-H reaction mechanisms are observed. 1,3-Butadiene bears no methyl group, so only H-loss products were expected. The H-loss product of 1-ethynyl-1,3-butadiene occurred mainly from the initial adduct from the terminal addition of ethynl radical to 1,3-butadiene. The aromatic product of benzene was also observed after cyclization and isomerization steps, followed by an H-loss. The reaction of CN + 1,3-butadiene was not studied in this work.

For the case of C_2H + 1,2-butadiene[97], CH_3-loss was expected to occur since 1,2-butadiene contains a terminal methyl group. Terminal addition of ethynyl radical to 1,3-

butadiene follows the C_2H-for-CH_3 mechanism producing 1,4-pentadiyne. However, central addition to both central carbons produces the C_2H-for-H product 2-ethynyl-1,3-butadiene. Unlike central ethynyl radical addition to methylacetylene reaction, central ethynyl radical addition to 1,2-butadiene could lose a CH_3, however the C_2H-for-H reaction is energetically favorable. The similar situation occurred for CN + 1,2-butadiene. Terminal addition of cyano radical to 1,2-butadiene had the CN-for-CH_3 mechanism, whch gave rise to 1-cyano-prop-3-yne. Central addition of cyano radical to 1,2-butadiene gave 2-cyano-1,3-butadiene from the CN-for-H mechanism, despite being able to produce the CN-for-CH_3 reaction path.

As previously mentioned, 1-butyne bears a terminal methyl group. So the terminal addition of ethynl radical to 1-butyne[89] produced the C_2H-for-CH_3 mechanism, leading to cyanoallene. Here, C2H-for-H products could be formed, but the C_2H-for-CH_3 is the preferred reaction path. For central addition, CH_3-loss would produce a diradical, so the C_2H-for-H reaction mechanism is preferred. For the case of CN + 1-butyne, similarly, terminal addition of cyano radical to 1-butyne gives rise to CN-for-CH_3 while central addition of cyano radical to 1-butyne gives CN-for-H.

Ethynyl radical addition to 2-butyne[89] leads to C_2H-for-CH_3 reaction mechanism, giving rise to methyldiacetylene. This is so since 2-butyne has two terminal methyl groups, any which can cleave upon ethynyl radical addition. Similarly, cyano radical addition to 2-butyne gives the CN-for-CH_3 reaction mechanism, giving rise to 1-cyano-prop-1-yne. Lastly, cyano radical addition to diacetylene gives the CN-for-H product cyanodiacetylene.[99] Diacetylene doesn’t contain any methyl group, so only H-loss products are expected.

To summarize, C_2H-for-H reaction mechanisms are preferred when the unsaturated hydrocarbon contains no methyl group. However, when there is a methyl group on the unsaturated hydrocarbon, the C_2H-for-CH_3 reaction mechanism prevails. If the CH_3-loss produces a diradical, then the H-loss would prevail in a methylated unsaturated hydrocarbon. The only exception to this was central addition of ethynyl radical to 1,2-butadiene, which could either follow a C_2H-for-CH_3 reaction mechanism or a C_2H-for-H reaction mechanism, in which the latter case was favorable from a significant difference in barrier heights (10.4 kcal/mol).

7.2 Isoelectronic Product Comparisons

Ethynyl radical is isoelectronic to cyano radical, so to address the products that form from ethynyl radical additions to unsaturated hydrocarbons versus cyano radical additions to the same unsaturated hydrocarbons, the products from both reactions are remarkably isoelectronic as well, and follow similar mechanisms as discussed in the previous section. In general, the CH group of ethnyl radical gets replaced by an N atom from the cyano group, producing isoelectronic reactants and consequently products. Here, ethynyl radical and cyano radical addition reactions to 1,2-butadiene, 1-butyne, and 2-butyne were compared, since they both used the same unsaturated hydrocarbon species.

For ethynl radical and cyano radical addition to 1,2-butadiene[97], terminal additions gave the CH_3-loss isoelectronic products of penta-1,4-diyne and 1-cyano-prop-3-yne, respectively. For these products, the terminal CH group from ethynyl radical was replaced by an N atom from cyano radical. Similarly, central addition gave rise to 2-

ethynyl-1,3-butadiene and 2-cyano-1,3-butadiene, respectively, from an H-loss mechanism.

Ethynyl radical additions and cyano radical additions to the terminal carbon of 1-butyne[89] also gave the CH_3-loss isoelectronic products of penta-1,4-diyne and cyanoallene, respectively. Central addition gave the H-loss isoelectronic products of 2-ethynyl-1,3-butadiene and 2-cyano-1,3-butadiene, respectively.

Finally, ethynyl radical addition and cyano radical addition to 2-butyne[89] gave the CH_3-loss isoelectronic products of methyldiacetylene and 1-cyano-prop-1-yne, respectively.

In general, C_2H and CN radical additions to unsaturated hydrocarbons can lead to a growth of larger and more complex organic molecules including aromatics in cold enviroments such as Titan and the interstellar medium.[86,89,97,99,112] The former radical reaction leads to a two carbon unit growth for C_2H-for-H reaction mechanisms and one carbon unit growth for C_2H-for-CH_3 reaction mechanisms. The latter radical reaction leads to a carbon and nitrogen unit growth in CN-for-H reaction mechanisms and a nitrogen unit growth in CN-for-CH_3 reaction mechanisms.

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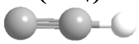
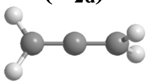
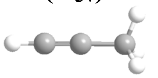
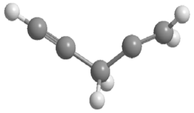
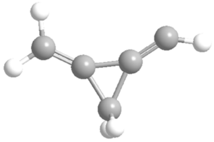
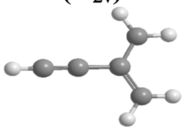
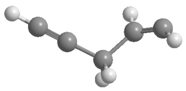
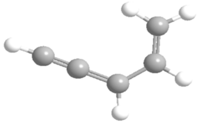
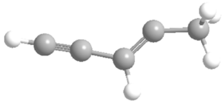
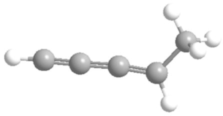
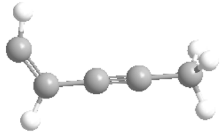
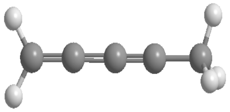
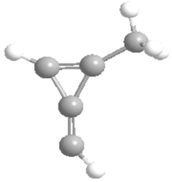
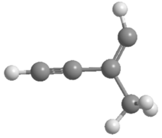
APPENDICES

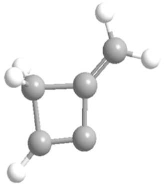
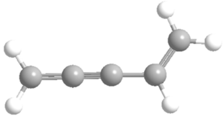
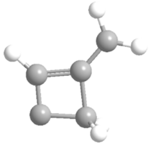
Table A1. B3LYP and CCSD(T) calculated total energies at 0 K, zero-point energy corrections (ZPE), B3LYP/6-311G** optimized Cartesian coordinates, unscaled vibrational frequencies (ν_i), and moments of inertia (I_i) of all species involved in the $C_2H + C_3H_4$ reaction.

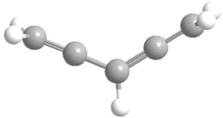
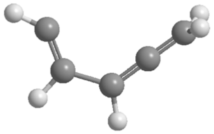
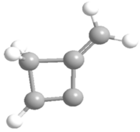
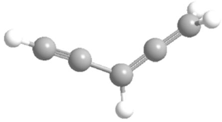
Species, (point group) electronic state	Energies, a.u.	*i*	I_i, a.u.	Cartesian coordinates, angstroms				ν_i, cm^{-1}
				Atom	X	Y	Z	
H (18-21)	ZPE(B3LYP/6-311G**) = 0.0 E(B3LYP/6-311G**) = -0.502155930011 E(CCSD(T)/CC-PVDZ) = -0.499278 E(CCSD(T)/CC-PVTZ) = -0.49980982 E(CCSD(T)/CC-PVQZ) = -0.499946 E(CCSD(T)/CC-PV5Z) = -0.499995 E(CCSD(T)/CBS) = -0.49999							
C_2H **($C_{\infty v}$)** 	ZPE(B3LYP/6-311G**) = 0.014445 E(B3LYP+ZPE) = -76.615013 E(CCSD(T)/CC-PVDZ) = -76.398687 E(CCSD(T)/CC-PVTZ) = -76.46769892 E(CCSD(T)/CC-PVQZ) = -76.4876915 E(CCSD(T)/CC-PV5Z) = -76.4936542 E(CCSD(T)/CBS) = -76.49585	A B C	0.00000 40.54466 40.54466	C H C	0.000000 0.000000 0.000000	0.000000 0.000000 0.000000	-0.473068 -1.536812 0.729203	370, 416, 2089, 3465
CH_2CCH_2 **Allene** **(D_{2d})** 	ZPE(B3LYP/6-311G**) = 0.054873 E(B3LYP+ZPE) = -116.638325 E(CCSD(T)/CC-PVDZ) = -116.314014 E(CCSD(T)/CC-PVTZ) = -116.43338571 E(CCSD(T)/CC-PVQZ) = -116.466524 E(CCSD(T)/CC-PV5Z) = -116.476317 E(CCSD(T)/CBS) = -116.47946	A B C	12.21789 203.15738 203.15833	C C H H C H H	0.000002 1.306511 1.877635 1.877580 -1.306511 -1.877613 -1.877615	0.000014 0.000001 0.662901 -0.662926 -0.000037 -0.639697 0.639851	0.000058 -0.000019 0.639704 -0.639744 -0.000055 0.662927 -0.662796	369, 369, 896, 921, 921, 1055, 1108, 1466, 1508, 2041, 3114, 3116, 3187, 3187

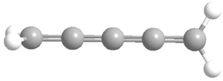
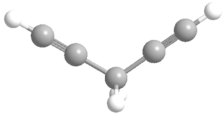
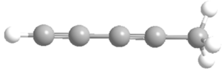
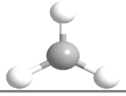
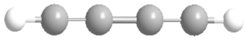
CH$_3$CCH **Methyl Acetylene** **(C_{3v})** 	ZPE(B3LYP/6-311G**) = 0.055468	A	11.25810	C	-1.420160	-0.000001	0.000001	339, 340, 666, 943, 1057, 1057, 1417, 1480, 1480, 2231, 3025, 3084, 3084, 3479
	E(B3LYP+ZPE) = -116.635302	B	210.15954	H	-2.482190	-0.000004	0.000006	
	E(CCSD(T)/CC-PVDZ) = -116.315233	C	210.15977	C	-0.219254	0.000001	-0.000005	
	E(CCSD(T)/CC-PVTZ) = -116.43520449			C	1.238135	0.000001	-0.000001	
	E(CCSD(T)/CC-PVQZ) = -116.46871			H	1.629948	1.011755	-0.138100	
	E(CCSD(T)/CBS) = -116.4817			H	1.629948	-0.386271	0.945252	
				H	1.629969	-0.625488	-0.807125	
HCCCH$_2$CCH$_2$ (1) **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.075116	A	88.19176	C	-2.365351	-0.508426	0.041871	89, 196, 316, 328, 434, 577, 669, 686, 859, 895, 909, 976, 1046, 1223, 1315, 1412, 1439, 1741, 2231, 2945, 3020, 3033, 3153, 3479
	E(B3LYP+ZPE) = -193.341599	B	694.82838	C	-1.318329	0.077818	0.026158	
	E(CCSD(T)/CC-PVTZ) = -192.99550682	C	747.59397	C	-0.044912	0.801351	0.008989	
				H	-0.129227	1.657627	-0.672050	
				C	1.114161	-0.033911	-0.386572	
				C	2.246218	-0.440266	0.125118	
				H	2.542024	-0.174286	1.144727	
				H	2.943916	-1.061725	-0.429228	
				H	-3.292194	-1.027136	0.053979	
				H	0.144756	1.226129	1.009186	
CH$_2$CCH$_2$CCH (2) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.075371	A	154.79121	C	1.864712	-0.790976	0.000436	228, 292, 440, 473, 528, 672, 703, 759, 792, 797, 816, 1037, 1061, 1113, 1219, 1358, 1469, 1500, 1783, 3142, 3143, 3234, 3234, 3246
	E(B3LYP+ZPE) = -193.329691	B	414.62452	H	2.929174	-0.621528	0.001276	
	E(CCSD(T)/CC-PVTZ) = -192.8706069	C	557.26723	C	0.763447	-0.117911	-0.000791	
				C	-0.653852	0.000629	-0.001027	
				C	-1.834567	-0.599390	0.000331	
				H	-2.754445	-0.025221	0.001721	
				H	-1.912396	-1.680414	-0.000044	
				C	0.096972	1.276890	0.000247	
				H	0.158070	1.854831	0.919553	
				H	0.159329	1.856887	-0.917688	
HCCC(CH$_2$)$_2$ (3) **(C_{2v})** 	ZPE(B3LYP/6-311G**) = 0.075198	A	172.72704	C	2.172908	0.000045	-0.001555	192, 265, 405, 526, 542, 571, 625, 657, 687, 767, 797, 800, 981, 1038, 1292, 1367, 1474, 1518, 2212, 3148, 3155, 3255, 3257, 3477
	E(B3LYP+ZPE) = -193.382714	B	438.31183	C	0.970003	-0.001116	0.002549	
	E(CCSD(T)/CC-PVTZ) = -193.03509924	C	611.03798	C	-0.468552	-0.000015	0.000278	
				C	-1.136488	1.222109	-0.000241	
				H	-0.595453	2.158006	0.001079	
				C	-1.138116	-1.221315	-0.000101	
				H	-0.598452	-2.158024	-0.000043	
				H	-2.220784	-1.250613	-0.001827	
				H	3.235223	-0.000981	-0.001871	
				H	-2.219064	1.253369	-0.002925	
HCCCH$_2$CHCH (4)	ZPE(B3LYP/6-311G**) = 0.075444	A	91.02892	C	-2.326649	-0.411202	-0.129762	90, 190, 335, 372, 489, 666,

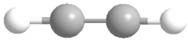
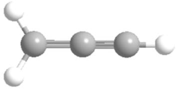
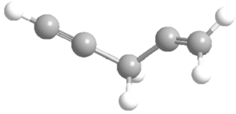
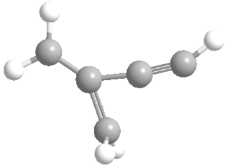
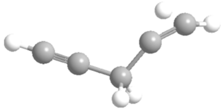
(C$_1$)	E(B3LYP+ZPE) = -193.336569	B	670.89859	C	-1.255792	0.127744	-0.053153	678, 682, 806, 843, 935, 968, 1016, 1206, 1271, 1317, 1464, 1668, 2222, 3014, 3064, 3107, 3236, 3477
	E(CCSD(T)/CC-PVTZ) = -192.99220308	C	704.65729	C	0.055066	0.763763	0.052778	
				H	0.304313	1.262707	-0.887986	
				C	1.159866	-0.229627	0.423064	
				C	2.245624	-0.427191	-0.274200	
				H	2.701276	-0.074222	-1.187797	
				H	-3.274741	-0.884725	-0.202589	
				H	0.013410	1.543497	0.823386	
				H	0.987057	-0.788181	1.342623	
CHCCHCHCH$_2$ (5)	ZPE(B3LYP/6-311G**) = 0.075850	A	130.93286	C	2.189719	2.189719	0.000000	158, 225, 383, 435, 559, 562, 651, 667, 736, 863, 943, 997, 1037, 1159, 1260, 1415, 1434, 1544, 2104, 3143, 3146, 3164, 3240, 3471
(C$_s$)	E(B3LYP+ZPE) = -193.394519	B	530.92725	H	3.087318	3.087318	0.000000	
	E(CCSD(T)/CC-PVTZ) = -193.04363509	C	661.86011	C	1.167048	1.167048	0.000000	
				C	0.000000	0.000000	0.000000	
				H	0.120051	0.120051	0.000000	
				C	-1.309155	-1.309155	0.000000	
				H	-2.114271	-2.114271	0.000000	
				C	-1.638382	-1.638382	0.000000	
				H	-2.673087	-2.673087	0.000000	
				H	-0.875400	-0.875400	0.000000	
CHCCHCCH$_3$ (6)	ZPE(B3LYP/6-311G**) = 0.075191	A	40.27641	C	2.618037	-0.254102	-0.000165	148, 154, 199, 328, 409, 526, 626, 684, 789, 889, 1042, 1046, 1059, 1284, 1397, 1451, 1471, 1727, 2206, 2966, 3009, 3048, 3070, 3478
(C$_s$)	E(B3LYP+ZPE) = -193.352873	B	812.27235	C	1.458463	0.070739	0.000131	
	E(CCSD(T)/CC-PVTZ) = -193.00374491	C	841.34594	C	0.104738	0.511669	-0.000252	
				C	-0.956317	-0.274313	-0.000904	
				C	-2.417319	-0.161949	0.000401	
				H	-2.731697	0.893098	0.001892	
				H	-2.852785	-0.642014	-0.881971	
				H	-2.851289	-0.644147	0.882316	
				H	3.635758	-0.557674	0.001956	
				H	-0.045599	1.598469	0.000546	
CHCCCHCH$_3$ (7)	ZPE(B3LYP/6-311G**) = 0.074183	A	47.69908	C	2.669314	-0.207850	0.000349	54, 144, 226, 292, 379, 440, 512, 610, 721, 788, 1035, 1048, 1087, 1324, 1399, 1482, 1487, 1810, 2010, 3016, 3046, 3063, 3120, 3469
(C$_s$)	E(B3LYP+ZPE) = -193.371149	B	805.87018	C	1.457646	0.013512	-0.000077	
	E(CCSD(T)/CC-PVTZ) = -193.01445218	C	842.40451	C	0.154860	0.214972	-0.001572	
				C	-1.112963	0.539260	0.000338	
				C	-2.269943	-0.429323	0.000225	
				H	-1.925628	-1.463697	-0.001322	
				H	-2.900626	-0.271043	0.881681	
				H	-2.902385	-0.268972	-0.879594	
				H	3.717227	-0.379286	0.001744	
				H	-1.382060	1.599571	0.001919	

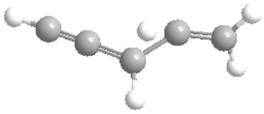
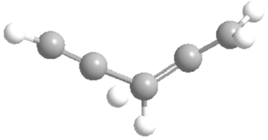
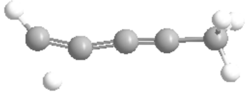
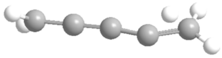
$CHCHCCCH_3$ (8) **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.075493	A	51.97354	C	-2.472756	0.159901	-0.000048	29, 139, 194, 313, 388, 501, 694, 718, 873, 911, 1050, 1054, 1178, 1268, 1416, 1478, 1478, 1623, 2330, 3020, 3075, 3081, 3087, 3237
	E(B3LYP+ZPE) = -193.350468	B	805.72700	H	-2.773300	0.796914	-0.837438	
	E(CCSD(T)/CC-PVTZ) = -193.00216449	C	846.45706	H	-3.016444	-0.785306	-0.085878	
				C	-1.033433	-0.061081	-0.000112	
				C	0.160479	-0.236549	0.000103	
				C	1.568754	-0.469596	0.000007	
				H	1.892762	-1.511266	-0.000069	
				C	2.476585	0.487705	-0.000023	
				H	2.495092	1.567891	0.000052	
				H	-2.795878	0.6494890	0.923768	
CH_2CCCCH_3 (9) **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.073725	A	17.41919	C	2.606751	0.004845	0.000011	26, 56, 136, 143, 324, 358, 550, 675, 871, 980, 1027, 1039, 1142, 1411, 1444, 1465, 1471, 1859, 2101, 3000, 3049, 3057, 3064, 3114
	E(B3LYP+ZPE) = -193.378718	B	924.78311	H	3.003110	-0.480185	0.898428	
	E(CCSD(T)/CC-PVTZ) = -193.01947811	C	930.95599	H	3.002317	1.027154	-0.028634	
				C	1.156707	-0.009818	-0.000198	
				C	-0.077120	-0.002344	-0.000034	
				C	-1.394209	0.002666	-0.000018	
				C	-2.700866	0.001581	0.000010	
				H	-3.280050	0.925357	0.000074	
				H	3.005384	-0.530542	-0.868576	
				H	-3.278347	-0.923363	0.000080	
$HCCCHCCH_3$ (10) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.075191	A	40.27641	C	2.618037	-0.254102	-0.000165	148, 154, 199, 328, 409, 526, 626, 684, 789, 889, 1042, 1046, 1059, 1284, 1397, 1451, 1471, 1727, 2206, 2966, 3009, 3048, 3070, 3478
	E(B3LYP+ZPE) = -193.352873	B	812.27235	C	1.458463	0.070739	0.000131	
	E(CCSD(T)/CC-PVTZ) = -193.00374491	C	841.34594	C	0.104738	0.511669	-0.000252	
				C	-0.956317	-0.274313	-0.000904	
				C	-2.417319	-0.161949	0.000401	
				H	-2.731697	0.893098	0.001892	
				H	-2.852785	-0.642014	-0.881971	
				H	-2.851289	-0.644147	0.882316	
				H	3.635758	-0.557674	0.001956	
				H	-0.045599	1.598469	0.000546	
$HCCC(CH)CH_3$ (11) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.075097	A	184.90177	C	0.606730	-2.071418	0.000000	171, 179, 271, 369, 532, 539, 643, 678, 692, 771, 853, 1029, 1053, 1194, 1404, 1481, 1482, 1642, 2191, 3031, 3089, 3124, 3242, 3476
	E(B3LYP+ZPE) = -193.34202	B	437.53394	C	0.337147	-0.896757	0.000000	
	E(CCSD(T)/CC-PVTZ) = -192.99616215	C	611.18936	C	0.000000	0.495810	0.000000	
				C	0.972514	1.390987	0.000000	
				H	2.051922	1.392526	0.000000	
				C	-1.476434	0.878336	0.000000	
				H	-1.718437	1.472235	0.883862	
				H	-1.718437	1.472235	-0.883862	
				H	-2.103331	-0.013036	0.000000	

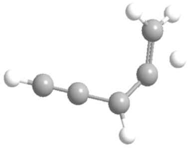
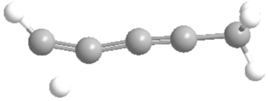
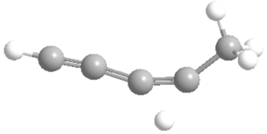
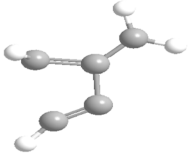
				H	0.848539	-3.105709	0.000000	
$CH_2CCCHCH_2$ (12) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.078256	A	123.22462	C	-1.887631	-0.044439	0.000132	219, 350, 525, 714, 715, 771, 837, 891, 899, 955, 981, 1086, 1099, 1180, 1219, 1432, 1459, 1563, 1740, 3023, 3085, 3140, 3224, 3243
	E(B3LYP+ZPE) = -193.34283	B	369.83729	H	-2.423036	0.897963	-0.000202	
	E(CCSD(T)/CC-PVTZ) = -193.00216744	C	481.36137	C	-0.562632	-0.083550	-0.000230	
				C	0.574426	0.970073	-0.000019	
				H	0.604309	1.588447	0.901971	
				C	1.541779	-0.228937	0.000014	
				C	0.512331	-1.082677	0.000016	
				H	-2.473768	-0.956071	-0.000035	
				H	0.604502	1.589700	-0.901094	
				H	2.618355	-0.302864	-0.000122	
$CH_2CCCHCH_2$ (13) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.075347	A	46.81254	C	-2.566363	0.178257	-0.000250	143, 178, 312, 330, 447, 536, 645, 749, 769, 893, 978, 1031, 1067, 1284, 1314, 1435, 1492, 1568, 2047, 3122, 3131, 3147, 3215, 3242
	E(B3LYP+ZPE) = -193.395824	B	793.15635	H	-2.966951	1.185527	0.000372	
	E(CCSD(T)/CC-PVTZ) = -193.03902804	C	839.96877	H	-3.271326	-0.645291	-0.000475	
				C	-1.236092	-0.042967	0.000839	
				C	-0.014198	-0.235980	-0.000688	
				C	1.355027	-0.487221	-0.000019	
				H	1.654973	-1.533577	0.000644	
				C	2.319247	0.467164	-0.000013	
				H	3.367615	0.196571	0.000483	
				H	2.069961	1.521248	-0.000240	
$CH_2CCHCCH_2$ (14) **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.078278	A	150.84209	C	1.790073	0.003270	0.000089	209, 351, 461, 692, 711, 828, 841, 876, 907, 999, 1059, 1125, 1148, 1215, 1436, 1470, 1558, 1711, 3059, 3109, 3137, 3224, 3235
	E(B3LYP+ZPE) = -193.341591	B	326.46169	H	2.373878	0.916533	-0.000198	
	E(CCSD(T)/CC-PVTZ) = -192.63246835	C	465.73102	C	0.459008	0.035917	-0.000265	
				C	-0.618607	-1.072974	0.000182	
				H	-0.653868	-1.693831	0.897510	
				C	-1.528814	0.149237	-0.000484	
				C	-0.576232	1.091317	0.000213	
				H	-0.545485	2.170652	0.000532	
				H	2.326826	-0.938055	-0.000576	
				H	-0.653918	-1.695897	-0.895680	
$CH_2CCHCCH_2$ (15) **(C_s)**	ZPE(B3LYP/6-311G**) = 0.073680	A	74.21263	C	-2.371748	-0.437567	0.002227	122, 134, 154, 351, 435, 497, 611, 868, 893, 895, 945, 975, 979, 1042, 1330, 1437, 1453, 1874, 1929, 3053, 3057, 3088, 3109, 3110
	E(B3LYP+ZPE) = -193.368438	B	739.56529	H	-2.882372	-0.692966	0.931639	
	E(CCSD(T)/CC-PVTZ) = -192.40831791	C	789.16665	C	-1.207599	0.135452	-0.008520	
				C	-0.000320	0.755923	0.000286	
				C	1.211277	0.143743	0.007565	
				C	2.370167	-0.439846	-0.002098	

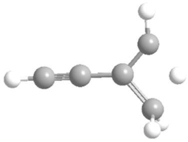
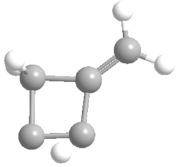
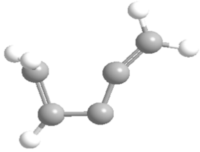
				H	2.892596	-0.704762	0.917902	
				H	2.881425	-0.696812	-0.930686	
				H	-2.897256	-0.698882	-0.916982	
				H	-0.005059	1.847198	0.001370	
CHCHCHCCH$_2$ (16) **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.074711 E(B3LYP+ZPE) = -193.347158 E(CCSD(T)/CC-PVTZ) = -192.99597397	A	124.38559	C	-2.165015	-0.461721	0.000220	88, 151, 324, 512, 631, 670, 828, 858, 876, 907, 924, 1008, 1149, 1276, 1368, 1472, 1642, 2035, 3026, 3107, 3131, 3176, 3249
		B	571.81295	H	-2.650249	-0.755769	0.927030	
		C	683.83396	C	-1.049928	0.206877	-0.000246	
				C	0.071346	0.886930	-0.000233	
				C	1.432164	0.318924	0.000328	
				C	1.773529	-0.950581	-0.000219	
				H	2.685567	-1.526950	-0.000009	
				H	-2.649806	-0.756925	-0.926491	
				H	0.006855	1.972634	-0.000877	
				H	2.235060	1.064440	0.001251	
CH$_2$CCCHCH$_2$ (17) **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.078256 E(B3LYP+ZPE) = -193.318882 E(CCSD(T)/CC-PVTZ) = -192.97455064	A	108.86016	C	-1.915316	0.000007	0.172090	217, 349, 530, 664, 703, 744, 775, 830, 842, 879, 1008, 1010, 1032, 1107, 1160, 1172, 1318, 1452, 1800, 3147, 3154, 3173, 3179, 3233
		B	403.20921	H	-2.466144	-0.929290	0.242033	
		C	451.59396	C	-0.599589	0.000118	0.013135	
				C	0.579933	-0.811345	-0.265808	
				H	0.723481	-1.488009	-1.099985	
				C	1.595069	-0.000565	0.400189	
				H	2.041897	-0.001259	1.387720	
				C	0.580611	0.812199	-0.265105	
				H	0.724534	1.487805	-1.100070	
				H	-2.468014	0.928268	0.243300	
CHCCHCCH$_2$ (18) **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.064999 E(B3LYP+ZPE) = -192.791208 E(CCSD(T)/CC-PVDZ) = -192.74687 E(CCSD(T)/CC-PVTZ) = -192.43544689 E(CCSD(T)/CC-PVQZ) = -192.989055 E(CCSD(T)/CBS) = -193.01056	A	67.01045	C	2.387584	-0.457475	-0.000060	141, 297, 350, 360, 606, 627, 644, 691, 883, 885, 951, 1005, 1140, 1353, 1465, 2042, 2209, 3109, 3114, 3182, 3478
		B	694.44424	C	1.306211	0.071666	0.000230	
		C	749.06097	C	0.054188	0.748983	-0.000010	
				C	-1.113745	0.147053	0.000000	
				C	-2.276429	-0.431525	-0.000001	
				H	-2.781054	-0.686694	-0.927852	
				H	-2.781744	-0.685251	0.927855	
				H	3.334931	-0.937879	-0.000071	
				H	0.081017	1.837618	-0.000884	
CH$_2$CCCCH$_2$ (19) **(D$_{2d}$)**	ZPE(B3LYP/6-311G**) = 0.064422 E(B3LYP+ZPE) = -192.796005 E(CCSD(T)/CC-PVDZ) = -192.742365 E(CCSD(T)/CC-PVTZ) = -192.43106043 E(CCSD(T)/CC-PVQZ) = -192.984279	A	12.37911	C	-2.583997	0.000715	0.000060	152, 152, 334, 335, 541, 541, 698, 754, 853, 853, 1006, 1006, 1323, 1432, 1512, 1955, 2228, 3113, 3114, 3187,
		B	860.38907	H	-3.149512	-0.189074	-0.907465	
		C	860.39132	C	-1.274193	-0.000807	0.000220	
				C	0.000012	0.000122	-0.000603	
				C	1.274214	-0.001202	0.000208	

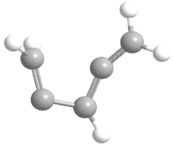
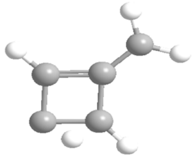
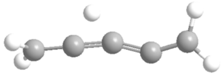
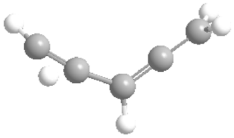
	E(CCSD(T)/CBS) = -193.00539			C	2.584047	0.000465	-0.000238	3187
				H	3.147368	0.909710	-0.188465	
				H	-3.149294	0.189591	0.907917	
				H	3.150940	-0.905985	0.190134	
CHCCH$_2$CCH (20)	ZPE(B3LYP/6-311G**) = 0.065461	A	92.35018	C	-2.243144	-0.569563	-0.000373	137, 307, 327, 334, 562, 670, 672, 689, 691, 903, 931, 999, 1243, 1341, 1455, 2231, 2237, 3013, 3037, 3477, 3478,
(C_{2v})	E(B3LYP+ZPE) = -192.776766	B	636.98044	C	-1.228322	0.070116	-0.000418	
	E(CCSD(T)/CC-PVDZ) = -192.738614	C	718.27985	C	1.227941	0.069409	0.000176	
	E(CCSD(T)/CC-PVTZ) = -192.42855099			C	2.243400	-0.569223	0.000457	
	E(CCSD(T)/CC-PVQZ) = -192.982539			H	3.138402	-1.141487	0.000724	
	E(CCSD(T)/CBS) = -193.00419			C	-0.000017	0.869907	0.000038	
				H	0.000518	1.529935	-0.875961	
				H	-3.138138	-1.141860	-0.000367	
				H	0.000067	1.529532	0.876324	
CHCCCCH$_3$ (21)	ZPE(B3LYP/6-311G**) = 0.065682	A	11.27539	C	-2.511633	-0.001382	0.002036	148, 148, 335, 335, 539, 540, 643, 644, 680, 1047, 1048, 1182, 1413, 1473, 1474, 2167, 2351, 3022, 3081, 3083, 3479
(C_{3v})	E(B3LYP+ZPE) = -192.800155	B	882.41245	H	-2.902582	-0.817579	-0.612142	
	E(CCSD(T)/CC-PVDZ) = -192.755153	C	882.41455	C	-1.058321	0.003766	-0.005300	
	E(CCSD(T)/CC-PVTZ) = -192.4454355			C	0.151062	-0.000120	-0.000792	
	E(CCSD(T)/CC-PVQZ) = -192.998799			C	1.515812	0.000239	-0.000041	
	E(CCSD(T)/CBS) = -193.0198			C	2.723345	-0.000989	0.001426	
				H	-2.895734	-0.129842	1.018489	
				H	3.785350	-0.000386	0.001796	
				H	-2.908628	0.938733	-0.392110	
CH$_3$ (22)	ZPE(B3LYP/6-311G**) = 0.029569	A	6.30449	C	0.000000	0.000000	0.000273	501, 1402, 1402, 3108, 3288, 3288
(D_{3h})	E(B3LYP+ZPE) = -39.853757	B	6.30449	H	0.000000	1.080657	-0.000545	
	E(CCSD(T)/CC-PVDZ) = -39.715785	C	12.60896	H	0.935876	-0.540328	-0.000545	
	E(CCSD(T)/CC-PVTZ) = -39.760817			H	-0.935876	-0.540328	-0.000545	
	E(CCSD(T)/CC-PVQZ) = -39.772271							
	E(CCSD(T)/CC-PV5Z) = -39.775614							
	E(CCSD(T)/CBS) = -39.77618							
HC$_4$H (22)	ZPE(B3LYP/6-311G**) = 0.037493	A	0.00000	C	0.000000	0.000000	1.889186	235, 236, 527, 527, 663, 663, 663, 663, 917, 2111, 2285, 3475, 3477
($C_{\infty v}$)	E(B3LYP+ZPE) = -153.528449693	B	408.53335	H	0.000000	0.000000	2.951597	
	E(CCSD(T)/CC-PVDZ) = -153.047959522	C	408.53335	C	0.000000	0.000000	0.682650	
	E(CCSD(T)/CC-PVTZ) = -153.195968803			C	0.000000	0.000000	-0.682650	
	E(CCSD(T)/CC-PVQZ) = -153.2379899667			C	0.000000	0.000000	-1.889186	
	E(CCSD(T)/CC-PV5Z) = -153.250397472			H	0.000000	0.000000	-2.951597	
	E(CCSD(T)/CBS) = -153.25465							
C$_2$H$_2$ (23)	ZPE(B3LYP/6-311G**) = 0.026978	A	0.00000	C	0.000000	0.000000	0.599026	642, 642, 773, 773, 2071, 3420, 3523
($D_{\infty h}$)	E(B3LYP+ZPE) = -77.354698	B	50.62104	H	0.000000	0.000000	1.661350	
	E(CCSD(T)/CC-PVDZ) = -77.108671	C	50.62104	C	0.000000	0.000000	-0.599026	
	E(CCSD(T)/CC-PVTZ) = -77.187388			H	0.000000	0.000000	-1.661350	

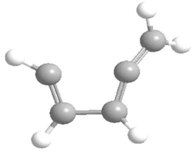
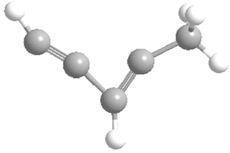
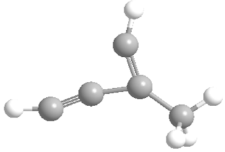
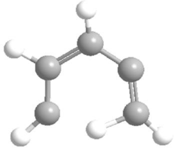
	E(CCSD(T)/CC-PVQZ) = -77.20918 E(CCSD(T)/CC-PV5Z) = -77.215664 E(CCSD(T)/CBS) = -77.21752							
C_3H_3 (23) **(C_{2v})** 	ZPE(B3LYP/6-311G**) = 0.040938 E(B3LYP+ZPE) = -116.037356 E(CCSD(T)/CC-PVDZ) = -115.662911 E(CCSD(T)/CC-PVTZ) = -115.777715 E(CCSD(T)/CC-PVQZ) = -115.810061 E(CCSD(T)/CC-PV5Z) = -115.819593 E(CCSD(T)/CBS) = -115.82275	A	6.22440	C	1.251382	-0.000031	-0.000030	352, 403, 468, 638, 681, 1031, 1089, 1455, 2013, 3140, 3230, 3469
		B	188.46833	H	1.806638	0.929996	0.000248	
		C	194.69273	H	1.806819	-0.929830	0.000248	
				C	-0.115826	-0.000114	-0.000084	
				C	-1.337807	0.000056	-0.000042	
				H	-2.399952	-0.000002	0.000445	
TS 1 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.075117 E(B3LYP+ZPE) = -193.341599 E(CCSD(T)/CC-PVTZ) = -192.99550331	A	88.25421	C	2.365364	-0.508112	0.041053	683i, 135, 190, 317, 355, 489, 509, 689, 853, 907, 938, 957, 1025, 1118, 1193, 1428, 1444, 1765, 1965, 3014, 3043, 3070, 3149, 3410
		B	694.68250	H	3.290389	-1.030182	0.053593	
		C	747.44558	C	1.318049	0.077640	0.026580	
				C	-1.114513	-0.032652	-0.387106	
				C	-2.245628	-0.440886	0.125008	
				H	-2.539416	-0.179149	1.146344	
				H	-2.944887	-1.059414	-0.430676	
				C	0.044965	0.801484	0.009595	
				H	-0.145004	1.225108	1.010276	
				H	0.129493	1.658787	-0.670313	
TS 2 **(C_s)** 	ZPE(B3LYP/6-311G**) = 0.072708 E(B3LYP+ZPE) = -193.323918 E(CCSD(T)/CC-PVTZ) = -192.9694158	A	161.50255	C	0.570890	-1.970145	0.000000	633i, 208, 245, 312, 390, 419, 611, 678, 768, 796, 850, 916, 950, 1021, 1168, 1417, 1451, 1704, 1904, 3123, 3141, 3228, 3233, 3385
		B	416.34377	C	0.223286	-0.766800	0.000000	
		C	565.39468	C	0.000000	0.625945	0.000000	
				C	0.664213	1.776277	0.000000	
				H	0.132486	2.720801	0.000000	
				H	1.747121	1.797287	0.000000	
				C	-1.349129	0.062109	0.000000	
				H	-1.894403	-0.045482	0.930019	
				H	1.253639	-2.791445	0.000000	
				H	-1.894403	-0.045482	-0.930019	
TS 3 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.068827 E(B3LYP+ZPE) = -193.265084 E(CCSD(T)/CC-PVTZ) = -192.91262339	A	87.54154	C	-2.358826	-0.498711	0.059510	1612i, 127, 144, 287, 374, 443, 518, 589, 680, 725, 768, 869, 1003, 1013, 1267, 1430, 1466, 1759, 1939, 2034, 3058, 3143, 3149, 3231
		B	696.43452	C	-1.314486	0.092304	0.031286	
		C	751.19732	C	-0.045346	0.816142	-0.001395	
				H	-0.092397	1.597989	-0.767676	
				C	1.145919	-0.062093	-0.275711	
				C	2.300635	-0.452790	0.147152	
				H	3.049517	-0.383746	0.936265	
				H	1.840850	-0.883803	-0.980033	
				H	-3.281910	-1.023625	0.085618	
				H	0.116571	1.324077	0.960777	

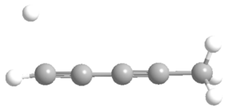
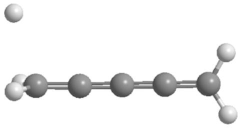
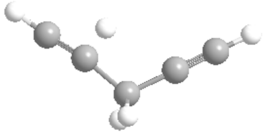
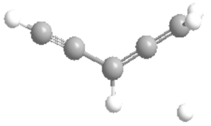
TS 4 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.070135	A	57.91029	C	2.494666	-0.361986	-0.077479	1936i, 130, 211, 313, 374, 504, 588, 658, 697, 822, 871, 914, 1015, 1086, 1127, 1283, 1434, 1686, 2108, 2182, 3058, 3071, 3177, 3476
	E(B3LYP+ZPE) = -193.284176	B	759.69038	C	1.373023	0.078652	-0.033589	
	E(CCSD(T)/CC-PVTZ) = -192.92729569	C	786.01678	C	0.067244	0.633584	0.020167	
				H	-0.411609	0.419537	1.224136	
				C	-1.112257	-0.159839	0.249537	
				C	-2.361047	-0.287206	-0.163833	
				H	-2.641598	-0.019716	-1.184809	
				H	-3.138594	-0.713000	0.460968	
				H	3.478228	-0.760426	-0.122460	
				H	-0.056203	1.654369	-0.346646	
TS 5 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.067262	A	81.86631	C	-2.359856	-0.529603	-0.108710	1683i, 126, 179, 326, 359, 425, 559, 614, 645, 753, 896, 902, 954, 993, 1100, 1206, 1340, 1449, 1908, 2044, 3054, 3127, 3133, 3433
	E(B3LYP+ZPE) = -193.274281	B	705.64046	C	-1.304775	0.085075	0.037428	
	E(CCSD(T)/CC-PVTZ) = -192.90903759	C	759.63745	C	-0.032815	0.761340	-0.047611	
				H	-0.086986	1.840726	-0.170518	
				C	1.164390	0.141943	-0.194089	
				C	2.291289	-0.457374	0.057692	
				H	2.626262	-0.645746	1.080049	
				H	2.953870	-0.801997	-0.733465	
				H	-3.280125	-1.005867	0.136607	
				H	-0.762418	0.604599	1.219075	
TS 6 **(C_s)**	ZPE(B3LYP/6-311G**) = 0.068305	A	21.09378	C	2.580507	-0.044832	-0.000010	2122i, 22, 137, 140, 228, 289, 369, 477, 583, 662, 851, 1044, 1045, 1141, 1413, 1471, 1475, 1868, 2258, 2316, 3013, 3041, 3066, 3074
	E(B3LYP+ZPE) = -193.288697	B	906.50110	H	2.956596	-0.571462	-0.882807	
	E(CCSD(T)/CC-PVTZ) = -192.92781170	C	916.35704	H	3.011405	0.961821	-0.001415	
				C	1.128187	-0.002667	-0.000014	
				C	-0.087195	0.000826	0.000013	
				C	-1.448164	0.168893	0.000045	
				H	-2.283534	1.125211	-0.000114	
				C	-2.712191	-0.119780	-0.000007	
				H	-3.407955	-0.961227	-0.000074	
				H	2.956622	-0.568988	0.884246	
TS 7 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.069880	A	26.84858	C	-2.632898	0.100677	0.027544	1825i, 125, 157, 254, 368, 507, 541, 600, 756, 811, 856, 1008, 1039, 1119, 1244, 1444, 1471, 1707, 2007, 2138, 3054, 3104, 3176, 3188
	E(B3LYP+ZPE) = -193.297773	B	863.30179	H	-3.132615	1.017173	-0.273050	
	E(CCSD(T)/CC-PVTZ) = -192.93017430	C	880.18384	H	-3.264442	-0.720480	0.354906	
				C	-1.317757	-0.012707	-0.006805	
				C	-0.050836	-0.104480	-0.037143	
				C	1.228457	-0.313333	-0.161965	
				H	2.025071	-0.858369	0.673471	
				C	2.499893	0.254696	0.037053	
				H	3.366634	-0.217839	-0.411592	

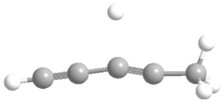
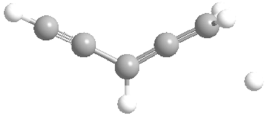
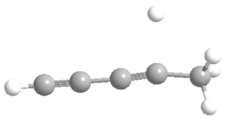
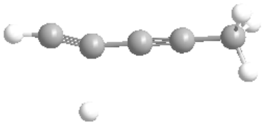
				H	**2.644203**	**1.230394**	**0.504153**	
TS 8 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.070596** **E(B3LYP+ZPE) = -193.288867** **E(CCSD(T)/CC-PVTZ) = -192.91833706**	**A**	**123.53907**	**C**	**2.223016**	**-0.557910**	**-0.034624**	**1808i, 126, 267, 298, 424, 521, 581, 641, 676, 792, 902, 957, 1038, 1090, 1150, 1348, 1461, 1557, 2158, 2164, 3042, 3141, 3177, 3476**
		B	**573.66116**	**C**	**1.232541**	**0.132787**	**0.017987**	
		C	**684.61966**	**C**	**0.072462**	**0.941339**	**0.061364**	
				**C**	**-1.162420**	**0.451085**	**-0.209748**	
				C	**-1.845487**	**-0.755929**	**0.038372**	
				H	**-2.270477**	**0.433268**	**0.466847**	
				H	**-2.687058**	**-1.029995**	**-0.590339**	
				H	**-1.467142**	**-1.513871**	**0.728678**	
				H	**3.094832**	**-1.162732**	**-0.078137**	
				H	**0.209177**	**2.005097**	**0.232837**	
TS 9 **(C_s)**	**ZPE(B3LYP/6-311G**) = 0.068305** **E(B3LYP+ZPE) = -193.288697** **E(CCSD(T)/CC-PVTZ) = -192.92781084**	**A**	**21.09372**	**C**	**2.580510**	**-0.044848**	**0.000026**	**2120i, 22, 137, 140, 228, 289, 369, 477, 583, 662, 850, 1044, 1045, 1141, 1413, 1471, 1475, 1868, 2258, 2315, 3013, 3040, 3066, 3074**
		B	**906.50213**	**H**	**2.956664**	**-0.563358**	**0.887587**	
		C	**916.35782**	**H**	**2.956573**	**-0.577059**	**-0.879429**	
				**C**	**1.128192**	**-0.002668**	**-0.000052**	
				C	**-0.087193**	**0.000872**	**-0.000045**	
				C	**-1.448169**	**0.168896**	**-0.000131**	
				H	**-2.283652**	**1.125176**	**0.000172**	
				C	**-2.712172**	**-0.119808**	**0.000109**	
				H	**-3.407996**	**-0.961205**	**-0.000027**	
				H	**3.011408**	**0.961777**	**-0.007752**	
TS 10 **(C_s)**	**ZPE(B3LYP/6-311G**) = 0.06934** **E(B3LYP+ZPE) = -193.286166** **E(CCSD(T)/CC-PVTZ) = -192.92707077**	**A**	**52.54852**	**C**	**2.637057**	**-0.298176**	**0.000051**	**2122i, 103, 134, 226, 270, 353, 504, 517, 545, 659, 714, 1020, 1021, 1068, 1386, 1463, 1473, 1901, 2151, 2299, 2992, 3073, 3090, 3475**
		B	**810.63449**	**C**	**1.454752**	**-0.023583**	**0.000002**	
		C	**851.99585**	**C**	**0.167825**	**0.455387**	**-0.000068**	
				C	**-1.129132**	**0.442443**	**-0.000086**	
				**C**	**-2.340230**	**-0.420612**	**0.000018**	
				H	**-2.956707**	**-0.222802**	**-0.880802**	
				H	**-2.053053**	**-1.480224**	**-0.001169**	
				H	**-2.955216**	**-0.224416**	**0.882250**	
				H	**3.661539**	**-0.577708**	**-0.000103**	
				H	**-0.438189**	**1.572395**	**0.000324**	
TS 11 **(C_s)**	**ZPE(B3LYP/6-311G**) = 0.073345** **E(B3LYP+ZPE) = -193.301073** **E(CCSD(T)/CC-PVDZ) = -192.76620644** **E(CCSD(T)/CC-PVTZ) = -192.953649** **E(CCSD(T)/CC-PVQZ) = -193.00753348** **E(CCSD(T)/CBS) = -193.00753348**	**A**	**153.16575**	**C**	**1.829353**	**-0.318068**	**-0.000062**	**698i, 65, 346, 374, 534, 596, 625, 708, 739, 808, 902, 923, 953, 1027, 1236, 1404, 1435, 1711, 1736, 3107, 3144, 3217, 3232, 3371**
		B	**380.50619**	**H**	**2.197717**	**-1.336617**	**-0.000062**	
		C	**521.25854**	**H**	**2.559311**	**0.483105**	**-0.000218**	
				**C**	**0.523901**	**-0.057841**	**0.000073**	
				C	**-0.215373**	**1.258555**	**0.000033**	
				H	**-0.275686**	**1.817948**	**-0.928366**	
				C	**-1.743812**	**-0.359047**	**-0.000116**	
				C	**-0.626783**	**-0.946300**	**0.000143**	

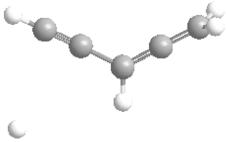
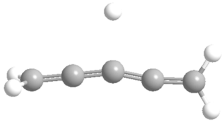
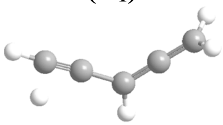
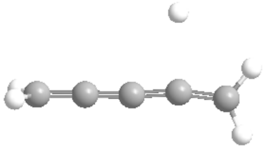
				H	-0.276798	1.817178	0.928813	
				H	-2.808262	-0.245409	-0.000593	
TS 12 **(C$_s$)**	ZPE(B3LYP/6-311G**) = 0.069824	A	141.90739	C	-2.276147	-0.096972	0.000101	2152i, 185, 236, 461, 511, 524, 569, 659, 670, 713, 849, 954, 984, 1047, 1102, 1210, 1420, 1639, 1857, 2202, 3069, 3145, 3169, 3476
	E(B3LYP+ZPE) = -193.285473	B	497.44486	C	-1.076117	0.014637	-0.000192	
	E(CCSD(T)/CC-PVTZ) = -192.93245570	C	627.12882	C	0.335326	0.107221	-0.000243	
				C	1.174858	1.141623	-0.000036	
				H	1.100997	2.226368	0.000792	
				C	1.355967	-1.005919	0.000121	
				H	1.488614	-1.571173	0.921463	
				H	1.489602	-1.570591	-0.921451	
				H	-3.334811	-0.185708	0.000285	
				H	2.172274	0.137568	0.000397	
TS 13 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.07173	A	130.73052	C	-1.860758	-0.068880	0.012333	941i, 179, 350, 430, 467, 715, 724, 841, 854, 876, 941, 947, 1101, 1143, 1156, 1401, 1423, 1438, 1735, 2208, 3063, 3134, 3137, 3224
	E(B3LYP+ZPE) = -193.246693	B	363.78264	H	-2.378542	-1.020663	-0.011915	
	E(CCSD(T)/CC-PVTZ) = -192.896689	C	475.30140	C	-0.539836	-0.015132	-0.027518	
				C	0.575462	1.005104	0.015570	
				H	0.662368	1.610343	0.917829	
				C	1.635647	-0.210197	-0.072790	
				C	0.561082	-1.051622	-0.100959	
				H	1.254861	-0.996569	0.946444	
				H	-2.461058	0.833034	0.067295	
				H	0.692782	1.618214	-0.879470	
TS 14 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.074465	A	135.04743	C	1.998726	0.171867	-0.085620	682i, 208, 264, 515, 531, 604, 713, 819, 835, 851, 965, 987, 1019, 1126, 1263, 1416, 1455, 1523, 1797, 3075, 3123, 3186, 3198, 3215
	E(B3LYP+ZPE) = -193.301102	B	424.14188	H	2.320809	1.196109	0.052090	
	E(CCSD(T)/CC-PVDZ) = -192.76351055	C	541.96621	C	0.748560	-0.191293	0.099829	
	E(CCSD(T)/CC-PVTZ) = -192.95052295			C	-1.063626	0.994006	0.020964	
	E(CCSD(T)/CC-PVQZ) = -193.00443295			H	-1.335456	1.729675	-0.737722	
	E(CCSD(T)/CBS) = -193.02627			C	-1.460051	-0.404611	-0.094692	
				C	-0.299050	-1.062667	0.136555	
				H	2.744657	-0.557174	-0.390455	
				H	-0.854602	1.388310	1.007905	
				H	-2.422761	-0.800734	-0.394028	
TS 15 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.074698	A	159.82214	C	1.878758	-0.329586	-0.075733	638i, 219, 283, 406, 579, 656, 702, 815, 870, 918, 961, 1011, 1038, 1134, 1270, 1422, 1478, 1511, 1758, 3094, 3094, 3175, 3195, 3200
	E(B3LYP+ZPE) = -193.298423	B	381.94223	H	2.627868	0.307357	-0.544214	
	E(CCSD(T)/CC-PVTZ) = -192.94847058	C	520.07059	C	0.664089	0.129587	0.142020	
				C	-1.179516	-0.983960	0.035942	
				H	-1.087354	-1.301227	1.070703	
				C	-1.393827	0.366367	-0.232371	
				C	-0.311540	1.134753	0.076281	

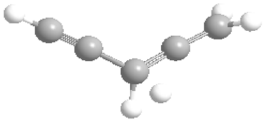
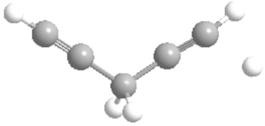
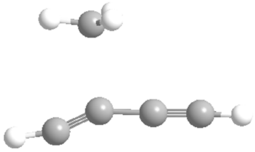
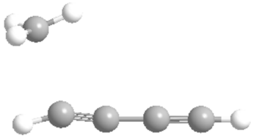
				H	-0.214096	2.195820	0.266797	
				H	2.179510	-1.333730	0.195287	
				H	-1.453713	-1.771187	-0.665405	
TS 16 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.071515	A	130.36624	C	1.860319	-0.066162	0.020885	1201i, 199, 341, 453, 654, 708, 719, 806, 861, 912, 920, 946, 1073, 1160, 1202, 1263, 1293, 1438, 1681, 2039, 3139, 3161, 3195, 3227
	E(B3LYP+ZPE) = -193.259869	B	358.14053	H	2.476132	0.826078	0.037863	
	E(CCSD(T)/CC-PVTZ) = -192.9106839	C	481.03667	C	0.527203	0.017086	-0.031417	
				C	-0.627028	-0.954280	-0.055842	
				H	-1.408461	-0.758413	0.949009	
				C	-1.637400	0.088934	-0.062226	
				C	-0.498831	1.054934	-0.009860	
				H	-0.468989	2.137110	0.027460	
				H	2.366149	-1.024264	0.045727	
				H	-0.710411	-2.023578	-0.229300	
TS 17 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.068384	A	23.25507	C	2.581159	0.074446	0.052075	1612i, 127, 144, 287, 374, 443, 518, 589, 680, 725, 768, 869, 1003, 1013, 1267, 1430, 1466, 1759, 1939, 2034, 3058, 3143, 3149, 3231
	E(B3LYP+ZPE) = -193.28886	B	862.07388	H	3.362945	-0.576070	0.434838	
	E(CCSD(T)/CC-PVTZ) = -192.91833706	C	874.49871	C	1.315894	-0.300226	0.036033	
				C	0.032321	-0.013847	-0.178784	
				C	-1.254093	0.021556	-0.001360	
				C	-2.585847	-0.032601	0.071153	
				H	-3.123527	-0.789094	-0.488090	
				H	-3.152109	0.662657	0.675970	
				H	2.905970	1.049823	-0.315014	
				H	-0.529877	1.156714	-0.182406	
TS 18 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.068079	A	91.33058	C	2.279424	-0.584546	-0.017549	2093i, 91, 183, 277, 281, 314, 504, 606, 647, 823, 861, 879, 914, 1003, 1099, 1328, 1458, 1886, 1994, 2319, 3038, 3094, 3124, 3161
	E(B3LYP+ZPE) = -193.280253	B	686.67776	H	2.743234	-1.287986	-0.712379	
	E(CCSD(T)/CC-PVTZ) = -192.918796	C	750.65042	C	1.268156	0.200701	0.135711	
				C	-0.004758	0.803046	-0.140025	
				C	-1.154719	0.160649	-0.062567	
				C	-2.285842	-0.469741	0.059595	
				H	-2.772683	-0.938404	-0.792098	
				H	-2.790106	-0.554550	1.019823	
				H	2.211326	0.250966	0.989799	
				H	-0.005341	1.869317	-0.356134	
TS 19 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.073879	A	141.53011	C	-1.973096	0.253200	0.098451	674i, 241, 270, 448, 583, 640, 719, 766, 839, 856, 899, 989, 1024, 1043, 1218, 1332, 1439,
	E(B3LYP+ZPE) = -193.314200	B	418.37554	H	-2.621665	-0.274438	0.793805	
	E(CCSD(T)/CC-PVTZ) = -192.96311109	C	543.13004	C	-0.742695	-0.155621	-0.124363	
				C	0.312195	-1.014724	-0.118901	

				C	1.466643	-0.195312	0.176304	1515, 1828, 3109, 3130, 3158, 3190, 3194
				C	1.069182	1.052960	-0.111364	
				H	-2.368345	1.147467	-0.369573	
				H	2.415410	-0.529991	0.589046	
				H	1.485836	2.052015	-0.052252	
				H	0.295388	-2.038065	-0.481789	
TS 20	ZPE(B3LYP/6-311G**) = 0.072673	A	123.82773	C	-2.137536	-0.599064	0.000006	667i, 128, 185, 228, 388, 426, 513, 517, 781, 870, 946, 1036, 1042, 1167, 1396, 1462, 1469, 1791, 1886, 2991, 3061, 3076, 3136, 3404
(C_s)	E(B3LYP+ZPE) = -193.311422	B	530.00290	H	-2.701422	-1.503851	0.000254	
	E(CCSD(T)/CC-PVTZ) = -192.95670401	C	642.68166	C	-1.099533	0.097533	0.000023	
				C	0.663410	0.098668	-0.000385	
				C	-0.128419	1.136049	-0.000006	
				H	-0.129143	2.222224	0.000516	
				C	1.998852	-0.511519	0.000087	
				H	2.129339	-1.148686	0.880229	
				H	2.130151	-1.148829	-0.879824	
				H	2.790432	0.249136	0.000475	
TS 21	ZPE(B3LYP/6-311G**) = 0.072473	A	159.25289	C	-2.022918	-0.618418	-0.000092	710i, 138, 227, 249, 419, 460, 507, 550, 646, 728, 777, 979, 1044, 1191, 1401, 1475, 1482, 1734, 1912, 3032, 3090, 3119, 3235, 3416
(C_s)	E(B3LYP+ZPE) = -193.310158	B	441.32817	H	-3.087719	-0.653871	0.001331	
	E(CCSD(T)/CC-PVTZ) = -192.957026	C	589.39571	C	-0.881320	-0.116934	-0.000233	
				C	0.518590	0.158859	-0.000270	
				C	0.059243	1.380793	0.000043	
				H	0.251556	2.443051	0.000470	
				C	1.762271	-0.662222	0.000125	
				H	1.786803	-1.308707	0.881780	
				H	1.787148	-1.309220	-0.881141	
				H	2.647019	-0.023715	0.000120	
TS 22	ZPE(B3LYP/6-311G**) = 0.070741	A	190.66106	C	-1.061477	-1.068328	-0.003118	1251i, 255, 360, 442, 529, 622, 666, 704, 786, 852, 890, 948, 1024, 1148, 1218, 1337, 1358, 1488, 1765, 1906, 3097, 3185, 3236, 3238
(C_1)	E(B3LYP+ZPE) = -193.295704	B	306.89863	C	-1.203290	0.265334	-0.066167	
	E(CCSD(T)/CC-PVTZ) = -192.941906	C	492.15912	C	-0.079047	1.175357	-0.006375	
				C	1.138143	0.564597	-0.059488	
				C	1.459107	-0.679905	0.067838	
				H	-1.753961	-1.895582	-0.060411	
				H	-2.199066	0.698042	0.038392	
				H	-0.239944	2.208548	0.275441	
				H	0.510712	-1.226841	0.586866	
				H	2.161651	-1.326494	-0.436431	
TS A	ZPE(B3LYP/6-311G**) = 0.066205	A	28.04697,	C	-2.601986	0.061610	-0.000065	349i, 17, 132,148, 234, 337, 353, 527, 539, 633, 681, 697, 1046, 1047, 1185, 1414, 1472,
(C_1)	E(B3LYP+ZPE) = -193.301336	B	917.30124,	H	-2.981133	0.320379	0.993055	
	E(CCSD(T)/CC-PVTZ) = -192.94211051	C	934.07103	H	-3.041591	-0.897620	-0.289725	

				C	-1.151606	-0.011249	0.000257	1473, 2138, 2334, 3021, 3080, 3081, 3473
				C	0.057200	-0.071356	0.000169	
				C	1.416395	-0.142979	0.000031	
				C	2.628666	-0.158016	-0.000121	
				H	3.678491	-0.319343	-0.000230	
				H	-2.955068	0.820528	-0.704703	
				H	3.207289	2.007997	-0.000018	
TS B	ZPE(B3LYP/6-311G**) = 0.064471	A	103.65530	C	2.504624	-0.167582	0.000097	25i, 7, 15, 152, 153, 335, 335, 541, 541, 698, 754, 852, 852, 1006, 1007, 1323, 1432, 1511, 1955, 2228, 3113, 3187, 3187
(C$_1$)	E(B3LYP+ZPE) = -193.298109	B	892.53269	H	3.058530	-0.236363	-0.931922	
	E(CCSD(T)/CC-PVDZ) = -192.74088721	C	983.80697	H	3.210866	2.000366	-0.000145	
	E(CCSD(T)/CC-PVTZ) = -192.92928836			C	1.180925	-0.126315	0.000128	
				C	-0.092692	-0.058128	-0.000284	
				C	-1.376869	0.000420	-0.000106	
				C	-2.688260	0.065946	0.000085	
				H	-3.293900	-0.836864	-0.000744	
				H	3.058563	-0.238083	0.931975	
				H	-3.200431	1.024902	0.001312	
TS C	ZPE(B3LYP/6-311G**) = 0.066832	A	101.69504	C	-2.291140	-0.539909	-0.072525	650i, 96, 160, 321, 347, 407, 459, 562, 656, 674, 691, 694, 900, 935, 997, 1242, 1340, 1456, 2146, 2236, 3022, 3051, 3466, 3478
(C$_1$)	E(B3LYP+ZPE) = -193.273502	B	668.21254	C	-1.265411	0.080781	-0.034406	
	E(CCSD(T)/CC-PVTZ) = -192.92133116	C	729.44174	C	-0.027965	0.862885	0.001477	
				H	0.028392	1.493478	-0.893661	
				C	1.197402	0.044043	0.058956	
				C	2.252558	-0.491682	-0.195003	
				H	3.167904	-1.024698	-0.285629	
				H	-3.194803	-1.097654	-0.101763	
				H	-0.052459	1.541453	0.860943	
				H	0.858303	-0.649285	1.869119	
TS D	ZPE(B3LYP/6-311G**) = 0.062052	A	181.40117	C	-2.541540	0.316583	-0.191139	569i, 94, 150, 324, 363, 393, 429, 608, 631, 651, 689, 870, 897, 953, 1003, 1130, 1352, 1459, 1987, 2197, 3117, 3119, 3203, 3476
(C$_1$)	E(B3LYP+ZPE) = -193.226775	B	788.98902	C	-1.420594	-0.076005	0.055095	
	E(CCSD(T)/CC-PVTZ) = -192.9253509	C	929.76742	C	-0.148054	-0.551614	0.364191	
				H	-0.078715	-1.332367	1.127366	
				C	1.023938	-0.105511	-0.225428	
				H	2.254261	5.983680	0.602139	
				C	2.341951	-0.327437	-0.173297	
				H	2.766281	-1.069880	0.506925	
				H	3.043012	0.214945	-0.798671	
				H	-3.519040	0.667531	-0.414287	
TS E	ZPE(B3LYP/6-311G**) = 0.066708	A	29.31110,	C	2.707186	-0.152710	0.000006	780i, 85, 140, 162, 308, 342, 488, 525, 560, 653, 654, 707,
	E(B3LYP+ZPE) = -193.294969	B	875.44956,	C	1.508559	-0.020480	-0.000002	

(C$_s$)	**E(CCSD(T)/CC-PVTZ) = -192.93576183**	**C**	**893.47955**	**C**	**0.143907**	**0.142060**	**-0.000005**	**1033, 1050, 1175, 1409, 1466, 1470, 2138, 2278, 3010, 3067, 3082, 3478**
	E(CCSD(T)/CC-PVDZ) = -192.74456623			**C**	**-1.056710**	**-0.090125**	**-0.000025**	
	E(CCSD(T)/CC-PVQZ) = -192.98987297			**C**	**-2.506015**	**-0.114107**	**0.000012**	
	E(CCSD(T)/CBS) = -193.01123			**H**	**-2.904580**	**0.907359**	**-0.000676**	
				**H**	**-2.892500**	**-0.628349**	**-0.884860**	
				H	**-2.892469**	**-0.627150**	**0.885593**	
				H	**3.762168**	**-0.275588**	**0.000019**	
				H	**0.145810**	**2.035908**	**0.000011**	
TS F **(C$_s$)**	**ZPE(B3LYP/6-311G**) = 0.066086**	**A**	**69.60471**	**C**	**-2.519677**	**-0.386181**	**0.000175**	**408i, 127, 167, 242, 345, 368, 378, 606, 637, 671, 6912, 8867, 899, 943, 1009, 1129, 1346, 1460, 2005, 2211, 3100, 3116, 3190, 3478**
	E(B3LYP+ZPE) = -193.291486	**B**	**750.73793**	**C**	**-1.415141**	**0.092035**	**0.000022**	
	E(CCSD(T)/CC-PVTZ) = -192.931495	**C**	**807.98144**	**C**	**-0.131529**	**0.707399**	**-0.000094**	
	E(CCSD(T)/CC-PVDZ) = -192.74178176			**C**	**1.005651**	**0.053069**	**-0.000620**	
	**E(CCSD(T)/CC-PVQZ) = -192.98565055**			**C**	**2.177914**	**-0.527290**	**0.000068**	
	E(CCSD(T)/CBS) = -193.00729			**H**	**3.591229**	**1.072050**	**0.001521**	
				H	**2.648384**	**-0.840995**	**0.927042**	
				H	**2.649405**	**-0.841461**	**-0.926224**	
				H	**-3.488860**	**-0.820939**	**0.000306**	
				H	**-0.103461**	**1.797149**	**0.000045**	
TS G **(C$_s$)**	**ZPE(B3LYP/6-311G**) = 0.06687**	**A**	**29.24966,**	**C**	**2.754632**	**-0.045447**	**0.000001**	**523i, 133, 146, 162, 346, 379, 395, 529, 534, 642, 644, 687, 1040, 1055, 1178, 1412, 1471, 1476, 2147, 2288, 3027, 3090, 3092, 3477**
	E(B3LYP+ZPE) = -193.298989	**B**	**885.48922,**	**C**	**1.545965**	**-0.036609**	**0.000001**	
	E(CCSD(T)/CC-PVTZ) = -192.94027766	**C**	**903.51365**	**C**	**0.185951**	**-0.034684**	**0.000001**	
				C	**-1.028753**	**0.046717**	**-0.000013**	
				**C**	**-2.472080**	**-0.164227**	**0.000004**	
				H	**-2.694569**	**-1.235377**	**-0.000138**	
				H	**-2.934348**	**0.284352**	**0.883115**	
				H	**-2.934408**	**0.284600**	**-0.882949**	
				H	**3.816778**	**-0.051748**	**0.000004**	
				H	**-1.167738**	**2.123672**	**0.000005**	
TS H **(C$_s$)**	**ZPE(B3LYP/6-311G**) = 0.066571**	**A**	**28.21390**	**C**	**-2.553271**	**-0.059205**	**0.000003**	**861i, 24, 150, 157, 346, 349, 466, 531, 544, 613, 648, 705, 1048, 1175, 1414, 1473, 1474, 2065, 2344, 3022, 3081, 3082, 3461**
	E(B3LYP+ZPE) = -193.293577	**B**	**885.61895**	**H**	**-2.927882**	**-0.582545**	**0.884726**	
	E(CCSD(T)/CC-PVTZ) = -192.93412939	**C**	**902.56663**	**H**	**-2.976533**	**0.949611**	**-0.000160**	
				C	**-1.101070**	**-0.012778**	**0.000012**	
				**C**	**0.106447**	**0.021234**	**-0.000033**	
				C	**1.479919**	**0.073857**	**0.000017**	
				H	**1.577770**	**1.936580**	**-0.000001**	
				C	**2.657543**	**-0.253254**	**-0.000003**	
				H	**3.717097**	**-0.339937**	**0.000021**	
				H	**-2.927866**	**-0.582829**	**-0.884559**	
TS I	**ZPE(B3LYP/6-311G**) = 0.065230**	**A**	**86.56636**	**C**	**2.416310**	**-0.301927**	**0.074511**	**3i, 27, 81, 141, 295, 350, 359,**

(C_1)	**E(B3LYP+ZPE) = -193.293238**	**B**	**747.75705**	**H**	**2.963118**	**-0.621138**	**-0.808262**	**606, 625, 642, 693, 883, 884, 951, 1004, 1139, 1352, 1465, 2042, 2208, 3111, 3115, 3183, 3478**
	E(CCSD(T)/CC-PVTZ) = -192.93529151	**C**	**818.65408**	**C**	**1.212546**	**0.177385**	**-0.012424**	
				**C**	**0.002031**	**0.680286**	**-0.102326**	
				C	**-1.192732**	**-0.091031**	**-0.043565**	
				C	**-2.226016**	**-0.707585**	**0.000712**	
				H	**-3.137485**	**-1.251438**	**0.040037**	
				H	**2.915521**	**-0.406414**	**1.033705**	
				H	**-0.109562**	**1.755877**	**-0.230322**	
				H	**-3.904425**	**1.980347**	**0.463398**	
TS J (C_s)	**ZPE(B3LYP/6-311G**) = 0.065456**	**A**	**31.81967**	**C**	**2.573627**	**-0.133868**	**0.000018**	**737i, 135, 152, 186, 309, 344, 462, 535, 556, 664, 766, 853, 858, 991, 1003, 1317, 1426, 1504, 1928, 2164, 3100, 3115, 3176, 3190**
	E(B3LYP+ZPE) = -193.291537	**B**	**852.69972**	**H**	**3.160625**	**0.782259**	**0.000422**	
	E(CCSD(T)/CC-PVTZ) = -192.92267825	**C**	**872.12636**	**C**	**1.266814**	**-0.095824**	**-0.000041**	
				**C**	**-0.000069**	**0.151130**	**0.000031**	
				C	**-1.271834**	**-0.000557**	**-0.000029**	
				C	**-2.570229**	**-0.150559**	**0.000011**	
				H	**-3.130568**	**-0.216829**	**-0.927800**	
				H	**-3.130412**	**-0.217689**	**0.927855**	
				H	**3.118139**	**-1.073431**	**-0.000421**	
				H	**-0.007642**	**2.103760**	**0.000000**	
TS K (C_1)	**ZPE(B3LYP/6-311G**) = 0.065638**	**A**	**86.34344**	**C**	**-2.344543**	**-0.458770**	**-0.044864**	**296i, 60, 141, 200, 310, 360, 365, 607, 633, 681, 686, 883, 884, 954, 1001, 1138, 1352, 1462, 2035, 2176, 3111, 3116, 3183, 3474**
	E(B3LYP+ZPE) = -193.292555	**B**	**736.25040**	**H**	**-2.787200**	**-0.950300**	**0.816951**	
	E(CCSD(T)/CC-PVTZ) = -192.9325076	**C**	**777.28364**	**C**	**-1.196000**	**0.140589**	**0.035697**	
				**C**	**-0.040997**	**0.764367**	**0.121846**	
				C	**1.215760**	**0.147692**	**-0.112849**	
				C	**2.307230**	**-0.350101**	**-0.256256**	
				H	**2.821920**	**-1.072399**	**1.829400**	
				H	**3.249652**	**-0.764582**	**-0.517875**	
				H	**-2.899206**	**-0.495409**	**-0.978304**	
				H	**-0.033865**	**1.820021**	**0.388386**	
TS L (C_s)	**ZPE(B3LYP/6-311G**) = 0.065644**	**A**	**31.39458**	**C**	**-2.620812**	**-0.029126**	**0.000098**	**503i, 145, 149, 171, 337, 365, 391, 541, 541, 691, 754, 853, 866, 1005, 1008, 1321, 1433, 1508, 1932, 2175, 3115, 3120, 3190, 3205**
	E(B3LYP+ZPE) = -193.295087	**B**	**865.39902**	**H**	**-3.185422**	**-0.023919**	**-0.927432**	
	E(CCSD(T)/CC-PVTZ) = -192.92734667	**C**	**884.40603**	**H**	**-3.185115**	**-0.023604**	**0.927814**	
	E(CCSD(T)/CC-PVDZ) = -192.73763885			**C**	**-1.308597**	**-0.039587**	**-0.000115**	
	**E(CCSD(T)/CC-PVQZ) = -192.98123192**			**C**	**-0.038123**	**-0.056460**	**-0.000136**	
	E(CCSD(T)/CBS) = -193.00261			**C**	**1.243327**	**0.014800**	**-0.000013**	
				H	**1.258263**	**2.202849**	**0.000018**	
				C	**2.543438**	**-0.164404**	**0.000057**	
				H	**3.242143**	**0.663483**	**-0.000011**	
				H	**2.954727**	**-1.170147**	**0.000268**	

TS M **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.066464	A	88.57461	C	2.373190	-0.511783	0.075322	758i, 137, 224, 299, 352, 422, 461, 591, 625, 644, 695, 886, 932, 944, 988, 1119, 1344, 1449, 1986, 2217, 3094, 3122, 3166, 3477
	E(B3LYP+ZPE) = -193.287252	B	702.11105	C	1.305960	0.029396	-0.041948	
	E(CCSD(T)/CC-PVDZ) = -192.73721161	C	756.50068	C	0.054952	0.701818	-0.211983	
	E(CCSD(T)/CC-PVTZ) = -192.9272013			H	0.123433	1.745097	1.401138	
	E(CCSD(T)/CC-PVQZ) = -192.98144698			C	-1.117594	0.078810	-0.117573	
	E(CCSD(T)/CBS) = -193.00312			C	-2.275561	-0.466827	0.086693	
				H	-2.777696	-1.051983	-0.679275	
				H	-2.785333	-0.360871	1.042709	
				H	3.311550	-0.996620	0.188181	
				H	0.082366	1.675891	-0.695827	
TS N **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.066255	A	100.48035	C	2.345559	-0.550846	0.084584	495i, 47, 135, 228, 315, 334, 401, 567, 674, 675, 694, 767, 901, 927, 999, 1239, 1339, 1450, 2179, 2236, 3004, 3032, 3462, 3478
	E(B3LYP+ZPE) = -193.276769	B	689.06848	C	1.323405	0.073127	0.017570	
	E(CCSD(T)/CC-PVTZ) = -192.923465	C	757.70184	C	0.086084	0.854270	-0.064788	
	E(CCSD(T)/CC-PVDZ) = -192.7324797			H	0.011986	1.511444	0.811860	
	E(CCSD(T)/CC-PVQZ) = -192.9780062			C	-1.125101	0.036990	-0.143974	
	E(CCSD(T)/CBS) = -192.99981			C	-2.169538	-0.567410	-0.110860	
				H	-3.014256	-1.196605	-0.255277	
				H	-3.140162	0.200648	1.540545	
				H	3.247273	-1.109328	0.145149	
				H	0.132706	1.517046	-0.937465	
TS O **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.069696	A	251.92532	C	2.173010	0.078516	0.000017	537i, 82, 153, 244, 265, 457, 477, 515, 553, 561, 644, 662, 671, 862, 918, 1416, 1420, 1953, 2223, 3090, 3254, 3256, 3440, 3477
	E(B3LYP+ZPE) = -193.295352	B	457.08837	C	1.010064	-0.240075	-0.000043	
	E(CCSD(T)/CC-PVTZ) = -192.939559	C	696.71458	C	-0.330042	-0.577759	-0.000030	
	E(CCSD(T)/CC-PVDZ) = -192.74704437			C	-1.250124	-1.398366	0.000038	
	E(CCSD(T)/CC-PVQZ) = -192.9933327			C	-1.158258	1.534194	0.000016	
	E(CCSD(T)/CBS) = -193.01417			H	3.202132	0.341407	0.000086	
				H	-2.216298	-1.845201	-0.000001	
				H	-2.227329	1.365452	-0.000197	
				H	-0.713335	1.879642	0.924367	
				H	-0.713069	1.879640	-0.924244	
TS P **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.069269	A	127.87370	C	2.596323	-0.496948	0.000192	377i, 51, 88, 239, 275, 409, 439, 497, 534, 612, 640, 659, 668, 774, 922, 1409, 1417, 2034, 2198, 3096, 3261, 3272, 3435, 3476
	E(B3LYP+ZPE) = -193.306685	B	826.58756	C	1.498866	0.013322	-0.000124	
	E(CCSD(T)/CC-PVTZ) = -192.947917	C	942.01434	C	0.275047	0.600528	-0.000490	
				C	-0.877163	1.006979	0.000306	
				C	-2.503755	-0.796398	-0.000019	
				H	3.558710	-0.946488	0.000510	
				H	-1.690875	1.692766	0.001210	
				H	-1.813102	-1.627401	-0.004513	
				H	-2.993665	-0.545410	0.931635	

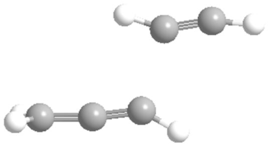
				H	-2.996982	-0.538367	-0.928033	
TS Q **(C_s)**	ZPE(B3LYP/6-311G**) = 0.069747 E(B3LYP+ZPE) = -193.302420 E(CCSD(T)/CC-PVTZ) = -192.942732	A	85.95354	C	-2.451418	0.034725	0.000000	599i, 24, 123, 262, 309, 381, 486, 548, 649, 713, 765, 767, 793, 875, 1029, 1150, 1463, 1836, 1951, 3127, 3208, 3347, 3355, 3455
		B	816.17722	C	-1.213466	0.530121	0.000000	
		C	889.73957	C	0.000000	0.861462	0.000000	
				C	1.341320	-0.831016	0.000000	
				C	2.536442	-0.558564	0.000000	
				H	-2.980031	-0.155144	0.927759	
				H	-2.980031	-0.155144	-0.927759	
				H	0.651469	1.710611	0.000000	
				H	0.546212	-1.545170	0.000000	
				H	3.485114	-0.075527	0.000000	

Table A2. RRKM calculated rate constants for individual reaction steps of the C_2H + C_3H_4 reaction on the C_5H_5 potential energy surface at collision energies of 0-5.3 kcal/mol.

Reaction step	Transition state	Collision Energy, kcal/mol					
		0.00	1.00	2.00	3.00	4.00	5.26
1 → 2	TS 1	9.84E+09	1.10E+10	1.23E+10	1.36E+10	1.51E+10	1.70E+10
2 → 1	TS 1	1.18E+08	1.40E+08	1.64E+08	1.93E+08	2.25E+08	2.71E+08
1 → 4	TS 3	1.20E+05	2.18E+05	3.78E+05	6.28E+05	1.01E+06	1.75E+06
4 → 1	TS 3	2.65E+05	4.79E+05	8.25E+05	1.36E+06	2.17E+06	3.74E+06
1 → 5	TS 4	8.45E+06	1.14E+07	1.53E+07	2.01E+07	2.61E+07	3.56E+07
5 → 1	TS 4	4.08E+04	5.89E+04	8.38E+04	1.17E+05	1.62E+05	2.38E+05
1 → 16	TS 5	1.48E+04	2.85E+04	5.19E+04	9.02E+04	1.51E+05	2.73E+05
16 → 1	TS 5	1.35E+04	2.62E+04	4.77E+04	8.30E+04	1.39E+05	2.52E+05
1 → 18	TS M	1.22E+08	1.60E+08	2.07E+08	2.65E+08	3.35E+08	4.44E+08
1 → 20	TS N	3.26E+08	4.44E+08	5.97E+08	7.91E+08	1.03E+09	1.43E+09
2 → 3	TS 2	3.06E+05	4.13E+05	5.51E+05	7.27E+05	9.49E+05	1.31E+06
3 → 2	TS 2	3.33E+07	4.25E+07	5.37E+07	6.72E+07	8.34E+07	1.08E+08
3 → 11	TS 12	6.71E+07	7.97E+07	9.42E+07	1.11E+08	1.30E+08	1.57E+08
11 → 3	TS 12	1.09E+11	1.23E+11	1.40E+11	1.57E+11	1.77E+11	2.03E+11
3 → 12	TS 11	3.17E+07	4.55E+07	6.40E+07	8.85E+07	1.20E+08	1.73E+08
12 → 3	TS 11	7.81E+02	1.31E+03	2.12E+03	3.35E+03	5.16E+03	8.63E+03
4 → 20	TS C	3.93E+04	6.26E+04	9.66E+04	1.45E+05	2.14E+05	3.37E+05
5 → 6	TS 8	4.67E+05	5.92E+05	7.43E+05	9.27E+05	1.15E+06	1.49E+06
6 → 5	TS 8	8.87E+07	1.05E+08	1.24E+08	1.46E+08	1.70E+08	2.05E+08
5 → 18	TS D	2.09E+06	2.88E+06	3.92E+06	5.27E+06	7.00E+06	9.87E+06
6 → 7	TS 10	1.54E+07	2.12E+07	2.89E+07	3.88E+07	5.13E+07	7.17E+07
7 → 6	TS 10	5.67E+05	7.98E+05	1.10E+06	1.50E+06	2.02E+06	2.88E+06
6 → 8	TS 9	2.67E+08	3.63E+08	4.87E+08	6.44E+08	8.42E+08	1.16E+09
8 → 6	TS 9	7.37E+07	1.00E+08	1.34E+08	1.77E+08	2.31E+08	3.17E+08
6 → 10	TS 20	5.14E+09	5.81E+09	6.54E+09	7.33E+09	8.19E+09	9.38E+09
10 → 6	TS 20	2.78E+12	2.91E+12	3.04E+12	3.18E+12	3.31E+12	3.48E+12
6 → 18	TS F	2.61E+08	3.34E+08	4.23E+08	5.30E+08	6.58E+08	8.55E+08
6 → 21	TS E	1.73E+09	2.15E+09	2.65E+09	3.24E+09	3.93E+09	4.96E+09
7 → 21	TS G	9.79E+07	1.21E+08	1.49E+08	1.82E+08	2.20E+08	2.77E+08
7 → 22	TS P	2.05E+09	2.47E+09	2.95E+09	3.50E+09	4.14E+09	5.06E+09
8 → 9	TS 6	7.42E+07	1.01E+08	1.35E+08	1.78E+08	2.32E+08	3.19E+08
9 → 8	TS 6	3.63E+05	5.06E+05	6.94E+05	9.40E+05	1.26E+06	1.78E+06
8 → 21	TS H	3.95E+09	4.80E+09	5.78E+09	6.91E+09	8.22E+09	1.01E+10
9 → 13	TS 7	1.24E+04	1.69E+04	2.26E+04	2.99E+04	3.91E+04	5.39E+04
13 → 9	TS 7	1.53E+05	2.12E+05	2.91E+05	3.93E+05	5.25E+05	7.44E+05
9 → 19	TS B	2.09E+07	2.97E+07	4.15E+07	5.72E+07	7.76E+07	1.12E+08
9 → 21	TS A	1.02E+08	1.25E+08	1.53E+08	1.86E+08	2.24E+08	2.81E+08
10 → 11	TS 21	2.76E+12	2.89E+12	3.01E+12	3.15E+12	3.28E+12	3.44E+12
11 → 10	TS 21	2.74E+10	3.05E+10	3.39E+10	3.75E+10	4.14E+10	4.67E+10
11 → 22	TS O	9.07E+09	1.12E+10	1.36E+10	1.65E+10	1.98E+10	2.47E+10
12 → 13	TS 14	8.95E+09	1.03E+10	1.18E+10	1.35E+10	1.53E+10	1.78E+10
13 → 12	TS 14	1.86E+06	2.25E+06	2.70E+06	3.23E+06	3.84E+06	4.74E+06
12 → 14	TS 13	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.65E+01

14 → 12	TS 13	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.57E+01
13 → 15	TS 17	6.18E+03	9.89E+03	1.54E+04	2.35E+04	3.50E+04	5.63E+04
15 → 13	TS 17	6.25E+04	9.65E+04	1.45E+05	2.14E+05	3.09E+05	4.77E+05
13 → 19	TS L	1.13E+06	1.58E+06	2.19E+06	3.00E+06	4.06E+06	5.83E+06
14 → 15	TS 15	3.07E+09	3.60E+09	4.19E+09	4.85E+09	5.59E+09	6.64E+09
15 → 14	TS 15	6.53E+06	7.76E+06	9.17E+06	1.08E+07	1.26E+07	1.52E+07
14 → 17	TS 16	8.95E+03	1.75E+04	3.23E+04	5.65E+04	9.48E+04	1.73E+05
17 → 14	TS 16	3.93E+01	8.07E+01	1.56E+02	2.85E+02	5.01E+02	9.66E+02
15 → 16	TS 18	7.76E+04	1.23E+05	1.89E+05	2.83E+05	4.15E+05	6.54E+05
16 → 15	TS 18	1.74E+06	2.69E+06	4.03E+06	5.91E+06	8.48E+06	1.30E+07
15 → 18	TS K	1.33E+08	1.72E+08	2.22E+08	2.82E+08	3.55E+08	4.70E+08
15 → 19	TS J	2.31E+06	3.31E+06	4.66E+06	6.44E+06	8.78E+06	1.27E+07
16 → 17	TS 19	5.72E+09	6.22E+09	6.74E+09	7.29E+09	7.87E+09	8.63E+09
17 → 16	TS 19	5.27E+08	6.06E+08	6.95E+08	7.93E+08	9.03E+08	1.06E+09
16 → 18	TS I	2.16E+08	2.89E+08	3.82E+08	4.99E+08	6.43E+08	8.73E+08
16 → 23	TS Q	3.23E+10	3.88E+10	4.62E+10	5.47E+10	6.44E+10	7.84E+10

Table A3. Optimized Cartesian coordinates of the C_2H + 1,3-butadiene reaction.

1) [i1], C_s, $^2A''$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.323343	-2.274031	0.000000
2	6	0	-1.329240	-1.072881	0.000000
3	6	0	-1.346653	0.387628	0.000000
4	6	0	0.000000	1.064440	0.000000
5	6	0	1.228778	0.430541	0.000000
6	6	0	2.450503	1.079131	0.000000
7	1	0	-1.323729	-3.336295	0.000000
8	1	0	-1.923322	0.732848	0.870774
9	1	0	-1.923322	0.732848	-0.870774
10	1	0	-0.032405	2.150982	0.000000
11	1	0	1.227606	-0.656798	0.000000
12	1	0	3.380514	0.525585	0.000000
13	1	0	2.514392	2.161859	0.000000

2) [i2], C_s, $^2A'$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.188922	-0.869676	0.000000
2	6	0	0.004410	-1.412820	0.000000
3	6	0	-1.333729	0.645941	0.000000
4	6	0	0.000000	1.348225	0.000000
5	6	0	1.180019	0.731477	0.000000
6	6	0	1.341700	-0.780308	0.000000
7	1	0	-2.099914	-1.463504	0.000000
8	1	0	-1.922474	0.964037	0.872407
9	1	0	-1.922474	0.964037	-0.872407
10	1	0	-0.026351	2.434773	0.000000
11	1	0	2.097265	1.315191	0.000000
12	1	0	1.926539	-1.095783	-0.874594
13	1	0	1.926539	-1.095783	0.874594

3) [i3], C_s, $^2A'$

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.958044	-1.970730	0.000000
2	6	0	-1.681030	-0.868852	0.000000
3	6	0	-1.253532	0.532525	0.000000
4	6	0	0.000000	1.035237	0.000000
5	6	0	1.240562	0.287413	0.000000
6	6	0	2.451597	0.860638	0.000000
7	1	0	-1.147906	-3.033553	0.000000
8	1	0	-2.770060	-1.002801	0.000000
9	1	0	-2.071003	1.246704	0.000000
10	1	0	0.100341	2.118363	0.000000
11	1	0	1.163305	-0.796759	0.000000
12	1	0	3.360034	0.270377	0.000000
13	1	0	2.567969	1.940286	0.000000

4) [i4], C_s, $^2A''$

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	1.401048	0.000000
2	6	0	-1.207021	0.768270	0.000000
3	6	0	1.296032	0.643067	0.000000
4	6	0	1.115934	-0.847260	0.000000
5	6	0	-0.118346	-1.425654	0.000000
6	6	0	-1.301819	-0.646270	0.000000
7	1	0	0.050163	2.484840	0.000000
8	1	0	-2.118664	1.357375	0.000000
9	1	0	1.911396	0.948871	0.865461
10	1	0	1.911396	0.948871	-0.865461
11	1	0	2.008768	-1.463671	0.000000
12	1	0	-0.199810	-2.508135	0.000000
13	1	0	-2.271932	-1.127358	0.000000

5) TS [i1]-H, C_1, ^2A

Center	Atomic	Atomic	Coordinates (Angstroms)

```
Number     Number      Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -2.529040   -0.935976   -0.012017
   2          6           0       -1.700433   -0.062178   -0.052368
   3          6           0       -0.749940    0.992810   -0.124184
   4          6           0        0.602528    0.817811   -0.132846
   5          6           0        1.284994   -0.440230    0.037448
   6          6           0        2.621414   -0.564328    0.033536
   7          1           0       -3.258772   -1.706916    0.029084
   8          1           0       -1.149249    1.978462   -0.338909
   9          1           0        1.221198    1.702028   -0.257052
  10          1           0        0.663703   -1.321045    0.171973
  11          1           0        3.102031   -1.526595    0.160830
  12          1           0        3.270681    0.295467   -0.098224
  13          1           0       -1.026734    1.731145    1.834885
---------------------------------------------------------------------
```

6) TS [i1]-[i2], C_1, ^2A

```
---------------------------------------------------------------------
Center     Atomic      Atomic              Coordinates (Angstroms)
Number     Number      Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        0.048309    1.715733   -0.260568
   2          6           0       -0.969909    1.037770   -0.091615
   3          6           0       -1.444607   -0.320228    0.223895
   4          6           0       -0.364399   -1.335078   -0.124065
   5          6           0        0.953575   -1.042433   -0.160825
   6          6           0        1.557270    0.180138    0.312722
   7          1           0        0.586374    2.611904   -0.478308
   8          1           0       -2.357228   -0.560555   -0.330527
   9          1           0       -1.719264   -0.371559    1.287308
  10          1           0       -0.709301   -2.299814   -0.481434
  11          1           0        1.614249   -1.760991   -0.643553
  12          1           0        1.368869    0.514219    1.324877
  13          1           0        2.534868    0.451389   -0.075620
---------------------------------------------------------------------
```

7) TS [i1]-[i3], C_1, ^2A

```
---------------------------------------------------------------------
Center     Atomic      Atomic              Coordinates (Angstroms)
Number     Number      Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -3.128632   -0.407060   -0.154021
   2          6           0       -1.997668    0.074897    0.021694
```

3	6	0	-0.652611	0.565997	-0.045543
4	6	0	0.502007	-0.218282	0.001231
5	6	0	1.812913	0.333155	-0.024181
6	6	0	2.960395	-0.385798	0.003020
7	1	0	-4.081706	-0.703015	0.227568
8	1	0	-0.558626	1.638047	-0.201058
9	1	0	0.392239	-1.295950	0.075030
10	1	0	1.884595	1.418388	-0.081552
11	1	0	2.947581	-1.469221	0.057509
12	1	0	3.929459	0.095321	-0.032746
13	1	0	-1.491964	0.538972	1.142044

8) TS [i2]-[i4], C_1, ^2A

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.892783	-1.106617	-0.174283
2	6	0	-0.405356	-1.370651	0.069200
3	6	0	1.406607	0.269892	0.218001
4	6	0	0.344772	1.312394	-0.092388
5	6	0	-0.967874	1.024713	-0.119662
6	6	0	-1.395300	-0.350853	0.170199
7	1	0	1.548162	-1.792482	-0.699177
8	1	0	2.328399	0.494649	-0.330359
9	1	0	1.684298	0.337731	1.282240
10	1	0	0.679203	2.329328	-0.278533
11	1	0	-1.707125	1.788805	-0.335746
12	1	0	-2.327121	-0.539675	0.695686
13	1	0	-1.459596	-1.291627	-0.760519

9) TS [i3]-[i4], C_1, ^2A

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.158517	1.288238	-0.087342
2	6	0	1.555412	0.023000	-0.083437
3	6	0	0.739823	-1.158509	0.164853
4	6	0	-0.611159	-1.245460	0.039355
5	6	0	-1.477301	-0.130962	-0.249135
6	6	0	-1.297335	1.116574	0.249128
7	1	0	1.658963	2.225236	-0.290609
8	1	0	2.595148	-0.191205	-0.352404
9	1	0	1.289874	-2.082189	0.317497

10	1	0	-1.052282	-2.239280	0.035426
11	1	0	-2.283262	-0.305192	-0.959744
12	1	0	-1.903124	1.948661	-0.092886
13	1	0	-0.713059	1.286685	1.142188

10) TS [i3]-H, C_s, $^2A'$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.226381	-2.172594	0.000000
2	6	0	-1.401525	-0.966395	0.000000
3	6	0	-1.208093	0.449274	0.000000
4	6	0	0.000000	1.054897	0.000000
5	6	0	1.291437	0.398974	0.000000
6	6	0	2.454196	1.063319	0.000000
7	1	0	-1.242142	-3.235606	0.000000
8	1	0	-2.101456	1.061416	0.000000
9	1	0	0.009413	2.141789	0.000000
10	1	0	1.292101	-0.686777	0.000000
11	1	0	3.404689	0.543695	0.000000
12	1	0	2.488507	2.148343	0.000000
13	1	0	-3.308917	-0.937712	0.000000

11) TS [i4]-H, C_1, ^2A

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.643728	-1.215319	-0.093169
2	6	0	0.740734	-1.210645	-0.000127
3	6	0	-1.356531	0.000879	-0.080717
4	6	0	-0.642148	1.216231	-0.093143
5	6	0	0.742407	1.209719	0.000151
6	6	0	1.437451	-0.000934	0.058078
7	1	0	-1.185054	-2.152806	-0.144772
8	1	0	1.284679	-2.148537	0.016948
9	1	0	-2.417330	0.001632	-0.301278
10	1	0	-1.182240	2.154488	-0.145552
11	1	0	1.287550	2.146911	0.017430
12	1	0	2.519137	-0.001675	0.130145
13	1	0	-1.975856	0.000406	1.680641

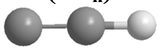
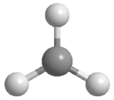
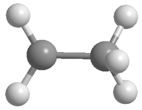
12) ac-C_6H_6, hexa-1,3-dien-5-yne, C_s, $^1A'$

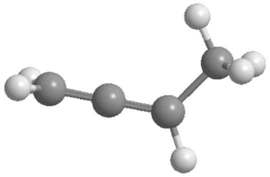
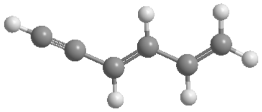
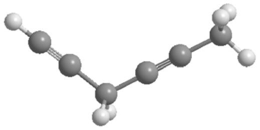
Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-1.648212	-2.155300	0.000000
2	6	0	-1.423481	-0.970491	0.000000
3	6	0	-1.208103	0.431186	0.000000
4	6	0	0.000000	1.035884	0.000000
5	6	0	1.281441	0.359699	0.000000
6	6	0	2.457052	1.000580	0.000000
7	1	0	-1.840877	-3.199937	0.000000
8	1	0	-2.102298	1.047677	0.000000
9	1	0	0.021371	2.122315	0.000000
10	1	0	1.259883	-0.726449	0.000000
11	1	0	3.397086	0.462290	0.000000
12	1	0	2.512657	2.084754	0.000000

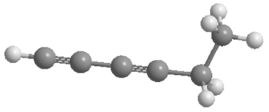
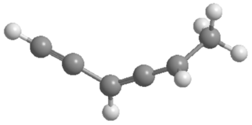
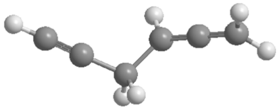
13) C_6H_6, benzene, D_{6h}, $^1A_{1g}$

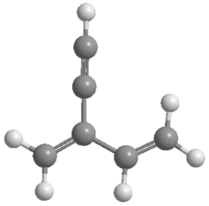
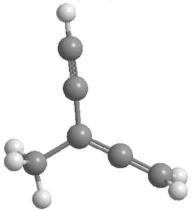
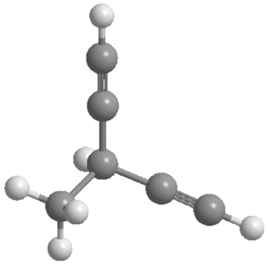
Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	1.393916	0.000000
2	6	0	1.207167	0.696958	0.000000
3	6	0	-1.207167	0.696958	0.000000
4	6	0	1.207167	-0.696958	0.000000
5	6	0	-1.207167	-0.696958	0.000000
6	6	0	0.000000	-1.393916	0.000000
7	1	0	0.000000	2.478341	0.000000
8	1	0	2.146306	1.239170	0.000000
9	1	0	-2.146306	1.239171	0.000000
10	1	0	2.146306	-1.239171	0.000000
11	1	0	-2.146306	-1.239171	0.000000
12	1	0	0.000000	-2.478341	0.000000

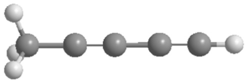
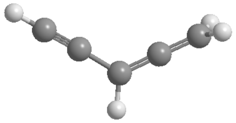
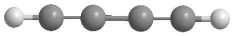
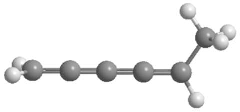
Table A4. B3LYP and CCSD(T) calculated total energies at 0 K, zero-point energy corrections (ZPE), B3LYP/6-311G** optimized Cartesian coordinates, unscaled vibrational frequencies (v_i), and moments of inertia (I_i) of all species involved in the C_2H + 1,2-butadiene reaction.

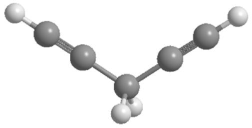
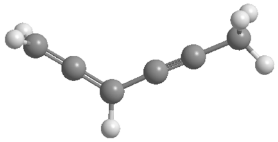
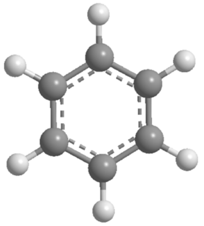
Species, (point group), electronic state	Energies, a.u.	*i*	I_i, a.u.	Cartesian coordinates, angstroms				v_i, cm^{-1}
				Atom	X	Y	Z	
H ^2S	ZPE(B3LYP/6-311G**) = 0.0 E(B3LYP/6-311G**) = -0.502155930011 E(CCSD(T)/CC-VDZ) = -0.499278 E(CCSD(T)/CC-VTZ) = -0.49980982 E(CCSD(T)/CC-VQZ) = -0.499946 E(CCSD(T)/CBS) = -0.49999							
C_2H ($D_{\infty h}$) 	ZPE(B3LYP/6-311G**) = 0.014445 E(B3LYP+ZPE) = -76.619455742 E(CCSD(T)/CC-VDZ) = -76.398687 E(CCSD(T)/CC-VTZ) = -76.46769892 E(CCSD(T)/CC-VQZ) = -76.4876915 E(CCSD(T)/CBS) = -76.49585	A B C	0.00000 40.54466 40.54466	C H C	0.000000 0.000000 0.000000	0.000000 0.000000 0.000000	-0.473068 -1.536812 0.729203	370, 416, 2089, 3465
CH_3 (C_1) 	ZPE(B3LYP/6-311G**) = 0.029569 E(B3LYP+ZPE) = -39.853757 E(CCSD(T)/CC-PVDZ) = -39.715785 E(CCSD(T)/CC-PVTZ) = -39.760817 E(CCSD(T)/CC-PVQZ) = -39.772271 E(CCSD(T)/CC-PV5Z) = -39.775614 E(CCSD(T)/CBS) = -39.77618	A B C	6.30449 6.30449 12.60896	C H H H	0.000000 0.000000 -0.935876 0.935876	0.000000 1.080657 -0.540328 -0.540328	0.000273 -0.000545 -0.000545 -0.000545	507, 1404, 1404, 3102, 3281, 3281
C_2H_5 (C_1) 	ZPE(B3LYP/6-311G**) = 0.058983 E(B3LYP+ZPE) = -79.124669 E(CCSD(T)/CC-VDZ) = -78.91573206 E(CCSD(T)/CC-VTZ) = -79.00226044 E(CCSD(T)/CC-VQZ) = -79.02545788 E(CCSD(T)/CBS) = -79.03395	A B C	17.39033 79.41224 85.68530	C H H C H H H	-0.794278 -1.351038 -1.351038 0.693124 1.107217 1.107217 1.094572	0.000000 -0.926566 0.926566 0.000000 -0.886126 0.886127 -0.000001	-0.019123 0.042622 0.042622 -0.001749 -0.492768 -0.492766 1.025521	105, 474, 813, 980, 1063, 1192, 1401, 1465, 1482, 1483, 2941, 3034, 3077, 3140, 3241

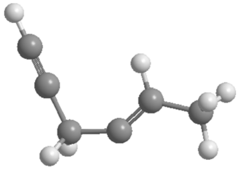
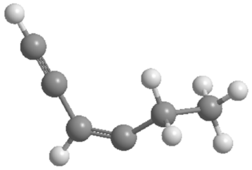
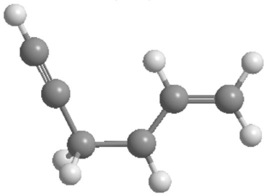
1,2-butadiene 	ZPE(B3LYP/6-311G**) = 0.083589 E(B3LYP+ZPE) = -155.937771 E(CCSD(T)/CC-VDZ) = -155.51539788 E(CCSD(T)/CC-VTZ) = -155.67550978 E(CCSD(T)/CC-VQZ) = -155.72038959 E(CCSD(T)/CBS) = -155.73787	A	52.08749	C	-1.937452	-0.214047	0.000671	168, 211, 340, 541, 572, 872, 879, 897, 1022, 1060, 1091, 1150, 1361, 1408, 1472, 1486, 1505, 2057, 3019, 3065, 3104, 3111, 3120, 3181
		B	431.02690	H	-2.476449	-0.382537	0.928581	
		C	459.59117	H	-2.482576	-0.381185	-0.923877	
				C	-0.692698	0.173968	-0.002479	
				C	0.553314	0.559152	0.000663	
				H	0.758980	1.628786	0.002691	
				C	1.746391	-0.364833	-0.000077	
				H	2.373927	-0.188003	-0.879758	
				H	2.371588	-0.191692	0.882119	
				H	1.437198	-1.410811	-0.002424	
hexa-1,3-diene-5-yne ((C_s)) 	ZPE(B3LYP/6-311G**) = 0.094365 E(B3LYP+ZPE) = -232.112802 E(CCSD(T)/CC-VDZ) = -231.47434583 E(CCSD(T)/CC-VTZ) = -231.70247712 E(CCSD(T)/CC-VQZ) = -231.76781018 E(CCSD(T)/CBS) = -231.79403	A	65.60308	C	-0.787242	2.809482	0.000000	134, 139, 207, 309, 446, 461, 555, 628, 668, 681, 880, 938, 960, 976, 1037, 1043, 1195, 1286, 1314, 1331, 1453, 1643, 1687, 2196, 3129, 3131, 3138, 3153, 3225, 3477
		B	1271.55338	H	0.226340	3.197324	0.000000	
		C	1337.15647	H	-1.590453	3.536090	0.000000	
				C	-1.031247	1.492856	0.000000	
				H	-2.060899	1.141318	0.000000	
				C	0.000000	0.475912	0.000000	
				H	1.032891	0.813954	0.000000	
				C	-0.254784	-0.849069	0.000000	
				H	-1.287394	-1.191738	0.000000	
				C	0.740856	-1.856011	0.000000	
				C	1.563266	-2.737928	0.000000	
				H	2.294416	-3.508395	0.000000	
hexa-1,4-diyne 	ZPE(B3LYP/6-311G**) = 0.093849 E(B3LYP+ZPE) = -232.024441 E(CCSD(T)/CC-VDZ) = -231.44560010 E(CCSD(T)/CC-VTZ) = -231.67620993 E(CCSD(T)/CC-VQZ) = -231.74160559 E(CCSD(T)/CBS) = -231.76749	A	145.03599	C	2.946786	-0.486889	0.000203	14, 92, 196, 248, 323, 365, 372, 522, 615, 636, 773, 937, 948, 1058, 1058, 1168, 1236, 1345, 1427, 1467, 1491, 1492, 2247, 2381, 3014, 3036, 3040, 3101, 3101, 3492
		B	1212.38035	H	3.134842	-1.105425	0.884717	
		C	1335.11507	H	3.681513	0.325930	0.000736	
				H	3.135699	-1.105029	-0.884401	
				C	1.582820	0.033719	-0.000378	
				C	0.452379	0.459991	-0.000373	
				C	-0.918667	0.988023	0.000193	
				H	-1.062991	1.636594	0.876059	
				H	-1.063396	1.637209	-0.875146	
				C	-1.955057	-0.053759	0.000055	
				C	-2.817337	-0.897594	-0.000045	
				H	-3.571219	-1.650230	0.000100	

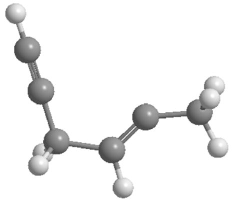
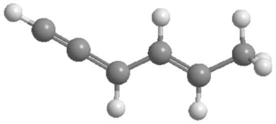
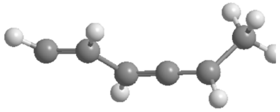
hexa-1,3-diyne **(C$_s$)** 	ZPE(B3LYP/6-311G**) = 0.094491	A	82.18487	C	2.348113	1.419454	0.000000	100, 132, 231, 240, 351, 464, 537, 553, 638, 642, 673, 787, 953, 1076, 1103, 1176, 1286, 1350, 1412, 1474, 1496, 1506, 2164, 2344, 3015, 3037, 3040, 3106, 3113, 3478
	E(B3LYP+ZPE) = -232.095506	B	1354.95574	H	2.622076	0.840218	0.883992	
	E(CCSD(T)/CC-VDZ) = -231.45392185	C	1414.83463	H	2.928835	2.345089	0.000000	
	E(CCSD(T)/CC-VTZ) = -231.68483829			H	2.622076	0.840218	-0.883992	
	E(CCSD(T)/CC-VQZ) = -231.74971853			C	0.840428	1.738845	0.000000	
	E(CCSD(T)/CBS) = -231.77507			H	0.591718	2.348869	0.876363	
				H	0.591718	2.348869	-0.876363	
				C	0.000000	0.548862	0.000000	
				C	-0.685553	-0.448562	0.000000	
				C	-1.459564	-1.572306	0.000000	
				C	-2.144899	-2.566670	0.000000	
				H	-2.747575	-3.441006	0.000000	
hexa-3,4-diene-1-yne **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.093476	A	137.96166	C	-2.638823	-0.582793	-0.291469	100, 147, 187, 229, 349, 447, 539, 611, 629, 688, 755, 874, 897, 985, 1059, 1090, 1156, 1303, 1407, 1438, 1485, 1501, 2044, 2207, 3023, 3072, 3100, 3107, 3122, 3479
	E(B3LYP+ZPE) = -232.091546	B	1176.58711	H	-2.235402	-0.878824	-1.260224	
	E(CCSD(T)/CC-VDZ) = -231.44919472	C	1240.61861	H	-3.541473	0.013841	-0.457456	
	E(CCSD(T)/CC-VTZ) = -231.67843565			H	-2.941046	-1.485333	0.249094	
	E(CCSD(T)/CC-VQZ) = -231.74368420			C	-1.627238	0.198908	0.510824	
	E(CCSD(T)/CBS) = -231.76964			H	-1.939744	0.537782	1.498601	
				C	-0.421689	0.490510	0.118805	
				C	0.791434	0.797613	-0.285586	
				H	0.947860	1.730515	-0.825857	
				C	1.940885	-0.013975	-0.063586	
				C	2.938780	-0.667349	0.101185	
				H	3.809708	-1.255468	0.254805	
hexa-4,5-diene-1-yne **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.093402	A	124.55056	C	2.846333	-0.431626	-0.246459	57, 165, 216, 327, 351, 459, 546, 600, 666, 682, 876, 879, 919, 956, 1020, 1021, 1144, 1218, 1306, 1374, 1466, 1478, 2058, 2224, 3010, 3066, 3115, 3135, 3187, 3479
	E(B3LYP+ZPE) = -232.084116	B	1172.53876	H	3.059024	-1.459943	-0.523168	
	E(CCSD(T)/CC-VDZ) = -231.44399277	C	1211.92123	H	3.657570	0.284382	-0.338713	
	E(CCSD(T)/CC-VTZ) = -231.67335978			C	1.669175	-0.074283	0.183582	
	E(CCSD(T)/CC-VQZ) = -231.73884848			C	0.489798	0.283507	0.606484	
	E(CCSD(T)/CBS) = -231.76502			H	0.263847	0.235244	1.669070	
				C	-0.626054	0.776670	-0.302294	
				H	-0.837201	1.829272	-0.075141	
				H	-0.293332	0.741054	-1.343332	
				C	-1.859762	0.005505	-0.149883	
				C	-2.867757	-0.632135	-0.007879	
				H	-3.760306	-1.195836	0.109974	

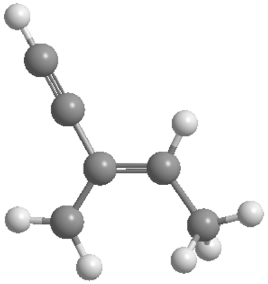
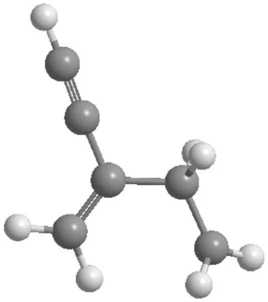
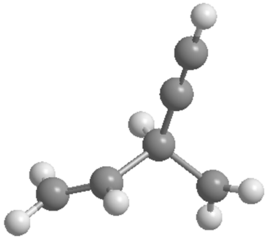
2-ethynyl-1,3-butadiene **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.094322	A	378.57720	C	-2.040225	-1.082399	0.000001	149, 162, 262, 309, 471, 499, 621, 652, 688, 717, 754, 775, 926, 946, 953, 1021, 1061, 1317, 1325, 1417, 1455, 1635, 1690, 2208, 3140, 3148, 3151, 3230, 3243, 3477
	E(B3LYP+ZPE) = -232.107249	B	512.23169	H	-2.860249	-1.757849	0.000049	
	E(CCSD(T)/CC-VDZ) = -231.47209420	C	890.80889	C	-1.121383	-0.304988	-0.000098	
	E(CCSD(T)/CC-VTZ) = -231.70074472			C	-0.011165	0.600579	-0.000004	
	E(CCSD(T)/CC-VQZ) = -231.76609711			C	-0.218293	1.931323	0.000062	
	E(CCSD(T)/CBS) = -231.79225			H	-1.215955	2.349834	0.000113	
				H	0.617918	2.620864	0.000165	
				C	1.351620	0.043609	-0.000102	
				H	2.145212	0.786131	-0.000278	
				C	1.660551	-1.254139	0.000079	
				H	0.893647	-2.020270	0.000336	
				H	2.692797	-1.582612	-0.000019	
1,1-ethynylmethylallene **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.093119	A	320.49455	C	0.180572	1.832358	-0.000206	136, 163, 200, 226, 343, 486, 531, 608, 631, 649, 686, 706, 884, 995, 1009, 1059, 1180, 1292, 1404, 1463, 1481, 1499, 2041, 2203, 3031, 3087, 3105, 3125, 3175, 3477
	E(B3LYP+ZPE) = -232.091295	B	685.71042	H	0.736449	2.160013	-0.883055	
	E(CCSD(T)/CC-VDZ) = -231.45011218	C	982.62420	H	-0.798102	2.312470	-0.000048	
	E(CCSD(T)/CC-VTZ) = -231.67940331			H	0.736817	2.160167	0.882351	
	E(CCSD(T)/CC-VQZ) = -231.74462982			C	0.037781	0.319436	-0.000044	
	E(CCSD(T)/CBS) = -231.77056			C	1.239191	-0.455976	-0.000044	
				C	2.281643	-1.058824	-0.000046	
				H	3.191561	-1.606725	-0.000063	
				C	-1.137672	-0.271589	0.000106	
				C	-2.307248	-0.839378	0.000261	
				H	-2.816081	-1.090961	0.927065	
				H	-2.816243	-1.091130	-0.926408	
3-ethynyl-1-butyne **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.093714	A	329.23816	C	0.000912	1.757258	-0.239490	133, 197, 207, 240, 346, 471, 562, 565, 675, 676, 685, 687, 787, 930, 1027, 1075, 1139, 1302, 1330, 1408, 1493, 1499, 2223, 2229, 3002, 3045, 3120, 3126, 3477, 3478
	E(B3LYP+ZPE) = -232.073636	B	655.70650	H	-0.888158	2.316549	0.056992	
	E(CCSD(T)/CC-VDZ) = -231.43960817	C	925.00665	H	0.890547	2.315505	0.057288	
	E(CCSD(T)/CC-VTZ) = -231.67002328			H	0.001025	1.647305	-1.324650	
	E(CCSD(T)/CC-VQZ) = -231.73552751			C	-0.000022	0.364662	0.439954	
	E(CCSD(T)/CBS) = -231.76155			H	-0.000054	0.522454	1.526770	
				C	1.214513	-0.392790	0.106477	
				C	2.223588	-0.983476	-0.165131	
				H	3.110477	-1.515847	-0.407019	
				C	-1.215255	-0.391580	0.106279	
				C	-2.224538	-0.982079	-0.164990	
				H	-3.109026	-1.517938	-0.407973	
methyldiacetylene **(C_1)**	ZPE(B3LYP/6-311G**) = 0.065681	A	11.27122	C	0.000000	0.000000	-2.511237	148, 148, 336, 336, 540, 540, 643, 643, 681, 1048, 1048,
	E(B3LYP+ZPE) = -192.800165	B	882.32687	H	0.000000	1.021724	-2.903005	

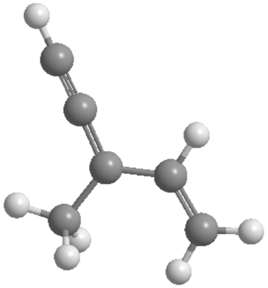
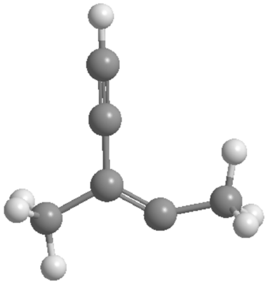
	E(CCSD(T)/CC-VDZ) = -192.25588599	C	882.32687	H	0.884839	-0.510862	-2.903005	1183, 1415, 1474, 1474, 2167,
	E(CCSD(T)/CC-VTZ) = -192.44543586			H	-0.884839	-0.510862	-2.903005	2351, 3020, 3079, 3079, 3479
	E(CCSD(T)/CC-VQZ) = -192.49885120			C	0.000000	0.000000	-1.058254	
	E(CCSD(T)/CBS) = -192.51981			C	0.000000	0.000000	0.151150	
				C	0.000000	0.000000	1.515712	
				C	0.000000	0.000000	2.723262	
				H	0.000000	0.000000	3.785214	
ethynylallene	ZPE(B3LYP/6-311G**) = 0.064997	A	67.05107	C	2.386836	-0.458322	0.000000	141, 295, 350, 359, 606, 626,
(C_1)	E(B3LYP+ZPE) = -192.791209	B	694.24010	H	3.334697	-0.937599	0.000028	643, 691, 883, 884, 951, 1004,
	E(CCSD(T)/CC-VDZ) = -192.24756563	C	748.90726	C	1.306493	0.072655	0.000014	1140, 1352, 1465, 2042, 2210,
	E(CCSD(T)/CC-VTZ) = -192.43544406			C	0.054208	0.749300	-0.000026	3111, 3115, 3184, 3478
	E(CCSD(T)/CC-VQZ) = -192.48910863			H	0.079958	1.837856	0.000051	
	E(CCSD(T)/CBS) = -192.51057			C	-1.113200	0.146341	-0.000028	
				C	-2.276359	-0.431301	0.000012	
				H	-2.781272	-0.686235	-0.927443	
				H	-2.781247	-0.686065	0.927529	
diacetylene	ZPE(B3LYP/6-311G**) = 0.037493	A	0.00000	C	0.000000	0.000000	1.889186	237, 237, 525, 525, 663, 663,
(C_1)	E(B3LYP+ZPE) = -153.490932	B	408.53335	H	0.000000	0.000000	2.951597	671, 671, 917, 2111, 2285,
	E(CCSD(T)/CC-VDZ) = -153.04796948	C	408.53335	C	0.000000	0.000000	0.682650	3476, 3478
	E(CCSD(T)/CC-VTZ) = -153.19597363			C	0.000000	0.000000	-0.682650	
	E(CCSD(T)/CC-VQZ) = -153.23799420			C	0.000000	0.000000	-1.889186	
	E(CCSD(T)/CBS) = -153.25465			H	0.000000	0.000000	-2.951597	
hexa-1,2,3,4-	ZPE(B3LYP/6-311G**) = 0.093073	A	65.29496	C	-2.882561	-0.555752	0.000009	104, 124, 176, 237, 319, 454,
tetraene	E(B3LYP+ZPE) = -232.096700	B	1406.66504	H	-3.529049	-0.474365	-0.880495	506, 537, 554, 719, 801, 855,
(C_1)	E(CCSD(T)/CC-VDZ) = -231.44520208	C	1448.42871	H	-2.418917	-1.542489	-0.000437	977, 1011, 1048, 1095, 1262,
	E(CCSD(T)/CC-VTZ) = -231.67456647			H	-3.528679	-0.474980	0.880841	1403, 1407, 1480, 1482, 1531,
	E(CCSD(T)/CC-VQZ) = -231.73936281			C	-1.848089	0.539056	0.000175	1957, 2222, 3016, 3061, 3104,
	E(CCSD(T)/CBS) = -231.76488			H	-2.216491	1.564515	0.000655	3109, 3123, 3181
				C	-0.549553	0.348935	-0.000111	
				C	0.711289	0.160862	-0.000414	
				C	1.972303	-0.024360	0.000003	
				C	3.268947	-0.215066	0.000164	
				H	3.829391	-0.297659	0.927058	
				H	3.829732	-0.297074	-0.926577	

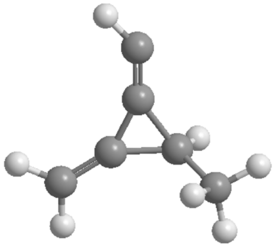
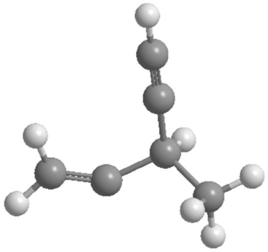
penta-1,4-diyne **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.065459**	**A**	**92.29024**	**C**	**2.243641**	**-0.569100**	**0.000002**	**137, 307, 327, 334, 562, 670, 672, 689, 691, 903, 931, 999, 1243, 1341, 1455, 2232, 2237, 3013, 3036, 3477, 3478**
	E(B3LYP+ZPE) = -192.776767	**B**	**637.14767**	**H**	**3.138749**	**-1.141176**	**0.000023**	
	E(CCSD(T)/CC-VDZ) = -192.23933457	**C**	**718.38928**	**C**	**1.228168**	**0.069521**	**-0.000014**	
	E(CCSD(T)/CC-VTZ) = -192.42855012			**C**	**-0.000002**	**0.869635**	**0.000006**	
	E(CCSD(T)/CC-VQZ) = -192.48259268			**H**	**0.000040**	**1.529580**	**0.876071**	
	E(CCSD(T)/CBS) = -192.5042			**H**	**0.000023**	**1.529600**	**-0.876045**	
				C	**-1.228232**	**0.069644**	**0.000005**	
				C	**-2.243603**	**-0.569146**	**-0.000018**	
				H	**-3.138641**	**-1.141330**	**0.000069**	
hexa-1,2-diene-4-yne **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.093219**	**A**	**104.600721**	**C**	**2.953259**	**-0.658506**	**0.000000**	**13, 95, 186, 250, 312, 380, 396, 551, 633, 802, 880, 887, 1007, 1051, 1054, 1070, 1207, 1365, 1416, 1471, 1478, 1479, 2040, 2340, 3019, 3073, 3078, 3103, 3107, 3176**
	E(B3LYP+ZPE) = -232.098292	**B**	**314.292301**	**C**	**1.888301**	**0.086096**	**0.000000**	
	E(CCSD(T)/CC-VDZ) = -231.43961046	**C**	**395.28034**	**C**	**0.823444**	**0.856322**	**0.000000**	
	E(CCSD(T)/CC-VTZ) = -231.67002641			**C**	**-0.519179**	**0.383272**	**0.000000**	
	E(CCSD(T)/CC-VQZ) =			**C**	**-1.671787**	**0.028128**	**0.000000**	
	E(CCSD(T)/CBS) =			**C**	**-3.057814**	**-0.419079**	**0.000000**	
				H	**3.416048**	**-0.986127**	**0.926967**	
				H	**3.416048**	**-0.986127**	**-0.926967**	
				H	**0.969595**	**1.936013**	**0.000000**	
				H	**-3.276672**	**-1.026281**	**0.883725**	
				H	**-3.745701**	**0.431437**	**-0.000019**	
				H	**-3.276661**	**-1.026313**	**-0.883706**	
benzene **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.100166**	**A**	**316.09731**	**C**	**-1.290906**	**-0.526176**	**-0.000001**	**413, 413, 623, 623, 689, 723, 862, 863, 981, 982, 1013, 1017, 1023, 1059, 1060, 1174, 1197, 1197, 1334, 1381, 1512, 1513, 1637, 1637, 3156, 3165, 3165, 3181, 3181, 3192**
	E(B3LYP+ZPE) = -232.208373	**B**	**316.14596**	**C**	**-1.101095**	**0.854806**	**0.000007**	
	E(CCSD(T)/CC-VDZ) = -231.58054764	**C**	**632.24327**	**C**	**0.189715**	**1.380922**	**-0.000011**	
	E(CCSD(T)/CC-VTZ) = -231.80581896			**C**	**1.290929**	**0.526122**	**0.000001**	
	E(CCSD(T)/CC-VQZ) = -231.87178577			**C**	**1.101131**	**-0.854759**	**0.000008**	
	E(CCSD(T)/CBS) = -231.8991			**C**	**-0.189773**	**-1.380914**	**-0.000005**	
				H	**-2.295091**	**-0.935474**	**0.000002**	
				H	**-1.957753**	**1.519697**	**0.000014**	
				H	**0.337277**	**2.455243**	**0.000001**	
				H	**2.295060**	**0.935551**	**0.000002**	
				H	**1.957705**	**-1.519760**	**0.000004**	
				H	**-0.337196**	**-2.455254**	**-0.000014**	
INT 1 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.103852**	**A**	**189.32461**	**C**	**2.548491**	**-0.991634**	**-0.000004**	**92, 103, 181, 241, 247, 325, 389, 642, 667, 678, 740, 823, 936, 941, 1034, 1060, 1096, 1233, 1284, 1319, 1406, 1457, 1485, 1490, 1769, 2217, 3007, 3017, 3025, 3027, 3065, 3111,**
	E(B3LYP+ZPE) = -232.642830	**B**	**1029.38255**	**H**	**3.191979**	**-1.836872**	**0.000006**	
	E(CCSD(T)/CC-VTZ) = -232.23979124	**C**	**1196.51923**	**C**	**1.833875**	**-0.026000**	**0.000000**	
				C	**0.927003**	**1.126369**	**0.000006**	
				H	**1.137657**	**1.753529**	**0.875246**	
				H	**1.137682**	**1.753554**	**-0.875210**	

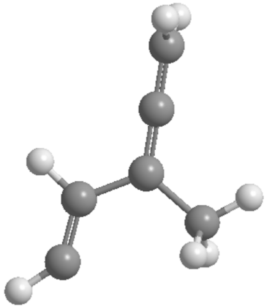
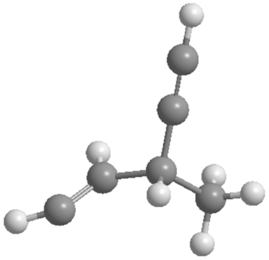
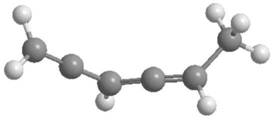
				C	-0.507719	0.736140	-0.000016	3476
				C	-1.253177	-0.339848	0.000001	
				H	-0.748136	-1.312831	0.000013	
				C	-2.759869	-0.370412	0.000001	
				H	-3.136803	-0.901265	0.880485	
				H	-3.177196	0.637496	-0.000016	
				H	-3.136803	-0.901303	-0.880457	
INT 2 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.104385	A	202.37243	C	2.660953	-0.859630	-0.046105	45, 116, 204, 231, 328, 374, 499, 624, 632, 683, 795, 804, 825, 968, 1028, 1083, 1100, 1271, 1296, 1335, 1411, 1455, 1498, 1506, 1703, 2193, 2962, 3024, 3036, 3103, 3104, 3108, 3477
	E(B3LYP+ZPE) = -232.648233	B	1017.42147	H	3.398396	-1.623255	-0.011026	
	E(CCSD(T)/CC-VTZ) = -232.24392426	C	1131.93657	C	1.825054	0.007552	-0.085379	
				C	0.842959	1.043811	-0.136526	
				H	1.192433	2.031942	-0.433794	
				C	-0.434148	0.859267	0.155464	
				C	-1.355993	-0.204413	0.576976	
				H	-1.786530	0.060274	1.550513	
				H	-0.773327	-1.125644	0.736123	
				C	-2.489883	-0.468833	-0.430380	
				H	-2.086470	-0.773232	-1.398468	
				H	-3.143698	-1.264654	-0.065684	
				H	-3.094458	0.428049	-0.581965	
INT 3 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.103749	A	218.13846	C	2.423233	-1.025899	0.000036	98, 130, 199, 292, 330, 420, 541, 664, 670, 684, 720, 790, 843, 923, 963, 1008, 1077, 1205, 1220, 1287, 1305, 1367, 1457, 1501, 1523, 2225, 2978, 2988, 3135, 3140, 3146, 3234, 3477
	E(B3LYP+ZPE) = -232.678518	B	908.93329	H	3.060762	-1.875612	0.000041	
	E(CCSD(T)/CC-VTZ) = -232.27389648	C	1116.15573	C	1.706910	-0.061738	0.000002	
				C	0.845193	1.117604	0.000097	
				H	1.099370	1.739364	0.871222	
				H	1.099924	1.740008	-0.870345	
				C	-0.638440	0.851419	-0.000244	
				H	-1.263937	1.740519	-0.000288	
				C	-1.241468	-0.392476	-0.000192	
				H	-0.588484	-1.261897	-0.000446	
				C	-2.608508	-0.605583	0.000166	
				H	-3.307712	0.223556	0.000559	
				H	-3.021448	-1.605908	0.000065	
INT 4 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.103386	A	243.59925	C	-2.359969	-1.171236	-0.000004	100, 103, 184, 229, 236, 332, 374, 654, 664, 676, 714, 815, 952, 955, 1045, 1050, 1067, 1235, 1265, 1350, 1399, 1455, 1466, 1475, 1777, 2229, 2959, 2998, 3010, 3019, 3046, 3071,
	E(B3LYP+ZPE) = -232.644276	B	918.91218	H	-2.913398	-2.077670	-0.000010	
	E(CCSD(T)/CC-VTZ) = -232.24019738	C	1140.32211	C	-1.727973	-0.150198	-0.000001	
				C	-0.977148	1.102007	0.000005	
				H	-1.272817	1.697884	-0.873413	
				H	-1.272809	1.697868	0.873437	

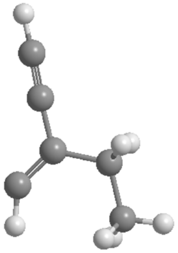
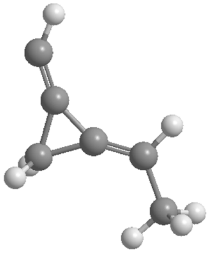
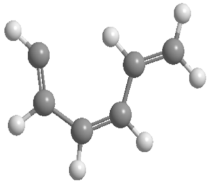
				C	0.533457	0.946724	-0.000008	3479
				C	1.201915	-0.178096	0.000018	
				C	2.581232	-0.678727	-0.000002	
				H	2.781398	-1.294858	-0.882325	
				H	3.304074	0.152316	-0.000010	
				H	2.781428	-1.294872	0.882303	
				H	1.083043	1.896492	-0.000037	
INT 5 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.103676	A	77.81082	C	-3.198641	-0.411704	0.000352	120, 129, 191, 237, 299, 430, 453, 527, 558, 666, 742, 804, 938, 984, 1031, 1040, 1130, 1189, 1278, 1303, 1410, 1430, 1476, 1488, 1555, 2091, 3001, 3037, 3092, 3128, 3134, 3144, 3473
	E(B3LYP+ZPE) = -232.698536	B	1330.81768	H	-4.176107	-0.826976	0.000443	
	E(CCSD(T)/CC-VTZ) = -232.28830833	C	1397.54097	C	-2.079414	0.058848	-0.000230	
				C	-0.803333	0.616038	-0.000193	
				H	-0.731050	1.700682	-0.000124	
				C	0.385103	-0.141188	-0.000302	
				H	0.281634	-1.224100	-0.000753	
				C	1.643389	0.394526	0.000186	
				H	1.743840	1.478265	0.000823	
				C	2.907326	-0.401825	0.000090	
				H	3.523491	-0.169566	-0.877302	
				H	3.523231	-0.170550	0.877892	
				H	2.708380	-1.475929	-0.000396	
INT 6 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.103466	A	105.72929	C	-3.116302	0.219307	-0.131814	100, 130, 177, 219, 287, 393, 525, 588, 634, 762, 777, 850, 898, 917, 1057, 1081, 1097, 1163, 1235, 1306, 1407, 1434, 1485, 1501, 1641, 2039, 3020, 3035, 3067, 3095, 3119, 3128, 3249
	E(B3LYP+ZPE) = -232.651657	B	1279.91939	H	-4.042702	0.719921	0.103680	
	E(CCSD(T)/CC-VTZ) = -232.24306173	C	1312.77508	C	-1.849355	0.303326	0.212645	
				H	-1.546605	1.065856	0.938072	
				C	-0.773801	-0.553290	-0.297791	
				H	-1.057566	-1.318416	-1.017015	
				C	0.484194	-0.446436	0.063990	
				C	1.733185	-0.340518	0.420098	
				H	2.074761	-0.918398	1.279258	
				C	2.764941	0.522130	-0.266115	
				H	3.186271	1.251136	0.433740	
				H	3.595310	-0.089299	-0.634176	
				H	2.333357	1.062087	-1.109634	

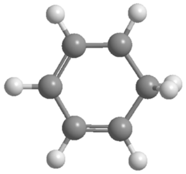
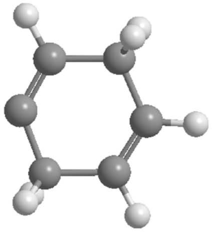
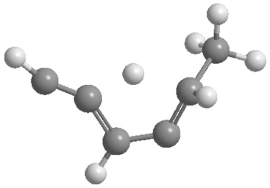
INT 7 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.103094**	**A**	**220.94625**	**C**	**0.155945**	**1.606798**	**0.000318**	**36, 151, 167, 288, 319, 481, 534, 555, 592, 640, 686, 703, 787, 808, 946, 1013, 1092, 1101, 1260, 1307, 1404, 1459, 1481, 1488, 1528, 2209, 2998, 3034, 3107, 3161, 3183, 3258, 3477**
	E(B3LYP+ZPE) = -232.683924	**B**	**804.29176**	**H**	**-0.640320**	**2.337944**	**-0.000101**	
	E(CCSD(T)/CC-VTZ) = -232.27798985	**C**	**1014.10236**	**H**	**1.175685**	**1.968265**	**0.002257**	
				C	**-0.124675**	**0.247150**	**-0.001084**	
				C	**-1.500802**	**-0.172001**	**-0.000853**	
				C	**-2.650685**	**-0.526763**	**0.000717**	
				H	**-3.666277**	**-0.837926**	**0.002676**	
				C	**0.860395**	**-0.751870**	**-0.001592**	
				H	**0.526336**	**-1.782456**	**0.003296**	
				C	**2.330988**	**-0.481585**	**0.000019**	
				H	**2.647239**	**0.038592**	**0.913441**	
				H	**2.900445**	**-1.409575**	**-0.065074**	
				H	**2.629899**	**0.154780**	**-0.841638**	
INT 8 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.102458**	**A**	**228.92736**	**C**	**0.222168**	**1.605547**	**0.054179**	**77, 121, 165, 269, 301, 445, 516, 531, 563, 646, 680, 745, 770, 858, 937, 940, 1049, 1098, 1213, 1251, 1353, 1428, 1456, 1465, 1672, 2200, 2939, 3035, 3142, 3150, 3239, 3246, 3476**
	E(B3LYP+ZPE) = -232.657429	**B**	**784.41894**	**H**	**-0.539241**	**2.374630**	**0.026660**	
	E(CCSD(T)/CC-VTZ) = -232.25472982	**C**	**992.41029**	**H**	**1.256939**	**1.920312**	**0.107945**	
				C	**-0.104839**	**0.307088**	**0.033690**	
				C	**0.914793**	**-0.830042**	**0.079079**	
				H	**0.623543**	**-1.548441**	**-0.705942**	
				H	**0.776238**	**-1.374064**	**1.020376**	
				C	**2.339211**	**-0.439403**	**-0.094071**	
				H	**3.117364**	**-0.895965**	**0.503060**	
				H	**2.638200**	**0.197830**	**-0.917588**	
				C	**-1.472805**	**-0.106845**	**-0.014550**	
				C	**-2.608135**	**-0.508082**	**-0.050292**	
				H	**-3.615401**	**-0.843889**	**-0.082712**	
INT 9 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.102431**	**A**	**307.24834**	**C**	**-2.204954**	**-0.793413**	**0.120037**	**95, 147, 179, 210, 299, 388, 483, 526, 552, 673, 676, 695, 817, 925, 945, 1023, 1065, 1083, 1111, 1261, 1313, 1326, 1440, 1448, 1689, 2220, 2996, 3127, 3145, 3152, 3213, 3262, 3477**
	E(B3LYP+ZPE) = -232.648143	**B**	**709.83164**	**H**	**-2.390260**	**-0.701012**	**1.185903**	
	E(CCSD(T)/CC-VTZ) = -232.24719167	**C**	**940.14899**	**H**	**-2.978892**	**-1.268889**	**-0.471575**	
				C	**-1.081893**	**-0.351081**	**-0.435306**	
				H	**-0.911394**	**-0.455371**	**-1.503180**	
				C	**0.032225**	**0.359472**	**0.330390**	
				H	**-0.225411**	**0.310118**	**1.396960**	
				C	**1.316761**	**-0.322639**	**0.137008**	
				C	**2.365800**	**-0.881796**	**-0.036644**	
				H	**3.293401**	**-1.378109**	**-0.183619**	
				C	**0.090433**	**1.803296**	**-0.086908**	

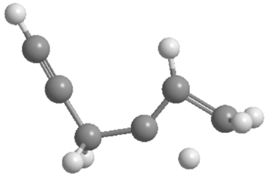
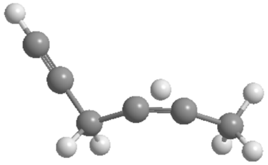
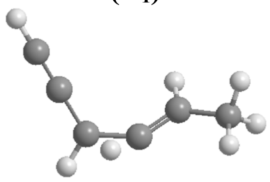
				H	-0.686344	2.478313	0.248945	
				H	0.788670	2.131923	-0.844890	
INT 10 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.103593	A	247.01869	C	0.264311	1.632423	0.000019	61, 160, 169, 280, 297, 464, 492, 529, 575, 641, 664, 739, 857, 973, 996, 1024, 1043, 1255, 1283, 1310, 1402, 1438, 1483, 1496, 1551, 2085, 3013, 3056, 3126, 3148, 3154, 3236, 3471
	E(B3LYP+ZPE) = -232.695830	B	756.12454	H	0.858021	1.897322	0.881872	
	E(CCSD(T)/CC-VTZ) = -232.28825483	C	991.95115	H	0.858428	1.897320	-0.881581	
				H	-0.637515	2.243345	-0.000232	
				C	-0.076614	0.162815	-0.000056	
				C	0.934134	-0.836551	-0.000056	
				H	0.587005	-1.865810	-0.000129	
				C	2.275911	-0.606532	0.000083	
				H	2.979773	-1.429085	0.000045	
				H	2.691244	0.393983	0.000158	
				C	-1.421245	-0.216544	-0.000137	
				C	-2.595795	-0.524826	0.000026	
				H	-3.621164	-0.801790	0.000598	
INT 11 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.103641	A	415.53350	C	-0.997120	1.782934	-0.000031	113, 128, 163, 214, 236, 292, 420, 565, 586, 624, 679, 704, 944, 1029, 1040, 61, 1108, 1191, 1391, 1403, 1455, 1468, 1481, 1488, 1725, 2186, 2978, 3027, 3 9, 3068, 3082, 3119, 3476
	E(B3LYP+ZPE) = -232.653490	B	577.83016	H	-1.641785	1.833572	0.882280	
	E(CCSD(T)/CC-VTZ) = -232.24878482	C	970.94005	H	-0.330523	2.646001	0.000041	
				H	-1.641812	1.833505	-0.882290	
				C	-0.196206	0.494155	0.000005	
				C	-0.932393	-0.736696	0.000219	
				C	-1.560200	-1.765903	-0.000125	
				H	-2.115615	-2.671305	-0.000053	
				C	1.128234	0.471100	-0.000120	
				C	2.242369	-0.482526	-0.000001	
				H	2.877014	-0.351991	-0.882597	
				H	2.876653	-0.351724	0.882845	
				H	1.867966	-1.516439	0.000092	

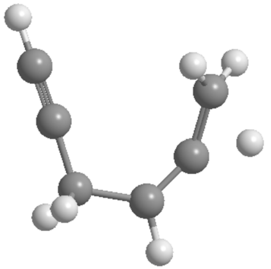
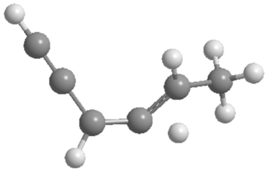
INT 12	**ZPE(B3LYP/6-311G**) = 0.103530**	**A**	**439.40585**	**C**	**1.602632**	**-1.395145**	**-0.140071**	**164, 192, 194, 226, 374, 395, 526, 642, 667, 719, 793, 818, 850, 910, 1016, 1051, 1091, 1110, 1144, 1327, 1408, 1449, 1489, 1497, 1681, 1823, 3026, 3078, 3087, 3108, 3127, 3211, 3251**
(C_1)	**E(B3LYP+ZPE) = -232.628818**	**B**	**454.18908**	**H**	**2.581603**	**-1.109620**	**-0.508616**	
	**E(CCSD(T)/CC-VTZ) = -232.22249192**	**C**	**818.88307**	**H**	**1.415898**	**-2.451848**	**0.020977**	
				C	**0.668557**	**-0.490044**	**0.107079**	
				C	**0.275603**	**0.894100**	**0.098473**	
				C	**0.467690**	**2.152456**	**-0.116563**	
				H	**1.240735**	**2.823927**	**-0.454860**	
				C	**-0.713518**	**-0.180283**	**0.538562**	
				H	**-0.895220**	**-0.209425**	**1.613696**	
				C	**-1.914629**	**-0.519698**	**-0.326483**	
				H	**-2.257711**	**-1.539384**	**-0.126617**	
				H	**-2.742746**	**0.164657**	**-0.124508**	
				H	**-1.660569**	**-0.446626**	**-1.386064**	
INT 13	**ZPE(B3LYP/6-311G**) = 0.103538**	**A**	**416.35699**	**C**	**0.381273**	**1.848971**	**-0.334104**	**113, 136, 204, 240, 295, 362, 486, 557, 598, 673, 676, 780, 889, 894, 995, 1031, 1078, 1126, 1296, 1315, 1402, 1408, 1493, 1500, 1737, 2209, 2998, 3042, 3051, 3116, 3121, 3153, 3476**
(C_1)	**E(B3LYP+ZPE) = -232.639512**	**B**	**543.82307**	**H**	**-0.340044**	**2.623388**	**-0.065682**	
	**E(CCSD(T)/CC-VTZ) = -232.23844946**	**C**	**887.35248**	**H**	**1.387492**	**2.207744**	**-0.110063**	
				H	**0.307821**	**1.659660**	**-1.406183**	
				C	**0.084550**	**0.554908**	**0.461080**	
				H	**0.178464**	**0.791180**	**1.529653**	
				C	**1.053299**	**-0.505165**	**0.151496**	
				C	**1.824217**	**-1.387486**	**-0.116734**	
				H	**2.516298**	**-2.158916**	**-0.350433**	
				C	**-1.308453**	**0.081356**	**0.227000**	
				C	**-1.961978**	**-0.969041**	**-0.195120**	
				H	**-1.440865**	**-1.879647**	**-0.501003**	
				H	**-3.046615**	**-0.984667**	**-0.257997**	
INT 14	**ZPE(B3LYP/6-311G**) = 0.103091**	**A**	**252.81483**	**C**	**-0.446541**	**1.642478**	**0.000055**	**136, 160, 164, 258, 278, 460, 487, 589, 593, 685, 706, 843, 852, 883, 1013, 1014, 1059, 1218, 1233, 1314, 1405, 1465, 1481, 1499, 1634, 2034, 3027, 3040, 3079, 3101, 3125, 3169, 3250**
(C_1)	**E(B3LYP+ZPE) = -232.651759**	**B**	**760.22800**	**H**	**-1.060158**	**1.852695**	**0.881162**	
	E(CCSD(T)/CC-VTZ) = -232.24474913	**C**	**989.52309**	**H**	**0.412514**	**2.313033**	**0.000024**	
				H	**-1.060347**	**1.852858**	**-0.880880**	
				C	**-0.010731**	**0.192991**	**-0.000084**	
				C	**1.259568**	**-0.145942**	**-0.000422**	
				C	**2.517780**	**-0.480461**	**0.000174**	
				H	**3.067780**	**-0.626035**	**0.926521**	
				H	**3.068722**	**-0.626257**	**-0.925575**	
				C	**-1.051661**	**-0.850890**	**-0.000014**	
				H	**-0.686955**	**-1.882936**	**0.000016**	

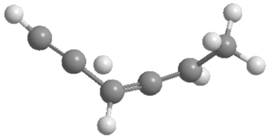
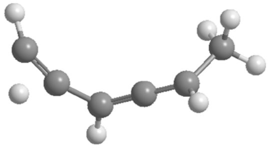
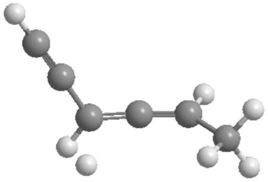
				C	-2.349233	-0.635547	0.000052	
				H	-3.256644	-1.219136	0.000169	
INT 15 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.103374	A	325.66157	C	-2.238439	-0.879910	-0.217612	92, 181, 205, 239, 327, 387, 511, 543, 669, 676, 679, 739, 839, 866, 936, 1053, 1083, 1141, 1235, 1309, 1333, 1406, 1494, 1498, 1670, 2217, 3026, 3035, 3040, 3107, 3112, 3248, 3477
	E(B3LYP+ZPE) = -232.634282	B	681.51375	H	-3.147184	-1.395662	0.052041	
	E(CCSD(T)/CC-VTZ) = -232.23441699	C	937.27643	C	-1.159655	-0.425659	0.360446	
				H	-1.022756	-0.546573	1.440930	
				C	-0.026524	0.305582	-0.352268	
				H	-0.242158	0.287614	-1.425432	
				C	1.246614	-0.386581	-0.129591	
				C	2.291297	-0.946188	0.069939	
				H	3.213822	-1.445019	0.238745	
				C	0.051291	1.778814	0.107498	
				H	0.862628	2.297316	-0.407569	
				H	-0.889693	2.287755	-0.111638	
				H	0.237835	1.838220	1.182454	
INT 16 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.102332	A	141.60120	C	-2.945252	0.626949	0.125651	76, 103, 130, 176, 238, 347, 434, 489, 602, 746, 852, 877, 892, 978, 984, 1054, 1057, 1097, 1302, 1369, 1401, 1447, 1485, 1492, 1876, 1934, 3018, 3037, 3054, 3067, 3081, 3108, 3116
	E(B3LYP+ZPE) = -232.668475	B	1253.10151	H	-3.574752	0.473471	1.002906	
	E(CCSD(T)/CC-VTZ) = -232.25317510	C	1313.55832	H	-3.275925	1.401998	-0.567176	
				C	-1.866451	-0.064969	-0.078587	
				C	-0.745440	-0.791085	-0.323551	
				H	-0.872927	-1.710800	-0.897686	
				C	0.514247	-0.475595	0.076230	
				C	1.716868	-0.215099	0.495059	
				H	2.028560	-0.599898	1.471099	
				C	2.758626	0.592867	-0.247959	
				H	3.065393	1.460674	0.345155	
				H	3.655374	-0.009303	-0.427882	
				H	2.378688	0.945448	-1.207474	

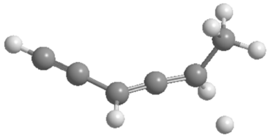
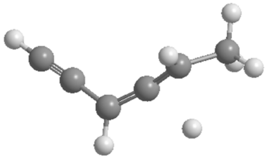
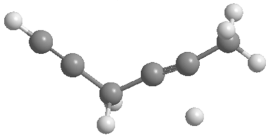
INT 17 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.103935**	**A**	**211.87286**	**C**	**-2.691573**	**-0.425309**	**0.000117**	**78, 157, 234, 279, 283, 428, 536, 544, 648, 675, 681, 754, 794, 825, 1004, 1074, 1089, 1140, 1287, 1347, 1413, 1475, 1498, 1507, 1643, 2202, 3022, 3031, 3049, 3095, 3098, 3253, 3477**
	E(B3LYP+ZPE) = -232.638741	**B**	**818.35328**	**H**	**-3.703806**	**-0.747366**	**0.000350**	
	E(CCSD(T)/CC-VTZ) = -232.23804379	**C**	**1007.95617**	**C**	**-1.551729**	**-0.037508**	**-0.000139**	
				C	**-0.173748**	**0.356058**	**-0.000400**	
				C	**0.157216**	**1.633773**	**0.000082**	
				H	**1.055897**	**2.230092**	**0.000569**	
				C	**0.840851**	**-0.793652**	**0.000088**	
				H	**0.624564**	**-1.417328**	**0.874631**	
				H	**0.624618**	**-1.417987**	**-0.874006**	
				C	**2.308383**	**-0.372499**	**0.000006**	
				H	**2.554426**	**0.220855**	**0.884555**	
				H	**2.953559**	**-1.254183**	**0.000026**	
				H	**2.554342**	**0.220735**	**-0.884645**	
INT 18 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.103532**	**A**	**170.71829**	**C**	**2.558306**	**-0.627940**	**0.000070**	**140, 160, 163, 302, 336, 384, 510, 645, 646, 801, 823, 851, 962, 963, 1020, 1030, 1048, 1057, 1126, 1348, 1410, 1446, 1481, 1490, 1695, 1835, 3012, 3053, 3069, 3103, 3136, 3148, 3254**
	E(B3LYP+ZPE) = -232.630789	**B**	**859.76801**	**H**	**2.980410**	**-1.620018**	**0.002525**	
	E(CCSD(T)/CC-VTZ) = -232.22322260	**C**	**1007.26453**	**C**	**1.405408**	**-0.044956**	**-0.000957**	
				C	**0.672721**	**1.290179**	**0.000016**	
				H	**0.704053**	**1.875782**	**0.916934**	
				H	**0.701038**	**1.875795**	**-0.917017**	
				C	**-0.027239**	**-0.015677**	**0.000595**	
				C	**-1.174404**	**-0.681318**	**-0.000384**	
				H	**-1.138266**	**-1.768404**	**-0.001572**	
				C	**-2.530187**	**-0.040099**	**0.000288**	
				H	**-3.108859**	**-0.347391**	**0.878804**	
				H	**-2.457039**	**1.048922**	**0.001267**	
				H	**-3.108962**	**-0.345816**	**-0.878705**	
INT 19 **(C_s)** 	**ZPE(B3LYP/6-311G**) = 0.104274**	**A**	**65.71132**	**C**	**-0.957972**	**-1.970663**	**0.000000**	**57, 137, 161, 323, 380, 441, 582, 684, 702, 796, 844, 867, 930, 938, 992, 1002, 1042, 1165, 1281, 1282, 1317, 1406, 1476, 1610, 1645, 1688, 3007, 3125, 3131, 3139, 3162, 3219, 3240**
	E(B3LYP+ZPE) = -232.665167	**B**	**1300.02267**	**H**	**-1.148052**	**-3.033462**	**0.000000**	
	E(CCSD(T)/CC-VTZ) = -232.26020277	**C**	**1365.73399**	**C**	**-1.681005**	**-0.868792**	**0.000000**	
				H	**-2.770013**	**-1.002869**	**0.000000**	
				C	**-1.253551**	**0.532575**	**0.000000**	
				H	**-2.070988**	**1.246791**	**0.000000**	
				C	**0.000000**	**1.035233**	**0.000000**	
				H	**0.100402**	**2.118355**	**0.000000**	
				C	**1.240522**	**0.287363**	**0.000000**	
				H	**1.163259**	**-0.796802**	**0.000000**	
				C	**2.451575**	**0.860545**	**0.000000**	
				H	**2.567995**	**1.940187**	**0.000000**	
				H	**3.359982**	**0.270241**	**0.000000**	

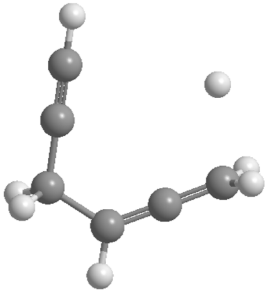
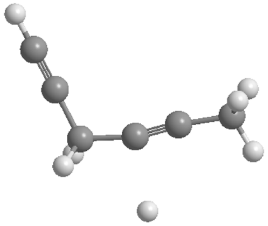
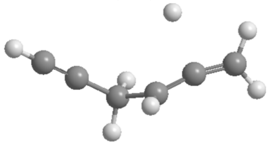
INT 20 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.108284** **E(B3LYP+ZPE) = -232.746121** **E(CCSD(T)/CC-VTZ) = -232.34640585**	**A**	**337.39947**	**C**	**0.624360**	**1.254359**	**-0.000186**	**173, 384, 527, 566, 593, 636, 726, 774, 870, 933, 968, 968, 974, 987, 997, 1110, 1171, 1182, 1198, 1307, 1369, 1416, 1437, 1455, 1545, 1610, 2902, 2918, 3150, 3152, 3170, 3171, 3194**
		B	**343.16379**	**C**	**-0.738240**	**1.225403**	**0.000000**	
		C	**669.78451**	**C**	**-1.453545**	**0.001588**	**0.000197**	
				C	**-0.741019**	**-1.223869**	**0.000000**	
				C	**0.621450**	**-1.255785**	**-0.000261**	
				C	**1.446697**	**-0.001448**	**0.000167**	
				H	**1.151537**	**2.202605**	**-0.000423**	
				H	**-1.291883**	**2.159124**	**0.000010**	
				H	**-2.536340**	**0.002939**	**-0.000377**	
				H	**-1.296699**	**-2.156388**	**0.000086**	
				H	**1.147058**	**-2.204878**	**-0.000429**	
				H	**2.133255**	**-0.002685**	**0.866104**	
				H	**2.134852**	**-0.002205**	**-0.864479**	
INT 21 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.108644** **E(B3LYP+ZPE) = -232.688062** **E(CCSD(T)/CC-VTZ) = -232.18661895**	**A**	**322.62762**	**C**	**-0.258158**	**1.323004**	**-0.000085**	**133, 365, 398, 525, 575, 655, 751, 850, 900, 907, 948, 963, 978, 1003, 1029, 1185, 1199, 1205, 1254, 1324, 1351, 1403, 1470, 1473, 1709, 1746, 2983, 2993, 2994, 3005, 3129, 3131, 3153**
		B	**371.08553**	**C**	**1.018369**	**0.944639**	**-0.000172**	
		C	**671.74715**	**C**	**1.465860**	**-0.508836**	**0.000216**	
				C	**0.274734**	**-1.385644**	**-0.000156**	
				C	**-1.000594**	**-1.081584**	**-0.000199**	
				C	**-1.432326**	**0.378469**	**0.000234**	
				H	**-0.493426**	**2.384144**	**-0.000251**	
				H	**1.807062**	**1.692719**	**-0.000475**	
				H	**2.100199**	**-0.706424**	**0.874981**	
				H	**-1.780237**	**-1.839481**	**-0.000410**	
				H	**-2.071288**	**0.577829**	**-0.871969**	
				H	**-2.070629**	**0.577610**	**0.872972**	
				H	**2.101010**	**-0.706687**	**-0.873881**	
TS 1 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.097660** **E(B3LYP+ZPE) = -232.576675** **E(CCSD(T)/CC-VTZ) = -232.16278271**	**A**	**241.33836**	**C**	**2.443404**	**-0.878500**	**-0.021668**	**2026i, 127, 177, 200, 281, 382, 461, 515, 575, 607, 708, 820, 872, 882, 939, 1033, 1068, 1108, 1135, 1238, 1382, 1404, 1474, 1487, 1496, 1701, 1887, 3020, 3073, 3078, 3111, 3203, 3425**
		B	**806.31815**	**H**	**3.137381**	**-1.682999**	**0.061301**	
		C	**974.31940**	**C**	**1.393030**	**-0.201670**	**0.023367**	
				C	**0.790867**	**1.131425**	**-0.220375**	
				H	**1.406673**	**1.952226**	**-0.564406**	
				C	**-0.505188**	**1.138338**	**0.048372**	
				C	**-1.213326**	**0.036256**	**0.520452**	
				H	**-1.431346**	**0.023046**	**1.591280**	
				H	**0.180104**	**-0.701169**	**0.444564**	
				C	**-2.217208**	**-0.708240**	**-0.332620**	
				H	**-1.896724**	**-0.747855**	**-1.375501**	
				H	**-2.348359**	**-1.729091**	**0.035280**	
				H	**-3.197209**	**-0.219811**	**-0.297684**	

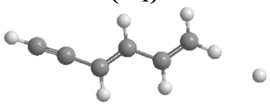
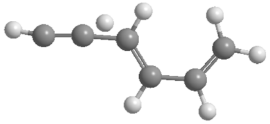
TS 2 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.098341	A	169.64077	C	-2.625532	-0.795188	0.000018	2166i, 88, 113, 231, 310, 328, 464, 470, 668, 672, 705, 812, 888, 940, 943, 990, 1046, 1051, 1117, 1225, 1227, 1312, 1430, 1456, 1724, 1822, 2215, 3015, 3036, 3059, 3150, 3182, 3478
	E(B3LYP+ZPE) = -232.578290	B	984.90200	H	-3.370644	-1.552308	0.000032	
	E(CCSD(T)/CC-VTZ) = -232.17018738	C	1131.36937	C	-1.793358	0.071760	0.000005	
				C	-0.748476	1.093881	-0.000011	
				H	-0.864776	1.744293	-0.875065	
				H	-0.864769	1.744319	0.875023	
				C	0.632896	0.502340	-0.000007	
				C	1.205546	-0.689992	-0.000028	
				H	0.777508	-1.685981	-0.000084	
				C	2.646883	-0.262820	0.000025	
				H	3.222264	-0.376471	-0.918630	
				H	1.970510	0.982560	-0.000046	
				H	3.222162	-0.376299	0.918766	
TS 3 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.097834	A	152.99259	C	-2.919013	-0.718376	-0.024336	2116i, 30, 106, 167, 201, 272, 330, 381, 434, 523, 666, 677, 789, 918, 942, 993, 1036, 1044, 1214, 1295, 1389, 1453, 1468, 1477, 1919, 2226, 2338, 2980, 2994, 3039, 3070, 3091, 3480
	E(B3LYP+ZPE) = -232.569091	B	1227.80928	H	-3.770449	-1.338482	-0.160718	
	E(CCSD(T)/CC-VTZ) = -232.15896047	C	1271.37002	C	-1.955065	-0.019197	0.129429	
				C	-0.782114	0.832294	0.316574	
				H	-1.043955	1.867445	0.071463	
				H	-0.490042	0.824035	1.376637	
				C	0.406542	0.413113	-0.517151	
				C	1.625096	-0.019604	-0.474799	
				H	1.036991	0.172543	-1.614874	
				C	2.788895	-0.456326	0.345746	
				H	3.052716	-1.492770	0.120186	
				H	3.666798	0.160440	0.137160	
				H	2.561896	-0.384635	1.417372	
TS 4 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.098588	A	170.84743	C	2.753711	-0.871561	0.099867	1941i, 90, 150, 195, 237, 276, 380, 447, 598, 638, 677, 695, 817, 861, 982, 1052, 1097, 1127, 1134, 1298, 1366, 1407, 1481, 1488, 1710, 2094, 2168, 3010, 3036, 3053, 3108, 3130, 3475
	E(B3LYP+ZPE) = -232.587158	B	1111.70864	H	3.498936	-1.625381	0.167721	
	E(CCSD(T)/CC-VTZ) = -232.17275664	C	1234.44543	C	1.906203	-0.017122	0.008037	
				C	0.899546	0.986136	-0.036279	
				H	0.153718	1.204574	1.011260	
				H	1.207149	1.995966	-0.296755	
				C	-0.514989	0.712653	-0.048476	
				C	-1.378949	-0.236143	-0.376806	
				H	-1.099531	-0.909749	-1.194033	
				C	-2.742248	-0.436262	0.220185	
				H	-2.829355	-1.433664	0.665722	
				H	-2.948273	0.305787	0.993202	
				H	-3.522288	-0.363738	-0.546279	

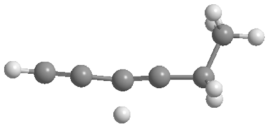
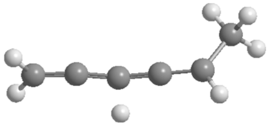
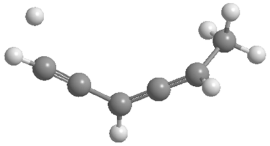
TS 5	ZPE(B3LYP/6-311G**) = 0.098668	A	340.48370	C	2.027117	-1.129742	-0.082994	1932i, 68, 121, 215, 331, 350, 388, 449, 661, 677, 701, 773, 822, 853, 938, 984, 1031, 1086, 1130, 1225, 1289, 1368, 1447, 1464, 1691, 2172, 2223, 2982, 3014, 3067, 3125, 3189, 3478
(C_1)	E(B3LYP+ZPE) = -232.575320	B	621.79606	H	2.536015	-2.058612	-0.162488	
	E(CCSD(T)/CC-VTZ) = -232.16474351	C	934.02602	C	1.446895	-0.081103	0.000963	
				C	0.773376	1.209932	0.101656	
				H	1.019452	1.662870	1.073127	
				H	1.199596	1.887426	-0.649423	
				C	-0.742773	1.193023	-0.057154	
				C	-1.509588	0.120211	-0.217808	
				C	-1.626238	-1.259093	0.116741	
				H	-1.089855	-1.704861	0.953723	
				H	-2.597919	-0.358722	0.296740	
				H	-2.086481	-1.929918	-0.600997	
				H	-1.193538	2.182447	-0.079102	
TS 6	ZPE(B3LYP/6-311G**) = 0.097151	A	207.63165	C	2.592955	-1.028167	0.009818	1587i, 96, 110, 120, 238, 267, 383, 430, 487, 565, 681, 688, 805, 844, 968, 1022, 1051, 1154, 1190, 1287, 1357, 1395, 1444, 1475, 1529, 2119, 2264, 2951, 2998, 3020, 3036, 3196, 3476
(C_1)	E(B3LYP+ZPE) = -232.545358	B	1024.16542	H	3.251292	-1.860780	0.030000	
	E(CCSD(T)/CC-VTZ) = -232.12728861	C	1210.17185	C	1.845211	-0.072675	-0.009194	
				C	0.977387	1.011444	-0.057255	
				H	-0.051966	1.010635	1.085658	
				H	1.360020	2.022987	-0.078065	
				C	-0.513600	0.875124	-0.013512	
				C	-1.267723	-0.281580	-0.122187	
				C	-2.683028	-0.637385	0.025291	
				H	-2.898674	-1.125328	0.986440	
				H	-3.320512	0.259239	-0.035134	
				H	-3.013715	-1.324535	-0.761984	
				H	-1.033662	1.817220	-0.224682	
TS 7	ZPE(B3LYP/6-311G**) = 0.098860	A	189.92971	C	2.652611	-0.917123	-0.049612	1674i, 98, 165, 204, 249, 316, 416, 508, 564, 620, 675, 765, 816, 884, 996, 1031, 1098, 1113, 1140, 1309, 1383, 1408, 1480, 1492, 1521, 2147, 2154, 3017, 3029, 3071, 3108, 3142, 3477
(C_1)	E(B3LYP+ZPE) = -232.590159	B	1027.10722	H	3.361064	-1.708074	-0.058173	
	E(CCSD(T)/CC-VTZ) = -232.17510583	C	1170.65428	C	1.849937	-0.012073	-0.036956	
				C	0.906928	1.039454	-0.041523	
				H	1.289120	2.055832	-0.059992	
				C	-0.434709	0.813370	-0.139589	
				C	-1.289292	-0.170745	0.399108	
				H	-1.376810	1.127407	0.696686	
				H	-0.911963	-0.836668	1.183259	
				C	-2.609568	-0.536596	-0.225699	
				H	-2.477783	-1.431093	-0.845255	
				H	-3.369477	-0.768476	0.525264	
				H	-2.969590	0.263353	-0.876171	

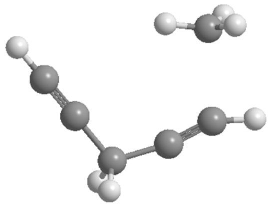
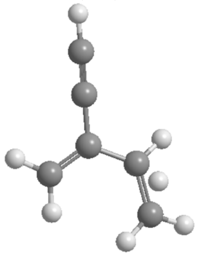
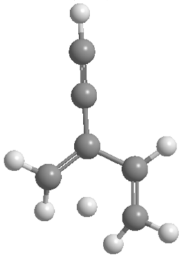
TS 8 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.095639	A	165.43867	C	-2.884543	0.625543	-0.312782	1663i, 74, 126, 172, 206, 339, 353, 471, 487, 586, 657, 748, 784, 845, 932, 965, 1052, 1065, 1091, 1161, 1312, 1386, 1399, 1484, 1493, 1921, 2048, 3018, 3068, 3071, 3114, 3119, 3435
	E(B3LYP+ZPE) = -232.574496	B	1155.85506	H	-3.694277	1.314905	-0.363077	
	E(CCSD(T)/CC-VTZ) = -232.15222058	C	1216.98765	C	-1.888633	0.040574	0.107241	
				C	-0.727993	-0.777061	0.372678	
				H	-1.192643	0.262958	1.317058	
				H	-0.917486	-1.664522	0.973173	
				C	0.476563	-0.633090	-0.231060	
				C	1.692018	-0.271277	-0.530862	
				H	2.153608	-0.671936	-1.435583	
				C	2.551025	0.679920	0.275523	
				H	2.826730	1.551797	-0.327011	
				H	2.031821	1.028146	1.169432	
				H	3.481622	0.190999	0.581586	
TS 9 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.096526		167.30879	C	-2.769759	0.843670	0.109535	2088i, 77, 135, 155, 179, 213, 284, 406, 491, 540, 640, 741, 826, 867, 879, 940, 1056, 1082, 1135, 1296, 1404, 1412, 1485, 1497, 1886, 1999, 2317, 3018, 3030, 3066, 3078, 3115, 3117
	E(B3LYP+ZPE) = -232.580462		1160.05338	H	-2.984989	-0.294745	0.721192	
	E(CCSD(T)/CC-VTZ) = -232.16166586		1252.04109	H	-3.011087	1.822952	-0.310769	
				C	-1.929219	-0.131307	0.027339	
				C	-0.748474	-0.847003	-0.362247	
				H	-0.899913	-1.737762	-0.969179	
				C	0.470265	-0.533200	0.039365	
				C	1.661298	-0.241764	0.478802	
				H	1.972542	-0.652850	1.440869	
				C	2.668846	0.627900	-0.234540	
				H	2.939443	1.490125	0.383613	
				H	3.590148	0.069463	-0.431086	
				H	2.276114	0.993044	-1.184162	
TS 10 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.095038	A	155.59388	C	2.924215	-0.689205	-0.043779	761i, 97, 133, 171, 214, 317, 351, 403, 480, 570, 610, 637, 692, 775, 869, 938, 977, 1057, 1082, 1139, 1296, 1403, 1413, 1485, 1496, 1989, 2215, 3025, 3076, 3091, 3115, 3125, 3478
	E(B3LYP+ZPE) = -232.587547	B	1197.51882	H	3.798005	-1.289578	-0.108694	
	E(CCSD(T)/CC-VTZ) = -232.17036273	C	1235.81355	C	1.927400	-0.020953	0.033252	
				C	0.766462	0.812541	0.116853	
				H	0.600039	0.787576	2.024260	
				H	0.941638	1.874986	0.274756	
				C	-0.435088	0.422473	-0.307673	
				C	-1.638105	0.031369	-0.602550	
				H	-1.954046	0.069829	-1.645802	
				C	-2.650698	-0.486400	0.393447	
				H	-2.951975	-1.505837	0.133555	
				H	-2.246922	-0.490389	1.405969	
				H	-3.551855	0.134463	0.378658	

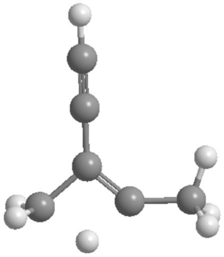
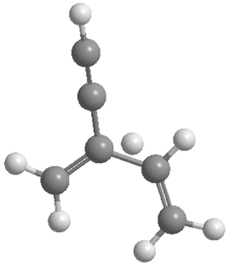
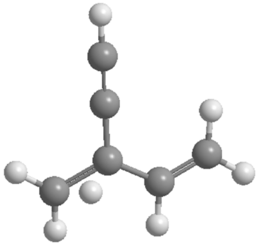
TS 11 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.094987**	**A**	**150.43376**	**C**	**-3.032230**	**-0.614975**	**0.110362**	**570i, 93, 138, 180, 216, 271, 382, 407, 454, 533, 613, 636, 690, 786, 869, 917, 980, 1055, 1090, 1144, 1297, 1407, 1424, 1488, 1498, 1990, 2209, 3032, 3088, 3092, 3111, 3129, 3478**
	E(B3LYP+ZPE) = -232.589955	**B**	**1209.58174**	**H**	**-3.928710**	**-1.162175**	**0.268867**	
	E(CCSD(T)/CC-VTZ) = -232.17293857	**C**	**1289.34552**	**C**	**-2.008386**	**-0.005563**	**-0.061527**	
				**C**	**-0.825507**	**0.753658**	**-0.291414**	
				H	**-0.938052**	**1.684062**	**-0.850061**	
				C	**0.371942**	**0.410883**	**0.122369**	
				C	**1.615799**	**0.179505**	**0.480080**	
				H	**1.916311**	**0.479584**	**1.482881**	
				H	**2.419032**	**1.939939**	**-0.059977**	
				C	**2.563794**	**-0.730587**	**-0.272591**	
				H	**2.222749**	**-0.898061**	**-1.294426**	
				H	**3.567322**	**-0.301663**	**-0.303778**	
				H	**2.628869**	**-1.699206**	**0.232828**	
TS 12 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.094495**	**A**	**155.13636**	**C**	**-2.941357**	**-0.723212**	**0.089316**	**511i, 41, 112, 144, 206, 277, 357, 431, 441, 524, 618, 627, 686, 756, 865, 891, 997, 1059, 1086, 1158, 1306, 1406, 1426, 1481, 1496, 1985, 2193, 3024, 3073, 3092, 3119, 3124, 3476**
	E(B3LYP+ZPE) = -232.589859	**B**	**1196.52770**	**H**	**-3.791463**	**-1.358458**	**0.134350**	
	E(CCSD(T)/CC-VTZ) = -232.17294381	**C**	**1262.31607**	**C**	**-1.967510**	**-0.015183**	**0.036667**	
				**C**	**-0.853015**	**0.861178**	**-0.026032**	
				H	**-1.053837**	**1.924028**	**0.093620**	
				C	**0.399997**	**0.449252**	**-0.168253**	
				H	**1.003201**	**1.354491**	**1.665673**	
				C	**1.543818**	**-0.049262**	**-0.553045**	
				H	**1.688608**	**-0.138485**	**-1.630789**	
				C	**2.684742**	**-0.506186**	**0.314217**	
				H	**2.912436**	**-1.557877**	**0.114085**	
				H	**3.589582**	**0.069104**	**0.093207**	
				H	**2.451430**	**-0.392325**	**1.372633**	
TS 13 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.095194**	**A**	**157.56344**	**C**	**2.881938**	**-0.866489**	**0.099419**	**562i, 47, 89, 147, 182, 250, 320, 387, 413, 488, 537, 671, 689, 779, 925, 945, 1050, 1062, 1155, 1238, 1342, 1415, 1451, 1478, 1483, 2233, 2286, 2996, 3026, 3032, 3095, 3096, 3478**
	E(B3LYP+ZPE) = -232.582071	**B**	**1238.64928**	**H**	**3.655073**	**-1.589081**	**0.191988**	
	E(CCSD(T)/CC-VTZ) = -232.17016156	**C**	**1351.82689**	**C**	**2.003434**	**-0.055785**	**-0.002393**	
				**C**	**0.944948**	**0.950714**	**-0.131624**	
				H	**1.035494**	**1.677309**	**0.687751**	
				H	**1.101003**	**1.518848**	**-1.056951**	
				C	**-0.408761**	**0.394889**	**-0.118753**	
				C	**-1.561151**	**0.049748**	**0.030295**	
				H	**-1.963119**	**1.213678**	**1.575895**	
				C	**-2.882785**	**-0.573723**	**-0.064733**	
				H	**-3.657155**	**0.175052**	**-0.248294**	
				H	**-2.899832**	**-1.296657**	**-0.884688**	
				H	**-3.137209**	**-1.095266**	**0.861034**	

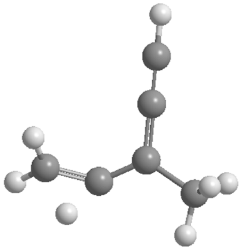
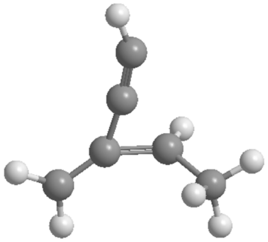
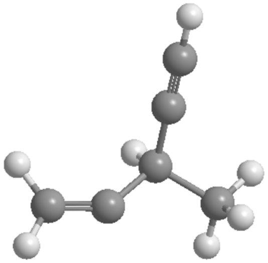
TS 14 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.094457	A	326.89573	C	1.995141	1.301045	-0.000137	432i, 80, 103, 212, 228, 317, 327, 341, 450, 588, 670, 684, 695, 828, 881, 898, 952, 1000, 1025, 1142, 1236, 1300, 1372, 1463, 1475, 2027, 2231, 3005, 3024, 3111, 3120, 3195, 3480
	E(B3LYP+ZPE) = -232.583146	B	714.46456	H	2.403146	2.281674	-0.000250	
	E(CCSD(T)/CC-VTZ) = -232.16882078	C	1018.01679	C	1.527240	0.195563	-0.000006	
				C	0.964369	-1.149321	0.000150	
				H	1.337570	-1.698432	-0.873762	
				H	1.337383	-1.698148	0.874321	
				C	-0.555403	-1.220352	0.000043	
				H	-0.965858	-2.229268	0.000109	
				C	-1.378790	-0.212347	-0.000439	
				C	-2.198665	0.812033	0.000028	
				H	-2.604688	1.205478	0.926316	
				H	-1.025724	2.572897	0.001228	
				H	-2.605177	1.206071	-0.925788	
TS 15 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.095034	A	192.83225	C	-2.717987	-0.998835	-0.000094	480i, 54, 101, 112, 198, 226, 322, 380, 388, 448, 568, 670, 688, 754, 933, 950, 1046, 1056, 1161, 1245, 1339, 1414, 1458, 1473, 1478, 2231, 2298, 3019, 3021, 3043, 3075, 3086, 3479
	E(B3LYP+ZPE) = -232.582909	B	1133.65400	H	-3.422512	-1.793816	-0.000170	
	E(CCSD(T)/CC-VTZ) = -232.17097465	C	1304.21341	C	-1.917337	-0.104977	-0.000011	
				C	-0.958608	1.003606	0.000093	
				H	-1.138394	1.640348	-0.873663	
				H	-1.138326	1.640123	0.874031	
				C	0.445346	0.557861	-0.000004	
				H	1.230225	2.421719	-0.001007	
				C	1.490084	-0.054156	0.000364	
				C	2.816025	-0.651141	-0.000097	
				H	2.969086	-1.274816	0.885082	
				H	2.968324	-1.275003	-0.885275	
				H	3.586458	0.127289	-0.000505	
TS 16 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.094764	A	127.97713	C	-2.923163	0.568421	0.006847	656i, 51, 79, 180, 222, 329, 409, 458, 493, 558, 618, 669, 685, 855, 895, 907, 956, 1017, 1022, 1135, 1218, 1301, 1375, 1462, 1471, 1986, 2224, 3005, 3069, 3122, 3139, 3208, 3478
	E(B3LYP+ZPE) = -232.581219	B	1201.45613	H	-3.825737	1.114531	0.131437	
	E(CCSD(T)/CC-VTZ) = -232.16721696	C	1247.34025	C	-1.901158	-0.044378	-0.142522	
				C	-0.652430	-0.789372	-0.302923	
				H	-0.839598	-1.846049	-0.070474	
				H	-0.326010	-0.750170	-1.345530	
				C	0.457329	-0.281682	0.599021	
				H	0.221120	-0.182798	1.655638	
				C	1.629534	0.132967	0.159489	
				H	1.002263	1.962997	-0.357849	
				C	2.878646	0.262814	-0.203288	
				H	3.546814	-0.592886	-0.159174	

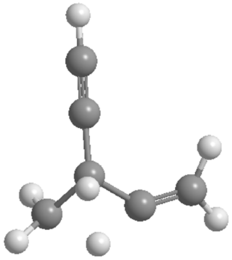
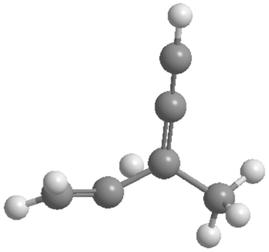
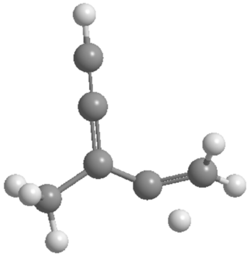
				H	3.288601	1.201750	-0.553796	
TS 17 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.094408	A	118.03208	C	-3.265465	-0.095010	0.304817	26i, 5, 18, 134, 139, 207, 308, 446, 461, 555, 627, 668, 681, 881, 937, 960, 976, 1037, 1043, 1195, 1286, 1315, 1331, 1453, 1643, 1687, 2196, 3129, 3131, 3138, 3153, 3224, 3476
	E(B3LYP+ZPE) = -232.614911	B	1412.99698	H	-4.273475	-0.317573	0.554971	
	E(CCSD(T)/CC-VTZ) = -232.20234012	C	1461.76804	C	-2.117587	0.148081	0.026549	
				C	-0.782532	0.467612	-0.321017	
				H	-0.641283	1.366733	-0.917139	
				C	0.294635	-0.262121	0.036384	
				H	0.149257	-1.159555	0.631898	
				C	1.653945	0.079414	-0.328553	
				H	1.785628	0.979680	-0.925160	
				C	2.728594	-0.638409	0.022099	
				H	3.728539	-0.345478	-0.273603	
				H	5.545028	2.820184	1.870321	
				H	2.636768	-1.541396	0.617037	
TS 18 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.097687	A	98.54634	C	-3.096685	0.030770	-0.116000	1690i, 94, 139, 207, 261, 420, 484, 553, 580, 622, 630, 773, 811, 863, 985, 1001, 1006, 1018, 1114, 1256, 1300, 1319, 1450, 1498, 1599, 1699, 1987, 3134, 3140, 3152, 3172, 3227, 3384
	E(B3LYP+ZPE) = -232.600752	B	1181.70319	H	-4.082924	0.057869	0.294202	
	E(CCSD(T)/CC-VTZ) = -232.18104339	C	1268.32619	C	-1.879898	-0.187043	0.011568	
				C	-0.458439	-0.334505	-0.106768	
				H	-1.268241	-0.618482	1.074956	
				H	-0.121905	-1.337351	-0.352886	
				C	0.467546	0.704264	0.008979	
				H	0.077167	1.709633	0.123363	
				C	1.889691	0.544102	-0.006813	
				H	2.451736	1.474436	-0.039829	
				C	2.599794	-0.608769	0.015691	
				H	2.130424	-1.584285	0.079567	
				H	3.681686	-0.594731	-0.019310	
TS 19 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.095537	A	103.80292	C	-3.289562	-0.361715	-0.061154	777i, 60, 102, 129, 239, 263, 318, 446, 498, 542, 554, 652, 653, 704, 786, 954, 1077, 1096, 1166, 1281, 1348, 1414, 1466, 1497, 1507, 2134, 2274, 2998, 3035, 3040, 3110, 3115, 3478
	E(B3LYP+ZPE) = -232.590328	B	1360.99460	H	-4.317957	-0.621685	-0.114703	
	E(CCSD(T)/CC-VTZ) = -232.17523560	C	1417.01005	C	-2.120360	-0.071318	-0.006136	
				C	-0.790496	0.267343	0.066177	
				H	-0.957452	1.526413	1.471860	
				C	0.412117	0.320425	-0.153748	
				C	1.847965	0.537029	-0.219704	

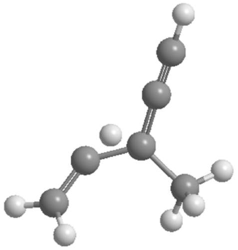
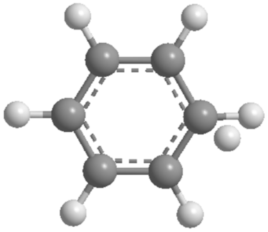
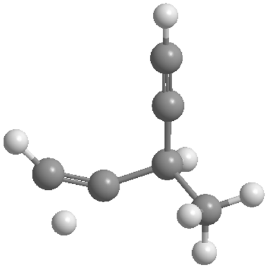
				H	2.100531	1.368041	0.452956	
				H	2.113607	0.870699	-1.229523	
				C	2.675293	-0.707592	0.154242	
				H	2.460752	-1.535922	-0.523670	
				H	3.741945	-0.479927	0.093678	
				H	2.448835	-1.032650	1.171348	
TS 20 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.094045	A	85.31246	H	3.236000	0.269388	-0.052914	736i, 92, 122, 135, 172, 249, 296, 421, 467, 511, 542, 569, 730, 795, 855, 974, 993, 1050, 1095, 1257, 1400, 1405, 1477, 1483, 1525, 1929, 2155, 3018, 3065, 309 6, 3106, 3125, 3172
	E(B3LYP+ZPE) = -232.592448	B	1415.40906	H	3.765242	0.760540	-0.864252	
	E(CCSD(T)/CC-VTZ) = -232.16630266	C	1441.20142	C	3.828073	-0.059225	0.799144	
				C	1.942803	0.076229	-0.089815	
				H	0.695283	-0.212417	0.081619	
				C	0.779389	-1.037844	1.841037	
				C	-0.566332	-0.335975	-0.103097	
				H	-1.858074	-0.461945	-0.278343	
				C	-2.221694	-1.362620	-0.771970	
				H	-2.891371	0.547675	0.148076	
				H	-3.466830	0.897399	-0.715526	
				H	-3.602533	0.094358	0.846776	
					-2.431497	1.409662	0.631632	
TS 21 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.094136	A	165.76401	C	2.863131	0.482262	-0.332677	299i, 59, 99, 145, 188, 195, 255, 352, 458, 540, 613, 675, 679, 756, 875, 897, 988, 1059, 1089, 1153, 1303, 1407, 1435, 1485, 1500, 2037, 2174, 3024, 3074, 3101, 3109, 3124, 3474
	E(B3LYP+ZPE) = -232.592914	B	1203.35129	H	2.909068	2.241718	1.078635	
	E(CCSD(T)/CC-VTZ) = -232.17543530	C	1278.25692	H	3.749768	0.914829	-0.726173	
				C	1.871301	-0.112595	0.017494	
				C	0.703464	-0.808327	0.429092	
				H	0.835362	-1.606058	1.158839	
				C	-0.505987	-0.543495	-0.019244	
				C	-1.705759	-0.292994	-0.453322	
				H	-2.048609	-0.824031	-1.341433	
				C	-2.670842	0.686203	0.169669	
				H	-2.946988	1.460985	-0.552254	
				H	-3.592405	0.177705	0.469927	
				H	-2.238049	1.168526	1.046378	
TS 22 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.097706	A	377.78863	C	-2.136881	1.280267	0.000038	468i, 21, 45, 69, 183, 310, 330, 343, 460, 500, 551, 657, 671, 688, 725, 833, 898, 932, 983, 1244, 1332, 1412, 1423, 1453, 2081, 2227, 3008, 3030, 3089, 3246, 3262, 3404, 3478
	E(B3LYP+ZPE) = -232.587816	B	804.42286	H	-2.577653	2.246882	-0.000086	
	E(CCSD(T)/CC-VTZ) = -232.17734193	C	1158.83561	C	-1.637872	0.188635	-0.000022	
				C	-1.038543	-1.151675	-0.000012	
				H	-1.400575	-1.705328	0.875273	
				H	-1.400508	-1.705313	-0.875334	
				C	0.426206	-1.145108	0.000031	

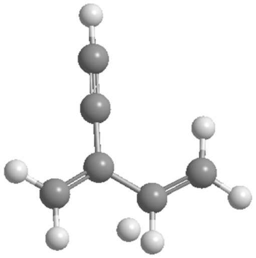
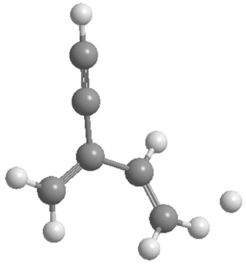
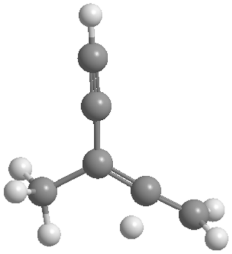
				C	1.621400	-0.900958	0.000022	
				H	2.658240	-1.148719	-0.000003	
				C	2.132594	1.353237	-0.000009	
				H	2.692500	1.398568	-0.925985	
				H	1.134431	1.768442	-0.000316	
				H	2.692132	1.399077	0.926165	
TS 23 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.098996 E(B3LYP+ZPE) = -232.609360 E(CCSD(T)/CC-VTZ) = -232.19865066	A	230.46509	C	-0.147918	1.639163	-0.023465	1813i, 125, 166, 272, 304, 410, 475, 552, 610, 630, 646, 671, 687, 782, 821, 860, 937, 1067, 1146, 1227, 1266, 1405, 1430, 1467, 1571, 2199, 2202, 3159, 3172, 3180, 3251, 3287, 3478
		B	784.99480	H	0.651453	2.363995	0.042958	
		C	1005.35302	H	-1.160280	2.014388	-0.096140	
				C	0.119748	0.304415	-0.037986	
				C	-0.900059	-0.731531	-0.069539	
				H	-1.518313	-0.909397	1.005373	
				H	-0.594942	-1.715717	-0.404665	
				C	-2.353964	-0.486042	0.002862	
				H	-3.036646	-1.277074	-0.269638	
				H	-2.739625	0.492686	0.243772	
				C	1.474430	-0.160926	0.004339	
				C	2.606223	-0.572322	0.028185	
				H	3.607584	-0.925420	0.051964	
TS 25 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.098173 E(B3LYP+ZPE) = -232.586727 E(CCSD(T)/CC-VTZ) = -232.17214560	A	208.66113	C	-0.423915	1.477098	0.046484	2887i, 146, 174, 349, 429, 489, 535, 564, 596, 610, 675, 716, 808, 861, 915, 931, 960, 1052, 1199, 1233, 1256, 1351, 1415, 1449, 1533, 1542, 2136, 3075, 3095, 3158, 3182, 3185, 3472
		B	767.71315	H	-1.253728	1.819781	-0.568916	
		C	959.84314	H	-1.582876	0.699461	0.793959	
				H	0.242784	2.277401	0.349777	
				C	0.120140	0.200166	-0.162534	
				C	-0.853922	-0.894767	-0.136902	
				H	-0.495335	-1.906938	0.012408	
				C	-2.172472	-0.525640	0.103572	
				H	-2.867532	-1.283624	0.452999	
				H	-2.661119	0.239739	-0.500013	
				C	1.487895	-0.094364	-0.030644	
				C	2.662568	-0.369814	0.065301	
				H	3.696043	-0.601893	0.148122	

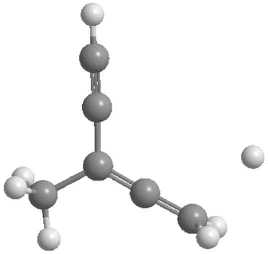
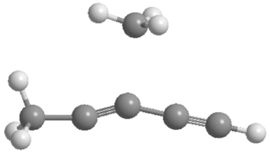
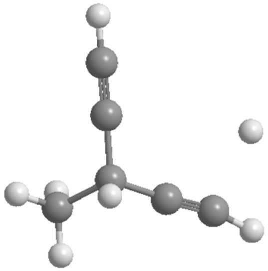
TS 26 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.097945	A	368.56792	C	0.027939	1.926737	0.000019	2164i, 125, 130, 196, 269, 296, 464, 495, 571, 619, 638, 673, 709, 965, 1016, 1038, 1046, 1068, 1114, 1217, 1389, 1425, 1461, 1473, 1716, 1839, 2195, 3003, 3065, 3069, 3073, 3160, 3476
	E(B3LYP+ZPE) = -232.592738	B	646.94404	H	-0.198234	2.464766	0.919948	
	E(CCSD(T)/CC-VTZ) = -232.18130163	C	992.14469	H	1.367916	1.466955	-0.000228	
				H	-0.198024	2.464684	-0.920010	
				C	-0.140434	0.427013	0.000032	
				C	-1.333186	-0.334909	0.000006	
				C	-2.358421	-0.969883	-0.000018	
				H	-3.260987	-1.529947	-0.000039	
				C	1.145375	0.065907	0.000007	
				C	1.955498	-1.175420	0.000000	
				H	2.603285	-1.222542	-0.880869	
				H	2.601865	-1.223403	0.881870	
				H	1.303553	-2.057182	-0.000940	
TS 27 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.097629	A	241.59931	C	0.161728	1.673389	-0.028855	1729i, 151, 172, 279, 290, 474, 494, 528, 553, 622, 646, 697, 703, 732, 771, 900, 934, 1059, 1135, 1210, 1276, 1372, 1421, 1503, 1551, 1672, 2212, 3158, 3168, 3176, 3249, 3268, 3477
	E(B3LYP+ZPE) = -232.596735	B	767.96524	H	-0.659479	2.374359	-0.020170	
	E(CCSD(T)/CC-VTZ) = -232.18319512	C	996.71455	H	1.170266	2.061043	-0.065494	
				C	-0.089224	0.305157	0.072948	
				C	0.981716	-0.753858	0.038088	
				H	0.588690	-1.764307	0.032659	
				H	0.439763	-0.252720	1.183893	
				C	2.332281	-0.548289	-0.111359	
				H	3.006768	-1.393333	-0.114982	
				H	2.767131	0.439252	-0.189755	
				C	-1.440956	-0.177317	-0.004131	
				C	-2.569646	-0.586352	-0.079315	
				H	-3.568532	-0.940682	-0.150408	
TS 28 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.098726	A	407.10682	C	-1.785148	-1.178021	-0.060049	1789i, 139, 153, 248, 289, 394, 442, 508, 573, 586, 611, 699, 703, 758, 905, 925, 1004, 1047, 1165, 1205, 1312, 1328, 1419, 1444, 1655, 2174, 2190, 3133, 3147, 3170, 3233, 3300, 3476,
	E(B3LYP+ZPE) = -232.608334	B	531.30620	H	-1.092737	-2.010410	-0.107220	
	E(CCSD(T)/CC-VTZ) = -232.19829604	C	926.08482	H	-2.843349	-1.404385	-0.097046	
				C	-1.358447	0.087154	0.033605	
				H	-2.088802	0.892508	0.069464	
				C	0.040990	0.523714	0.101874	
				H	0.201902	1.276765	1.073763	
				C	1.089998	-0.437882	0.023598	
				C	1.979350	-1.250567	-0.025889	
				H	2.763602	-1.965041	-0.076808	
				C	0.378182	1.968218	-0.131275	
				H	-0.422299	2.675576	-0.288398	
				H	1.412132	2.259293	-0.224941	

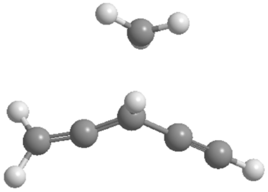
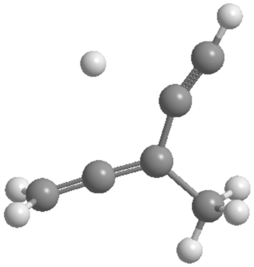
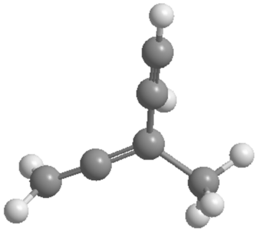
TS 29 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.098339 E(B3LYP+ZPE) = -232.589747 E(CCSD(T)/CC-VTZ) = -232.17586200	A	406.85059	C	-0.646618	1.884651	0.076343	1806i, 126, 138, 209, 243, 273, 400, 493, 556, 589, 618, 672, 723, 904, 980, 1033, 1052, 1140, 1189, 1241, 1404, 1462, 1478, 1487, 1565, 2152, 2157, 3017, 3040, 3064, 3113, 3173, 3476
		B	568.01582	H	-1.144618	2.028020	1.040784	
		C	947.23067	H	0.165763	2.607239	-0.012209	
				H	-1.386668	2.095818	-0.702775	
				C	-0.114250	0.475639	-0.048634	
				C	-1.043638	-0.597448	-0.019772	
				C	-1.834831	-1.511489	-0.010492	
				H	-2.531080	-2.313373	-0.000201	
				C	1.198686	0.203578	-0.277879	
				C	2.078663	-0.833332	0.098315	
				H	2.969299	-1.016281	-0.495233	
				H	2.277746	0.446660	0.406197	
				H	1.821491	-1.577676	0.856150	
TS 30 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.101178 E(B3LYP+ZPE) = -232.624667 E(CCSD(T)/CC-VTZ) = -232.21352992	A	442.80125	C	-0.417687	2.053221	-0.147217	36i, 151, 167, 288, 319, 481, 534, 555, 592, 640, 686, 703, 787, 808, 946, 1092, 1101, 1260, 1307, 1404, 1459, 1481, 1488, 1528, 2209, 2998, 3034, 3106, 3183, 3258, 3477
		B	463.28481	H	-1.358397	2.427349	-0.532718	
		C	830.18610	H	0.385336	2.762680	0.017374	
				C	-0.248998	0.762102	0.120400	
				C	-0.928744	-0.472378	0.034501	
				C	-1.642908	-1.495001	-0.102365	
				H	-2.560348	-1.989521	-0.344431	
				C	0.745859	-0.215942	0.562406	
				H	0.819430	-0.399211	1.630280	
				C	1.864669	-0.692692	-0.320985	
				H	2.767914	-0.087634	-0.168708	
				H	2.123749	-1.733050	-0.106927	
				H	1.589162	-0.616470	-1.375310	
TS 31 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.101065 E(B3LYP+ZPE) = -232.608832 E(CCSD(T)/CC-VTZ) = -232.20001398	A	414.19635	C	-1.964689	-1.023760	-0.141842	665i, 120, 173, 191, 223, 296, 366, 475, 490, 617, 689, 816, 837, 905, 1016, 1046, 1077, 1087, 1206, 1310, 1404, 1435, 1492, 1495, 1760, 1957, 3022, 3036, 3042, 3106, 3118, 3145, 3409
		B	521.46898	H	-2.060469	-2.049606	-0.487826	
		C	862.98255	H	-2.897009	-0.464468	-0.026901	
				C	-0.802377	-0.487393	0.131958	
				C	1.023821	-0.423269	0.132087	
				C	2.008006	-1.114354	-0.156287	
				H	2.534288	-1.984212	-0.478116	
				C	0.064931	0.626008	0.508544	
				H	0.074444	0.827006	1.585762	
				C	0.043047	1.916688	-0.314889	
				H	-0.847336	2.501722	-0.071945	
				H	0.928709	2.517625	-0.096554	
				H	0.030943	1.688419	-1.381841	

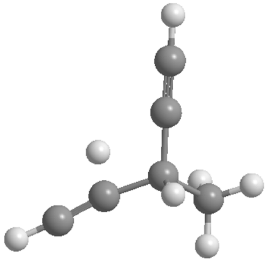
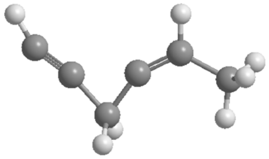
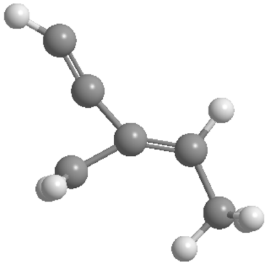
TS 33	ZPE(B3LYP/6-311G**) = 0.098179	A	361.64004	C	-0.415537	1.725273	-0.337453	2080i, 117, 151, 202, 332, 383, 498, 567, 593, 665, 668, 674, 800, 900, 928, 978, 1026, 1052, 1109, 1206, 1229, 1328, 1407, 1428, 1698, 1839, 2217, 3025, 3090, 3100, 3194, 3212, 3477
(C_1)	E(B3LYP+ZPE) = -232.580911	B	602.56494	H	-0.486408	2.693300	0.151778	
	E(CCSD(T)/CC-VTZ) = -232.17197475	C	889.06201	H	-0.098565	1.734728	-1.375461	
				H	-1.636423	1.046832	-0.292350	
				C	0.053995	0.514098	0.499896	
				H	0.086694	0.788985	1.560247	
				C	1.302436	-0.132106	0.126219	
				C	2.323893	-0.687310	-0.180048	
				H	3.229700	-1.169310	-0.455020	
				C	-1.238129	-0.198943	0.186235	
				C	-1.617320	-1.420632	-0.137950	
				H	-2.611309	-1.631630	-0.515210	
				H	-0.939713	-2.265187	-0.015371	
TS 34	ZPE(B3LYP/6-311G**) = 0.098572	A	396.77853	C	-0.443520	1.895353	0.158220	1901i, 124, 184, 212, 227, 301, 413, 544, 584, 618, 628, 672, 706, 854, 962, 976, 1038, 1116, 1180, 1250, 1410, 1430, 1480, 1499, 1665, 2084, 2166, 3026, 3066, 3086, 3113, 3180, 3475
(C_1)	E(B3LYP+ZPE) = -232.585360	B	598.48816	H	0.365009	2.557336	-0.159462	
	E(CCSD(T)/CC-VTZ) = -232.17273481	C	954.45435	H	-1.370530	2.187117	-0.339329	
				H	-0.581033	2.026877	1.236189	
				C	-0.084979	0.450125	-0.137841	
				H	0.601007	0.466615	-1.256697	
				C	-1.110653	-0.536126	-0.031478	
				C	-1.980981	-1.371351	0.005458	
				H	-2.743100	-2.110008	0.049759	
				C	1.304119	0.069847	-0.186848	
				C	2.114600	-0.919365	0.159464	
				H	1.886525	-1.549077	1.021390	
				H	3.050616	-1.109760	-0.353701	
TS 35	ZPE(B3LYP/6-311G**) = 0.098336	A	406.81577	C	0.646210	1.884697	0.076548	1806i, 126, 138, 209, 243, 273, 400, 493, 556, 589, 618, 672, 723, 904, 980, 1033, 1052, 1140, 1189, 1241, 1404, 1462, 1478, 1487, 1565, 2152, 2157, 3017, 3040, 3064, 3113, 3173, 3476
(C_1)	E(B3LYP+ZPE) = -232.589749	B	568.13666	H	1.387299	2.096073	-0.701519	
	E(CCSD(T)/CC-VTZ) = -232.17586032	C	947.30255	H	-0.166162	2.607174	-0.013012	
				H	1.142859	2.028021	1.041697	
				C	0.114253	0.475600	-0.049310	
				C	1.043895	-0.597273	-0.019771	
				C	1.835337	-1.511101	-0.010495	
				H	2.531778	-2.312810	0.000457	
				C	-1.198812	0.203268	-0.278000	
				C	-2.078736	-0.833604	0.098403	
				H	-2.277468	0.446280	0.406612	
				H	-2.969788	-1.016266	-0.494624	
				H	-1.821404	-1.577990	0.856141	

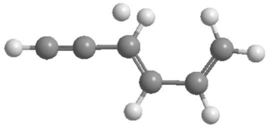
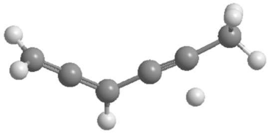
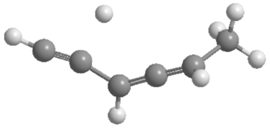
TS 36	ZPE(B3LYP/6-311G**) = 0.098431	A	275.75636	C	0.113274	1.705351	0.024667	1887i, 131, 179, 185, 217, 337, 427, 491, 540, 597, 660, 696, 718, 851, 973, 1008, 1037, 1064, 1178, 1237, 1397, 1436, 1480, 1491, 1664, 2089, 2182, 3023, 3061, 3088, 3120, 3174, 3476
(C_1)	E(B3LYP+ZPE) = -232.584640	B	764.09443	H	1.062430	2.026878	-0.408396	
	E(CCSD(T)/CC-VTZ) = -232.17218890	C	996.05825	H	-0.704848	2.270067	-0.425247	
				H	0.135684	1.932211	1.095912	
				C	-0.077360	0.209752	-0.176100	
				H	0.360532	-0.343086	-1.286786	
				C	-1.391701	-0.320500	-0.002588	
				C	-2.519750	-0.720103	0.143706	
				H	-3.506878	-1.087870	0.279828	
				C	1.050578	-0.684537	-0.193853	
				C	2.316379	-0.731386	0.197116	
				H	2.651524	-0.197900	1.088789	
				H	3.053037	-1.351755	-0.301786	
TS 37	ZPE(B3LYP/6-311G**) = 0.101705	A	330.45782	C	-0.642990	-1.215779	-0.093230	772i, 289, 367, 422, 471, 618, 619, 696, 733, 848, 890, 980, 993, 996, 1017, 1041, 1047, 1057, 1173, 1188, 1197, 1328, 1379, 1498, 1508, 1606, 1621, 3160, 3169, 3170, 3184, 3185, 3194
(C_1)	E(B3LYP+ZPE) = -232.704756	B	341.54836	C	0.741569	-1.210171	-0.000050	
	E(CCSD(T)/CC-VTZ) = -232.29721921	C	648.66883	C	1.437427	0.000010	0.058141	
				C	0.741552	1.210181	-0.000051	
				C	-0.643007	1.215769	-0.093230	
				C	-1.356574	-0.000008	-0.080550	
				H	-1.183711	-2.153681	-0.145513	
				H	1.286106	-2.147720	0.016986	
				H	2.519108	0.000018	0.130284	
				H	1.286075	2.147737	0.016985	
				H	-1.183740	2.153664	-0.145512	
				H	-1.974235	-0.000012	1.681229	
				H	-2.417473	-0.000017	-0.300637	
TS 38	ZPE(B3LYP/6-311G**) = 0.097119	A	411.56535	C	0.219168	1.859820	-0.324199	2089i, 104, 129, 193, 205, 242, 317, 400, 530, 594, 648, 666, 673, 757, 813, 881, 1028, 1078, 1120, 1279, 1318, 1405, 1492, 1501, 1837, 2207, 2352, 3016, 3040, 3095, 3114, 3119, 3477
(C_1)	E(B3LYP+ZPE) = -232.563724	B	555.91293	H	-0.590994	2.545317	-0.066625	
	E(CCSD(T)/CC-VTZ) = -232.15622049	C	897.36967	H	1.173299	2.327523	-0.074635	
				H	0.192315	1.676262	-1.399640	
				C	0.052774	0.535803	0.451688	
				H	0.081702	0.763725	1.524109	
				C	1.122100	-0.418927	0.154303	
				C	1.964157	-1.233691	-0.115199	
				H	2.719464	-1.943914	-0.346549	
				C	-1.293604	-0.099762	0.172901	
				C	-1.923495	-1.156565	-0.213464	
				H	-1.846072	-2.191345	-0.542756	
				H	-2.576324	-0.097639	0.149918	

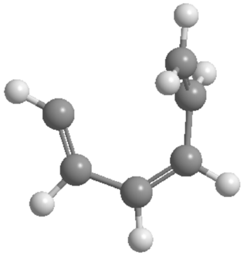
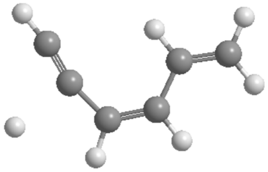
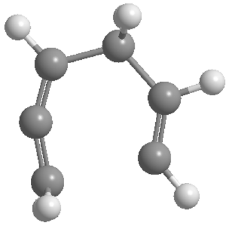
TS 39	ZPE(B3LYP/6-311G**) = 0.095706	A	395.53436	C	-0.228602	1.930624	-0.100731	715i, 114, 162, 251, 310, 354, 418, 473, 521, 622, 652, 691, 715, 749, 754, 918, 931, 942, 1027, 1058, 1304, 1309, 1409, 1451, 1597, 1657, 2208, 3147, 3149, 3157, 3240, 3244, 3476
(C_1)	E(B3LYP+ZPE) = -232.604030	B	536.05847	H	-1.219775	2.362280	-0.141241	
	E(CCSD(T)/CC-VTZ) = -232.19351107	C	900.57829	C	-0.043771	0.600975	-0.023273	
				C	-1.162295	-0.290658	0.016129	
				C	-2.088751	-1.058364	0.050209	
				H	-2.916132	-1.724035	0.083580	
				C	1.318611	0.020625	0.007991	
				H	1.602949	0.195638	1.935282	
				H	2.122961	0.747687	-0.047008	
				C	1.597901	-1.289718	-0.164569	
				H	2.622198	-1.636027	-0.220927	
				H	0.811579	-2.033847	-0.202843	
				H	0.617659	2.607403	-0.121371	
TS 40	ZPE(B3LYP/6-311G**) = 0.094583	A	274.02864	C	-2.217869	-0.467077	0.006536	88i, 75, 105, 146, 172, 272, 294, 437, 547, 566, 648, 686, 723, 758, 790, 931, 945, 951, 1022, 1089, 1246, 1324, 1428, 1452, 1640, 1676, 2205, 3139, 3151, 3153, 3227, 3244, 3476
(C_1)	E(B3LYP+ZPE) = -232.604656	B	768.62325	H	-2.535836	0.330091	0.669319	
	E(CCSD(T)/CC-VTZ) = -232.19525356	C	979.68374	H	-2.232160	-1.880821	2.155919	
				H	-2.973441	-1.177821	-0.305408	
				C	-0.958495	-0.565140	-0.427821	
				H	-0.672576	-1.408072	-1.050647	
				C	0.134125	0.377531	-0.094101	
				C	-0.058225	1.697765	0.075732	
				H	-1.037433	2.139583	-0.060586	
				H	0.761006	2.355033	0.336803	
				C	1.442419	-0.194783	0.018577	
				C	2.525434	-0.714426	0.100472	
				H	3.486108	-1.161212	0.178226	
TS 41	ZPE(B3LYP/6-311G**) = 0.094296	A	341.25676	C	0.218836	1.834187	-0.073476	472i, 102, 143, 148, 207, 231, 369, 393, 488, 549, 607, 636, 659, 686, 709, 895, 992, 1006, 1054, 1186, 1282, 1403, 1456, 1479, 1495, 1992, 2194, 3031, 3087, 3112, 3128, 3193, 3476
(C_1)	E(B3LYP+ZPE) = -232.590727	B	704.30406	H	-0.756717	2.317192	-0.125776	
	E(CCSD(T)/CC-VTZ) = -232.17583125	C	986.04315	H	0.740040	2.185562	0.821704	
				H	0.812759	2.131447	-0.942019	
				C	0.071243	0.325255	-0.037761	
				C	-1.117083	-0.262210	0.026339	
				H	-1.278687	0.097704	2.142408	
				C	-2.266163	-0.850242	-0.148803	
				H	-2.908706	-1.128819	0.678700	
				H	-2.613639	-1.084102	-1.152253	
				C	1.261926	-0.457197	-0.009956	
				C	2.298316	-1.071479	0.003647	
				H	3.202501	-1.628874	0.017292	

TS 42	ZPE(B3LYP/6-311G**) = 0.094237	A	355.30557	C	-0.450239	1.871202	0.000176	429i, 118, 157, 197, 198, 209, 287, 347, 489, 546, 606, 638, 688, 704, 707, 901, 991, 1014, 1057, 1175, 1277, 1403, 1458, 1480, 1496, 2003, 2203, 3031, 3089, 3110, 3125, 3183, 3477
(C_1)	E(B3LYP+ZPE) = -232.591404	B	693.33427	H	-1.041420	2.127564	0.883545	
	E(CCSD(T)/CC-VTZ) = -232.17546033	C	1025.07345	H	0.462620	2.466995	-0.000502	
				H	-1.042725	2.127520	-0.882324	
				C	-0.125308	0.386271	-0.000034	
				C	-1.223865	-0.529769	-0.000061	
				C	-2.181858	-1.259092	-0.000079	
				H	-3.015577	-1.917295	-0.000097	
				C	1.110783	-0.059840	-0.000148	
				C	2.329265	-0.540443	-0.000202	
				H	2.878876	-0.682587	-0.926219	
				H	2.878958	-0.682741	0.925731	
				H	2.126596	-2.649420	0.001953	
TS 43	ZPE(B3LYP/6-311G**) = 0.098041	A	319.64357	C	0.308237	2.015861	0.000009	533i, 75, 85, 112, 148, 153, 336, 345, 463, 475, 540, 564, 638, 646, 675, 87 1023, 1049, 1163, 1408, 1418, 1419, 1466, 1470, 2071, 2229, 2995, 3053, 3074 089, 3246, 3254, 3479
(C_1)	E(B3LYP+ZPE) = -232.604437	B	877.23177	H	0.863658	2.119699	-0.923217	
	E(CCSD(T)/CC-VTZ) = -232.18924278	C	1173.36634	H	-0.714349	2.372598	0.000113	
				H	0.863695	2.119113	0.923271	
				C	0.077364	-0.235768	-0.000015	
				C	1.418559	-0.568294	-0.000007	
				C	2.596572	-0.828758	0.000009	
				H	3.629107	-1.076731	-0.000011	
				C	-1.120040	-0.539396	-0.000047	
				C	-2.571191	-0.513430	0.000015	
				H	-2.947672	0.517910	-0.000259	
				H	-2.975766	-1.017162	-0.883377	
				H	-2.975688	-1.016714	0.883700	
TS 44	ZPE(B3LYP/6-311G**) = 0.094477	A	367.45172	C	0.226613	1.807765	-0.316786	530i, 26, 118, 195, 206, 234, 288, 384, 477, 562, 570, 661, 678, 688, 772, 789, 926, 1026, 1075, 1137, 1301, 1327, 1407, 1493, 1500, 2169, 2226, 3001, 3045, 3121, 3128, 3461, 3478
(C_1)	E(B3LYP+ZPE) = -232.573220	B	652.87169	H	-0.585833	2.481543	-0.038859	
	E(CCSD(T)/CC-VTZ) = -232.16482711	C	952.53691	H	1.180381	2.275531	-0.067092	
				H	0.190054	1.637429	-1.393419	
				C	0.085072	0.464946	0.443565	
				H	0.126685	0.682171	1.519355	
				C	1.195720	-0.446781	0.134030	
				C	2.117598	-1.171333	-0.122349	
				H	2.926433	-1.821384	-0.350092	
				C	-1.212195	-0.167874	0.174479	
				C	-2.238037	-0.751700	-0.082857	
				H	-1.651701	-2.576508	-0.815372	
				H	-3.234642	-1.088915	-0.235018	

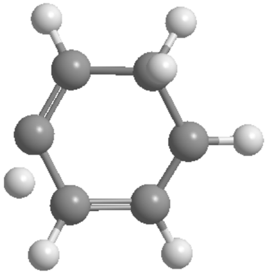
TS 45 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.097845 E(B3LYP+ZPE) = -232.597554 E(CCSD(T)/CC-VTZ) = -232.18134165	A	396.16016	C	0.287520	2.077946	-0.200057	516i, 111, 115, 133, 153, 323, 351, 382, 532, 552, 563, 599, 631, 691, 822, 888, 925, 952, 984, 1101, 1336, 1419, 1424, 1446, 1927, 2213, 3067, 3084, 3118, 3138, 3241, 3250, 3478
		B	737.90944	H	-0.599631	2.579349	0.168235	
		C	1037.36873	H	1.228159	2.337059	0.270804	
				H	0.322430	1.861423	-1.259941	
				C	0.017903	-0.004690	0.616012	
				H	0.074331	0.422799	1.614653	
				C	1.232171	-0.576928	0.109999	
				C	2.264176	-1.044137	-0.294278	
				H	3.169548	-1.465808	-0.655558	
				C	-1.183840	-0.463489	0.213389	
				C	-2.358285	-0.684593	-0.293729	
				H	-2.933987	-1.576424	-0.055391	
				H	-2.818722	0.016944	-0.990822	
TS 46 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.094195 E(B3LYP+ZPE) = -232.587350 E(CCSD(T)/CC-VTZ) = -232.17171860	A	298.83437	C	0.242182	1.792603	0.000014	656i, 70, 164, 168, 213, 246, 354, 452, 495, 531, 589, 636, 649, 657, 719, 884, 998, 1007, 1060, 1163, 1293, 1404, 1462, 1480, 1499, 2043, 2110, 3032, 3089, 3108, 3126, 3178, 3465
		B	738.23381	H	0.815759	2.087981	-0.882674	
		C	1013.47574	H	-0.709029	2.324876	-0.000297	
				H	0.815203	2.088036	0.883048	
				C	0.014581	0.288236	-0.000009	
				C	-1.197268	-0.222473	-0.000002	
				C	-2.416186	-0.674210	-0.000012	
				H	-2.943858	-0.881407	-0.927040	
				H	-2.943874	-0.881406	0.927007	
				C	1.200496	-0.524066	-0.000012	
				H	0.333822	-2.307546	0.000216	
				C	2.371449	-0.850599	-0.000025	
				H	3.340454	-1.287481	0.000014	
TS 47 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.094921 E(B3LYP+ZPE) = -232.585017 E(CCSD(T)/CC-VTZ) = -232.16987990	A	338.32904	C	0.184217	1.825798	-0.114997	821i, 133, 179, 189, 221, 308, 442, 477, 496, 559, 593, 628, 646, 690, 717, 886, 990, 992, 1058, 1164, 1275, 1405, 1446, 1484, 1496, 1976, 2210, 3039, 3087, 3107, 3134, 3159, 3477
		B	701.15266	H	-0.762231	2.329591	0.081031	
		C	984.76703	H	0.947150	2.226503	0.553103	
				H	0.488590	2.029681	-1.145446	
				C	0.040304	0.318406	0.085756	
				H	0.027387	0.427256	1.966258	
				C	1.242777	-0.465570	0.012085	
				C	2.275880	-1.076034	-0.068996	
				H	3.180548	-1.629126	-0.132340	
				C	-1.141457	-0.283750	-0.069484	
				C	-2.308873	-0.849299	-0.052128	
				H	-2.825037	-1.135982	-0.964838	
				H	-2.813496	-1.065223	0.888820	

TS 48	ZPE(B3LYP/6-311G**) = 0.095064	A	337.05796	C	-2.286061	-0.914271	-0.009418	624i, 114, 176, 206, 241, 256, 385, 452, 475, 558, 569, 653, 675, 688, 690, 786, 930, 1026, 1076, 1139, 1301, 1324, 1406, 1491, 1500, 2140, 2227, 3009, 3044, 3120, 3126, 3466, 3478
(C_1)	E(B3LYP+ZPE) = -232.570378	B	687.94752	H	-3.212170	-1.414432	0.139785	
	E(CCSD(T)/CC-VTZ) = -232.16307390	C	949.26209	C	-1.205080	-0.369111	-0.020200	
				H	-0.729956	-0.485518	1.908547	
				C	0.019311	0.355199	-0.426105	
				H	-0.042376	0.457131	-1.517519	
				C	1.236654	-0.408561	-0.126372	
				C	2.253584	-1.004371	0.100918	
				H	3.146020	-1.540905	0.311267	
				C	0.076074	1.777905	0.178793	
				H	0.958603	2.301646	-0.192274	
				H	-0.817298	2.338690	-0.102208	
				H	0.130281	1.722647	1.266710	
TS 49	ZPE(B3LYP/6-311G**) = 0.101461	A	152.50580	C	2.694545	-0.617707	0.000125	661i, 64, 118, 160, 283, 313, 368, 476, 549, 678, 763, 812, 898, 941, 1017, 1049, 1084, 1117, 1195, 1335, 1399, 1443, 1482, 1490, 1776, 1967, 3009, 3014, 3062, 3064, 3090, 3109, 3410
(C_1)	E(B3LYP+ZPE) = -232.608812	B	981.69611	H	3.259098	-1.522219	0.000436	
	E(CCSD(T)/CC-VTZ) = -232.19889103	C	1111.31092	C	1.679776	0.087732	0.000026	
				C	0.675600	1.155778	-0.000039	
				H	0.652910	1.774873	0.902383	
				H	0.653192	1.774953	-0.902407	
				C	-0.143812	-0.052381	-0.000276	
				C	-1.294580	-0.681122	-0.000185	
				H	-1.302013	-1.771198	-0.000397	
				C	-2.651300	-0.011089	0.000198	
				H	-3.229487	-0.310541	0.881040	
				H	-2.565241	1.077099	0.000368	
				H	-3.229838	-0.310234	-0.880518	
TS 50	ZPE(B3LYP/6-311G**) = 0.101243	A	174.48938	C	2.559960	-0.670050	0.000097	619i, 136, 168, 169, 303, 315, 376, 502, 596, 619, 705, 783, 818, 859, 1007, 1016, 1054, 1059, 1145, 1350, 1411, 1435, 1481, 1489, 1718, 1910, 3012, 3053, 3103, 3120, 3152, 3224, 3355
(C_1)	E(B3LYP+ZPE) = -232.628859	B	856.05986	H	3.612685	-0.476603	-0.000035	
	E(CCSD(T)/CC-VTZ) = -232.21766821	C	1007.00248	C	1.383978	-0.226075	0.000000	
				C	0.526632	1.349069	0.000025	
				H	0.633341	1.895885	0.929592	
				H	0.633943	1.896009	-0.929395	
				C	-0.004647	-0.018814	-0.000217	
				C	-1.154189	-0.692434	-0.000006	
				H	-1.107277	-1.777992	0.000069	
				C	-2.506619	-0.051586	0.000037	
				H	-3.085818	-0.357552	0.878623	
				H	-2.431532	1.037476	-0.000176	
				H	-3.086032	-0.357888	-0.878289	

TS 51 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.095353	A	106.48851	C	3.085758	0.006943	-0.022475	483i, 98, 145, 182, 254, 279, 303, 445, 503, 591, 632, 643, 684, 873, 938, 978, 995, 1005, 1026, 1110, 1298, 1316, 1344, 1455, 1599, 1669, 2199, 3136, 3142, 3149, 3163, 3226, 3477
	E(B3LYP+ZPE) = -232.606490	B	1170.45186	H	4.139624	0.128490	0.031249	
	E(CCSD(T)/CC-VTZ) = -232.19373011	C	1250.26729	C	1.889225	-0.125631	-0.073713	
				C	0.483620	-0.304203	-0.166014	
				H	0.146627	-1.231441	-0.620091	
				H	0.258318	-1.524307	1.603284	
				C	-0.415242	0.677299	0.110762	
				H	-0.028509	1.631863	0.454835	
				C	-1.860615	0.569306	-0.010848	
				H	-2.394073	1.516091	-0.040824	
				C	-2.575102	-0.563524	-0.054633	
				H	-2.114452	-1.541771	0.027980	
				H	-3.653394	-0.540056	-0.154909	
TS 52 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.094569	A	124.11695	C	2.984521	-0.663581	0.014841	429i, 57, 93, 138, 196, 256, 319, 370, 399, 436, 556, 633, 803, 882, 885, 1002, 1045, 1060, 1068, 1203, 1364, 1414, 1467, 1476, 1480, 2030, 2280, 3026, 3085, 3092, 3107, 3110, 3178
	E(B3LYP+ZPE) = -232.598119	B	1335.87696	H	3.440939	-0.943879	0.960294	
	E(CCSD(T)/CC-VTZ) = -232.17907902	C	1400.20060	H	3.449169	-1.042149	-0.891622	
				C	1.924488	0.085168	-0.029022	
				C	0.861454	0.860359	-0.075469	
				H	1.008913	1.938122	-0.132477	
				C	-0.475250	0.387535	-0.057079	
				C	-1.630627	0.028297	0.032911	
				H	-1.724108	0.100894	2.143753	
				C	-3.007075	-0.430327	-0.139488	
				H	-3.170269	-1.383307	0.370079	
				H	-3.716791	0.292255	0.271265	
				H	-3.232918	-0.566647	-1.201457	
TS 53 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.094564	A	127.06443	C	-3.063933	0.458795	-0.027143	656i, 81, 114, 154, 204, 243, 383, 450, 457, 531, 602, 632, 659, 757, 873, 895, 978, 1058, 1090, 1159, 1298, 1407, 1437, 1485, 1501, 2046, 2115, 3024, 3073, 3103, 3109, 3124, 3466
	E(B3LYP+ZPE) = -232.588080	B	1250.35871	H	-4.014045	0.929549	0.045234	
	E(CCSD(T)/CC-VTZ) = -232.17088167	C	1300.49224	C	-1.914865	0.062493	-0.027342	
				H	-1.004597	1.559853	0.888780	
				C	-0.753000	-0.747313	-0.236407	
				H	-0.934382	-1.685620	-0.759325	
				C	0.472762	-0.461290	0.141035	
				C	1.701682	-0.220678	0.493364	
				H	2.025768	-0.559771	1.477109	
				C	2.718503	0.515254	-0.343668	
				H	3.062880	1.413841	0.177693	
				H	3.596112	-0.114021	-0.522462	
				H	2.301369	0.812596	-1.306062	

TS 54 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.103469** **E(B3LYP+ZPE) = -232.654717** **E(CCSD(T)/CC-VTZ) = -232.25136952**	**A**	**311.47599**	**C**	**-1.313797**	**-1.372197**	**0.210189**	**117i, 81, 141, 280, 342, 487, 574, 657, 734, 751, 843, 858, 940, 958, 987, 994, 1018, 1097, 1245, 1279, 1314, 1414, 1456, 1630, 1673, 1698, 3014, 3099, 3115, 3133, 3154, 3217, 3235**
		B	**611.51720**	**H**	**-1.782835**	**-2.342632**	**0.278152**	
		C	**847.25230**	**C**	**-1.694522**	**-0.154155**	**-0.113379**	
				H	**-2.749152**	**-0.006498**	**-0.375001**	
				C	**-0.879145**	**1.067809**	**-0.149114**	
				H	**-1.423285**	**1.975926**	**-0.392266**	
				C	**0.433926**	**1.177761**	**0.100671**	
				H	**0.869937**	**2.175116**	**0.074216**	
				C	**1.356232**	**0.077673**	**0.454222**	
				H	**1.586665**	**-0.032573**	**1.514433**	
				C	**1.948434**	**-0.731884**	**-0.421701**	
				H	**1.757509**	**-0.652638**	**-1.486595**	
				H	**2.634384**	**-1.506744**	**-0.098267**	
TS 55 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.095868** **E(B3LYP+ZPE) = -232.607078** **E(CCSD(T)/CC-VTZ) = -232.19367632**	**A**	**208.86028**	**C**	**2.627108**	**-0.501928**	**0.000024**	**732i, 26, 134, 147, 285, 332, 452, 483, 520, 622, 665, 690, 734, 811, 894, 946, 983, 990, 1044, 1170, 1271, 1318, 1396, 1466, 1619, 1683, 2092, 3133, 3145, 3162, 3185, 3223, 3461**
		B	**897.35999**	**H**	**3.266012**	**0.375714**	**0.000015**	
		C	**1106.22027**	**H**	**3.120453**	**-1.466322**	**0.000043**	
				C	**1.292073**	**-0.396835**	**0.000012**	
				H	**0.681669**	**-1.294756**	**0.000022**	
				C	**0.593571**	**0.872078**	**-0.000018**	
				H	**1.212931**	**1.765283**	**-0.000028**	
				C	**-0.745901**	**1.051185**	**-0.000036**	
				H	**-1.140003**	**2.059897**	**-0.000059**	
				C	**-1.702342**	**-0.010297**	**-0.000022**	
				H	**-3.263051**	**1.086672**	**0.000449**	
				C	**-2.236276**	**-1.105970**	**-0.000043**	
				H	**-2.847409**	**-1.975893**	**0.000048**	
TS 56 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.103095** **E(B3LYP+ZPE) = -232.626656** **E(CCSD(T)/CC-VTZ) = -232.22077838**	**A**	**353.29763**	**C**	**-1.226158**	**0.839288**	**0.000013**	**414i, 150, 185, 356, 368, 476, 558, 630, 720, 825, 860, 870, 889, 919, 968, 1010, 1028, 1117, 1219, 1245, 1317, 1367, 1462, 1480, 1665, 1955, 2987, 3001, 3012, 3113, 3127, 3187, 3188**
		B	**438.19913**	**C**	**-0.152477**	**1.599789**	**-0.000650**	
		C	**768.33465**	**C**	**1.861628**	**0.309105**	**0.000443**	
				C	**1.118737**	**-0.790232**	**-0.000135**	
				C	**-0.011654**	**-1.436970**	**-0.000479**	
				C	**-1.324059**	**-0.673046**	**0.000392**	
				H	**-2.205188**	**1.333660**	**-0.000028**	
				H	**-0.054898**	**2.678731**	**-0.000269**	
				H	**2.283737**	**0.696304**	**0.923112**	
				H	**-0.067545**	**-2.522812**	**-0.001851**	
				H	**-1.919775**	**-0.985639**	**-0.868816**	
				H	**-1.916629**	**-0.984396**	**0.872289**	
				H	**2.284202**	**0.696545**	**-0.921936**	

TS 57
(C_1)



ZPE(B3LYP/6-311G**) = 0.103188
E(B3LYP+ZPE) = -232.625123
E(CCSD(T)/CC-VTZ) = -232.22199700

A	329.13791
B	350.74785
C	643.25417

C	-0.344624	1.312394	-0.092324
C	0.968038	1.024588	-0.120092
C	1.394837	-0.350872	0.170453
C	0.405366	-1.370412	0.069193
C	-0.892784	-1.106496	-0.174563
C	-1.406424	0.269895	0.218140
H	-0.679070	2.329448	-0.277799
H	1.707281	1.788641	-0.336344
H	2.326303	-0.539806	0.696534
H	-1.548207	-1.792278	-0.699339
H	-2.328122	0.494700	-0.330379
H	-1.684460	0.337786	1.282293
H	1.459817	-1.293070	-0.759798

1867i, 205, 401, 473, 521, 581, 663, 752, 815, 841, 889, 945, 963, 987, 992, 1098, 1157, 1188, 1195, 1281, 1317, 1391, 1394, 1464, 1538, 1633, 2010, 2948, 3028, 3141, 3146, 3166, 3171

Table A5. RRKM calculated rate constants for individual reaction steps of the C_2H + 1,2-butadiene reaction on the C_6H_7 potential energy surface at collision energies of 0-7.0 kcal/mol.

Channel	Barrier	0.00	1.00	2.00	3.00	4.00	5.00	6.00	7.00
INT 1 → INT 3	TS 2	6.38E+05	8.93E+05	1.23E+06	1.67E+06	2.24E+06	2.96E+06	3.88E+06	5.02E+06
INT 3 → INT 1	TS 2	1.44E+03	2.14E+03	3.12E+03	4.48E+03	6.34E+03	8.85E+03	1.22E+04	1.66E+04
INT 1 → INT 4	TS 3	1.71E+04	3.00E+04	5.07E+04	8.27E+04	1.31E+05	2.02E+05	3.05E+05	4.51E+05
INT 4 → INT 1	TS 3	1.41E+04	2.47E+04	4.17E+04	6.82E+04	1.08E+05	1.67E+05	2.53E+05	3.73E+05
INT 1 → INT 5	TS 4	1.77E+06	2.42E+06	3.26E+06	4.33E+06	5.69E+06	7.39E+06	9.49E+06	1.21E+07
INT 5 → INT 1	TS 4	5.19E+02	7.64E+02	1.11E+03	1.58E+03	2.23E+03	3.11E+03	4.27E+03	5.81E+03
INT 1 → INT 6	TS 8	5.81E+02	1.17E+03	2.23E+03	4.06E+03	7.09E+03	1.19E+04	1.95E+04	3.09E+04
INT 6 → INT 1	TS 8	2.71E+02	5.51E+02	1.06E+03	1.94E+03	3.41E+03	5.78E+03	9.50E+03	1.52E+04
INT 1 → INT 18	TS 49	2.07E+09	2.36E+09	2.68E+09	3.03E+09	3.41E+09	3.82E+09	4.27E+09	4.75E+09
INT 18 → INT 1	TS 49	2.56E+11	2.80E+11	3.06E+11	3.33E+11	3.61E+11	3.91E+11	4.22E+11	4.55E+11
INT 1 → 1,4-hexadiyne + H	TS 13	1.62E+07	2.25E+07	3.08E+07	4.15E+07	5.53E+07	7.28E+07	9.47E+07	1.22E+08
INT 1 → 3,4-diene-1-hexyne + H	TS 10	6.77E+06	9.32E+06	1.27E+07	1.69E+07	2.24E+07	2.93E+07	3.80E+07	4.87E+07
INT 1 → + CH_3	TS 22	9.57E+08	1.27E+09	1.67E+09	2.18E+09	2.80E+09	3.56E+09	4.49E+09	5.61E+09
INT 2 → INT 5	TS 7	1.28E+06	1.72E+06	2.28E+06	2.99E+06	3.87E+06	4.97E+06	6.31E+06	7.94E+06
INT 5 → INT 2	TS 7	7.17E+02	1.03E+03	1.46E+03	2.04E+03	2.81E+03	3.84E+03	5.18E+03	6.93E+03
INT 2 → INT 6	TS 1	6.49E+03	1.01E+04	1.54E+04	2.30E+04	3.36E+04	4.82E+04	6.79E+04	9.44E+04
INT 6 → INT 2	TS 1	5.79E+03	9.03E+03	1.37E+04	2.05E+04	2.99E+04	4.28E+04	6.04E+04	8.38E+04
INT 2 → 3,4-diene-1-hexyne + H	TS 11	1.10E+07	1.49E+07	1.98E+07	2.61E+07	3.40E+07	4.38E+07	5.59E+07	7.07E+07
INT 2 → 1,3-hexadiyne + H	TS 19	2.73E+07	3.62E+07	4.74E+07	6.15E+07	7.89E+07	1.00E+08	1.26E+08	1.58E+08
INT 3 → INT 4	TS 5	1.65E+02	2.67E+02	4.22E+02	6.53E+02	9.89E+02	1.47E+03	2.15E+03	3.10E+03
INT 4 → INT 3	TS 5	5.98E+04	9.16E+04	1.37E+05	2.01E+05	2.89E+05	4.08E+05	5.66E+05	7.75E+05
INT 3 → INT 12	TS 18	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 12 → INT 3	TS 18	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 3 → 4,5-diene-1-hexyne + H	TS 16	1.57E+04	2.37E+04	3.53E+04	5.16E+04	7.43E+04	1.05E+05	1.48E+05	2.04E+05
INT 3 → 3,5-diene-1-hexyne + H	TS 51	8.13E+07	9.93E+07	1.21E+08	1.46E+08	1.75E+08	2.09E+08	2.49E+08	2.95E+08
INT 4 → INT 5	TS 6	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
INT 5 → INT 4	TS 6	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09

INT 4 → 1,4-hexadiyne + H	TS 15	2.13E+07	2.93E+07	3.97E+07	5.32E+07	7.04E+07	9.21E+07	1.19E+08	1.53E+08
INT 4 → 4,5-diene-1-hexyne + H	TS 14	8.00E+06	1.12E+07	1.54E+07	2.10E+07	2.81E+07	3.72E+07	4.88E+07	6.32E+07
INT 5 → 3,4-diene-1-hexyne + H	TS 12	2.55E+04	3.67E+04	5.22E+04	7.33E+04	1.02E+05	1.39E+05	1.89E+05	2.54E+05
INT 5 → 3,5-diene-1-hexyne + H	TS 17	5.53E+10	6.62E+10	7.87E+10	9.33E+10	1.10E+11	1.29E+11	1.51E+11	1.77E+11
INT 6 → INT 16	TS 9	5.97E+04	9.61E+04	1.50E+05	2.30E+05	3.43E+05	5.01E+05	7.20E+05	1.02E+06
INT 16 → INT 6	TS 9	3.43E+03	5.63E+03	8.97E+03	1.40E+04	2.12E+04	3.16E+04	4.62E+04	6.63E+04
INT 7 → INT 8	TS 23	3.03E+06	3.66E+06	4.40E+06	5.26E+06	6.27E+06	7.42E+06	8.76E+06	1.03E+07
INT 8 → INT 7	TS 23	9.69E+07	1.13E+08	1.32E+08	1.52E+08	1.75E+08	2.01E+08	2.30E+08	2.62E+08
INT 7 → INT 10	TS 25	2.64E+02	3.81E+02	5.44E+02	7.64E+02	1.06E+03	1.45E+03	1.97E+03	2.64E+03
INT 10 → INT 7	TS 25	1.17E+02	1.71E+02	2.47E+02	3.52E+02	4.94E+02	6.85E+02	9.40E+02	1.27E+03
INT 7 → INT 11	TS 26	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
INT 11 → INT 7	TS 26	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
INT 7 → INT 12	TS 30	3.57E+07	4.08E+07	4.65E+07	5.28E+07	5.97E+07	6.74E+07	7.58E+07	8.50E+07
INT 12 → INT 7	TS 30	8.55E+12	8.79E+12	9.03E+12	9.27E+12	9.51E+12	9.75E+12	9.98E+12	1.02E+13
INT 7 → INT 18	TS 50	7.26E+07	8.19E+07	9.20E+07	1.03E+08	1.15E+08	1.28E+08	1.43E+08	1.59E+08
INT 18 → INT 7	TS 50	1.17E+13	1.19E+13	1.21E+13	1.23E+13	1.25E+13	1.27E+13	1.29E+13	1.31E+13
INT 7 → 2-ethynyl-1,3-butadiene + H	TS 40	9.20E+07	1.12E+08	1.36E+08	1.64E+08	1.97E+08	2.35E+08	2.80E+08	3.31E+08
INT 8 → INT 9	TS 27	1.20E+06	1.53E+06	1.93E+06	2.42E+06	3.01E+06	3.71E+06	4.54E+06	5.53E+06
INT 9 → INT 8	TS 27	2.49E+06	3.13E+06	3.89E+06	4.81E+06	5.90E+06	7.19E+06	8.69E+06	1.05E+07
INT 8 → INT 17	TS 32	4.78E+08	5.34E+08	5.95E+08	6.61E+08	7.32E+08	8.08E+08	8.91E+08	9.79E+08
INT 17 → INT 8	TS 32	5.78E+10	6.25E+10	6.74E+10	7.26E+10	7.79E+10	8.36E+10	8.94E+10	9.55E+10
INT 8 → 2-ethynyl-1,3-butadiene + H	TS 39	1.31E+08	1.56E+08	1.84E+08	2.17E+08	2.54E+08	2.96E+08	3.44E+08	3.97E+08
INT 9 → INT 10	TS 28	2.41E+08	2.78E+08	3.19E+08	3.65E+08	4.16E+08	4.72E+08	5.33E+08	6.01E+08
INT 10 → INT 9	TS 28	1.61E+06	1.98E+06	2.41E+06	2.92E+06	3.53E+06	4.23E+06	5.05E+06	6.01E+06
INT 9 → INT 13	TS 33	4.71E+04	6.54E+04	8.95E+04	1.21E+05	1.61E+05	2.12E+05	2.77E+05	3.58E+05
INT 13 → INT 9	TS 33	1.95E+06	2.66E+06	3.57E+06	4.75E+06	6.22E+06	8.07E+06	1.04E+07	1.32E+07
INT 10 → INT 13	TS 34	1.74E+02	2.57E+02	3.73E+02	5.33E+02	7.51E+02	1.05E+03	1.44E+03	1.96E+03
INT 13 → INT 10	TS 34	1.08E+06	1.47E+06	1.97E+06	2.61E+06	3.42E+06	4.43E+06	5.67E+06	7.20E+06
INT 10 → 3-ethynyl-1,2-butadiene + H	TS 41	1.97E+04	2.76E+04	3.83E+04	5.24E+04	7.10E+04	9.53E+04	1.27E+05	1.67E+05
INT 11 → INT 13	TS 35	1.21E+06	1.63E+06	2.17E+06	2.84E+06	3.69E+06	4.74E+06	6.04E+06	7.62E+06
INT 13 → INT 11	TS 35	5.48E+06	7.21E+06	9.37E+06	1.21E+07	1.54E+07	1.94E+07	2.42E+07	3.00E+07

INT 11 → pentadiyne + CH_3	TS 43	1.67E+09	2.05E+09	2.49E+09	3.02E+09	3.63E+09	4.33E+09	5.15E+09	6.09E+09
INT 11 → 3-ethynyl-1,2-butadiene + H	TS 42	2.18E+07	2.89E+07	3.80E+07	4.94E+07	6.36E+07	8.11E+07	1.03E+08	1.29E+08
INT 12 → INT 13	TS 31	3.19E+11	3.47E+11	3.76E+11	4.06E+11	4.38E+11	4.71E+11	5.05E+11	5.40E+11
INT 13 → INT 12	TS 31	3.67E+09	4.14E+09	4.66E+09	5.23E+09	5.84E+09	6.50E+09	7.22E+09	7.98E+09
INT 13 → INT 14	TS 36	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
INT 14 → INT 13	TS 36	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
INT 13 → INT 15	TS 38	5.73E+03	1.07E+04	1.92E+04	3.29E+04	5.46E+04	8.77E+04	1.37E+05	2.10E+05
INT 15 → INT 13	TS 38	7.18E+03	1.33E+04	2.36E+04	4.01E+04	6.60E+04	1.05E+05	1.63E+05	2.48E+05
INT 13 → ethynylallene + CH_3	TS 45	3.14E+08	3.99E+08	5.02E+08	6.26E+08	7.75E+08	9.52E+08	1.16E+09	1.40E+09
INT 13 → 3-ethynyl-1-butyne + H	TS 44	1.19E+07	1.76E+07	2.57E+07	3.68E+07	5.17E+07	7.16E+07	9.78E+07	1.32E+08
INT 13 → 3-ethynyl-1,2-butadiene + H	TS 47	3.19E+06	4.40E+06	5.97E+06	8.01E+06	1.06E+07	1.39E+07	1.80E+07	2.30E+07
INT 15 → 3-ethynyl-1-butyne + H	TS 48	5.46E+05	8.30E+05	1.23E+06	1.79E+06	2.56E+06	3.59E+06	4.96E+06	6.75E+06
INT 16 → 1,2,3,4-hexatetraene	TS 20	6.31E+04	9.33E+04	1.35E+05	1.93E+05	2.71E+05	3.76E+05	5.14E+05	6.94E+05
INT 16 → 1,2-hexadiene-4-yne	TS 52	1.23E+07	1.60E+07	2.05E+07	2.62E+07	3.30E+07	4.14E+07	5.15E+07	6.36E+07
INT 17 → diacetylene + C_2H_5	TS 24	1.39E+09	1.74E+09	2.16E+09	2.66E+09	3.24E+09	3.93E+09	4.73E+09	5.65E+09
INT 19 → INT 20	TS 54	1.02E+12	1.03E+12	1.05E+12	1.06E+12	1.07E+12	1.09E+12	1.10E+12	1.12E+12
INT 20 → INT 19	TS 54	2.11E+09	2.34E+09	2.59E+09	2.87E+09	3.16E+09	3.48E+09	3.83E+09	4.20E+09
INT 20 → benzene	TS 37	4.37E+11	4.55E+11	4.73E+11	4.92E+11	5.11E+11	5.30E+11	5.50E+11	5.70E+11

Table A6. Statistical branching ratios of all products via the formation of the indicated initial adduct on the C_2H + 1,2-butadiene reaction at collision energies of 0-7.0 kcal/mol.

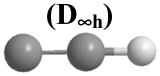
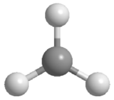
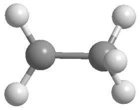
Product	**Initial Adduct**	**0.0**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
hexa-1,4-diyne + H	INT 1	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

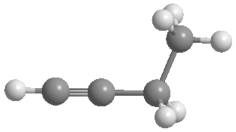
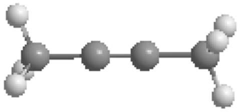
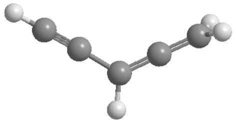
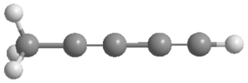
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
hexa-3,4-diene-1-yne + H	INT 1	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
hexa-1,2,3,4-tetraene + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethynylallene + CH_3	INT 1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	INT 7	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
	INT 12	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0
	INT 13	8.2	9.1	10.1	11.1	12.2	13.2	14.3	15.4
	INT 18	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
3-ethynyl-1-butyne + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1
	INT 13	0.3	0.4	0.5	0.7	0.8	1.0	1.2	1.5
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-ethynl-1,3-butadiene + H	INT 1	66.8	63.3	59.8	56.2	52.9	49.6	46.5	43.6
	INT 7	99.2	99.1	99.0	99.0	98.9	98.8	98.7	98.7
	INT 12	98.9	98.7	98.6	98.4	98.3	98.1	98.0	97.8
	INT 13	90.6	89.4	88.3	87.0	85.7	84.3	82.9	81.5
	INT 18	98.5	98.3	98.1	97.8	97.6	97.3	97.1	96.8
3-ethynyl-1,2-butadiene + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

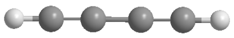
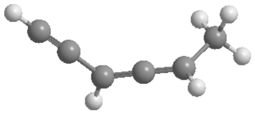
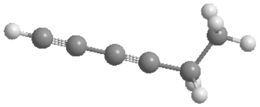
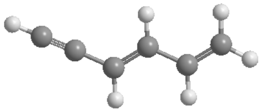
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
penta-1,4-diyne + CH_3	INT 1	32.2	35.5	38.9	42.4	45.5	48.6	51.6	54.4
	INT 7	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.8
	INT 12	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.8
	INT 13	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7
	INT 18	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
benzene + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
diacetlyne + C_2H_5	INT 1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	INT 7	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	INT 12	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2
	INT 13	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	INT 18	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2
hexa-4,5-diene-1-yne + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
hexa-3,5-diene-1-yne + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

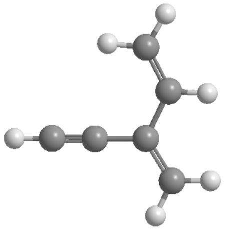
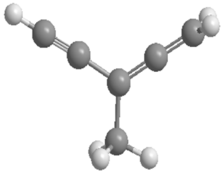
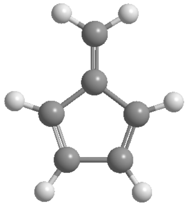
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
hexa-1,2-diene-4-yne + H	INT 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	INT 18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

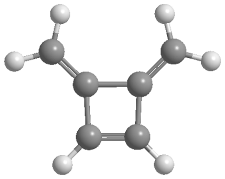
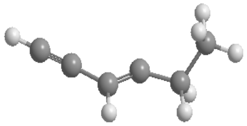
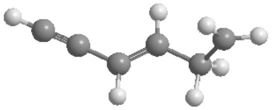
Table A7. B3LYP, CCSD(T), MP2, and G3 calculated energies at 0 K, zero-point energy corrections (ZPE), B3LYP/6-311G** optimized Cartesian coordinates, unscaled vibrational frequencies (v_i), moments of inertia (I_i), and rotational constants (B_i) of all species involved in the studied indene formation mechanisms.

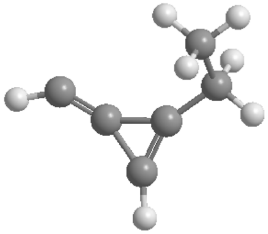
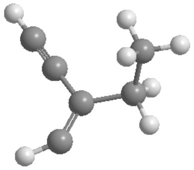
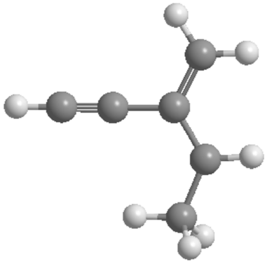
Species, (point group), electronic state	Energies, a.u.	*i*	I_i, a.u.	Cartesian coordinates, angstroms				v_i, cm^{-1}
				Atom	X	Y	Z	
H ^{2}S	ZPE(B3LYP/6-311G**) = 0.0 1. E(B3LYP/6-311G**) = - 0.502155930011 E(CCSD(T)/CC-VDZ) = -0.499278 E(CCSD(T)/CC-VTZ) = -0.49980982 E(CCSD(T)/CC-VQZ) = -0.499946 E(CCSD(T)/CBS) = -0.49999							
C_2H ($D_{\infty h}$) 	ZPE(B3LYP/6-311G**) = 0.014445 E(B3LYP+ZPE) = -76.619455742 E(CCSD(T)/CC-VDZ) = -76.398687 E(CCSD(T)/CC-VTZ) = -76.46769892 E(CCSD(T)/CC-VQZ) = -76.4876915 E(CCSD(T)/CBS) = -76.49585	A B C	0.00000 40.54466 40.54466	C H C	0.000000 0.000000 0.000000	0.000000 0.000000 0.000000	-0.473068 -1.536812 0.729203	370, 416, 2089, 3465
CH_3 (C_1) 	ZPE(B3LYP/6-311G**) = 0.029569 E(B3LYP+ZPE) = -39.824188 E(CCSD(T)/CC-VDZ) = -39.44618541 E(CCSD(T)/CC-VTZ) = -39.50031087 E(CCSD(T)/CC-VQZ) = -39.51444526 E(CCSD(T)/CBS) = -39.51944	A B C	6.30449 6.30449 12.60896	C H H H	0.000000 0.000000 -0.935876 0.935876	0.000000 1.080657 -0.540328 -0.540328	0.000273 -0.000545 -0.000545 -0.000545	507, 1404, 1404, 3102, 3281, 3281
C_2H_5 (C_1) 	ZPE(B3LYP/6-311G**) = 0.058983 E(B3LYP+ZPE) = -79.124669 E(CCSD(T)/CC-VDZ) = -78.91573206 E(CCSD(T)/CC-VTZ) = -79.00226044 E(CCSD(T)/CC-VQZ) = -79.02545788 E(CCSD(T)/CBS) = -79.03395	A B C	17.39033 79.41224 85.68530	C H H C H H H	-0.794278 -1.351038 -1.351038 0.693124 1.107217 1.107217 1.094572	0.000000 -0.926566 0.926566 0.000000 -0.886126 0.886127 -0.000001	-0.019123 0.042622 0.042622 -0.001749 -0.492768 -0.492766 1.025521	105, 474, 813, 980, 1063, 1192, 1401, 1465, 1482, 1483, 2941, 3034, 3077, 3140, 3241

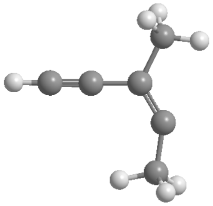
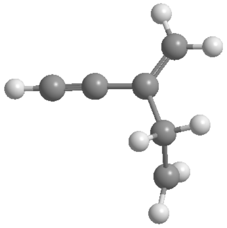
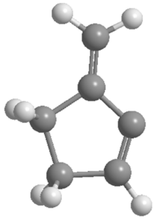
1-butyne	ZPE(B3LYP/6-311G**) = 0.084380	A	65.43102	C	1.960054	-0.262471	0.000000	201, 224, 360, 519, 665, 673,
(C_1)	E(B3LYP+ZPE) = -155.930477	B	400.10341	H	2.955614	-0.632552	0.000000	789, 846, 1020, 1089, 1109,
	E(CCSD(T)/CC-VDZ) = -155.51300878	C	443.24411	C	0.833687	0.156349	0.000000	1288, 1349, 1411, 1479, 1497,
	E(CCSD(T)/CC-VTZ) = -155.67431685			C	-0.542362	0.647396	0.000000	1507, 2222, 3020, 3035, 3045,
	E(CCSD(T)/CC-VQZ) = -155.71932538			H	-0.691652	1.288389	0.876126	3103, 3110, 3478
	E(CCSD(T)/CBS) = -155.73674			H	-0.691652	1.288389	-0.876126	
				C	-1.588182	-0.482763	0.000000	
				H	-2.598554	-0.065958	0.000000	
				H	-1.476467	-1.114665	-0.883611	
				H	-1.476467	-1.114665	0.883611	
2-butyne	ZPE(B3LYP/6-311G**) =0.083756	A	22.47396	C	-2.060490	-0.000003	0.000019	15, 201, 202, 383, 384, 725,
(C_1)	E(B3LYP+ZPE) = -155.941156	B	536.41053	H	-2.456450	0.388735	-0.943151	1054, 1054, 1057, 1057, 1170,
	E(CCSD(T)/CC-VDZ) = -155.52061932	C	536.41124	H	-2.456369	0.622455	0.808283	1417, 1420, 1482, 1482, 1482,
	E(CCSD(T)/CC-VTZ) = -155.68158969			H	-2.456280	-1.011240	0.134966	1482, 2365, 3018, 3019, 3074,
	E(CCSD(T)/CC-VQZ) = -155.72674319			C	-0.601495	0.000018	-0.000037	3074, 3074, 3074
	E(CCSD(T)/CBS) = -155.74435			C	0.601495	-0.000026	-0.000028	
				C	2.060490	0.000007	0.000014	
				H	2.456434	-0.622458	-0.808213	
				H	2.456282	1.011245	-0.134918	
				H	2.456383	-0.388717	0.943219	
ethynylallene	ZPE(B3LYP/6-311G**) = 0.064997	A	67.05107	C	2.386836	-0.458322	0.000000	141, 295, 350, 359, 606, 626,
(C_1)	E(B3LYP+ZPE) = -192.791209	B	694.24010	H	3.334697	-0.937599	0.000028	643, 691, 883, 884, 951, 1004,
	E(CCSD(T)/CC-VDZ) = -192.24756563	C	748.90726	C	1.306493	0.072655	0.000014	1140, 1352, 1465, 2042, 2210,
	E(CCSD(T)/CC-VTZ) = -192.43544406			C	0.054208	0.749300	-0.000026	3111, 3115, 3184, 3478
	E(CCSD(T)/CC-VQZ) = -192.48910863			H	0.079958	1.837856	0.000051	
	E(CCSD(T)/CBS) = -192.51057			C	-1.113200	0.146341	-0.000028	
				C	-2.276359	-0.431301	0.000012	
				H	-2.781272	-0.686235	-0.927443	
				H	-2.781247	-0.686065	0.927529	
pentadiyne	ZPE(B3LYP/6-311G**) = 0.065681	A	11.27122	C	0.000000	0.000000	-2.511237	148, 148, 336, 336, 540, 540,
(C_1)	E(B3LYP+ZPE) = -192.800165	B	882.32687	H	0.000000	1.021724	-2.903005	643, 643, 681, 1048, 1048,
	E(CCSD(T)/CC-VDZ) = -192.25588599	C	882.32687	H	0.884839	-0.510862	-2.903005	1183, 1415, 1474, 1474, 2167,
	E(CCSD(T)/CC-VTZ) = -192.44543586			H	-0.884839	-0.510862	-2.903005	2351, 3020, 3079, 3079, 3479
	E(CCSD(T)/CC-VQZ) = -192.49885120			C	0.000000	0.000000	-1.058254	
	E(CCSD(T)/CBS) = -192.51981			C	0.000000	0.000000	0.151150	
				C	0.000000	0.000000	1.515712	
				C	0.000000	0.000000	2.723262	
				H	0.000000	0.000000	3.785214	
diacetylene	ZPE(B3LYP/6-311G**) = 0.037493	A	0.00000	C	0.000000	0.000000	1.889186	237, 237, 525, 525, 663, 663,

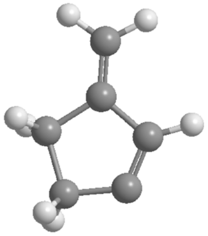
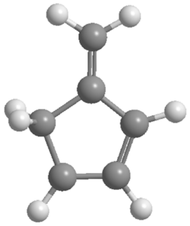
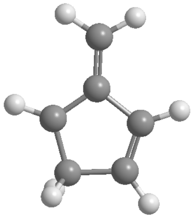
(C$_1$) 	E(B3LYP+ZPE) = -153.490932 E(CCSD(T)/CC-VDZ) = -153.04796948 E(CCSD(T)/CC-VTZ) = -153.19597363 E(CCSD(T)/CC-VQZ) = -153.23799420 E(CCSD(T)/CBS) = -153.25465	B C	408.53335 408.53335	H C C C H	0.000000 0.000000 0.000000 0.000000 0.000000	0.000000 0.000000 0.000000 0.000000 0.000000	2.951597 0.682650 -0.682650 -1.889186 -2.951597	671, 671, 917, 2111, 2285, 3476, 3478
3,4-hexadiene-1-yne (C$_1$) 	ZPE(B3LYP/6-311G**) = 0.094491 E(B3LYP+ZPE) = -232.095506 E(CCSD(T)/CC-VDZ) = -231.45392185 E(CCSD(T)/CC-VTZ) = -231.68483829 E(CCSD(T)/CC-VQZ) = -231.74971853 E(CCSD(T)/CBS) = -231.77507	A B C	82.18487 1354.95574 1414.83463	C H H H C H H C C C C H	2.348113 2.622076 2.928835 2.622076 0.840428 0.591718 0.591718 0.000000 -0.685553 -1.459564 -2.144899 -2.747575	1.419454 0.840218 2.345089 0.840218 1.738845 2.348869 2.348869 0.548862 -0.448562 -1.572306 -2.566670 -3.441006	0.000000 0.883992 0.000000 -0.883992 0.000000 0.876363 -0.876363 0.000000 0.000000 0.000000 0.000000 0.000000	100, 132, 231, 240, 351, 464, 537, 553, 638, 642, 673, 787, 953, 1076, 1103, 1176, 1286, 1350, 1412, 1474, 1496, 1506, 2164, 2344, 3015, 3037, 3040, 3106, 3113, 3478
1,3-hexadiyne (C$_1$) 	ZPE(B3LYP/6-311G**) = 0.093476 E(B3LYP+ZPE) = -232.091546 E(CCSD(T)/CC-VDZ) = -231.44919472 E(CCSD(T)/CC-VTZ) = -231.67843565 E(CCSD(T)/CC-VQZ) = -231.74368420 E(CCSD(T)/CBS) = -231.76964	A B C	137.96166 1176.58711 1240.61861	C H H H C H C C H C C H	-2.638823 -2.235402 -3.541473 -2.941046 -1.627238 -1.939744 -0.421689 0.791434 0.947860 1.940885 2.938780 3.809708	-0.582793 -0.878824 0.013841 -1.485333 0.198908 0.537782 0.490510 0.797613 1.730515 -0.013975 -0.667349 -1.255468	-0.291469 -1.260224 -0.457456 0.249094 0.510824 1.498601 0.118805 -0.285586 -0.825857 -0.063586 0.101185 0.254805	100, 147, 187, 229, 349, 447, 539, 611, 629, 688, 755, 874, 897, 985, 1059, 1090, 1156, 1303, 1407, 1438, 1485, 1501, 2044, 2207, 3023, 3072, 3100, 3107, 3122, 3479
1,3-hexadiene-5-yne (C$_s$) 	ZPE(B3LYP/6-311G**) = 0.094365 E(B3LYP+ZPE) = -232.112802 E(CCSD(T)/CC-VDZ) = -231.47434583 E(CCSD(T)/CC-VTZ) = -231.70247712 E(CCSD(T)/CC-VQZ) = -231.76781018 E(CCSD(T)/CBS) = -231.79403	A B C	65.60308 1271.55338 1337.15647	C H H C H C H C H C	-0.787242 0.226340 -1.590453 -1.031247 -2.060899 0.000000 1.032891 -0.254784 -1.287394 0.740856	2.809482 3.197324 3.536090 1.492856 1.141318 0.475912 0.813954 -0.849069 -1.191738 -1.856011	0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000	134, 139, 207, 309, 446, 461, 555, 628, 668, 681, 880, 938, 960, 976, 1037, 1043, 1195, 1286, 1314, 1331, 1453, 1643, 1687, 2196, 3129, 3131, 3138, 3153, 3225, 3477

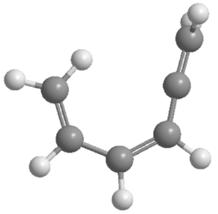
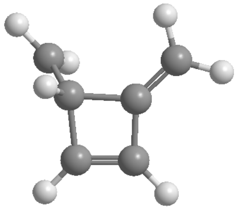
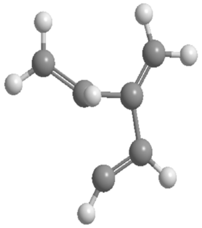
				C	**1.563266**	**-2.737928**	**0.000000**	
				H	**2.294416**	**-3.508395**	**0.000000**	
2-ethynylbutadiene **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.094322** **E(B3LYP+ZPE) = -232.107249** **E(CCSD(T)/CC-VDZ) = -231.47209420** **E(CCSD(T)/CC-VTZ) = -231.70074472** **E(CCSD(T)/CC-VQZ) = -231.76609711** **E(CCSD(T)/CBS) = -231.79225**	**A**	**378.57720**	**C**	**-2.040225**	**-1.082399**	**0.000001**	**149, 162, 262, 309, 471, 499, 621, 652, 688, 717, 754, 775, 926, 946, 953, 1021, 1061, 1317, 1325, 1417, 1455, 1635, 1690, 2208, 3140, 3148, 3151, 3230, 3243, 3477**
		B	**512.23169**	**H**	**-2.860249**	**-1.757849**	**0.000049**	
		C	**890.80889**	**C**	**-1.121383**	**-0.304988**	**-0.000098**	
				C	**-0.011165**	**0.600579**	**-0.000004**	
				C	**-0.218293**	**1.931323**	**0.000062**	
				H	**-1.215955**	**2.349834**	**0.000113**	
				H	**0.617918**	**2.620864**	**0.000165**	
				C	**1.351620**	**0.043609**	**-0.000102**	
				H	**2.145212**	**0.786131**	**-0.000278**	
				C	**1.660551**	**-1.254139**	**0.000079**	
				H	**0.893647**	**-2.020270**	**0.000336**	
				H	**2.692797**	**-1.582612**	**-0.000019**	
3-methyl-3,4-diene-1-pentyne **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.093119** **E(B3LYP+ZPE) = -232.091295** **E(CCSD(T)/CC-VDZ) = -231.45010853** **E(CCSD(T)/CC-VTZ) = -231.67940149** **E(CCSD(T)/CC-VQZ) = -231.74462829** **E(CCSD(T)/CBS) = -231.77056**	**A**	**320.49545**	**C**	**0.180327**	**1.832375**	**0.000056**	**135, 163, 199, 226, 343, 486, 530, 608, 630, 649, 686, 706, 884, 995, 1009, 1059, 1180, 1292, 1404, 1463, 1481, 1499, 2041, 2203, 3031, 3087, 3105, 3125, 3175, 3477**
		B	**685.69629**	**H**	**0.736322**	**2.160330**	**-0.882602**	
		C	**982.61139**	**H**	**-0.798444**	**2.312308**	**0.000145**	
				H	**0.736343**	**2.160045**	**0.882805**	
				C	**0.037808**	**0.319403**	**-0.000193**	
				C	**-1.137617**	**-0.271726**	**-0.000059**	
				C	**-2.307131**	**-0.839504**	**0.000064**	
				H	**-2.816129**	**-1.091262**	**-0.926604**	
				H	**-2.816061**	**-1.091011**	**0.926836**	
				C	**1.239323**	**-0.455739**	**-0.000058**	
				C	**2.281676**	**-1.058780**	**0.000068**	
				H	**3.191645**	**-1.606591**	**0.000155**	
fulvene **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.097539** **E(B3LYP+ZPE) = -232.154466** **E(CCSD(T)/CC-VDZ) = -231.52854118** **E(CCSD(T)/CC-VTZ) = -231.75340884** **E(CCSD(T)/CC-VQZ) = -231.81924966** **E(CCSD(T)/CBS) = -231.84651**	**A**	**219.73865**	**C**	**0.125762**	**1.178086**	**-0.000153**	**208, 345, 492, 636, 680, 691, 779, 791, 808, 909, 930, 943, 962, 963, 1000, 1102, 1104, 1253, 1334, 1369, 1453, 1532, 1616, 1701, 3136, 3197, 3207, 3221, 3224, 3230**
		B	**473.08717**	**C**	**1.402604**	**0.737479**	**0.000133**	
		C	**692.82581**	**C**	**1.402654**	**-0.737440**	**-0.000086**	
				C	**0.125817**	**-1.178084**	**-0.000045**	
				H	**-0.219030**	**2.202277**	**-0.000359**	
				H	**2.294628**	**1.349622**	**0.000590**	
				H	**2.294702**	**-1.349562**	**-0.000229**	
				H	**-0.218912**	**-2.202293**	**0.000259**	
				C	**-0.759635**	**-0.000012**	**0.000032**	
				C	**-2.100227**	**-0.000023**	**0.000080**	
				H	**-2.666593**	**-0.924931**	**-0.000038**	

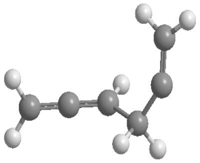
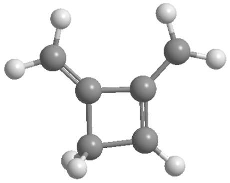
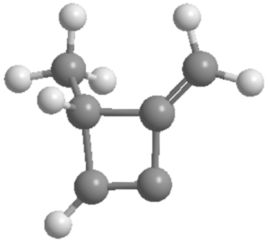
				H	**-2.666634**	**0.924859**	**0.000015**	
DMCB **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.095572** **E(B3LYP+ZPE) = -232.110019** **E(CCSD(T)/CC-VDZ) = -231.47933896** **E(CCSD(T)/CC-VTZ) = -231.70492116** **E(CCSD(T)/CC-VQZ) = -231.77052116** **E(CCSD(T)/CBS) = -231.79742**	**A**	**321.68822**	**C**	**-1.361972**	**-1.487204**	**0.000000**	**202, 244, 297, 416, 695, 698, 723, 765, 770, 822, 889, 893, 905, 918, 948, 1070, 1155, 1191, 1295, 1435, 1451, 1540, 1721, 1764, 3139, 3139, 3199, 3222, 3222, 3226**
		B	**425.11889**	**H**	**-2.355935**	**-1.055313**	**0.000000**	
		C	**746.80711**	**H**	**-1.288690**	**-2.568757**	**0.000000**	
				C	**-0.277141**	**-0.718603**	**0.000000**	
				C	**0.000000**	**0.769243**	**0.000000**	
				C	**1.191418**	**-0.913690**	**0.000000**	
				H	**1.821633**	**-1.793185**	**0.000000**	
				C	**-0.732042**	**1.879288**	**0.000000**	
				H	**-0.270852**	**2.860173**	**0.000000**	
				C	**1.440349**	**0.421865**	**0.000000**	
				H	**2.345231**	**1.014941**	**0.000000**	
				H	**-1.815061**	**1.836744**	**0.000000**	
INT A **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.103935** **E(B3LYP+ZPE) = -232.648342** **E(CCSD(T)/CC-VTZ) = -232.24312927**	**A**	**111.89615**	**C**	**-3.186171**	**0.454680**	**-0.102140**	**97, 110, 138, 232, 326, 369, 455, 534, 627, 684, 770, 806, 883, 969, 1055, 1087, 1098, 1246, 1299, 1341, 1411, 1455, 1497, 1506, 1720, 2206, 2944, 3008, 3023, 3036, 3105, 3109, 3478**
		B	**1301.71146**	**H**	**-4.158327**	**0.853546**	**-0.256206**	
		C	**1356.24956**	**C**	**-2.077370**	**0.014098**	**0.061113**	
				C	**-0.788811**	**-0.545988**	**0.290896**	
				H	**-0.747861**	**-1.376077**	**1.007195**	
				C	**0.332813**	**-0.149482**	**-0.283666**	
				C	**1.763021**	**-0.484605**	**-0.275160**	
				H	**1.915416**	**-1.357898**	**0.381284**	
				H	**2.063844**	**-0.802987**	**-1.280871**	
				C	**2.665048**	**0.675572**	**0.184271**	
				H	**2.413364**	**0.984893**	**1.200972**	
				H	**3.714358**	**0.371537**	**0.166664**	
				H	**2.548026**	**1.541333**	**-0.470921**	
INT B **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.102422** **E(B3LYP+ZPE) = -232.659855** **E(CCSD(T)/CC-VTZ) = -232.25491033**	**A**	**99.42838**	**C**	**-3.153614**	**-0.342130**	**0.035745**	**86, 114, 131, 175, 342, 381, 474, 494, 560, 631, 682, 782, 851, 982, 991, 1035, 1073, 1098, 1203, 1307, 1329, 1340, 1458, 1458, 1684, 2203, 2944, 3017, 3123, 3138, 3151, 3246, 3478**
		B	**1274.41547**	**H**	**-4.158043**	**-0.665184**	**0.157586**	
		C	**1308.21648**	**C**	**-2.010474**	**0.016566**	**-0.093158**	
				C	**-0.675094**	**0.467508**	**-0.276419**	
				H	**-0.530205**	**1.248341**	**-1.020779**	
				C	**0.382994**	**-0.000515**	**0.400282**	
				H	**0.234284**	**-0.785245**	**1.137346**	
				C	**1.797573**	**0.471857**	**0.198580**	
				H	**2.175193**	**0.897197**	**1.137238**	
				H	**1.793925**	**1.302300**	**-0.526654**	
				C	**2.716557**	**-0.616143**	**-0.257118**	
				H	**2.394045**	**-1.318785**	**-1.015673**	
				H	**3.743149**	**-0.661485**	**0.083461**	

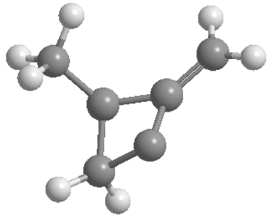
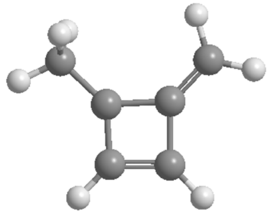
INT C-T	**ZPE(B3LYP/6-311G**) = 0.103512**	**A**	**256.19103**	**C**	**-2.052553**	**-1.196684**	**0.135356**	**63, 141, 192, 265, 368, 430, 464, 570, 632, 750, 793, 808, 841, 937, 1006, 1037, 1087, 1155, 1290, 1342, 1415, 1476, 1499, 1508, 1649, 1861, 3019, 3039, 3060, 3106, 3113, 3240, 3282**
(C_1)	**E(B3LYP+ZPE) = -232.615309**	**B**	**728.58134**	**H**	**-3.069024**	**-1.520956**	**0.002659**	
	**E(CCSD(T)/CC-VTZ) = -232.20940060**	**C**	**912.27383**	**C**	**-1.313149**	**-0.141332**	**0.015035**	
				C	**-1.041408**	**1.268001**	**-0.298871**	
				H	**-1.431595**	**2.218181**	**-0.628652**	
				C	**-0.026773**	**0.544349**	**0.110911**	
				C	**1.406988**	**0.397169**	**0.451737**	
				H	**1.919929**	**1.349522**	**0.286137**	
				H	**1.473879**	**0.175444**	**1.523547**	
				C	**2.083767**	**-0.733427**	**-0.341489**	
				H	**3.125080**	**-0.843031**	**-0.030662**	
				H	**1.572550**	**-1.683835**	**-0.175695**	
				H	**2.067956**	**-0.523783**	**-1.413408**	
INT 1	**ZPE(B3LYP/6-311G**) = 0.104105**	**A**	**360.99887**	**C**	**-0.347802**	**1.894276**	**-0.263915**	**80, 155, 212, 241, 333, 376, 535, 619, 645, 678, 696, 731, 805, 852, 973, 1069, 1094, 1192, 1289, 1344, 1411, 1484, 1497, 1508, 1633, 2189, 3029, 3031, 3077, 3096, 3106, 3239, 3476**
(C_1)	**E(B3LYP+ZPE) = -232.640085**	**B**	**612.55375**	**H**	**-1.172395**	**2.495849**	**-0.616976**	
	**E(CCSD(T)/CC-VTZ) = -232.23908322**	**C**	**887.65055**	**C**	**-0.141826**	**0.639240**	**0.094187**	
				C	**-1.226239**	**-0.297872**	**0.046115**	
				C	**-2.127399**	**-1.097365**	**0.015405**	
				H	**-2.926561**	**-1.796725**	**-0.013025**	
				C	**1.216559**	**0.128647**	**0.557586**	
				H	**1.094629**	**-0.311508**	**1.553304**	
				H	**1.885616**	**0.985997**	**0.660686**	
				C	**1.823442**	**-0.909722**	**-0.395424**	
				H	**2.783586**	**-1.265137**	**-0.012388**	
				H	**1.164150**	**-1.773370**	**-0.509689**	
				H	**1.990566**	**-0.478326**	**-1.385642**	
INT 2	**ZPE(B3LYP/6-311G**) = 0.103166**	**A**	**403.93313**	**C**	**-1.929655**	**-0.879932**	**0.000044**	**94, 160, 189, 272, 299, 460, 532, 615, 621, 650, 685, 731, 757, 771, 918, 1021, 1043, 1145, 1250, 1372, 1411, 1434, 1478, 1490, 1512, 2206, 2996, 3028, 3113, 3146, 3152, 3256, 3476**
(C_1)	**E(B3LYP+ZPE) = -232.685188**	**B**	**536.94373**	**C**	**-1.208411**	**0.424022**	**-0.000291**	
	**E(CCSD(T)/CC-VTZ) = -232.27941324**	**C**	**929.79308**	**C**	**0.177447**	**0.604011**	**-0.000095**	
				C	**1.047703**	**-0.541453**	**-0.000191**	
				C	**0.760783**	**1.870217**	**0.000157**	
				C	**1.786297**	**-1.491715**	**-0.000001**	
				H	**-2.588777**	**-0.964368**	**-0.873380**	
				H	**-2.577460**	**-0.970242**	**0.881474**	
				H	**-1.242669**	**-1.726835**	**-0.006827**	
				H	**-1.813309**	**1.326726**	**0.000038**	
				H	**1.834558**	**1.993078**	**0.000196**	
				H	**0.140663**	**2.758234**	**0.000287**	
				H	**2.442010**	**-2.327487**	**0.000474**	

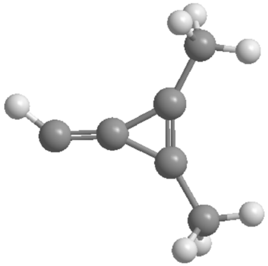
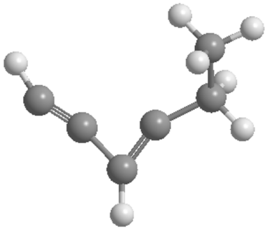
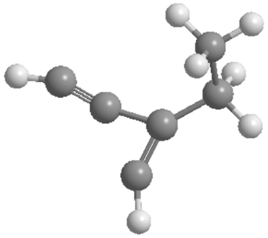
INT 3 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.103641	A	415.53350	C	-0.997120	1.782934	-0.000031	113, 128, 163, 214, 236, 292, 420, 565, 586, 624, 679, 704, 944, 1029, 1040, 1061, 1108, 1191, 1391, 1403, 1455, 1468, 1481, 1488, 1725, 2186, 2978, 3027, 3049, 3068, 3082, 3119, 3476
	E(B3LYP+ZPE) = -232.653490	B	577.83016	H	-1.641785	1.833572	0.882280	
	E(CCSD(T)/CC-VTZ) = -232.24878482	C	970.94005	H	-0.330523	2.646001	0.000041	
				H	-1.641812	1.833505	-0.882290	
				C	-0.196206	0.494155	0.000005	
				C	-0.932393	-0.736696	0.000219	
				C	-1.560200	-1.765903	-0.000125	
				H	-2.115615	-2.671305	-0.000053	
				C	1.128234	0.471100	-0.000120	
				C	2.242369	-0.482526	-0.000001	
				H	2.877014	-0.351991	-0.882597	
				H	2.876653	-0.351724	0.882845	
				H	1.867966	-1.516439	0.000092	
INT 4 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.102330	A	376.73722	C	-0.111765	1.865492	-0.218043	72, 90, 169, 226, 328, 393, 478, 557, 644, 660, 677, 742, 758, 834, 935, 952, 1046, 1091, 1183, 1288, 1339, 1436, 1458, 1464, 1669, 2201, 2953, 3039, 3141, 3142, 3233, 3249, 3476
	E(B3LYP+ZPE) = -232.657592	B	590.63838	H	-1.034159	2.333401	-0.538499	
	E(CCSD(T)/CC-VTZ) = -232.25478985	C	881.71152	C	-0.059127	0.565486	0.101519	
				C	-1.223029	-0.262571	0.034043	
				C	-2.182845	-0.989644	0.003322	
				H	-3.035003	-1.622791	-0.032156	
				C	1.229805	-0.115575	0.541657	
				H	1.068008	-0.595806	1.513104	
				H	1.982154	0.671002	0.711626	
				C	1.734629	-1.119425	-0.441644	
				H	2.243622	-2.016024	-0.112446	
				H	1.675252	-0.920200	-1.504387	
				H	0.774118	2.487841	-0.162357	
INT 5 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.107974	A	225.95006	C	-1.519368	0.585953	0.006012	43, 280, 356, 516, 611, 716, 752, 755, 843, 847, 894, 897, 944, 1004, 1008, 1154, 1188, 1229, 1241, 1300, 1310, 1441, 1470, 1493, 1633, 1696, 3020, 3046, 3052, 3090, 3141, 3200, 3226
	E(B3LYP+ZPE) = -232.679660	B	529.65649	H	-2.075256	0.911135	0.891981	
	E(CCSD(T)/CC-VTZ) = -232.28445820	C	733.32957	H	-2.093135	0.918992	-0.865355	
				C	-0.061333	1.143712	-0.005766	
				H	0.135190	1.770757	0.866827	
				C	0.863033	-0.084969	-0.001297	
				C	-1.341424	-0.927072	-0.000854	
				H	-2.168892	-1.624749	-0.001188	
				C	-0.046904	-1.212234	-0.003735	
				C	2.198448	-0.093847	0.003837	
				H	2.751526	-1.025060	0.005509	
				H	2.771008	0.826577	0.006219	
				H	0.124841	1.753094	-0.893172	

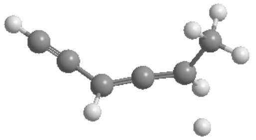
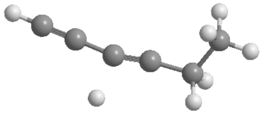
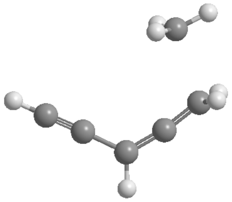
INT 6 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.107984** **E(B3LYP+ZPE) = -232.680926** **E(CCSD(T)/CC-VTZ) = -232.28611197**	**A** **B** **C**	**236.96932** **506.18497** **720.82673**	**C** **H** **H** **C** **H** **C** **C** **C** **C** **H** **H** **H** **H**	**-1.656997** **-2.242957** **-2.269397** **-0.262655** **-0.148076** **0.790173** **-1.236048** **0.067995** **2.115636** **2.792701** **2.562696** **-0.160064** **0.556467**	**-0.412397** **-0.661248** **-0.668973** **-1.133733** **-1.785649** **-0.020401** **1.016698** **1.263955** **-0.187542** **0.659007** **-1.175699** **-1.756587** **2.229674**	**-0.008581** **-0.898613** **0.860940** **0.008837** **-0.860035** **0.001683** **0.000921** **0.004407** **-0.005863** **-0.008771** **-0.009489** **0.900453** **0.007093**	**43, 296, 360, 491, 607, 671, 761, 814, 836, 873, 881, 914, 960, 969, 1014, 1154, 1209, 1223, 1233, 1271, 1310, 1441, 1468, 1493, 1632, 1691, 3033, 3053, 3058, 3092, 3132, 3201, 3213**
INT 7 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.106970** **E(B3LYP+ZPE) = -232.738830** **E(CCSD(T)/CC-VTZ) = -232.33821563**	**A** **B** **C**	**226.38596** **507.05360** **722.33024**	**C** **H** **C** **H** **C** **C** **C** **C** **H** **H** **H** **H** **H**	**-1.504999** **-2.411437** **-0.117179** **0.065459** **0.785757** **-1.426327** **-0.071899** **2.145797** **2.714669** **2.706002** **0.064260** **0.269648** **-2.275499**	**-0.610384** **-1.199899** **-1.192200** **-1.824382** **0.038817** **0.757330** **1.175944** **0.025312** **0.947824** **-0.902277** **-1.822270** **2.202630** **1.429458**	**-0.000518** **-0.000697** **0.000421** **-0.877097** **0.000060** **-0.000208** **0.000355** **-0.000426** **-0.000403** **-0.000472** **0.879815** **0.000969** **-0.000218**	**183, 355, 394, 529, 617, 638, 661, 779, 819, 820, 856, 927, 944, 952, 987, 1043, 1109, 1147, 1258, 1268, 1308, 1395, 1416, 1443, 1510, 1567, 3016, 3039, 3137, 3189, 3206, 3219, 3223**
INT 8 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.106566** **E(B3LYP+ZPE) = -232.729189** **E(CCSD(T)/CC-VTZ) = -232.32921337**	**A** **B** **C**	**225.32654** **513.28453** **727.56777**	**C** **H** **H** **C** **H** **C** **C** **H** **C** **H** **C** **H** **H**	**1.482387** **2.038100** **2.038129** **0.052367** **-0.263752** **-0.803089** **1.355377** **2.204944** **0.063862** **-0.320079** **-2.185008** **-2.743723** **-2.748998**	**-0.688500** **-1.054860** **-1.055051** **-1.140344** **-2.174780** **-0.028072** **0.815913** **1.486301** **1.172422** **2.185123** **-0.022278** **0.905315** **-0.946897**	**-0.000041** **0.875870** **-0.875823** **0.000057** **0.000314** **0.000114** **-0.000153** **-0.000401** **0.000174** **0.000411** **-0.000114** **-0.000295** **-0.000292**	**217, 351, 356, 532, 586, 643, 655, 744, 773, 792, 915, 918, 939, 953, 960, 1016, 1108, 1126, 1251, 1273, 1320, 1365, 1430, 1443, 1514, 1630, 2985, 2997, 3144, 3188, 3207, 3212, 3235**

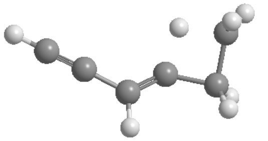
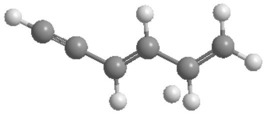
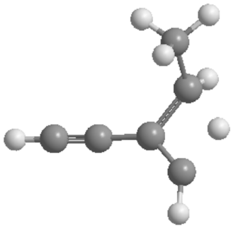
INT 9 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.104036**	**A**	**285.76703**	**C**	**2.346568**	**0.676925**	**0.000791**	**93, 152, 273, 277, 315, 478, 544, 584, 762, 768, 868, 869, 878, 911, 993, 1001, 1046, 1094, 1204, 1276, 1364, 1436, 1451, 1478, 1569, 1952, 3084, 3106, 3127, 3148, 3153, 3168, 3246**
	E(B3LYP+ZPE) = -232.695742	**B**	**705.31924**	**H**	**2.763444**	**1.070507**	**-0.924321**	
	E(CCSD(T)/CC-VTZ) = -232.28415688	**C**	**978.74796**	**H**	**2.762531**	**1.068419**	**0.927205**	
				C	**1.391744**	**-0.205788**	**-0.000581**	
				C	**0.470812**	**-1.166562**	**-0.000887**	
				H	**0.865213**	**-2.182381**	**-0.001119**	
				C	**-0.953578**	**-1.066562**	**0.000262**	
				H	**-1.470954**	**-2.020058**	**0.000857**	
				C	**-1.777901**	**0.084689**	**0.000731**	
				H	**-2.845547**	**-0.123746**	**0.002307**	
				C	**-1.403492**	**1.395171**	**-0.000701**	
				H	**-2.152821**	**2.177514**	**-0.000176**	
				H	**-0.366785**	**1.702502**	**-0.002450**	
INT 10 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.104154**	**A**	**341.45957**	**C**	**1.565977**	**-1.111252**	**-0.353335**	**133, 174, 234, 317, 396, 537, 647, 698, 714, 796, 803, 882, 893, 925, 957, 1039, 1095, 1138, 1155, 1181, 1296, 1338, 1440, 1461, 1585, 1725, 3043, 3132, 3136, 3180, 3211, 3215, 3242**
	E(B3LYP+ZPE) = -232.662755	**B**	**442.18774**	**H**	**2.161297**	**-1.895993**	**0.095593**	
	E(CCSD(T)/CC-VTZ) = -232.26304406	**C**	**714.24430**	**H**	**1.557534**	**-1.026449**	**-1.433786**	
				C	**0.732228**	**-0.201636**	**0.460662**	
				C	**-0.780345**	**-0.078094**	**0.068571**	
				C	**0.745303**	**1.295570**	**0.092257**	
				H	**1.550791**	**2.019420**	**0.080438**	
				C	**-1.783015**	**-0.949278**	**0.006723**	
				H	**-2.775219**	**-0.648320**	**-0.312295**	
				C	**-0.563402**	**1.343512**	**-0.220479**	
				H	**-1.222849**	**2.133332**	**-0.559601**	
				H	**-1.638519**	**-1.990488**	**0.271670**	
				H	**0.866491**	**-0.384428**	**1.531588**	
INT 11 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.104054**	**A**	**423.73801**	**C**	**-1.909692**	**-0.637440**	**0.000182**	**95, 169, 238, 352, 399, 447, 587, 609, 733, 735, 772, 847, 864, 925, 946, 984, 1018, 1070, 1263, 1329, 1347, 1417, 1460, 1629, 1652, 1697, 3010, 3125, 3131, 3143, 3215, 3228, 3240**
	E(B3LYP+ZPE) = -232.663753	**B**	**440.71944**	**H**	**-2.743784**	**0.054376**	**0.000342**	
	E(CCSD(T)/CC-VTZ) = -232.26155974	**C**	**864.45743**	**H**	**-2.147746**	**-1.694505**	**0.000280**	
				C	**-0.632823**	**-0.206268**	**-0.000103**	
				C	**-0.383784**	**1.248620**	**-0.000155**	
				H	**-1.299172**	**1.853053**	**0.000106**	
				C	**0.760175**	**1.894438**	**-0.000047**	
				H	**1.077130**	**2.926562**	**0.000096**	
				C	**0.455115**	**-1.195768**	**-0.000207**	
				H	**0.111350**	**-2.227756**	**-0.000832**	
				C	**1.769161**	**-0.964515**	**0.000212**	
				H	**2.476253**	**-1.786317**	**-0.000058**	

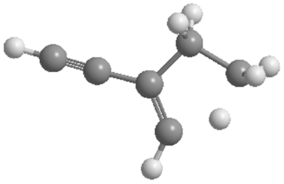
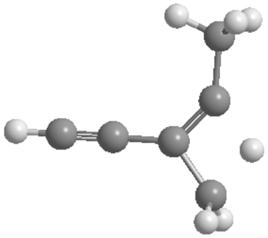
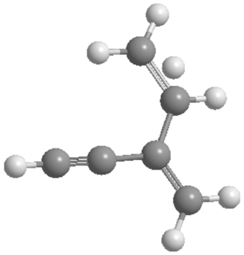
				H	2.177059	0.040179	0.000772	
INT 12	ZPE(B3LYP/6-311G**) = 0.103165	A	193.38011	C	-2.724367	-0.496432	-0.292561	51, 147, 181, 220, 343, 424, 468, 552, 609, 864, 875, 886, 906, 910, 1000, 1017, 1019, 1136, 1208, 1297, 1359, 1408, 1460, 1474, 1740, 2048, 3008, 3040, 3058, 3114, 3131, 3144, 3186
(C_1)	E(B3LYP+ZPE) = -232.648708	B	1012.93945	H	-2.837191	-1.504406	-0.680547	
	E(CCSD(T)/CC-VTZ) = -232.24038753	C	1111.55300	H	-3.602192	0.142653	-0.309992	
				C	-1.584387	-0.073854	0.178253	
				C	-0.444138	0.359012	0.637547	
				H	-0.203822	0.223330	1.689697	
				C	0.620923	1.035396	-0.218733	
				H	0.852363	2.019584	0.208237	
				H	0.226043	1.218817	-1.222611	
				C	1.864654	0.242343	-0.309481	
				C	2.344390	-0.932258	0.008637	
				H	1.731373	-1.690752	0.503560	
				H	3.370977	-1.214462	-0.210326	
INT 13	ZPE(B3LYP/6-311G**) = 0.104863	A	339.13828	C	1.478763	-1.350857	-0.000133	159, 248, 294, 420, 508, 571, 664, 691, 743, 763, 779, 877, 901, 941, 969, 974, 1085, 1160, 1210, 1249, 1308, 1400, 1439, 1467, 1508, 1736, 3006, 3037, 3131, 3144, 3200, 3211, 3237
(C_1)	E(B3LYP+ZPE) = -232.689598	B	440.23569	H	1.066957	-2.354510	-0.000293	
	E(CCSD(T)/CC-VTZ) = -232.28583447	C	767.99788	H	2.559430	-1.260082	-0.000156	
				C	0.694746	-0.279825	0.000183	
				C	-0.777235	-0.030024	0.000024	
				C	0.947034	1.238752	0.000136	
				H	1.459170	1.626300	-0.888692	
				C	-1.884049	-0.849586	0.000063	
				H	-2.885047	-0.435295	0.000051	
				C	-0.565893	1.357540	-0.000249	
				H	-1.234365	2.208959	-0.000415	
				H	-1.784991	-1.927822	0.000169	
				H	1.458650	1.626444	0.889198	
INT 14	ZPE(B3LYP/6-311G**) = 0.106223	A	332.02336	C	0.615803	-0.153891	0.474635	176, 223, 253, 328, 402, 625, 705, 710, 780, 794, 847, 900, 922, 1045, 1060, 1090, 1095, 1185, 1219, 1325, 1406, 1434, 1491, 1494, 1561, 1736, 3020, 3024, 3085, 3098, 3137, 3220, 3235
(C_1)	E(B3LYP+ZPE) = -232.642565	B	454.61698	C	-0.856960	0.086720	0.036221	
	E(CCSD(T)/CC-VTZ) = -232.24568978	C	719.55060	C	-0.421135	1.442570	-0.311973	
				C	0.860780	1.310630	0.043407	
				C	-1.961579	-0.646042	0.002699	
				C	1.380375	-1.239168	-0.276633	
				H	0.688767	-0.283137	1.560902	
				H	1.739821	1.937699	0.050221	
				H	-2.893959	-0.238223	-0.370461	
				H	-1.965740	-1.674379	0.345932	
				H	2.445054	-1.204624	-0.026806	
				H	1.277134	-1.110058	-1.356895	

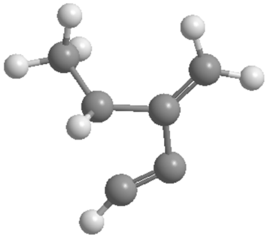
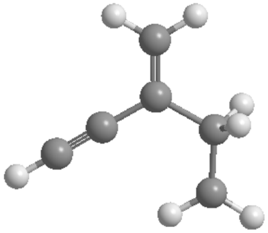
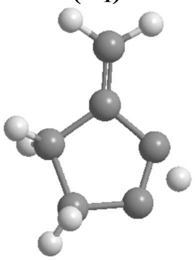
				H	1.005213	-2.232201	-0.013031	
INT 15	ZPE(B3LYP/6-311G**) = 0.104079	A	303.48609	C	-0.498853	0.176854	-0.354246	102, 200, 278, 307, 406, 549, 573, 610, 694, 778, 796, 929, 957, 1015, 1021, 1049, 1099, 1152, 1225, 1302, 1402, 1438, 1475, 1488, 1491, 1557, 3008, 3065, 3074, 3109, 3135, 3152, 3249
(C$_1$)	E(B3LYP+ZPE) = -232.621247	B	491.03569	C	0.866217	-0.158421	-0.040793	
	E(CCSD(T)/CC-VTZ) = -232.21944549	C	707.90255	C	0.108206	-1.109553	0.685151	
				C	-1.102550	-1.166226	-0.272445	
				C	2.136997	0.330869	-0.107615	
				C	-1.196769	1.410744	0.152047	
				H	-2.100155	-1.255965	0.156745	
				H	-0.934735	-1.866249	-1.088580	
				H	2.917916	-0.102559	0.503730	
				H	2.391690	1.139691	-0.779738	
				H	-1.826243	1.178458	1.019776	
				H	-1.849128	1.820757	-0.625354	
				H	-0.478836	2.180262	0.440828	
INT 16	ZPE(B3LYP/6-311G**) = 0.104574	A	336.40874	C	0.681937	0.079982	-0.000411	94, 210, 219, 247, 411, 509, 668, 680, 726, 754, 848, 878, 889, 927, 1013, 1018, 1138, 1153, 1241, 1346, 1404, 1439, 1468, 1469, 1510, 1735, 2996, 3031, 3093, 3137, 3196, 3219, 3237
(C$_1$)	E(B3LYP+ZPE) = -232.686715	B	460.31749	C	-0.780485	-0.253858	-0.000049	
	E(CCSD(T)/CC-VTZ) = -232.28363230	C	785.59039	C	-1.032643	1.214051	0.000174	
				C	0.357311	1.449661	-0.000146	
				C	-1.510765	-1.367748	-0.000054	
				C	1.923811	-0.729527	0.000210	
				H	-1.917014	1.833172	0.000841	
				H	0.958744	2.350316	-0.000292	
				H	-2.594101	-1.332396	0.000230	
				H	-1.044879	-2.346722	-0.000334	
				H	2.811422	-0.092646	0.000938	
				H	1.976042	-1.383392	-0.879371	
				H	1.974791	-1.383700	0.879644	
INT CYC	ZPE(B3LYP/6-311G**) = 0.103089	A	452.28841	C	1.843434	-1.194150	0.000164	128, 135, 163, 195, 200, 402, 453, 500, 530, 664, 687, 810, 893, 1035, 1050, 1088, 1121, 1194, 1401, 1406, 1474, 1475, 1480, 1482, 1661, 1940, 3022, 3025, 3076, 3079, 3099, 3105, 3276
(C$_1$)	E(B3LYP+ZPE) = -232.627267	B	492.50342	C	2.453456	-0.968013	0.880227	
	E(CCSD(T)/CC-VTZ) = -232.21912408	C	922.51645	C	1.607255	-2.260743	-0.000015	
				C	2.454182	-0.967965	-0.879381	
				C	0.620405	-0.365059	-0.000300	
				C	0.075690	1.002328	-0.000286	
				H	0.156973	2.296265	0.000332	
				H	0.895533	3.078087	-0.000223	
				H	-0.687729	-0.238289	-0.000295	
				H	-2.042725	-0.830088	0.000160	
				H	-2.600080	-0.493256	-0.879210	
				H	-2.006898	-1.921518	0.000439	

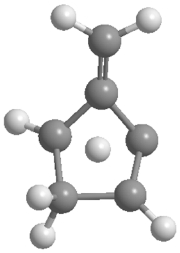
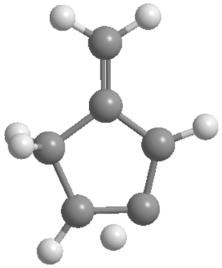
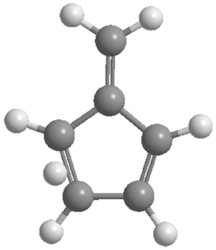
				H	-2.599731	-0.492631	0.879506	
TS A-1	ZPE(B3LYP/6-311G**) = 0.101420	A	234.43474	C	-2.385696	-1.003508	0.087673	664i, 60, 124, 170, 257, 364, 412, 474, 512, 526, 771, 802, 813, 945, 1001, 1081, 1092, 1164, 1276, 1331, 1412, 1464, 1497, 1507, 1783, 1883, 2974, 3030, 3038, 3106, 3111, 3135, 3402
(C_1)	E(B3LYP+ZPE) = -232.606854	B	849.21563	H	-2.674538	-2.001084	0.329151	
	E(CCSD(T)/CC-VTZ) = -232.19645236	C	1013.40169	C	-1.587508	-0.049260	-0.038646	
				C	-0.950115	1.198230	-0.280878	
				H	-1.245942	2.187349	-0.618567	
				C	0.079230	0.504652	0.123849	
				C	1.509237	0.366216	0.448120	
				H	2.018270	1.321240	0.251036	
				H	1.601352	0.177566	1.524408	
				C	2.198650	-0.770118	-0.327347	
				H	3.249828	-0.841145	-0.038467	
				H	1.717577	-1.728022	-0.120217	
				H	2.150661	-0.593174	-1.403966	
TS 1-A	ZPE(B3LYP/6-311G**) = 0.101161	A	283.95122	C	-2.093516	-1.164830	0.084624	710i, 63, 156, 192, 265, 350, 434, 489, 506, 578, 662, 721, 747, 800, 964, 1045, 1086, 1188, 1294, 1342, 1414, 1478, 1499, 1507, 1728, 1909, 3025, 3036, 3069, 3103, 3108, 3234, 3414
(C_1)	E(B3LYP+ZPE) = -232.605579	B	697.62189	H	-3.048856	-1.626171	-0.014369	
	E(CCSD(T)/CC-VTZ) = -232.19692925	C	904.83206	C	-1.239116	-0.257029	0.051043	
				C	-0.930691	1.447548	-0.303339	
				H	-1.146187	2.463101	-0.599339	
				C	-0.068791	0.559504	0.112443	
				C	1.362339	0.336119	0.483876	
				H	1.900117	1.282876	0.381673	
				H	1.397193	0.054688	1.542469	
				C	2.023675	-0.763224	-0.360569	
				H	3.052452	-0.930036	-0.033023	
				H	1.479229	-1.705651	-0.268268	
				H	2.042644	-0.487331	-1.417610	
TS A1	ZPE(B3LYP/6-311G**) = 0.095539	A	103.81970	C	3.289494	-0.361835	-0.061183	777i, 60, 102, 129, 239, 263, 319, 446, 498, 542, 554, 652, 653, 704, 786, 954, 1077,
(C_1)	E(B3LYP+ZPE) = -232.590326	B	1360.95148	H	4.317869	-0.621875	-0.114796	
	E(CCSD(T)/CC-VTZ) = -232.17523393	C	1416.99030	C	2.120318	-0.071347	-0.006114	

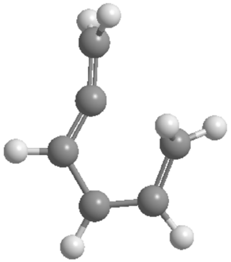
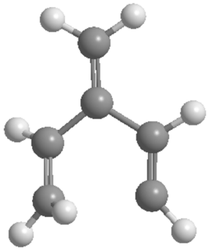
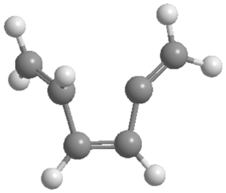
				C	0.790502	0.267512	0.066232	1096, 1166, 1281, 1348, 1414, 1466, 1497, 1507, 2134, 2274, 2998, 3035, 3040, 3110, 3115, 3478
				H	0.957790	1.526922	1.471429	
				C	-0.412109	0.320520	-0.153649	
				C	-1.847984	0.536997	-0.219756	
				H	-2.100726	1.368068	0.452763	
				H	-2.113575	0.870521	-1.229635	
				C	-2.675233	-0.707663	0.154265	
				H	-2.448702	-1.032689	1.171364	
				H	-3.741899	-0.480053	0.093753	
				H	-2.460685	-1.535995	-0.523643	
TS A2	ZPE(B3LYP/6-311G**) = 0.094985	A	150.50340	C	-3.031988	-0.615141	0.110286	569i, 93, 138, 180, 216, 270, 382, 407, 454, 533, 613, 636, 690, 785, 869, 917, 980, 1055, 1090, 1144, 1297, 1407, 1424, 1488, 1498, 1990, 2209, 3032, 3088, 3092, 3111, 3129, 3478
(C$_1$)	E(B3LYP+ZPE) = -232.589956	B	1209.39980	H	-3.928319	-1.162565	0.268864	
	E(CCSD(T)/CC-VTZ) = -232.17294478	C	1289.21216	C	-2.008278	-0.005486	-0.061541	
				C	-0.825444	0.753801	-0.291409	
				H	-0.937996	1.684104	-0.850211	
				C	0.371960	0.411268	0.122711	
				C	1.615824	0.179467	0.480191	
				H	2.419145	1.940148	-0.061099	
				H	1.916554	0.479731	1.482838	
				C	2.563434	-0.730836	-0.272674	
				H	2.221956	-0.898478	-1.294337	
				H	3.566994	-0.302015	-0.304352	
				H	2.628620	-1.699357	0.232915	
TS A3	ZPE(B3LYP/6-311G**) = 0.098047	A	335.14923	C	2.502954	1.039261	0.000043	438i, 62, 73, 136, 188, 335, 348, 384, 514, 520, 580, 627, 687, 720, 805, 867, 908, 934, 1032, 1105, 1334, 1416, 1424, 1451, 1929, 2203, 3087, 3088, 3114, 3188, 3244, 3255, 3477
(C$_1$)	E(B3LYP+ZPE) = -232.602265	B	909.58922	H	3.135464	1.892497	0.000070	
	E(CCSD(T)/CC-VTZ) = -232.18503241	C	1220.29814	C	1.775903	0.079111	-0.000127	
				C	0.951889	-1.086012	0.000053	
				H	1.468899	-2.046145	0.000049	
				C	-0.361061	-1.057670	0.000036	
				C	-1.670287	-0.842783	0.000014	
				H	-2.232849	-0.957128	-0.921224	
				H	-2.232940	-0.955984	0.921343	
				C	-2.135564	1.413400	-0.000043	
				H	-1.651325	1.709544	-0.921420	
				H	-3.218865	1.375840	-0.000022	
				H	-1.651388	1.709536	0.921347	
TS AB	ZPE(B3LYP/6-311G**) = 0.098596	A	145.68249	C	-2.999438	0.491091	-0.030381	2019i, 95, 149, 167, 343, 386, 473, 533, 619, 646, 682, 780, 823, 949, 959, 997, 1062,
(C$_1$)	E(B3LYP+ZPE) = -232.587854	B	1102.53077	H	-3.942791	0.975014	-0.091163	
	E(CCSD(T)/CC-VTZ) = -232.17604097	C	1210.00652	C	-1.922882	-0.047791	0.027033	

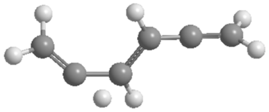
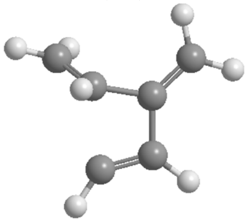
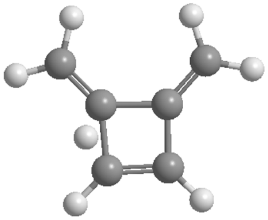
				**C**	**-0.676451**	**-0.718307**	**0.130462**	**1083, 1189, 1222, 1240, 1279, 1424, 1480, 1659, 1855, 2200, 3043, 3065, 3085, 3102, 3211, 3478**
				H	**-0.696495**	**-1.710849**	**0.587297**	
				C	**0.493076**	**-0.245582**	**-0.313581**	
				C	**1.929306**	**-0.565605**	**-0.060198**	
				H	**2.137107**	**-1.210060**	**0.797287**	
				H	**2.446307**	**-0.963624**	**-0.937091**	
				C	**2.193432**	**0.933328**	**0.144091**	
				H	**2.194641**	**1.304692**	**1.163811**	
				H	**2.855517**	**1.442623**	**-0.551105**	
				H	**0.903458**	**1.079404**	**-0.353591**	
TS B1 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.095701**	**A**	**83.16458**	**C**	**3.180723**	**-0.340887**	**0.026469**	**758i, 131, 138, 170, 306, 360, 417, 461, 471, 556, 631, 642, 683, 874, 898, 953, 976, 1034, 1047, 1180, 1284, 1293, 1326, 1443, 1588, 1668, 2197, 3131, 3139, 3143, 3159, 3234, 3476**
	**E(B3LYP+ZPE) = -232.608944**	**B**	**1299.41594**	**H**	**4.180399**	**-0.695640**	**0.082365**	
	E(CCSD(T)/CC-VTZ) = -232.19456301	**C**	**1355.19576**	**C**	**2.042277**	**0.051522**	**-0.032452**	
				C	**0.719329**	**0.551299**	**-0.112109**	
				H	**0.617001**	**1.612808**	**-0.327596**	
				C	**-0.387254**	**-0.196225**	**0.062024**	
				H	**-0.282827**	**-1.254459**	**0.284158**	
				C	**-1.743498**	**0.327325**	**-0.048290**	
				H	**-1.838877**	**1.376443**	**-0.315422**	
				H	**-1.896780**	**1.005043**	**1.756164**	
				C	**-2.841358**	**-0.468229**	**-0.106864**	
				H	**-2.772504**	**-1.536526**	**0.066283**	
				H	**-3.827720**	**-0.056494**	**-0.278618**	
TS 1-2 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.098190**	**A**	**315.20161**	**C**	**0.182569**	**1.759977**	**-0.220120**	**2119i, 123, 168, 219, 228, 341, 521, 557, 598, 655, 670, 722, 766, 827, 950, 1017, 1060, 1082, 1148, 1210, 1326, 1403, 1484, 1488, 1635, 1847, 2198, 3000, 3064, 3080, 3102, 3136, 3476**
	**E(B3LYP+ZPE) = -232.586892**	**B**	**694.83678**	**H**	**-0.308609**	**2.655402**	**-0.595042**	
	E(CCSD(T)/CC-VTZ) = -232.17688561	**C**	**938.14899**	**C**	**-0.184621**	**0.514567**	**0.079072**	
				C	**-1.423545**	**-0.166210**	**0.017058**	
				C	**-2.459857**	**-0.780970**	**-0.022717**	
				H	**-3.379845**	**-1.310784**	**-0.061277**	
				C	**1.159676**	**-0.021303**	**0.525716**	
				H	**1.276148**	**-0.114396**	**1.607190**	
				H	**1.467693**	**1.305182**	**0.205175**	
				C	**1.863558**	**-1.060382**	**-0.308963**	
				H	**2.897005**	**-1.198457**	**0.017500**	
				H	**1.354830**	**-2.030055**	**-0.227712**	
				H	**1.866095**	**-0.780965**	**-1.366113**	
TS 1-4 **(C_1)**	**ZPE(B3LYP/6-311G**) = 0.099176**	**A**	**186.60310**	**C**	**-0.424981**	**1.420092**	**-0.000170**	**1732i, 110, 165, 254, 452, 509, 524, 547, 632, 648, 671, 755, 842, 852, 946, 989, 1081,**
	E(B3LYP+ZPE) = -232.616575	**B**	**809.12453**	**H**	**-0.011962**	**2.420541**	**0.000116**	
	E(CCSD(T)/CC-VTZ) = -232.20826355	**C**	**972.84213**	**C**	**0.141516**	**0.212291**	**-0.000102**	

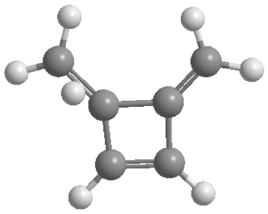
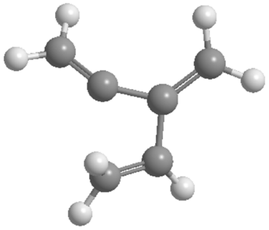
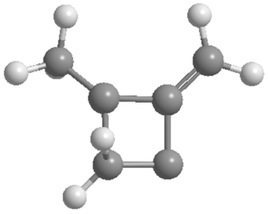
				**C**	**1.540270**	**-0.038877**	**0.000036**	**1083, 1181, 1226, 1256, 1299, 1455, 1491, 1621, 1696, 2195, 3036, 3066, 3094, 3172, 3209, 3476**
				C	**2.719445**	**-0.289091**	**0.000126**	
				H	**3.761463**	**-0.495546**	**0.000234**	
				C	**-0.879099**	**-0.928678**	**-0.000233**	
				H	**-0.734546**	**-1.565874**	**0.877462**	
				H	**-0.734946**	**-1.565301**	**-0.878417**	
				C	**-2.238531**	**-0.231465**	**0.000268**	
				H	**-2.835119**	**-0.327307**	**-0.904470**	
				H	**-2.834470**	**-0.327379**	**0.905423**	
				H	**-1.762137**	**0.995224**	**0.000099**	
TS 2-3	**ZPE(B3LYP/6-311G**) = 0.097946**	**A**	**368.43400**	**C**	**0.027867**	**1.926475**	**0.000009**	**2164i, 125, 130, 196, 269, 296, 464, 495, 571, 619, 638, 673, 709, 965, 1016, 1038, 1046, 1067, 1114, 1217, 1389, 1425, 1461, 1473, 1716, 1840, 2195, 3003, 3065, 3069, 3073, 3161, 3476**
(C_1)	**E(B3LYP+ZPE) = -232.592737**	**B**	**647.25090**	**H**	**-0.197899**	**2.464316**	**0.920118**	
	**E(CCSD(T)/CC-VTZ) = -232.18130382**	**C**	**992.31382**	**H**	**1.367503**	**1.466561**	**0.000000**	
				H	**-0.197844**	**2.464352**	**-0.920094**	
				C	**-0.140642**	**0.426734**	**-0.000010**	
				C	**-1.333540**	**-0.334966**	**-0.000008**	
				C	**-2.358884**	**-0.969766**	**0.000005**	
				H	**-3.261570**	**-1.529638**	**0.000002**	
				C	**1.145338**	**0.065872**	**-0.000013**	
				C	**1.956238**	**-1.175036**	**0.000006**	
				H	**2.603329**	**-1.222132**	**-0.881375**	
				H	**2.603316**	**-1.222109**	**0.881399**	
				H	**1.304900**	**-2.057221**	**0.000014**	
TS 2-4	**ZPE(B3LYP/6-311G**) = 0.098670**	**A**	**406.40968**	**C**	**0.629385**	**1.905745**	**-0.043982**	**1828i, 144, 155, 258, 297, 397, 455, 601, 603, 637, 651, 665, 687, 749, 809, 859, 923, 1029, 1150, 1231, 1306, 1371, 1421, 1456, 1566, 2196, 2200, 3149, 3165, 3169, 3248, 3291, 3476**
(C_1)	**E(B3LYP+ZPE) = -232.609020**	**B**	**522.76845**	**H**	**1.690325**	**2.111247**	**-0.065402**	
	**E(CCSD(T)/CC-VTZ) = -232.19774150**	**C**	**919.07086**	**C**	**0.160319**	**0.626118**	**-0.002694**	
				C	**1.080652**	**-0.471585**	**0.003349**	
				C	**1.828043**	**-1.416164**	**0.012487**	
				H	**2.503785**	**-2.235788**	**0.019496**	
				C	**-1.256346**	**0.317778**	**0.053726**	
				H	**-1.938281**	**1.156999**	**-0.030238**	
				H	**-1.585283**	**-0.354760**	**1.057533**	
				C	**-1.855197**	**-1.031061**	**-0.103461**	
				H	**-2.922692**	**-1.114104**	**-0.238705**	
				H	**-1.216681**	**-1.896213**	**-0.199035**	
				H	**-0.052310**	**2.747637**	**-0.060200**	
TS 2-14	**ZPE(B3LYP/6-311G**) = 0.102007**	**A**	**405.77420**	**C**	**-0.679396**	**-0.286052**	**0.485992**	**641i, 101, 173, 234, 248, 409, 576, 596, 624, 680, 731, 776, 816, 916, 948, 998, 1066,**
(C_1)	**E(B3LYP+ZPE) = -232.603262**	**B**	**449.92895**	**C**	**0.508505**	**0.564443**	**0.102486**	
	E(CCSD(T)/CC-VTZ) = -232.19843707	**C**	**794.43410**	**C**	**1.468860**	**-0.496748**	**-0.158172**	

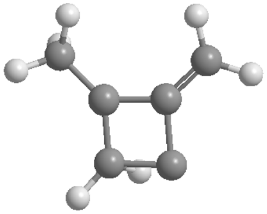
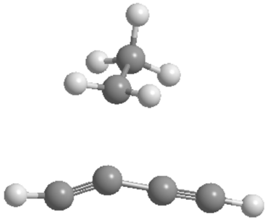
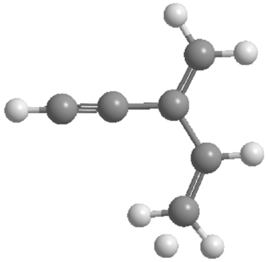
				**C**	**0.972597**	**-1.657938**	**-0.090191**	**1111, 1234, 1337, 1399, 1433, 1478, 1480, 1702, 1726, 2963, 3052, 3096, 3139, 3143, 3230, 3360**
				C	**0.605768**	**1.885566**	**-0.045417**	
				C	**-1.972539**	**-0.195621**	**-0.261769**	
				H	**-0.716612**	**-0.557366**	**1.537991**	
				H	**0.953099**	**-2.727358**	**-0.148910**	
				H	**1.531923**	**2.346575**	**-0.365812**	
				H	**-0.238424**	**2.537365**	**0.148491**	
				H	**-2.646625**	**-1.012802**	**0.005792**	
				H	**-1.809952**	**-0.214026**	**-1.343093**	
				H	**-2.496179**	**0.745709**	**-0.032032**	
TS 4-5 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.101670**	**A**	**407.11040**	**C**	**-1.648235**	**-1.274137**	**-0.000013**	**110i, 40, 170, 265, 309, 435, 440, 537, 601, 641, 682, 724, 735, 879, 918, 933, 1016, 1113, 1193, 1280, 1335, 1437, 1446, 1458, 1661, 2197, 2958, 2962, 3140, 3153, 3233, 3262, 3477**
	E(B3LYP+ZPE) = -232.654344	**B**	**518.18242**	**H**	**-2.673193**	**-1.622341**	**0.000021**	
	E(CCSD(T)/CC-VTZ) = -232.25087170	**C**	**914.41896**	**H**	**-0.850381**	**-2.002772**	**-0.000107**	
				C	**-1.376938**	**0.187875**	**0.000021**	
				H	**-1.865262**	**0.655542**	**0.869132**	
				C	**0.091187**	**0.628445**	**0.000000**	
				C	**1.969049**	**-1.216804**	**0.000023**	
				H	**2.731590**	**-1.956425**	**-0.000028**	
				C	**1.115161**	**-0.366552**	**-0.000005**	
				C	**0.419263**	**1.928164**	**-0.000012**	
				H	**1.452002**	**2.251786**	**-0.000016**	
				H	**-0.346405**	**2.696693**	**-0.000018**	
				H	**-1.865273**	**0.655566**	**-0.869072**	
TS 5-6 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.101938**	**A**	**240.86963**	**C**	**1.549262**	**-0.508269**	**0.196304**	**1393i, 111, 279, 367, 473, 542, 624, 671, 744, 769, 847, 895, 906, 934, 938, 999, 1134, 1172, 1219, 1264, 1292, 1431, 1468, 1482, 1660, 1701, 2194, 3031, 3054, 3084, 3101, 3137, 3224**
	E(B3LYP+ZPE) = -232.589686	**B**	**506.09050**	**H**	**1.800904**	**-0.651518**	**1.250750**	
	E(CCSD(T)/CC-VTZ) = -232.18484478	**C**	**705.00358**	**H**	**2.384911**	**-0.895583**	**-0.388711**	
				C	**0.171187**	**-1.148882**	**-0.172005**	
				H	**-0.103309**	**-1.988045**	**0.470854**	
				C	**-0.820102**	**0.021623**	**-0.084735**	
				C	**1.291044**	**0.977598**	**-0.071887**	
				H	**0.675354**	**1.776755**	**0.751384**	
				C	**0.008865**	**1.252600**	**-0.232881**	
				C	**-2.131509**	**-0.030532**	**0.139179**	
				H	**-2.726305**	**0.874086**	**0.171049**	
				H	**-2.643657**	**-0.973290**	**0.300439**	
				H	**0.199626**	**-1.527227**	**-1.199613**	
TS 5-8 **(C$_1$)**	**ZPE(B3LYP/6-311G**) = 0.100181**	**A**	**232.36029**	**C**	**-1.390560**	**-0.609328**	**-0.442688**	**1475i, 173, 279, 348, 399, 545, 598, 694, 776, 828, 871, 909, 934, 947, 966, 981, 1034,**
	E(B3LYP+ZPE) = -232.552416	**B**	**536.33049**	**H**	**-1.310358**	**-1.046030**	**-1.447397**	
	E(CCSD(T)/CC-VTZ) = -232.15015531	**C**	**625.37810**	**C**	**-2.335290**	**-0.957961**	**-0.007177**	

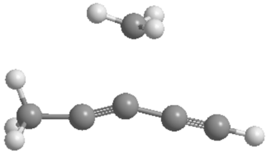
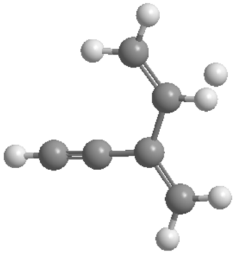
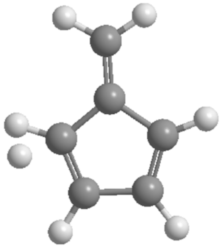
				C	-0.182999	-0.916378	0.463215	1098, 1162, 1181, 1268, 1276, 1322, 1447, 1457, 1770, 1980, 2990, 3023, 3132, 3144, 3216, 3227
				H	-0.030867	-1.810028	1.062738	
				C	0.903060	0.022713	0.126277	
				H	-1.215834	0.876428	-0.306132	
				C	-1.819833	1.685433	-0.688649	
				H	-0.112393	0.971581	0.675308	
				H	2.120867	0.009157	-0.382922	
				C	2.686515	0.926991	-0.497991	
				H	2.588840	-0.916044	-0.700109	
				H	-0.511847	-0.007405	1.480237	
TS 6-7 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.101545	A	226.17853	C	1.523434	-0.501522	-0.014130	1168i, 176, 351, 401, 461, 537, 645, 696, 794, 818, 836, 875, 917, 955, 983, 1040, 1144, 1174, 1229, 1285, 1291, 1328, 1376, 1411, 1443, 1525, 2096, 3030, 3065, 3138, 3146, 3179, 3228
	E(B3LYP+ZPE) = -232.619875	B	512.52211	H	1.913539	0.223637	0.960970	
	E(CCSD(T)/CC-VTZ) = -232.21447760	C	719.68788	H	2.438765	-1.058946	-0.197603	
				C	0.160734	-1.175913	-0.005298	
				H	-0.004938	-1.830851	0.855991	
				C	-0.777596	0.019799	-0.016840	
				C	1.453086	0.912731	-0.109380	
				C	0.023439	1.184678	-0.002991	
				C	-2.147836	-0.040364	0.010947	
				H	-2.741243	0.866340	-0.006661	
				H	-2.681391	-0.982468	0.055650	
				H	0.053435	-1.799359	-0.900694	
				H	-0.389734	2.185194	0.058498	
TS 7-8 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.102947	A	218.29342	C	1.477108	-0.647054	-0.030307	1408i, 254, 344, 464, 584, 603, 662, 668, 740, 770, 842, 901, 934, 953, 958, 1009, 1073, 1090, 1232, 1246, 1282, 1364, 1392, 1460, 1487, 1507, 2104, 3148, 3199, 3216, 3226, 3234, 3242
	E(B3LYP+ZPE) = -232.683975	B	508.42149	H	0.886365	-1.089786	1.021645	
	E(CCSD(T)/CC-VTZ) = -232.27911736	C	718.29308	H	2.340524	-1.268187	-0.220299	
				C	0.075277	-1.137729	-0.045264	
				H	-0.208490	-2.169575	-0.192131	
				C	-0.781782	0.008252	-0.020965	
				C	1.407589	0.774842	-0.016317	
				H	2.264644	1.431279	0.025690	
				C	0.080456	1.157281	-0.011625	
				H	-0.277410	2.176717	0.052365	
				C	-2.179908	-0.001316	0.007067	
				H	-2.741738	0.923679	0.007230	
				H	-2.736332	-0.929783	0.009962	
TS 7-9 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.102133	A	257.56905	C	0.486954	1.372862	0.120708	681i, 155, 252, 299, 335, 510, 511, 555, 699, 740, 768, 819, 881, 930, 948, 1008, 1017,
	E(B3LYP+ZPE) = -232.656717	B	571.90079	C	1.602968	0.489379	-0.113572	
	E(CCSD(T)/CC-VTZ) = -232.24634539	C	800.94473	C	1.349102	-0.838426	-0.035265	

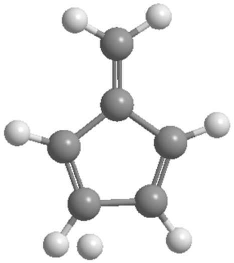
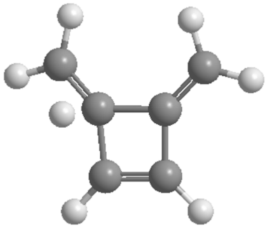
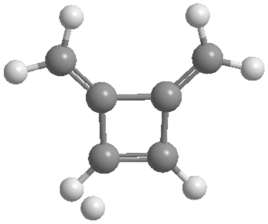
				C	-0.050756	-1.189813	0.117065	1075, 1103, 1170, 1329, 1399, 1450, 1462, 1566, 1804, 3098, 3110, 3131, 3147, 3182, 3186, 3192
				H	0.093441	1.429401	1.133190	
				H	2.578689	0.870053	-0.406281	
				H	2.112253	-1.602903	-0.117587	
				H	-0.344115	-2.211311	0.343191	
				C	-0.997150	-0.258803	-0.004769	
				C	-2.266862	0.161990	-0.105307	
				H	-2.812376	0.056888	-1.038771	
				H	-2.737344	0.753057	0.674172	
				H	0.363926	2.281680	-0.461076	
TS 8-11 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.103334	A	309.14269	C	1.455899	-1.043936	0.212020	585i, 178, 309, 359, 429, 530, 608, 651, 726, 734, 779, 850, 871, 882, 903, 942, 969, 1048, 1211, 1256, 1309, 1399, 1449, 1551, 1608, 1645, 3092, 3125, 3139, 3160, 3201, 3218, 3225
	E(B3LYP+ZPE) = -232.645783	B	486.66445	H	1.735146	-0.518370	1.116866	
	E(CCSD(T)/CC-VTZ) = -232.24049308	C	771.55800	H	2.210168	-1.723816	-0.173264	
				C	0.149474	-1.167656	-0.176428	
				H	-0.159040	-1.986360	-0.818751	
				C	-0.762902	-0.041344	0.010973	
				C	1.289765	1.211242	-0.183670	
				H	2.070463	1.959690	-0.164705	
				C	-0.017380	1.235505	0.011689	
				H	-0.572938	2.164748	0.144905	
				C	-2.105880	-0.123921	0.074331	
				H	-2.722037	0.764518	0.151106	
				H	-2.615616	-1.079750	0.050357	
TS 9-10 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.102354	A	315.85612	C	1.784322	-1.045317	-0.313552	544i, 152, 200, 260, 337, 474, 516, 590, 705, 790, 795, 866, 879, 924, 930, 960, 1074, 1099, 1100, 1253, 1317, 1404, 1425, 1512, 1622, 1726, 3067, 3107, 3134, 3138, 3167, 3180, 3226
	E(B3LYP+ZPE) = -232.642737	B	557.12153	H	2.074112	-2.015429	0.072169	
	E(CCSD(T)/CC-VTZ) = -232.23465451	C	812.59790	H	2.022590	-0.828886	-1.348877	
				C	1.033369	-0.171104	0.446140	
				C	-1.002350	-0.086878	0.082329	
				C	0.725309	1.238358	0.031558	
				H	1.456876	2.029207	-0.094592	
				C	-2.002944	-0.935493	-0.034682	
				H	-2.973339	-0.622971	-0.424563	
				C	-0.603343	1.278270	-0.141369	
				H	-1.244769	2.121870	-0.383794	
				H	-1.904307	-1.980378	0.242525	
				H	0.962654	-0.370428	1.514586	
TS 9-12 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.098434	A	93.67281	C	3.057842	-0.052819	0.106189	1874i, 80, 126, 202, 324, 365, 486, 496, 554, 630, 799, 828, 879, 903, 990, 1008, 1022,
	E(B3LYP+ZPE) = -232.593147	B	1245.91427	H	3.548301	-0.333553	1.034745	
	E(CCSD(T)/CC-VTZ) = -232.17435817	C	1307.30206	H	3.687920	0.362263	-0.676503	

				C	1.777014	-0.210831	-0.063247	1090, 1148, 1164, 1284, 1395, 1437, 1475, 1653, 2010, 2082, 3057, 3101, 3129, 3143, 3169, 3178
				C	0.481206	-0.359491	-0.222164	
				H	0.095491	-1.296710	-0.617539	
				C	-0.508807	0.684223	0.081531	
				H	-1.255363	1.192054	-0.873364	
				H	-0.140185	1.597186	0.541855	
				C	-1.921903	0.489651	0.054459	
				C	-2.809214	-0.499355	0.091792	
				H	-2.603542	-1.406329	0.664617	
				H	-3.789456	-0.423179	-0.365169	
TS 10-11	ZPE(B3LYP/6-311G**) = 0.102780	A	390.59190	C	1.832721	-0.718380	-0.310625	620i, 157, 259, 277, 384, 486, 575, 673, 705, 749, 802, 816, 842, 903, 920, 952, 966, 1067, 1182, 1257, 1285, 1405, 1445, 1522, 1596, 1709, 3120, 3128, 3135, 3137, 3211, 3222, 3227
(C_1)	E(B3LYP+ZPE) = -232.637525	B	425.12167	H	1.641611	-1.076574	-1.315726	
	E(CCSD(T)/CC-VTZ) = -232.23225933	C	756.45575	H	2.861006	-0.708813	0.031380	
				C	0.822857	-0.184178	0.455134	
				C	-0.642826	-0.299050	0.092666	
				C	0.194668	1.726615	-0.023901	
				H	0.589091	2.730675	-0.111661	
				C	-1.370979	-1.412684	-0.006480	
				H	-2.419221	-1.377746	-0.282238	
				C	-0.971771	1.101367	-0.146845	
				H	-1.951727	1.517822	-0.372627	
				H	-0.937058	-2.386464	0.187592	
				H	1.028284	0.018950	1.503586	
TS 10-13	ZPE(B3LYP/6-311G**) = 0.098974	A	339.43575	C	1.729215	-1.061073	-0.117050	1840i, 214, 248, 325, 414, 531, 632, 691, 697, 709, 737, 786, 858, 886, 905, 919, 1030, 1096, 1135, 1164, 1242, 1379, 1423, 1442, 1521, 1577, 1690, 3141, 3148, 3209, 3226, 3232, 3240
(C_1)	E(B3LYP+ZPE) = -232.602947	B	433.93712	H	1.479857	-2.113809	-0.106654	
	E(CCSD(T)/CC-VTZ) = -232.19171558	C	759.38605	H	2.774208	-0.787748	-0.195002	
				C	0.750121	-0.119520	0.091038	
				C	-0.778793	-0.148161	-0.000667	
				C	0.606863	1.379244	-0.000208	
				H	1.354910	2.155190	-0.089073	
				C	-1.664346	-1.149512	0.026940	
				H	-2.725702	-0.966480	-0.095668	
				C	-0.790241	1.302604	-0.125537	
				H	-1.576345	2.042310	-0.096429	
				H	-1.345883	-2.177369	0.153775	
				H	0.922041	0.626407	1.181955	
TS 10-16	ZPE(B3LYP/6-311G**) = 0.099627	A	338.02408	C	1.886174	-0.858192	-0.118012	1913i 203, 228, 264, 350, 407, 607, 653, 685, 730, 737, 756, 846, 881, 889, 920, 1054,
(C_1)	E(B3LYP+ZPE) = -232.606926	B	449.47203	H	1.733793	-1.918815	-0.254915	
	E(CCSD(T)/CC-VTZ) = -232.19829409	C	774.93506	H	2.851246	-0.416690	-0.322474	

				C	0.715666	0.009387	0.111899	1088, 1144, 1169, 1253, 1404, 1433, 1448, 1467, 1737, 2163, 3137, 3153, 3201, 3219, 3232, 3273
				C	-0.776386	-0.219836	0.019359	
				C	0.431874	1.441007	0.003200	
				H	1.070504	2.314355	-0.019653	
				C	-1.570611	-1.286727	-0.005969	
				H	-2.645470	-1.184777	-0.101112	
				C	-0.926145	1.253670	-0.066813	
				H	-1.780446	1.912950	-0.114555	
				H	-1.171339	-2.292138	0.064951	
				H	1.378278	-0.450744	1.085778	
TS 12-13 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.101922	A	406.66084	C	1.762159	-1.150116	-0.154072	753i, 180, 233, 251, 351, 516, 563, 638, 652, 704, 757, 771, 829, 849, 926, 946, 1011, 1022, 1202, 1281, 1336, 1425, 1432, 1506, 1520, 1744, 3079, 3092, 3149, 3168, 3180, 3183, 3244
	E(B3LYP+ZPE) = -232.631725	B	438.10782	H	1.644430	-2.086938	-0.699453	
	E(CCSD(T)/CC-VTZ) = -232.22149321	C	803.19711	H	2.770742	-0.873525	0.131907	
				C	0.720396	-0.398260	0.127907	
				C	-0.688657	-0.213162	-0.006084	
				C	0.502900	1.714838	0.220226	
				H	1.006434	2.564807	-0.240744	
				C	-1.712071	-1.122587	0.144411	
				H	-2.745686	-0.819302	0.034593	
				C	-0.682960	1.189170	-0.307132	
				H	-1.328217	1.689273	-1.021698	
				H	-1.508813	-2.159139	0.379484	
				H	0.750500	1.565524	1.264381	
TS 14-15 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.099339	A	341.00041	C	-0.631130	-0.099992	-0.251844	1631i, 156, 178, 190, 261, 378, 538, 621, 698, 721, 751, 807, 886, 971, 1008, 1052, 1091, 1139, 1159, 1288, 1332, 1400, 1433, 1472, 1476, 1711, 2254, 2966, 3051, 3087, 3133, 3173, 3223
	E(B3LYP+ZPE) = -232.542675	B	463.12823	C	0.839225	-0.085812	-0.065407	
	E(CCSD(T)/CC-VTZ) = -232.13015041	C	765.19461	C	0.843863	1.376556	0.298795	
				C	-0.542233	1.447211	-0.061229	
				C	1.791572	-1.020226	-0.030745	
				C	-1.708958	-1.041213	0.155033	
				H	-0.635781	1.032583	-1.182309	
				H	-1.319463	2.180756	0.125464	
				H	2.801186	-0.750099	0.257968	
				H	1.593242	-2.059965	-0.270034	
				H	-2.682015	-0.705717	-0.215312	
				H	-1.782889	-1.109663	1.251280	
				H	-1.528321	-2.047032	-0.234682	
TS 15-17 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.099544	A	341.26020	C	-0.659823	-0.014837	-0.135398	1049i, 92, 126, 200, 236, 396, 624, 644, 677, 746, 856, 869, 925, 933, 985, 1018, 1131,
	E(B3LYP+ZPE) = -232.565930	B	463.85277	C	0.779142	-0.208252	-0.003074	
	E(CCSD(T)/CC-VTZ) = -232.15809569	C	783.13873	C	1.058753	1.307478	0.005636	

				C C C H H H H H H H	-0.398750 1.647271 -1.856786 -1.000676 0.076182 2.707626 1.333254 -2.724277 -2.137220 -1.673724	1.443710 -1.228464 -0.872441 2.312300 1.723674 -1.031757 -2.258613 -0.471262 -0.948402 -1.889112	-0.081381 -0.004994 0.056346 -0.338915 1.011895 0.103811 -0.139342 -0.476202 1.118140 -0.302197	1160, 1239, 1290, 1370, 1403, 1435, 1472, 1477, 1667, 2116, 2968, 3048, 3090, 3132, 3144, 3223
TS 1x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.098671 E(B3LYP+ZPE) = -232.595613 E(CCSD(T)/CC-VTZ) = -232.18258138	A B C	455.14828 629.91984 987.98827	C H C C C H C H H C H H H	-0.591112 -0.228138 -0.625662 -1.305528 -1.868973 -2.388702 1.396507 1.033182 1.875686 1.914708 2.882322 1.231476 2.074530	2.049957 3.048590 0.831243 -0.372172 -1.438498 -2.364581 0.059262 -0.412264 1.020606 -0.817609 -1.262715 -1.644761 -0.257974	-0.223967 -0.296447 -0.022770 0.002047 0.031319 0.050794 0.656441 1.563959 0.807612 -0.436379 -0.158076 -0.645957 -1.362025	522i, 35, 132, 166, 203, 260, 270, 453, 509, 531, 590, 640, 658, 672, 819, 828, 901, 1021, 1069, 1215, 1400, 1469, 1482, 1489, 1936, 2216, 2969, 3051, 3093, 3117, 3209, 3431, 3478
TS 2x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.096236 E(B3LYP+ZPE) = -232.613423 E(CCSD(T)/CC-VTZ) = -232.19837457	A B C	404.58119 534.95667 915.92149	C C C C C C H H H H H H H	1.815695 1.255333 -0.164125 -1.090136 -0.622686 -1.854039 2.137528 2.871715 1.193207 1.907467 -1.680867 0.068167 -2.537462	-0.915354 0.337224 0.621866 -0.472742 1.897542 -1.402560 -1.417174 -1.026446 -1.789796 1.205333 2.115967 2.732299 -2.216046	-0.125892 -0.087002 -0.011562 -0.012052 0.055172 -0.011452 1.678159 -0.336017 -0.271500 -0.069725 0.103367 0.060225 -0.007778	1000i, 158, 202, 267, 304, 421, 465, 595, 607, 620, 657, 690, 693, 762, 816, 897, 935, 939, 982, 1066, 1273, 1314, 1394, 1437, 1539, 1581, 2209, 3148, 3150, 3157, 3241, 3248, 3476
TS 3x **(C_1)**	ZPE(B3LYP/6-311G**) = 0.098041 E(B3LYP+ZPE) = -232.604437 E(CCSD(T)/CC-VTZ) = -232.18924278	A B C	319.64357 877.23177 1173.36634	C H H	0.308237 0.863658 -0.714349	2.015861 2.119699 2.372598	0.000009 -0.923217 0.000113	533i, 75, 85, 112, 148, 153, 336, 345, 463, 475, 540, 564, 638, 646, 675, 874, 1023,

				H	0.863695	2.119113	0.923271	1049, 1163, 1408, 1418, 1419, 1466, 1470, 2071, 2229, 2995, 3053, 3074, 3089, 3246, 3254, 3479
				C	0.077364	-0.235768	-0.000015	
				C	1.418559	-0.568294	-0.000007	
				C	2.596572	-0.828758	0.000009	
				H	3.629107	-1.076731	-0.000011	
				C	-1.120040	-0.539396	-0.000047	
				C	-2.571191	-0.513430	0.000015	
				H	-2.947672	0.517910	-0.000259	
				H	-2.975766	-1.017162	-0.883377	
				H	-2.975688	-1.016714	0.883700	
TS 4x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.095706 E(B3LYP+ZPE) = -232.604030 E(CCSD(T)/CC-VTZ) = -232.19351107	A	395.53436	C	-0.228602	1.930624	-0.100731	715i, 114, 162, 251, 310, 354, 418, 473, 521, 622, 652, 691, 715, 749, 754, 918, 931, 942, 1027, 1058, 1304, 1309, 1409, 1451, 1597, 1657, 2208, 3147, 3149, 3157, 3240, 3244, 3476
		B	536.05847	H	-1.219775	2.362280	-0.141241	
		C	900.57829	C	-0.043771	0.600975	-0.023273	
				C	-1.162295	-0.290658	0.016129	
				C	-2.088751	-1.058364	0.050209	
				H	-2.916132	-1.724035	0.083580	
				C	1.318611	0.020625	0.007991	
				H	1.602949	0.195638	1.935282	
				H	2.122961	0.747687	-0.047008	
				C	1.597901	-1.289718	-0.164569	
				H	2.622198	-1.636027	-0.220927	
				H	0.811579	-2.033847	-0.202843	
				H	0.617659	2.607403	-0.121371	
TS 7x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.098270 E(B3LYP+ZPE) = -232.656258 E(CCSD(T)/CC-VTZ) = -232.25216216	A	250.44535	C	-0.127157	1.126352	-0.169997	102i, 147, 151, 215, 345, 492, 642, 679, 701, 781, 790, 809, 910, 928, 944, 963, 967, 1005, 1101, 1104, 1253, 1335, 1371, 1450, 1511, 1604, 1701, 3138, 3200, 3211, 3224, 3227, 3235
		B	493.30568	C	-1.406525	0.677827	-0.139692	
		C	705.15156	C	-1.399903	-0.782403	0.026999	
				C	-0.119874	-1.215189	0.083704	
				H	0.211569	2.139867	-0.325706	
				H	-2.299521	1.282636	-0.221126	
				H	-2.288947	-1.395062	0.092968	
				H	0.226470	-2.231563	0.205422	
				C	0.762537	-0.043991	-0.043508	
				C	2.103174	-0.041078	-0.052909	
				H	2.671567	-0.960022	0.039273	
				H	2.666697	0.880149	-0.150851	
				H	-0.061351	1.954889	2.132436	
TS 8x **(C_1)**	ZPE(B3LYP/6-311G**) = 0.098345 E(B3LYP+ZPE) = -232.655601 E(CCSD(T)/CC-VTZ) = -232.25103466	A	240.12066	C	1.388413	-0.643939	-0.152631	305i, 164, 182, 244, 345, 504, 635, 678, 686, 778, 798, 809, 909, 928, 941, 960, 963, 996,
		B	503.94155	H	2.014943	-1.034965	2.000660	
		C	710.80106	H	2.298638	-1.208899	-0.296846	

				C	0.125536	-1.143343	-0.126024	1098, 1105, 1254, 1335, 1366, 1450, 1513, 1601, 1690, 3138, 3203, 3212, 3224, 3227, 3233
				H	-0.170762	-2.181023	-0.178181	
				C	-0.805364	-0.013028	-0.008501	
				C	1.319530	0.829523	-0.073434	
				H	2.181930	1.482013	-0.078105	
				C	0.026155	1.204018	0.013385	
				H	-0.363843	2.208785	0.092337	
				C	-2.144646	-0.076506	0.060715	
				H	-2.750187	0.819444	0.141116	
				H	-2.668466	-1.025707	0.037959	
TS 10x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.097026 E(B3LYP+ZPE) = -232.605255 E(CCSD(T)/CC-VTZ) = -232.19672282	A	338.22436	C	1.697435	-1.049356	-0.179315	766i, 204, 242, 293, 336, 421, 488, 639, 695, 719, 746, 769, 815, 865, 895, 905, 920, 948, 1070, 1154, 1189, 1290, 1432, 1449, 1547, 1639, 1748, 3141, 3142, 3203, 3224, 3231, 3232
		B	444.00727	H	1.455796	-2.102959	-0.249176	
		C	748.68948	H	2.741738	-0.767519	-0.242344	
				C	0.739958	-0.132979	0.069455	
				C	-0.778584	-0.136745	-0.009156	
				C	0.651117	1.351894	0.002604	
				H	1.398056	2.133728	0.012378	
				C	-1.726834	-1.067361	-0.003331	
				H	-2.775510	-0.804650	-0.081326	
				C	-0.700736	1.336598	-0.097800	
				H	-1.450700	2.108290	-0.209442	
				H	-1.481255	-2.119007	0.085852	
				H	0.817739	-0.260193	1.989310	
TS 13x **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.096349 E(B3LYP+ZPE) = -232.611021 E(CCSD(T)/CC-VTZ) = -232.20264255	A	349.67762	C	1.516500	-1.332039	-0.031316	310i, 155, 168, 243, 251, 317, 416, 685, 704, 724, 765, 767, 824, 890, 896, 905, 915, 937, 1067, 1155, 1192, 1292, 1434, 1451, 1503, 1713, 1758, 3140, 3140, 3205, 3223, 3224, 3231
		B	447.18851	H	1.133487	-2.343125	0.042996	
		C	763.28944	H	2.592074	-1.208963	-0.083601	
				C	0.697328	-0.285879	-0.055173	
				C	-0.798726	-0.073974	-0.008314	
				C	0.825397	1.190483	-0.153221	
				H	1.666548	1.852589	-0.303740	
				C	-1.872939	-0.855616	0.083609	
				H	-2.874314	-0.440817	0.090229	
				C	-0.527782	1.372465	-0.124650	
				H	-1.165976	2.244627	-0.170909	
				H	-1.779091	-1.932950	0.153029	
				H	1.388600	1.736005	2.006388	
TS 3x2 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.094235 E(B3LYP+ZPE) = -232.591407 E(CCSD(T)/CC-VTZ) = -232.17547018	A	355.23344	C	0.449940	1.871091	0.000100	427i, 118, 157, 196, 198, 209, 287, 347, 489, 546, 606, 638, 688, 704, 707, 901, 991, 1014,
		B	693.47579	H	1.042026	2.127575	-0.882623	
		C	1025.14329	H	-0.463025	2.466723	-0.000178	

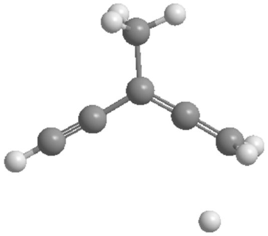
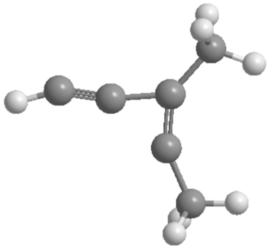
				**H**	**1.041432**	**2.127500**	**0.883245**	**1057, 1174, 1277, 1403, 1458, 1480, 1496, 2003, 2203, 3031, 3089, 3110, 3125, 3183, 3477**
				C	**0.125260**	**0.386091**	**-0.000060**	
				C	**1.224052**	**-0.529651**	**-0.000040**	
				C	**2.182305**	**-1.258633**	**0.000005**	
				H	**3.016265**	**-1.916530**	**0.000046**	
				C	**-1.110836**	**-0.060103**	**-0.000271**	
				C	**-2.329434**	**-0.540414**	**0.000029**	
				H	**-2.878864**	**-0.682537**	**0.926161**	
				H	**-2.879471**	**-0.682419**	**-0.925758**	
				H	**-2.126088**	**-2.650600**	**0.000536**	
TS CTS (C$_1$) 	**ZPE(B3LYP/6-311G**) = 0.100916** **E(B3LYP+ZPE) = -232.617316** **E(CCSD(T)/CC-VTZ) = -232.20565845**	**A**	**433.97582**	**C**	**-2.208355**	**-0.592720**	**0.000023**	**657i, 115, 131, 149, 166, 216, 387, 465, 468, 516, 547, 695, 890, 1024, 1033, 1047, 1067, 1191, 1395, 1402, 1464, 1471, 1476, 1487, 1826, 1924, 2987, 3029, 3055, 3071, 3086, 3113, 3404**
		B	**546.13604**	**H**	**-2.469468**	**-1.187959**	**0.880711**	
		C	**957.76963**	**H**	**-2.831243**	**0.311631**	**-0.000537**	
				H	**-2.469446**	**-1.189033**	**-0.879941**	
				C	**-0.775042**	**-0.267455**	**-0.000117**	
				C	**0.960792**	**-0.642013**	**0.000156**	
				C	**1.830164**	**-1.539223**	**-0.000151**	
				H	**2.195924**	**-2.540622**	**0.000396**	
				C	**0.222386**	**0.577720**	**-0.000053**	
				C	**0.566625**	**2.030881**	**0.000019**	
				H	**1.164866**	**2.278486**	**-0.881454**	
				H	**-0.334950**	**2.645964**	**0.000066**	
				H	**1.164897**	**2.278399**	**0.881494**	

Table A8. Single Collission Rate Constants for C_2H + 1-butyne

Channel	Barrier	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
INT 1 → INT 2	TS 1-2	1.37E+07	1.76E+07	2.22E+07	2.79E+07	3.48E+07	4.29E+07	5.26E+07	6.40E+07
INT 2 → INT 1	TS 1-2	6.75E+03	9.20E+03	1.24E+04	1.66E+04	2.19E+04	2.86E+04	3.72E+04	4.78E+04
INT 1 → INT 4	TS 1-4	5.17E+10	5.59E+10	6.02E+10	4.32E+10	4.63E+10	4.96E+10	5.31E+10	5.67E+10
INT 4 → INT 1	TS 1-4	3.38E+08	3.76E+08	4.18E+08	4.62E+08	5.10E+08	5.62E+08	6.17E+08	6.76E+08
INT 1 → C_2H_5 + diacetylene	TS 1x	1.12E+09	1.40E+09	1.73E+09	4.25E+09	5.18E+09	6.27E+09	7.54E+09	9.01E+09
INT 1 → INT C-T	TS 1-A	3.25E+09	3.71E+09	4.22E+09	9.56E+09	1.08E+10	1.21E+10	1.36E+10	1.52E+10
INT C-T → INT 1	TS 1-A	1.62E+12	1.71E+12	1.80E+12	3.77E+12	3.95E+12	4.13E+12	4.31E+12	4.50E+12

INT 2 → INT 3	TS 2-3	2.65E+04	3.50E+04	4.56E+04	1.18E+05	1.52E+05	1.93E+05	2.44E+05	3.07E+05
INT 3 → INT 2	TS 2-3	1.08E+07	1.36E+07	1.70E+07	1.40E+07	1.73E+07	2.11E+07	2.57E+07	3.10E+07
INT 2 → INT 4	TS 2-4	4.88E+06	5.89E+06	7.05E+06	5.61E+06	6.66E+06	7.87E+06	9.26E+06	1.08E+07
INT 4 → INT 2	TS 2-4	6.49E+07	7.56E+07	8.77E+07	1.01E+08	1.17E+08	1.33E+08	1.52E+08	1.73E+08
INT 2 → 3-methylene-4-ene-1-pentyne + H	TS 2x	9.17E+06	1.09E+07	1.30E+07	1.02E+07	1.21E+07	1.41E+07	1.65E+07	1.92E+07
INT 2 → 19	TS 2-14	4.39E+05	5.31E+05	6.38E+05	1.52E+06	1.81E+06	2.15E+06	2.53E+06	2.97E+06
19 → INT 2	TS 31	8.08E+09	9.29E+09	1.06E+10	2.42E+10	2.75E+10	3.11E+10	3.51E+10	3.94E+10
INT 3 → CH_3 + pentadiyne	TS 18	2.07E+09	2.52E+09	3.04E+09	7.31E+09	8.73E+09	1.04E+10	1.22E+10	1.44E+10
INT 3 → 3-methyl-3,4-diene-1-pentyne + H	TS 32	3.15E+07	4.13E+07	5.35E+07	4.58E+07	5.82E+07	7.35E+07	9.19E+07	1.14E+08
INT 4 → INT 5	TS 5	2.66E+12	2.68E+12	2.70E+12	5.43E+12	5.46E+12	5.50E+12	5.53E+12	5.56E+12
INT 5 → INT 4	TS 5	1.00E+13	1.05E+13	1.10E+13	2.30E+13	2.40E+13	2.50E+13	2.61E+13	2.71E+13
INT 4 → 3-methylene-4-ene-1-pentyne + H	TS 4x	1.01E+08	1.19E+08	1.40E+08	1.63E+08	1.90E+08	2.20E+08	2.54E+08	2.92E+08
INT 5 → INT 6	TS 5-6	8.12E+04	1.05E+05	1.36E+05	3.46E+05	4.39E+05	5.53E+05	6.91E+05	8.58E+05
INT 6 → INT 5	TS 5-6	6.51E+04	8.46E+04	1.09E+05	2.79E+05	3.54E+05	4.47E+05	5.59E+05	6.96E+05
INT 6 → INT 7	TS 6-7	1.95E+08	2.22E+08	2.51E+08	2.83E+08	3.19E+08	3.58E+08	4.01E+08	4.48E+08
INT 7 → INT 6	TS 6-7	2.95E+05	3.51E+05	4.17E+05	9.85E+05	1.16E+06	1.36E+06	1.60E+06	1.86E+06
INT 7 → INT 8	TS 7-8	2.46E+10	2.60E+10	2.74E+10	2.89E+10	3.05E+10	3.21E+10	3.38E+10	3.55E+10
INT 8 → INT 7	TS 7-8	6.24E+10	6.55E+10	6.86E+10	7.19E+10	7.53E+10	7.88E+10	8.24E+10	8.61E+10
INT 7 → INT 9	TS 7-9	5.47E+08	6.09E+08	6.76E+08	1.50E+09	1.66E+09	1.83E+09	2.02E+09	2.22E+09
INT 9 → INT 7	TS 7-9	8.13E+09	8.62E+09	9.14E+09	1.93E+10	2.04E+10	2.16E+10	2.28E+10	2.40E+10
INT 7 → fulvene + H	TS 7x	2.67E+09	2.98E+09	3.32E+09	3.70E+09	4.11E+09	4.55E+09	5.04E+09	5.56E+09
INT 8 → INT 11	TS 8-11	2.13E+08	2.37E+08	2.64E+08	5.86E+08	6.49E+08	7.17E+08	7.91E+08	8.71E+08
INT 11 → INT 8	TS 8-11	5.59E+10	5.80E+10	6.01E+10	1.24E+11	1.29E+11	1.33E+11	1.38E+11	1.42E+11
INT 8 → fulvene + H	TS 8x	2.70E+10	2.94E+10	3.20E+10	3.48E+10	3.78E+10	4.09E+10	4.43E+10	4.79E+10
INT 9 → INT 10	TS 9-10	1.04E+09	1.13E+09	1.22E+09	2.65E+09	2.86E+09	3.09E+09	3.33E+09	3.59E+09
INT 10 → INT 9	TS 9-10	8.80E+10	9.28E+10	9.77E+10	2.06E+11	2.16E+11	2.27E+11	2.38E+11	2.49E+11
INT 9 → INT 12	TS 9-12	4.56E+03	6.42E+03	8.92E+03	2.45E+04	3.32E+04	4.46E+04	5.94E+04	7.83E+04
INT 12 → INT 9	TS 9-12	1.08E+07	1.40E+07	1.79E+07	2.28E+07	2.86E+07	3.57E+07	4.41E+07	5.40E+07

INT 10 → INT 11	TS 10-11	3.12E+10	3.31E+10	3.50E+10	7.41E+10	7.83E+10	8.27E+10	8.71E+10	9.17E+10
INT 11 → INT 10	TS 10-11	1.64E+10	1.74E+10	1.85E+10	3.91E+10	4.13E+10	4.36E+10	4.60E+10	4.85E+10
INT 10 → INT 13	TS 10-13	3.51E+06	4.27E+06	5.17E+06	1.24E+07	1.49E+07	1.77E+07	2.10E+07	2.47E+07
INT 13 → INT 10	TS 10-13	7.92E+05	9.94E+05	1.24E+06	1.54E+06	1.89E+06	2.32E+06	2.82E+06	3.42E+06
INT 10 → DMCB + H	TS 10x	6.39E+07	7.56E+07	8.90E+07	2.09E+08	2.43E+08	2.83E+08	3.27E+08	3.78E+08
INT 13 → DMCB + H	TS 13x	2.87E+08	3.42E+08	4.04E+08	4.76E+08	5.59E+08	6.53E+08	7.61E+08	8.83E+08
INT 14 → INT 15	TS 14-15	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 15 → INT 14	TS 14-15	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 15 → INT 16	TS 15-16	7.51E+05	1.20E+06	1.86E+06	2.79E+06	4.10E+06	5.89E+06	8.28E+06	1.15E+07
INT 16 → INT 15	TS 15-16	3.17E+00	5.70E+00	9.90E+00	3.33E+01	5.46E+01	8.72E+01	1.36E+02	2.09E+02
INT A → INT B	TS AB	9.67E+07	1.29E+08	1.71E+08	1.49E+08	1.93E+08	2.46E+08	3.13E+08	3.93E+08
INT B → INT A	TS AB	1.14E+06	1.56E+06	2.11E+06	5.62E+06	7.41E+06	9.68E+06	1.25E+07	1.60E+07
INT A → 1,3-hexadiyne + H	TS A2	2.48E+07	3.29E+07	4.31E+07	1.12E+08	1.44E+08	1.83E+08	2.30E+08	2.88E+08
INT A → 3,4-hexadiene-1-yne + H	TS A1	3.66E+07	4.78E+07	6.17E+07	7.90E+07	1.00E+08	1.26E+08	1.57E+08	1.94E+08
INT A → ethynylallene + CH_3	TS A3	8.78E+08	1.08E+09	1.33E+09	3.23E+09	3.91E+09	4.69E+09	5.60E+09	6.65E+09
INT A → C-T	TS A-1	8.50E+08	9.81E+08	1.13E+09	2.58E+09	2.94E+09	3.34E+09	3.78E+09	4.26E+09
INT C-T → INT A	TS A-1	1.51E+12	1.60E+12	1.68E+12	3.54E+12	3.72E+12	3.89E+12	4.07E+12	4.26E+12
INT B → 1,3-hexadiene-5-yne + H	TS B1	1.85E+08	2.18E+08	2.55E+08	2.96E+08	3.43E+08	3.97E+08	4.56E+08	5.22E+08

Single Collission Rate Constants for C_2H + 2-butyne

Channel	**Barrier**	**0.0**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
INT 1 → INT 2	TS 1-2	3.34E+06	4.56E+06	6.12E+06	8.11E+06	1.06E+07	1.37E+07	1.76E+07	2.22E+07
INT 2 → INT 1	TS 1-2	1.17E+03	1.71E+03	2.46E+03	3.50E+03	4.89E+03	6.75E+03	9.20E+03	1.24E+04
INT 1 → INT 4	TS 1-4	3.40E+10	3.71E+10	4.05E+10	4.41E+10	4.78E+10	5.17E+10	5.59E+10	6.02E+10
INT 4 → INT 1	TS 1-4	1.89E+08	2.13E+08	2.41E+08	2.70E+08	3.03E+08	3.38E+08	3.76E+08	4.18E+08
INT 1 → C_2H_5 + diacetylene	TS 1x	3.16E+08	4.16E+08	5.42E+08	6.97E+08	8.88E+08	1.12E+09	1.40E+09	1.73E+09
INT 1 → INT C-T	TS 1-A	1.54E+09	1.81E+09	2.11E+09	2.45E+09	2.83E+09	3.25E+09	3.71E+09	4.22E+09
INT C-T → INT 1	TS 1-A	1.20E+12	1.29E+12	1.37E+12	1.45E+12	1.53E+12	1.62E+12	1.71E+12	1.80E+12
INT 2 → INT 3	TS 2-3	5.65E+03	7.89E+03	1.09E+04	1.48E+04	1.99E+04	2.65E+04	3.50E+04	4.56E+04
INT 3 → INT 2	TS 2-3	2.90E+06	3.86E+06	5.07E+06	6.58E+06	8.45E+06	1.08E+07	1.36E+07	1.70E+07
INT 2 → INT 4	TS 2-4	1.76E+06	2.19E+06	2.70E+06	3.31E+06	4.03E+06	4.88E+06	5.89E+06	7.05E+06
INT 4 → INT 2	TS 2-4	2.79E+07	3.34E+07	3.98E+07	4.71E+07	5.54E+07	6.49E+07	7.56E+07	8.77E+07
INT 2 → 3-methylene-4-ene-1-pentyne + H	TS 2x	3.49E+06	4.28E+06	5.22E+06	6.33E+06	7.64E+06	9.17E+06	1.09E+07	1.30E+07
INT 2 → 19	TS 2-14	1.56E+05	1.94E+05	2.41E+05	2.96E+05	3.62E+05	4.39E+05	5.31E+05	6.38E+05
19 → INT 2	TS 31	3.74E+09	4.41E+09	5.17E+09	6.03E+09	7.00E+09	8.08E+09	9.29E+09	1.06E+10
INT 3 → CH_3 + pentadiyne	TS 18	6.88E+08	8.73E+08	1.10E+09	1.37E+09	1.69E+09	2.07E+09	2.52E+09	3.04E+09
INT 3 → 3-methyl-3,4-diene-1-pentyne + H	TS 32	6.81E+06	9.52E+06	1.31E+07	1.78E+07	2.38E+07	3.15E+07	4.13E+07	5.35E+07
INT 4 → INT 5	TS 5	2.57E+12	2.59E+12	2.61E+12	2.63E+12	2.64E+12	2.66E+12	2.68E+12	2.70E+12
INT 5 → INT 4	TS 5	7.87E+12	8.28E+12	8.70E+12	9.13E+12	9.58E+12	1.00E+13	1.05E+13	1.10E+13
INT 4 → 3-methylene-4-ene-1-pentyne + H	TS 4x	4.02E+07	4.89E+07	5.91E+07	7.10E+07	8.48E+07	1.01E+08	1.19E+08	1.40E+08
INT 5 → INT 6	TS 5-6	1.90E+04	2.60E+04	3.51E+04	4.69E+04	6.20E+04	8.12E+04	1.05E+05	1.36E+05
INT 6 → INT 5	TS 5-6	1.51E+04	2.06E+04	2.79E+04	3.74E+04	4.96E+04	6.51E+04	8.46E+04	1.09E+05
INT 6 → INT 7	TS 6-7	9.84E+07	1.14E+08	1.31E+08	1.50E+08	1.71E+08	1.95E+08	2.22E+08	2.51E+08
INT 7 → INT 6	TS 6-7	1.16E+05	1.41E+05	1.70E+05	2.05E+05	2.46E+05	2.95E+05	3.51E+05	4.17E+05
INT 7 → INT 8	TS 7-8	1.85E+10	1.96E+10	2.08E+10	2.20E+10	2.33E+10	2.46E+10	2.60E+10	2.74E+10
INT 8 → INT 7	TS 7-8	4.84E+10	5.10E+10	5.37E+10	5.65E+10	5.94E+10	6.24E+10	6.55E+10	6.86E+10
INT 7 → INT 9	TS 7-9	3.11E+08	3.50E+08	3.93E+08	4.40E+08	4.91E+08	5.47E+08	6.09E+08	6.76E+08

INT 9 → INT 7	TS 7-9	5.94E+09	6.34E+09	6.76E+09	7.20E+09	7.66E+09	8.13E+09	8.62E+09	9.14E+09
INT 7 → fulvene + H	TS 7x	1.49E+09	1.68E+09	1.89E+09	2.13E+09	2.39E+09	2.67E+09	2.98E+09	3.32E+09
INT 8 → INT 11	TS 8-11	1.20E+08	1.35E+08	1.52E+08	1.71E+08	1.91E+08	2.13E+08	2.37E+08	2.64E+08
INT 11 → INT 8	TS 8-11	4.59E+10	4.78E+10	4.98E+10	5.18E+10	5.38E+10	5.59E+10	5.80E+10	6.01E+10
INT 8 → fulvene + H	TS 8x	1.72E+10	1.89E+10	2.07E+10	2.27E+10	2.48E+10	2.70E+10	2.94E+10	3.20E+10
INT 9 → INT 10	TS 9-10	6.63E+08	7.28E+08	7.98E+08	8.72E+08	9.52E+08	1.04E+09	1.13E+09	1.22E+09
INT 10 → INT 9	TS 9-10	6.63E+10	7.04E+10	7.46E+10	7.89E+10	8.34E+10	8.80E+10	9.28E+10	9.77E+10
INT 9 → INT 12	TS 9-12	6.54E+02	1.00E+03	1.50E+03	2.21E+03	3.19E+03	4.56E+03	6.42E+03	8.92E+03
INT 12 → INT 9	TS 9-12	2.40E+06	3.35E+06	4.59E+06	6.18E+06	8.22E+06	1.08E+07	1.40E+07	1.79E+07
INT 10 → INT 11	TS 10-11	2.27E+10	2.43E+10	2.59E+10	2.76E+10	2.93E+10	3.12E+10	3.31E+10	3.50E+10
INT 11 → INT 10	TS 10-11	1.19E+10	1.28E+10	1.36E+10	1.45E+10	1.55E+10	1.64E+10	1.74E+10	1.85E+10
INT 10 → INT 13	TS 10-13	1.18E+06	1.49E+06	1.87E+06	2.32E+06	2.86E+06	3.51E+06	4.27E+06	5.17E+06
INT 13 → INT 10	TS 10-13	2.27E+05	2.96E+05	3.83E+05	4.92E+05	6.27E+05	7.92E+05	9.94E+05	1.24E+06
INT 10 → DMCB + H	TS 10x	2.53E+07	3.08E+07	3.73E+07	4.49E+07	5.37E+07	6.39E+07	7.56E+07	8.90E+07
INT 13 → DMCB + H	TS 13x	1.12E+08	1.37E+08	1.66E+08	2.01E+08	2.41E+08	2.87E+08	3.42E+08	4.04E+08
INT 14 → INT 15	TS 14-15	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 15 → INT 14	TS 14-15	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08	1.00E-08
INT 15 → INT 16	TS 15-16	3.53E+04	7.40E+04	1.44E+05	2.62E+05	4.53E+05	7.51E+05	1.20E+06	1.86E+06
INT 16 → INT 15	TS 15-16	7.91E-02	1.90E-01	4.19E-01	8.67E-01	1.70E+00	3.17E+00	5.70E+00	9.90E+00
INT A → INT B	TS AB	1.80E+07	2.61E+07	3.71E+07	5.18E+07	7.13E+07	9.67E+07	1.29E+08	1.71E+08
INT B → INT A	TS AB	1.89E+05	2.81E+05	4.09E+05	5.85E+05	8.23E+05	1.14E+06	1.56E+06	2.11E+06
INT A → 1,3-hexadiyne + H	TS A2	4.87E+06	6.97E+06	9.79E+06	1.35E+07	1.84E+07	2.48E+07	3.29E+07	4.31E+07
INT A → 3,4-hexadiene-1-yne + H	TS A1	7.95E+06	1.11E+07	1.53E+07	2.07E+07	2.77E+07	3.66E+07	4.78E+07	6.17E+07
INT A → ethynylallene + CH_3	TS A3	2.67E+08	3.45E+08	4.42E+08	5.61E+08	7.05E+08	8.78E+08	1.08E+09	1.33E+09

INT A → C-T	TS A-1	3.81E+08	4.53E+08	5.34E+08	6.27E+08	7.32E+08	8.50E+08	9.81E+08	1.13E+09
INT C-T → INT A	TS A-1	1.11E+12	1.19E+12	1.27E+12	1.35E+12	1.43E+12	1.51E+12	1.60E+12	1.68E+12
INT B → 1,3-hexadiene-5-yne + H	TS B1	7.61E+07	9.20E+07	1.11E+08	1.32E+08	1.57E+08	1.85E+08	2.18E+08	2.55E+08

Table A9. Product Branching Ratios of the C_2H + 1- and 2-butyne reaction

Product Branching Ratios
Initial Adduct: INT 1

Product	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
CH_3 + pentadiyne	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3
C_2H_5 + diacetylene	6.4	7.0	7.7	19.4	20.8	22.2	23.6	25.1
3-methylene-4-e-ene-1-pentyne + H	87.3	86.5	85.6	65.0	63.4	61.8	60.3	58.8
fulvene + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiyne + H	0.1	0.2	0.2	0.5	0.5	0.5	0.6	0.6
3,4-hexadiene-1-yne + H	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4
1,3-hexadiene-5-yne + H	0.6	0.6	0.7	0.6	0.7	0.7	0.8	0.8
ethynylallene + CH_3	5.3	5.4	5.5	13.9	14.0	14.0	14.1	14.1
3-methyl-3,4-diene-1-pentyne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Product Branching Ratios
Initial Adduct: INT 22

Product	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
CH_3 + pentadiyne	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1
C_2H_5 + diacetylene	1.9	2.0	2.1	5.3	5.4	5.5	5.6	5.7
3-methylene-4-e-ene-1-pentyne + H	26.0	24.4	22.9	17.7	16.4	15.3	14.2	13.3
fulvene + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiyne + H	1.7	1.9	2.0	2.4	2.6	2.8	2.9	3.1
3,4-hexadiene-1-yne + H	2.5	2.7	2.9	1.7	1.8	1.9	2.0	2.1
1,3-hexadiene-5-yne + H	6.7	7.3	7.9	3.2	3.4	3.6	3.9	4.1
ethynylallene + CH_3	61.1	61.7	62.2	69.7	70.4	70.9	71.3	71.7
3-methyl-3,4-diene-1-pentyne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Product Branching Ratios
Initial Adduct: INT 28

Product	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
CH_3 + pentadiyne	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2
C_2H_5 + diacetylene	4.2	4.6	5.0	12.5	13.3	14.1	14.9	15.6
3-methylene-4-e-ene-1-pentyne + H	57.8	56.5	55.3	42.1	40.6	39.3	37.9	36.6
fulvene + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiyne + H	0.9	1.0	1.1	1.4	1.5	1.6	1.7	1.8
3,4-hexadiene-1-yne + H	1.3	1.4	1.5	1.0	1.1	1.1	1.2	1.2
1,3-hexadiene-5-yne + H	3.5	3.9	4.2	1.9	2.0	2.1	2.3	2.4
ethynylallene + CH_3	32.2	32.6	32.9	40.9	41.4	41.6	41.9	42.1
3-methyl-3,4-diene-1-pentyne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Product Branching Ratios
Initial Adduct: INT 3

Product	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0

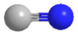
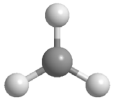
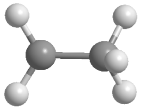
CH_3 + pentadiyne	98.6	98.5	98.4	98.3	98.1	98.0	97.9	97.7
C_2H_5 + diacetylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-methylene-4-e-ene-1-pentyne + H	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5
fulvene + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMCB + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiyne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3,4-hexadiene-1-yne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3-hexadiene-5-yne + H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ethynylallene + CH_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-methyl-3,4-diene-1-pentyne + H	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7

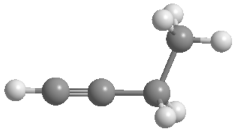
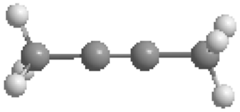
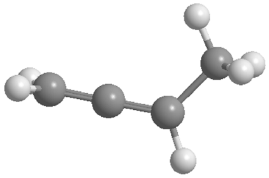
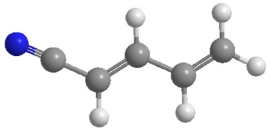
Table A10. Ionization Energies of he C_2H + 1- and 2-butyne reaction products

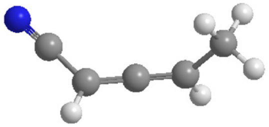
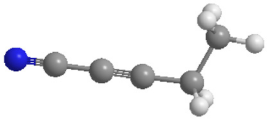
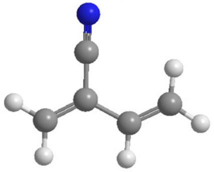
Ionization Energies (eV)

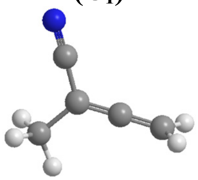
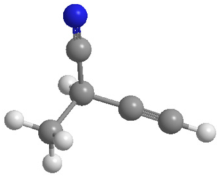
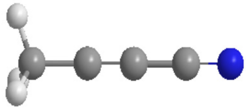
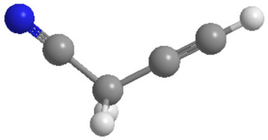
		cc-pvdz	**cc-pvtz**	**cc-pvqz**	**CBS**
vertical	1,3-hexadiene-5-yne	8.503295	8.722518	8.795023	8.829624
	3,4-hexadiene-1-yne	9.297934	9.504969	9.570829	9.600801
	1,3-hexadiyne	8.939517	9.159169	9.231264	9.265009
	2-ethynylbutadiene	8.831276	9.05452	9.126615	9.838278
	3-methyl-3,4-diene-1-pentyne	9.246934	9.498239	9.579974	9.618216
	fulvene	8.340183	8.537585	8.60805	8.644585
	DMCB	8.702689	8.90634	8.977961	9.01439
adiabatic	1,3-hexadiene-5-yne	8.28799	8.54737	8.626267	8.660422
	3,4-hexadiene-1-yne	9.093108	9.347942	9.357979	9.450375
	1,3-hexadiyne	8.706645	8.954533	8.983913	9.060705
	2-ethynylbutadiene	8.612086	8.885267	8.951758	9.001927
	3-methyl-3,4-diene-1-pentyne	8.61131	8.862504	8.859475	8.965736
	fulvene	8.035538	8.279901	8.361746	8.395653
	DMCB	8.446448	8.695872	8.751632	8.811446

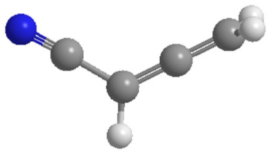
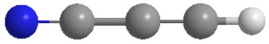
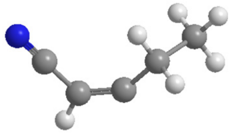
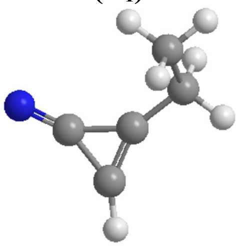
Table A11. B3LYP, and CCSD(T) calculated energies at 0 K, zero-point energy corrections (ZPE), B3LYP/6-311G** optimized Cartesian coordinates, unscaled vibrational frequencies (v_i), and moments of inertia (I_i) of all species involved in the studied CN + 1/2-butyne and CN + 1,2-butadiene reactions.

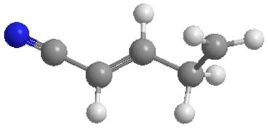
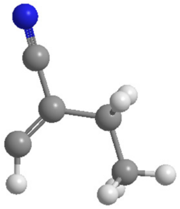
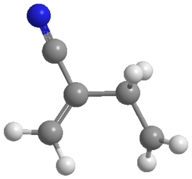
Species, (point group), electronic state	Energies, a.u.	*i*	I_i, a.u.	Cartesian coordinates, angstroms				v_i, cm^{-1}
				Atom	X	Y	Z	
H, **^{2}S**	ZPE(B3LYP/6-311G**) = 0.0 2. E(B3LYP/6-311G**) = - 0.502155930011 E(CCSD(T)/CC-VDZ) = -0.499278 E(CCSD(T)/CC-VTZ) = -0.49980982 E(CCSD(T)/CC-VQZ) = -0.499946 E(CCSD(T)/CBS) = -0.49999							
CN **(C_{∞}v)** 	ZPE(B3LYP/6-311G**) = 0.004902 E(B3LYP+ZPE) = -92.731965 E(CCSD(T)/CC-VDZ) = -92.4892179 E(CCSD(T)/CC-VTZ) = -92.5662682 E(CCSD(T)/CC-VQZ) = -92.5905486 E(CCSD(T)/CC-V5Z) = -92.59801244 E(CCSD(T)/CC-CBS) = -92.60152	A	0.00000	N	0.000000	0.000000	0.538005	2152
		B	31.35694	C	0.000000	0.000000	-0.627672	
		C	31.35694					
CH_3 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.029569 E(B3LYP+ZPE) = -39.853757 E(CCSD(T)/CC-VDZ) = -39.715785 E(CCSD(T)/CC-VTZ) = -39.760817 E(CCSD(T)/CC-VQZ) = -39.772271 E(CCSD(T)/CC-V5Z) = -39.775614 E(CCSD(T)/CBS) = -39.77618	A	6.30449	C	0.000000	0.000000	0.000273	507, 1404, 1404, 3102, 3281, 3281
		B	6.30449	H	0.000000	1.080657	-0.000545	
		C	12.60896	H	-0.935876	-0.540328	-0.000545	
				H	0.935876	-0.540328	-0.000545	
C_2H_5 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.058983 E(B3LYP+ZPE) = -79.124669 E(CCSD(T)/CC-VDZ) = -78.91573206 E(CCSD(T)/CC-VTZ) = -79.00226044 E(CCSD(T)/CC-VQZ) = -79.02545788 E(CCSD(T)/CBS) = -79.03395	A	17.39033	C	-0.794278	0.000000	-0.019123	105, 474, 813, 980, 1063, 1192, 1401, 1465, 1482, 1483, 2941, 3034, 3077, 3140, 3241
		B	79.41224	H	-1.351038	-0.926566	0.042622	
		C	85.68530	H	-1.351038	0.926566	0.042622	
				C	0.693124	0.000000	-0.001749	
				H	1.107217	-0.886126	-0.492768	
				H	1.107217	0.886127	-0.492766	
				H	1.094572	-0.000001	1.025521	

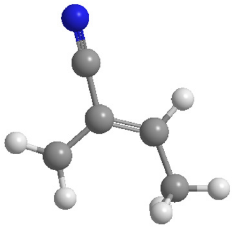
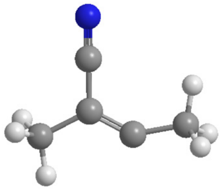
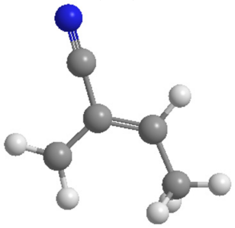
1-butyne	ZPE(B3LYP/6-311G**) = 0.084380	A	65.43102	C	1.960054	-0.262471	0.000000	201, 224, 360, 519, 665, 673, 789, 846, 1020, 1089, 1109, 1288, 1349, 1411, 1479, 1497, 1507, 2222, 3020, 3035, 3045, 3103, 3110, 3478
(C_1)	E(B3LYP+ZPE) = -155.930477	B	400.10341	H	2.955614	-0.632552	0.000000	
	E(CCSD(T)/CC-VDZ) = -155.51300878	C	443.24411	C	0.833687	0.156349	0.000000	
	E(CCSD(T)/CC-VTZ) = -155.67431685			C	-0.542362	0.647396	0.000000	
	E(CCSD(T)/CC-VQZ) = -155.71932538			H	-0.691652	1.288389	0.876126	
	E(CCSD(T)/CBS) = -155.73674			H	-0.691652	1.288389	-0.876126	
				C	-1.588182	-0.482763	0.000000	
				H	-2.598554	-0.065958	0.000000	
				H	-1.476467	-1.114665	-0.883611	
				H	-1.476467	-1.114665	0.883611	
2-butyne	ZPE(B3LYP/6-311G**) =0.083756	A	22.47396	C	-2.060490	-0.000003	0.000019	15, 201, 202, 383, 384, 725, 1054, 1054, 1057, 1057, 1170, 1417, 1420, 1482, 1482, 1482, 1482, 2365, 3018, 3019, 3074, 3074, 3074, 3074
(C_1)	E(B3LYP+ZPE) = -155.941156	B	536.41053	H	-2.456450	0.388735	-0.943151	
	E(CCSD(T)/CC-VDZ) = -155.52061932	C	536.41124	H	-2.456369	0.622455	0.808283	
	E(CCSD(T)/CC-VTZ) = -155.68158969			H	-2.456280	-1.011240	0.134966	
	E(CCSD(T)/CC-VQZ) = -155.72674319			C	-0.601495	0.000018	-0.000037	
	E(CCSD(T)/CBS) = -155.74435			C	0.601495	-0.000026	-0.000028	
				C	2.060490	0.000007	0.000014	
				H	2.456434	-0.622458	-0.808213	
				H	2.456282	1.011245	-0.134918	
				H	2.456383	-0.388717	0.943219	
1,2-butadiene	ZPE(B3LYP/6-311G**) = 0.083589	A	52.08749	C	-1.937452	-0.214047	0.000671	168, 211, 340, 541, 572, 872, 879, 897, 1022, 1060, 1091, 1150, 1361, 1408, 1472, 1486, 1505, 2057, 3019, 3065, 3104, 3111, 3120, 3181
	E(B3LYP+ZPE) = -155.937771	B	431.02690	H	-2.476449	-0.382537	0.928581	
	E(CCSD(T)/CC-VDZ) = -155.51539788	C	459.59117	H	-2.482576	-0.381185	-0.923877	
	E(CCSD(T)/CC-VTZ) = -155.67550978			C	-0.692698	0.173968	-0.002479	
	E(CCSD(T)/CC-VQZ) = -155.72038959			C	0.553314	0.559152	0.000663	
	E(CCSD(T)/CBS) = -155.73787			H	0.758980	1.628786	0.002691	
				C	1.746391	-0.364833	-0.000077	
				H	2.373927	-0.188003	-0.879758	
				H	2.371588	-0.191692	0.882119	
				H	1.437198	-1.410811	-0.002424	
1-cyano-1,3-butadiene	ZPE(B3LYP/6-311G**) = 0.084197	A	66.99305	N	-3.096438	-0.403589	-0.000704	139, 144, 209, 322, 461, 497, 579, 671, 873, 958, 962, 986, 1027, 1045, 1196, 1288, 1318, 1332, 1454, 1648, 1691, 2327, 3137, 3144, 3156, 3164, 3229
(C_1)	E(B3LYP+ZPE) = -248.222149	B	1253.59640	C	-2.022480	0.025561	0.000622	
	E(CCSD(T)/CC-VDZ) = -247.55440575	C	1320.58934	C	-0.712910	0.576179	0.000282	
	E(CCSD(T)/CC-VTZ) = -247.79172558			H	-0.650036	1.660002	-0.000049	
	E(CCSD(T)/CC-VQZ) = -247.86142996			C	0.402399	-0.179476	0.000315	
	E(CCSD(T)/CBS) = -247.89042			H	0.306225	-1.261790	0.000890	
				C	1.743935	0.366771	-0.000225	
				H	1.833117	1.450381	-0.000666	

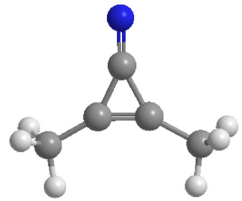
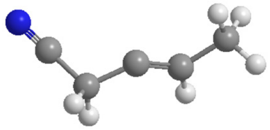
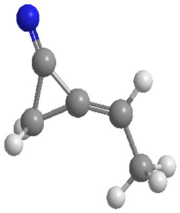
				C	2.848243	-0.389333	-0.000153	
				H	3.837548	0.051362	-0.000551	
				H	2.793085	-1.473049	0.000262	
1-cyano-1,2-butadiene (C$_1$) 	ZPE(B3LYP/6-311G**) = 0.083206	A	137.83879	C	2.608238	-0.552194	-0.289338	101, 151, 192, 235, 372, 492, 549, 621, 755, 878, 894, 979, 1060, 1090, 1153, 1298, 1409, 1435, 1485, 1500, 2049, 2339, 3029, 3081, 3111, 3129, 3134
	E(B3LYP+ZPE) = -248.201843	B	1156.60713	H	2.212089	-0.863167	-1.255950	
	E(CCSD(T)/CC-VDZ) = -247.52978988	C	1220.43463	H	2.919540	-1.443525	0.263332	
	E(CCSD(T)/CC-VTZ) = -247.76816959			H	3.501253	0.057609	-0.455898	
	E(CCSD(T)/CC-VQZ) = -247.83787017			C	1.586155	0.222144	0.504648	
	E(CCSD(T)/CBS) = -247.86667			H	1.886152	0.575995	1.490501	
				C	0.378631	0.494077	0.109836	
				C	-0.838185	0.777939	-0.296646	
				H	-1.039838	1.694501	-0.845643	
				C	-1.956278	-0.075205	-0.050572	
				N	-2.878652	-0.745998	0.133727	
1-cyano-1-butyne (C$_1$) 	ZPE(B3LYP/6-311G**) = 0.084281	A	82.06122	C	2.377717	1.299234	0.000000	100, 131, 228, 245, 373, 490, 565, 576, 670, 787, 954, 1076, 1104, 1173, 1285, 1348, 1415, 1470, 1497, 1506, 2257, 2395, 3023, 3043, 3051, 3114, 3119
	E(B3LYP+ZPE) = -248.200855	B	1345.63622	H	2.629713	0.711407	0.884341	
	E(CCSD(T)/CC-VDZ) = -247.53034501	C	1405.36695	H	2.990563	2.202978	0.000000	
	E(CCSD(T)/CC-VTZ) = -247.76985572			H	2.629713	0.711407	-0.884341	
	E(CCSD(T)/CC-VQZ) = -247.83930102			C	0.884479	1.679589	0.000000	
	E(CCSD(T)/CBS) = -247.86766			H	0.653705	2.294804	0.876981	
				H	0.653705	2.294804	-0.876981	
				C	0.000000	0.524222	0.000000	
				C	-0.718514	-0.446757	0.000000	
				C	-1.536111	-1.542173	0.000000	
				N	-2.228974	-2.471442	0.000000	
2-cyano-1,3-butadiene (C$_1$) 	ZPE(B3LYP/6-311G**) = 0.083994	A	374.37622	N	-1.690595	-1.529757	0.000684	146, 162, 285, 311, 477, 512, 641, 732, 748, 777, 943, 951, 966, 1018, 1061, 1318, 1325, 1420, 1461, 1643, 1693, 2342, 3143, 3154, 3156, 3233, 3250
	E(B3LYP+ZPE) = -248.217116	B	498.46031	C	-1.022919	-0.587967	-0.000905	
	E(CCSD(T)/CC-VDZ) = -247.55242773	C	872.83638	C	-0.165908	0.566895	-0.000491	
	E(CCSD(T)/CC-VTZ) = -247.79006761			C	-0.716406	1.793109	0.000167	
	E(CCSD(T)/CC-VQZ) = -247.85975661			H	-1.788618	1.936159	-0.000121	
	E(CCSD(T)/CBS) = -247.88867			H	-0.088940	2.676421	0.001303	
				C	1.285303	0.341398	0.000105	
				H	1.884450	1.247398	0.000481	
				C	1.879560	-0.853076	0.000043	
				H	1.310376	-1.776158	-0.000226	
				H	2.959120	-0.937670	0.000260	
3-cyano-1,2-butadiene	ZPE(B3LYP/6-311G**) = 0.082797	A	323.04248	C	2.326780	-0.690411	-0.000046	138, 152, 209, 229, 370, 503, 541, 618, 663, 702, 893, 994, 1003, 1061, 1183, 1291, 1409, 1459,
	E(B3LYP+ZPE) = -248.201441	B	666.81430	H	2.847488	-0.908330	-0.928069	
	E(CCSD(T)/CC-VDZ) = -247.53042300	C	966.22810	H	2.847965	-0.908206	0.927715	
	E(CCSD(T)/CC-VTZ) = -247.76881075							

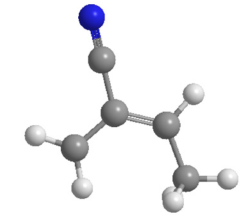
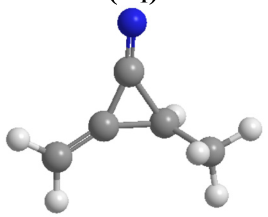
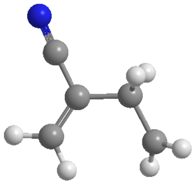
(C_1)	E(CCSD(T)/CC-VQZ) = -247.83852772			C	1.125028	-0.198926	0.000100	1481, 1498, 2047, 2332, 3036,
	E(CCSD(T)/CBS) = -247.86734			C	-0.085274	0.313871	0.000050	3094, 3115, 3133, 3189
				C	-0.365476	1.805519	-0.000054	
				H	-0.946573	2.084194	-0.883005	
				H	-0.945118	2.084471	0.883742	
				H	0.569513	2.364909	-0.000899	
				C	-1.216354	-0.567341	0.000145	
				N	-2.154501	-1.241902	-0.000094	
3-cyano-1-butyne	ZPE(B3LYP/6-311G**) = 0.083353	A	326.57074	C	-0.182292	1.737995	-0.225694	136, 201, 215, 238, 366, 482, 572,
(C_1)	E(B3LYP+ZPE) = -248.184417	B	642.90892	H	-1.122054	2.208971	0.066498	585, 687, 702, 788, 926, 1028,
	E(CCSD(T)/CC-VDZ) = -247.52044520	C	910.29751	H	0.648781	2.367921	0.093638	1078, 1140, 1301, 1332, 1412,
	E(CCSD(T)/CC-VTZ) = -247.76000324			H	-0.155493	1.643708	-1.311516	1494, 1500, 2233, 2361, 3019,
	E(CCSD(T)/CC-VQZ) = -247.82996282			C	-0.054832	0.344781	0.439434	3051, 3129, 3135, 3476
				H	-0.098103	0.476783	1.527840	
				C	1.215598	-0.310370	0.110418	
				C	2.268932	-0.817334	-0.158301	
				H	3.196926	-1.276445	-0.397906	
				C	-1.197593	-0.511072	0.077641	
				N	-2.109847	-1.154991	-0.205648	
1-cyano-prop-1-yne	ZPE(B3LYP/6-311G**) = 0.055432	A	11.29792	C	0.000000	0.000000	-2.468335	149, 149, 361, 361, 567, 567, 674,
(C_{3v})	E(B3LYP+ZPE) = -208.905399	B	869.21136	H	0.000000	1.022933	-2.855041	1048, 1048, 1182, 1414, 1469,
	E(CCSD(T)/CC-VDZ) = -208.33226649	C	869.21136	H	0.885886	-0.511466	-2.855041	1469, 2263, 2400, 3029, 3092,
	E(CCSD(T)/CC-VTZ) = -208.53035466			H	-0.885886	-0.511466	-2.855041	3092
	E(CCSD(T)/CC-VQZ) = -208.58832442			C	0.000000	0.000000	-1.017732	
	E(CCSD(T)/CBS) = -208.61231			C	0.000000	0.000000	0.189213	
				C	0.000000	0.000000	1.556422	
				N	0.000000	0.000000	2.715387	
1-cyano-prop-3-yne	ZPE(B3LYP/6-311G**) = 0.055113	A	89.37575	C	-1.258536	-0.000033	0.000003	141, 309, 355, 369, 578, 685, 706,
(C_1)	E(B3LYP+ZPE) = -208.887101	B	624.46795	C	-0.063647	0.852080	0.000003	902, 935, 994, 1247, 1343, 1452,
	E(CCSD(T)/CC-VDZ) = -208.32003860	C	702.73692	H	-0.107917	1.505760	-0.878348	2242, 2371, 3028, 3057, 3476
	E(CCSD(T)/CC-VTZ) = -208.51823167			H	-0.107902	1.505737	0.878373	
	E(CCSD(T)/CC-VQZ) = -208.57670202			C	1.187641	0.094444	-0.000012	
	E(CCSD(T)/CBS) = -208.60117			C	2.222240	-0.510742	-0.000002	
				H	3.136038	-1.053297	0.000034	
				N	-2.206630	-0.653242	-0.000001	
cyanoallene	ZPE(B3LYP/6-311G**) = 0.054678	A	67.54524	C	-2.234011	-0.398838	0.000038	145, 316, 379, 383, 615, 654, 875,
(C_1)	E(B3LYP+ZPE) = -208.900741	B	674.05016	H	-2.738854	-0.646258	0.928931	892, 951, 997, 1136, 1348, 1459,
	E(CCSD(T)/CC-VDZ) = -208.32756605	C	729.17480	H	-2.738926	-0.646363	-0.928788	2048, 2342, 3122, 3142, 3197

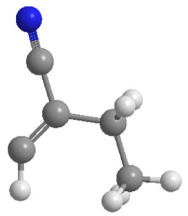
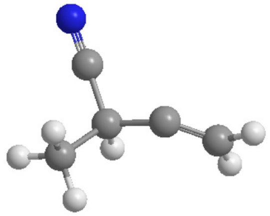
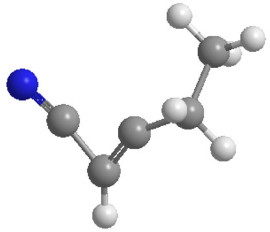
	E(CCSD(T)/CC-VTZ) = -208.52450404 E(CCSD(T)/CC-VQZ) = -208.58257862 E(CCSD(T)/CBS) = -208.60687			C	-1.066256	0.164538	-0.000043	
				C	0.109015	0.749450	-0.000126	
				H	0.182155	1.833829	0.000477	
				C	1.336422	0.022399	-0.000028	
				N	2.346372	-0.538072	0.000047	
cyanoacetylene **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.027214 E(B3LYP+ZPE) = -169.593283 E(CCSD(T)/CC-VDZ) = -169.12226083 E(CCSD(T)/CC-VTZ) = -169.27862615 E(CCSD(T)/CC-VQZ) = -169.32493353 E(CCSD(T)/CBS) = -169.34442	A	0.00000	N	0.000000	0.000000	1.895560	242.7358, 242.7358, 561.7284, 561.7284, 706.9050, 706.9050, 904.7721, 2172.1912, 2375.9517, 3469.9009
		B	393.99863	C	0.000000	0.000000	0.737693	
		C	393.99863	C	0.000000	0.000000	-0.631447	
				C	0.000000	0.000000	-1.834684	
				H	0.000000	0.000000	-2.898295	
INT A1 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.094101 E(B3LYP+ZPE) = -248.758956 E(CCSD(T)/CC-VTZ) = -248.33401841	A	198.63435	C	1.838411	-0.072911	-0.086250	49, 116, 208, 231, 348, 412, 523, 647, 789, 799, 827, 962, 1023, 1082, 1101, 1271, 1291, 1334, 1414, 1453, 1499, 1506, 1709, 2325, 2963, 3031, 3041, 3111, 3113, 3131
		B	1002.06419	C	0.901076	1.008978	-0.135946	
		C	1112.56991	H	1.295411	1.978300	-0.431241	
				C	-0.376351	0.848006	0.159979	
				C	-1.328094	-0.186801	0.577310	
				H	-1.746907	0.093265	1.551319	
				H	-0.775997	-1.127041	0.735195	
				C	-2.470181	-0.409166	-0.431906	
				H	-2.077854	-0.723355	-1.401082	
				H	-3.145356	-1.186185	-0.067521	
				H	-3.047361	0.506155	-0.577473	
				N	2.586986	-0.952825	-0.044045	
INT A2 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.093236 E(B3LYP+ZPE) = -248.719124 E(CCSD(T)/CC-VTZ) = -248.29020659	A	249.87831	C	-1.339295	-0.215837	0.014499	59, 141, 196, 275, 400, 480, 576, 624, 765, 801, 838, 914, 1011, 1032, 1087, 112, 1287, 1339, 1417, 1474, 1500, 1507, 1643, 1841, 3024, 3041, 3061, 3110, 3115 3226
		B	726.04415	C	-1.124571	1.195292	-0.298707	
		C	904.99139	C	-0.068577	0.526215	0.109424	
				C	1.372172	0.446540	0.442616	
				C	2.092424	-0.667823	-0.335032	
				H	-1.558112	2.127019	-0.631309	
				H	1.838233	1.418900	0.254656	
				H	1.453827	0.250870	1.517956	
				H	3.140366	-0.719440	-0.032756	
				H	1.630234	-1.638009	-0.142549	
				H	2.056392	-0.482167	-1.410660	
				N	-2.021979	-1.237642	0.121123	
INT A3	ZPE(B3LYP/6-311G**) = 0.092211 E(B3LYP+ZPE) = -248.770108	A	101.08164	C	2.673753	-0.604980	-0.261553	68, 107, 135, 182, 358, 385, 500,

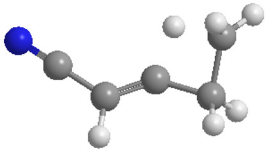
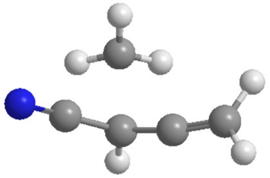
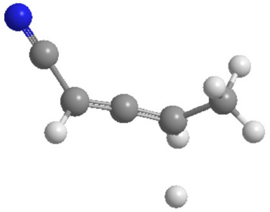
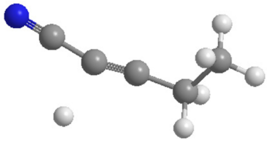
(C$_1$)	E(CCSD(T)/CC-VTZ) = -248.34481641	B	1255.43038	H	3.670325	-0.711258	0.146029	524, 582, 781, 849, 982, 995,
		C	1289.06372	H	2.373404	-1.260021	-1.069892	1034, 1070, 1102, 1210, 1311,
				C	1.760519	0.486729	0.198438	1326, 1339, 1459, 1460, 1687,
				H	2.131413	0.902681	1.142768	2335, 2958, 3033, 3143, 3152,
				H	1.756518	1.319216	-0.522784	3159, 3252
				C	0.348752	0.007981	0.397805	
				H	0.201319	-0.774292	1.137340	
				C	-0.706561	0.465501	-0.287149	
				H	-0.591161	1.241666	-1.038037	
				C	-2.032538	-0.016231	-0.085900	
				N	-3.115053	-0.393141	0.062104	
INT B1	ZPE(B3LYP/6-311G**) = 0.093665	A	210.86924	C	-1.576046	-0.092794	-0.000100	78, 167, 241, 281, 302, 425, 569,
(C$_1$)	E(B3LYP+ZPE) = -248.748475	B	806.89759	C	-0.203286	0.336545	-0.000772	569, 710, 747, 796, 817, 1004,
	E(CCSD(T)/CC-VTZ) = -248.32717828	C	995.46347	C	0.064892	1.626178	0.000049	1075, 1092, 1137, 1289, 1351,
				H	0.929730	2.270138	0.000602	1417, 1474, 1500, 1506, 1654,
				C	0.835234	-0.788669	-0.000277	2334, 3026, 3034, 3054, 3099,
				H	0.636021	-1.417089	0.874632	3104, 3262
				H	0.636755	-1.417087	-0.875348	
				C	2.287648	-0.319510	0.000349	
				H	2.514249	0.280126	0.885652	
				H	2.958862	-1.180873	0.000714	
				H	2.515046	0.279995	-0.884837	
				N	-2.663045	-0.483673	0.000441	
INT B2	ZPE(B3LYP/6-311G**) = 0.092266	A	226.88408	C	-2.323369	-0.368885	-0.095216	80, 133, 173, 293, 301, 444, 529,
(C$_1$)	E(B3LYP+ZPE) = -248.767348	B	773.60201	H	-2.593871	0.278015	-0.920953	545, 592, 755, 772, 859, 934, 968,
	E(CCSD(T)/CC-VTZ) = -248.34425165	C	979.34371	H	-3.119928	-0.802331	0.494113	1051, 1099, 1213, 1254, 1360,
				C	-0.916467	-0.816666	0.082374	1431, 1457, 1466, 1681, 2332,
				H	-0.800149	-1.361033	1.026376	2942, 3038, 3145, 3155, 3246,
				H	-0.650918	-1.547883	-0.699831	3251
				C	0.134611	0.286663	0.036088	
				C	1.494191	-0.169994	-0.018319	
				C	-0.121691	1.598485	0.057555	
				H	0.676535	2.328942	0.028409	
				H	-1.140114	1.961977	0.112447	
				N	2.574971	-0.576472	-0.059351	
INT B3	ZPE(B3LYP/6-311G**) = 0.092833	A	221.62664	C	0.065469	1.607618	0.000260	27, 157, 175, 283, 350, 475, 541,
(C$_1$)	E(B3LYP+ZPE) = -248.794938	B	789.04728	H	-0.760699	2.304419	-0.000069	586, 611, 720, 801, 804, 946,
	E(CCSD(T)/CC-VTZ) = -248.36846294	C	999.53194	H	1.069752	2.008847	0.001758	1016, 1093, 1103, 1258, 1323,
				C	-0.152663	0.237632	-0.000794	1405, 1463, 1481, 1486, 1528,

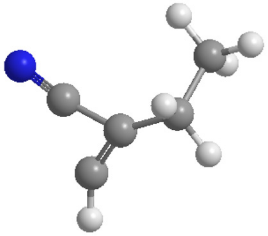
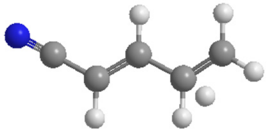
				**C**	**-1.518333**	**-0.225584**	**-0.000222**	**2342, 3002, 3041, 3115, 3166, 3187, 3266**
				C	**0.849124**	**-0.739937**	**-0.001320**	
				H	**0.538388**	**-1.777673**	**0.004004**	
				C	**2.310503**	**-0.431604**	**-0.000387**	
				H	**2.610177**	**0.096151**	**0.913961**	
				H	**2.904024**	**-1.343633**	**-0.066562**	
				H	**2.589247**	**0.214143**	**-0.841498**	
				N	**-2.610784**	**-0.598714**	**0.000454**	
INT C1	**ZPE(B3LYP/6-311G**) = 0.093381**	**A**	**410.75541**	**C**	**1.307609**	**-1.565405**	**0.000013**	**125, 128, 160, 219, 241, 318, 425, 592, 612, 697, 940, 1029, 1043, 1061, 1112, 1186, 1395, 1407, 1451, 1465, 1482, 1489, 1733, 2315, 2980, 3033, 3056, 3077, 3090, 3128**
(C$_1$)	**E(B3LYP+ZPE) = -248.764663**	**B**	**565.40885**	**H**	**1.949570**	**-1.505150**	**0.883063**	
	**E(CCSD(T)/CC-VTZ) = -248.33916477**	**C**	**953.71494**	**H**	**0.797159**	**-2.528390**	**0.000002**	
				H	**1.949624**	**-1.505161**	**-0.882999**	
				C	**0.292890**	**-0.439873**	**-0.000026**	
				C	**0.802102**	**0.905831**	**-0.000010**	
				C	**-1.017858**	**-0.616224**	**-0.000018**	
				C	**-2.269456**	**0.143295**	**0.000011**	
				H	**-2.871659**	**-0.092763**	**-0.882897**	
				H	**-2.871500**	**-0.092579**	**0.883076**	
				H	**-2.070934**	**1.224873**	**-0.000121**	
				N	**1.203716**	**1.990489**	**0.000009**	
INT C2	**ZPE(B3LYP/6-311G**) = 0.092833**	**A**	**221.62664**	**C**	**0.065469**	**1.607618**	**0.000260**	**27, 157, 175, 283, 350, 475, 541, 586, 611, 720, 801, 804, 946, 1016, 1093, 1103, 1258, 1323, 1405, 1463, 1481, 1486, 1528, 2342, 3002, 3041, 3115, 3166, 3187, 3266**
(C$_1$)	**E(B3LYP+ZPE) = -248.794938**	**B**	**789.04728**	**H**	**-0.760699**	**2.304419**	**-0.000069**	
	**E(CCSD(T)/CC-VTZ) = -248.36846294**	**C**	**999.53194**	**H**	**1.069752**	**2.008847**	**0.001758**	
				C	**-0.152663**	**0.237632**	**-0.000794**	
				C	**-1.518333**	**-0.225584**	**-0.000222**	
				C	**0.849124**	**-0.739937**	**-0.001320**	
				H	**0.538388**	**-1.777673**	**0.004004**	
				C	**2.310503**	**-0.431604**	**-0.000387**	
				H	**2.610177**	**0.096151**	**0.913961**	
				H	**2.904024**	**-1.343633**	**-0.066562**	
				H	**2.589247**	**0.214143**	**-0.841498**	
				N	**-2.610784**	**-0.598714**	**0.000454**	
INT C3	**ZPE(B3LYP/6-311G**) = 0.092839**	**A**	**443.12308**	**C**	**1.950127**	**-0.992783**	**0.000007**	**116, 122, 171, 194, 212, 446, 532, 555, 652, 685, 875, 1034, 1050, 1082, 1114, 1174, 1401, 1405, 1473, 1474, 1479, 1480, 1650, 1921, 3030, 3030, 3089, 3089, 3106, 3107**
(C$_1$)	**E(B3LYP+ZPE) = -248.731673**	**B**	**490.46528**	**C**	**0.658714**	**-0.271789**	**-0.000013**	
	E(CCSD(T)/CC-VTZ) = -248.30051131	**C**	**911.29449**	**C**	**0.000491**	**1.039853**	**-0.000032**	
				C	**-0.659024**	**-0.271470**	**-0.000006**	
				C	**-1.950883**	**-0.991539**	**0.000008**	
				H	**2.536226**	**-0.713424**	**0.880026**	
				H	**1.803068**	**-2.074983**	**-0.000108**	

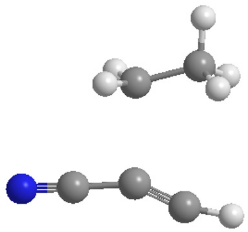
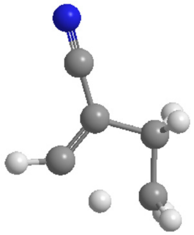
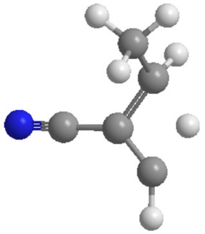
				**H**	**2.536349**	**-0.713244**	**-0.879871**	
				H	**-2.536841**	**-0.711772**	**-0.879978**	
				H	**-1.804602**	**-2.073859**	**0.000091**	
				H	**-2.536906**	**-0.711646**	**0.879910**	
				N	**0.000879**	**2.275041**	**0.000021**	
INT D1 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.093319**	**A**	**141.67623**	**C**	**2.800705**	**-0.505724**	**-0.115122**	**77, 110, 193, 214, 297, 374, 433, 565, 752, 868, 917, 935, 1061, 1062, 1096, 1211, 1291, 1331, 1407, 1437, 1485, 1488, 1768, 2366, 2965, 3006, 3024, 3037, 3072, 3119**
	E(B3LYP+ZPE) = -248.753861	**B**	**1213.92106**	**H**	**2.651096**	**-0.984580**	**-1.083189**	
	E(CCSD(T)/CC-VTZ) = -248.32952837	**C**	**1299.95622**	**H**	**3.636450**	**0.196407**	**-0.197975**	
				H	**3.093577**	**-1.271529**	**0.610114**	
				C	**1.554132**	**0.203822**	**0.341979**	
				H	**1.620522**	**0.716083**	**1.310661**	
				C	**0.415635**	**0.257523**	**-0.302274**	
				C	**-0.918090**	**0.876070**	**-0.117614**	
				H	**-0.917886**	**1.500921**	**0.789767**	
				H	**-1.153948**	**1.544722**	**-0.953806**	
				C	**-2.003755**	**-0.103213**	**0.001652**	
				N	**-2.860225**	**-0.867555**	**0.096101**	
INT D2 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.092303**	**A**	**165.17565**	**C**	**-1.418273**	**-0.153228**	**0.000017**	**135, 163, 165, 324, 333, 414, 421, 540, 803, 810, 913, 922, 1000, 1017, 1038, 1060, 1131, 1351, 1410, 1433, 1480, 1488, 1724, 1841, 3018, 3062, 3085, 3110, 3149, 3176**
	E(B3LYP+ZPE) = -248.728693	**B**	**858.01034**	**C**	**-0.718887**	**1.260503**	**0.000014**	
	E(CCSD(T)/CC-VTZ) = -248.29700877	**C**	**999.84204**	**H**	**-0.803734**	**1.830396**	**-0.921849**	
				H	**-0.803395**	**1.830377**	**0.921918**	
				C	**0.009905**	**-0.024223**	**-0.000158**	
				C	**1.173554**	**-0.660803**	**-0.000024**	
				H	**1.159138**	**-1.747710**	**0.000019**	
				C	**2.510331**	**0.013693**	**0.000041**	
				H	**3.093427**	**-0.283896**	**-0.878335**	
				H	**2.413656**	**1.100526**	**-0.000056**	
				H	**3.093262**	**-0.283751**	**0.878577**	
				N	**-2.498876**	**-0.723085**	**0.000056**	
INT E1 **(C$_1$)**	**ZPE(B3LYP/6-311G**) = 0.092833**	**A**	**221.62664**	**C**	**0.065469**	**1.607618**	**0.000260**	**27, 157, 175, 283, 350, 475, 541, 586, 611, 720, 801, 804, 946, 1016, 1093, 1103, 1258, 1323, 1405, 1463, 1481, 1486, 1528, 2342, 3002, 3041, 3115, 3166, 3187, 3266**
	E(B3LYP+ZPE) = -248.794938	**B**	**789.04728**	**H**	**-0.760699**	**2.304419**	**-0.000069**	
	E(CCSD(T)/CC-VTZ) = -248.36846294	**C**	**999.53194**	**H**	**1.069752**	**2.008847**	**0.001758**	
				C	**-0.152663**	**0.237632**	**-0.000794**	
				C	**-1.518333**	**-0.225584**	**-0.000222**	
				C	**0.849124**	**-0.739937**	**-0.001320**	
				H	**0.538388**	**-1.777673**	**0.004004**	
				C	**2.310503**	**-0.431604**	**-0.000387**	

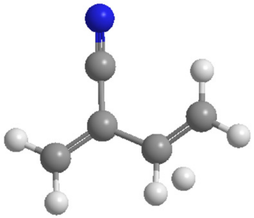
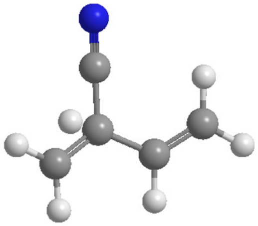
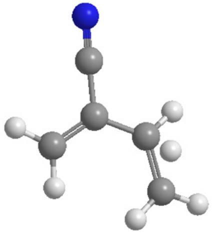
				H	2.610177	0.096151	0.913961	
				H	2.904024	-1.343633	-0.066562	
				H	2.589247	0.214143	-0.841498	
				N	-2.610784	-0.598714	0.000454	
INT E2 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.092030	A	431.84707	C	1.852925	-1.017986	-0.136421	146, 186, 199, 225, 288, 369, 422, 559, 727, 796, 826, 940, 956, 1029, 1082, 1096, 1142, 1317, 1410, 1449, 1487, 1495, 1718, 1847, 3024, 3087, 3101, 3116, 3134, 3225
	E(B3LYP+ZPE) = -248.726516	B	452.47169	H	2.745912	-0.539538	-0.520623	
	E(CCSD(T)/CC-VTZ) = -248.29570245	C	810.45997	H	1.886109	-2.087700	0.041754	
				C	0.755987	-0.320231	0.111279	
				C	0.147000	0.981739	0.051098	
				C	-0.653834	-0.310938	0.546632	
				H	-0.824817	-0.298184	1.622250	
				C	-1.767845	-0.873274	-0.308802	
				H	-1.901553	-1.940773	-0.104347	
				H	-2.711885	-0.365469	-0.099460	
				H	-1.541481	-0.757794	-1.370674	
				N	0.048902	2.176229	-0.164516	
INT E3 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.092260	A	226.89305	C	0.122025	1.598504	0.057269	80, 131, 173, 293, 300, 444, 529, 544, 592, 755, 772, 859, 934, 968, 1051, 1099, 1213, 1254, 1360, 1431, 1457, 1466, 1681, 2332, 2943, 3039, 3145, 3155, 3246, 3251
	E(B3LYP+ZPE) = -248.767354	B	773.65291	H	-0.675964	2.329208	0.028400	
	E(CCSD(T)/CC-VTZ) = -248.34425139	C	979.36641	H	1.140637	1.961586	0.111705	
				C	-0.134579	0.286755	0.035851	
				C	0.916290	-0.817063	0.081548	
				H	0.650971	-1.547002	-0.701841	
				H	0.799152	-1.362298	1.024872	
				C	2.323364	-0.369212	-0.094641	
				H	3.118702	-0.797170	0.500306	
				H	2.595444	0.273647	-0.923017	
				C	-1.494311	-0.169680	-0.018135	
				N	-2.575096	-0.576256	-0.058825	
INT E4 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.093665	A	210.86924	C	-1.576046	-0.092794	-0.000100	78, 167, 241, 281, 302, 425, 569, 569, 710, 747, 796, 817, 1004, 1075, 1092, 1137, 1289, 1351, 1417, 1474, 1500, 1506, 1654, 2334, 3026, 3034, 3054, 3099, 3104, 3262
	E(B3LYP+ZPE) = -248.748475	B	806.89759	C	-0.203286	0.336545	-0.000772	
	E(CCSD(T)/CC-VTZ) = -248.32717828	C	995.46347	C	0.064892	1.626178	0.000049	
				H	0.929730	2.270138	0.000602	
				C	0.835234	-0.788669	-0.000277	
				H	0.636021	-1.417089	0.874632	
				H	0.636755	-1.417087	-0.875348	

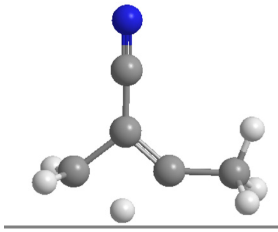
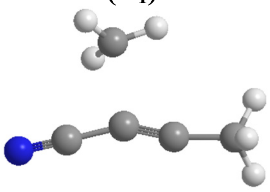
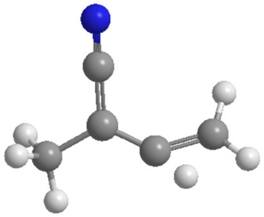
				C	2.287648	-0.319510	0.000349	
				H	2.514249	0.280126	0.885652	
				H	2.958862	-1.180873	0.000714	
				H	2.515046	0.279995	-0.884837	
				N	-2.663045	-0.483673	0.000441	
INT F1 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.092998	A	330.18975	C	2.322735	-0.670148	0.007415	86, 195, 210, 227, 294, 367, 509,
	E(B3LYP+ZPE) = -248.749985	B	686.51561	H	2.614489	-0.762794	1.057773	555, 611, 780, 905, 910, 959,
	E(CCSD(T)/CC-VTZ) = -248.32769894	C	957.80598	H	3.062939	-0.978646	-0.725307	1043, 1086, 1144, 1273, 1305,
				C	1.145687	-0.220336	-0.338973	1408, 1414, 1494, 1500, 1740,
				C	-0.074443	0.311729	0.320109	2358, 2949, 3040, 3049, 3126,
				H	0.100673	0.300813	1.408934	3129, 3158
				C	-0.389605	1.764882	-0.109456	
				H	-0.574208	1.812794	-1.183306	
				H	-1.272346	2.133217	0.415661	
				H	0.460796	2.405156	0.129264	
				C	-1.230156	-0.564611	0.073849	
				N	-2.148235	-1.234235	-0.117240	
TS A1-A2 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.091674	A	237.76558	C	-2.157480	-0.714386	-0.319976	639i, 58, 126, 179, 263, 396, 453,
	E(B3LYP+ZPE) = -248.714613	B	799.37252	H	-3.209843	-0.754918	-0.031506	529, 757, 799, 809, 922, 999,
	E(CCSD(T)/CC-VTZ) = -248.28301027	C	968.32334	H	-1.696268	-1.675634	-0.086795	1083, 1096, 1134, 1276, 1330,
				H	-2.104201	-0.564275	-1.400194	1415, 1463, 1498, 1507, 1784,
				C	-1.449625	0.427197	0.431114	1908, 2990, 3040, 3043, 3111,
				H	-1.929912	1.390214	0.209281	3118, 3155
				H	-1.543050	0.266317	1.511303	
				C	-0.015676	0.520783	0.111364	
				C	1.053413	1.155469	-0.291591	
				H	1.436415	2.110061	-0.636659	
				C	1.545790	-0.155507	-0.019915	
				N	2.169761	-1.167585	0.138371	
TS A1-A3 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.088549	A	146.77738	C	-1.932342	-0.003537	0.025794	1967i, 104, 160, 175, 362, 410,
	E(B3LYP+ZPE) = -248.698644	B	1073.27745	C	-0.702822	-0.707067	0.151150	523, 555, 653, 780, 810, 954, 965,
	E(CCSD(T)/CC-VTZ) = -248.26635126	C	1179.18318	C	0.461215	-0.255032	-0.330037	995, 1059, 1093, 1191, 1228,
				C	1.891989	-0.582170	-0.070654	1239, 1276, 1425, 1480, 1648,
				C	2.131078	0.915862	0.158486	1871, 2329, 3054, 3100, 3101,
				H	-0.751549	-1.677841	0.644384	3108, 3220

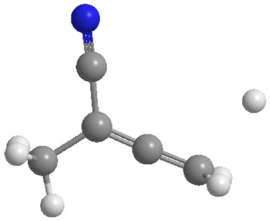
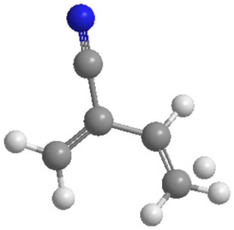
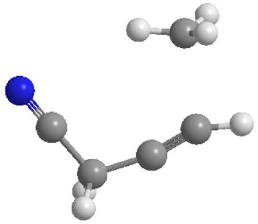
				H	2.092688	-1.238864	0.777990	
				H	2.416492	-0.958921	-0.951453	
				H	2.105523	1.277894	1.180722	
				H	2.784284	1.447315	-0.527798	
				H	0.855946	1.066766	-0.366079	
				N	-2.942585	0.553617	-0.052314	
TS A2-1 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.087586	A	394.75279	C	0.608891	2.016410	0.206269	497i, 105, 116, 135, 157, 327, 374, 404, 557, 563, 571, 606, 826, 897, 932, 952, 979, 1098, 1333, 1419, 1424, 1444, 1938, 2345, 3076, 3086, 3138, 3148, 3245, 3252
	E(B3LYP+ZPE) = -248.708389	B	724.48856	H	-0.199344	2.620070	0.273918	
	E(CCSD(T)/CC-VTZ) = -248.27130151	C	1023.74757	H	1.581832	2.134240	-1.252045	
				H	0.599007	1.817333	0.612710	
				C	0.031843	-0.016365	1.617998	
				H	0.162679	0.374000	0.072612	
				C	1.164429	-0.716252	0.211655	
				C	-1.211272	-0.340048	-0.276479	
				C	-2.407174	-0.453971	-0.037621	
				H	-3.049483	-1.298559	-0.955694	
				H	-2.817305	0.293738	-0.349579	
				N	2.086045	-1.268496		
TS A2-2 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.084692	A	150.51954	C	-2.025207	-0.062223	-0.047855	619i, 94, 141, 184, 221, 281, 391, 432, 496, 540, 621, 781, 874, 918, 974, 1056, 1090, 1141, 1293, 1409, 1421, 1488, 1497, 1992, 2340, 3038, 3099, 3113, 3119, 3134
	E(B3LYP+ZPE) = -248.699469	B	1190.25378	C	-0.869531	0.737467	-0.300871	
	E(CCSD(T)/CC-VTZ) = -248.26204271	C	1270.07565	H	-1.026711	1.654199	-0.867359	
				C	0.331268	0.413815	0.115280	
				C	1.577329	0.203396	0.473102	
				H	1.867091	0.516261	1.474810	
				H	2.372091	1.956187	-0.073940	
				C	2.533668	-0.704903	-0.270242	
				H	2.199732	-0.881291	-1.292605	
				H	3.533963	-0.269508	-0.296543	
				H	2.599070	-1.668347	0.244044	
				N	-2.975770	-0.690401	0.142158	
TS A2-3 **(C1)**	ZPE(B3LYP/6-311G**) = 0.085176	A	107.12840	C	2.141041	-0.100708	-0.008868	757i, 51, 105, 134, 239, 271, 331, 458, 502, 557, 565, 698, 785, 954, 1076, 1097, 1164, 1280, 1345, 1416, 1463, 1498, 1507, 2193, 2365, 3008, 3043, 3045, 3117, 3120
	E(B3LYP+ZPE) = -248.695775	B	1344.26806	C	0.819918	0.276340	0.075360	
	E(CCSD(T)/CC-VTZ) = -248.26042269	C	1402.93531	H	1.127055	1.599691	1.451431	
				C	-0.380224	0.338676	-0.136058	
				C	-1.814623	0.541366	-0.232683	
				H	-2.058421	0.841475	-1.258112	
				H	-2.082862	1.391110	0.408724	
				C	-2.635582	-0.700808	0.164911	

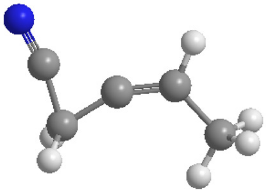
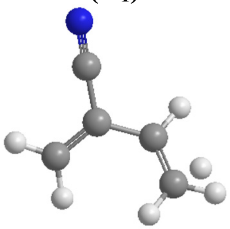
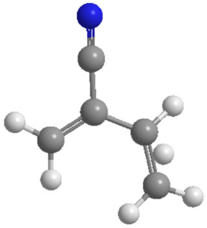
				H	**-2.425728**	**-0.992318**	**1.195372**	
				H	**-3.701698**	**-0.482141**	**0.077994**	
				H	**-2.402827**	**-1.546359**	**-0.484575**	
				N	**3.251614**	**-0.420094**	**-0.080972**	
TS A2-B1	**ZPE(B3LYP/6-311G**) = 0.091477**	**A**	**269.24124**	**C**	**-2.053451**	**-0.670134**	**-0.356081**	**692i, 60, 155, 199, 276, 381, 458, 577, 691, 722, 763, 800, 958, 1040, 1086, 1172, 1292, 1340, 1417, 1476, 1500, 1507, 1739, 1938, 3031, 3039, 3074, 3108, 3111, 3240**
(C_1)	**E(B3LYP+ZPE) = -248.712487**	**B**	**702.46352**	**H**	**-3.094152**	**-0.758850**	**-0.037333**	
	**E(CCSD(T)/CC-VTZ) = -248.28258762**	**C**	**895.98474**	**H**	**-1.576418**	**-1.645207**	**-0.235217**	
				H	**-2.042285**	**-0.416952**	**-1.418580**	
				C	**-1.333266**	**0.402092**	**0.475129**	
				H	**-1.807506**	**1.379408**	**0.350265**	
				H	**-1.391301**	**0.145013**	**1.538342**	
				C	**0.109569**	**0.533011**	**0.112173**	
				C	**1.054072**	**1.331448**	**-0.306014**	
				H	**1.386843**	**2.309454**	**-0.619225**	
				C	**1.248119**	**-0.338879**	**0.054549**	
				N	**2.053509**	**-1.222584**	**0.077603**	
TS A3-1	**ZPE(B3LYP/6-311G**) = 0.085496**	**A**	**84.89742**	**C**	**2.800344**	**-0.462072**	**-0.106733**	**764i, 135, 143, 169, 319, 365, 416, 470, 504, 578, 646, 868, 917, 955, 985, 1024, 1046, 1182, 1286, 1296, 1327, 1445, 1593, 1676, 2329, 3143, 3149, 3159, 3167, 3238**
(C_1)	**E(B3LYP+ZPE) = -248.718000**	**B**	**1281.09380**	**H**	**3.788820**	**-0.058990**	**-0.286282**	
	**E(CCSD(T)/CC-VTZ) = -248.28365388**	**C**	**1338.10594**	**H**	**2.723983**	**-1.529183**	**0.069978**	
				C	**1.710318**	**0.341724**	**-0.048815**	
				H	**1.814270**	**1.027372**	**1.766154**	
				H	**1.807458**	**1.389641**	**-0.317912**	
				C	**0.354842**	**-0.185291**	**0.063779**	
				H	**0.254518**	**-1.242401**	**0.292315**	
				C	**-0.752694**	**0.555216**	**-0.117294**	
				H	**-0.684119**	**1.615384**	**-0.340929**	
				C	**-2.065395**	**0.017694**	**-0.029626**	
				N	**-3.141346**	**-0.400778**	**0.035545**	
TS B1-1	**ZPE(B3LYP/6-311G**) = 0.088325**	**A**	**307.28129**	**C**	**1.620802**	**-0.110275**	**-0.000082**	**462i, 39, 125, 160, 180, 258, 289, 474, 515, 524, 583, 713, 810, 829, 893, 1017, 1074, 1214, 1398, 1470, 1481, 1490, 1976, 2339, 2988, 3054, 3093, 3123, 3218, 3442**
(C_1)	**E(B3LYP+ZPE) = -248.703366**	**B**	**822.18543**	**C**	**0.511154**	**0.718182**	**0.000163**	
	E(CCSD(T)/CC-VTZ) = -248.26986802	**C**	**1106.05580**	**C**	**0.009764**	**1.841050**	**0.000159**	
				H	**-0.655653**	**2.672063**	**-0.000007**	
				C	**-1.023109**	**-0.992564**	**0.000724**	
				H	**-0.665501**	**-1.452664**	**-0.914256**	
				H	**-0.666583**	**-1.451238**	**0.916846**	
				C	**-2.368449**	**-0.352078**	**-0.000544**	
				H	**-2.521795**	**0.266667**	**-0.888756**	
				H	**-3.160000**	**-1.115301**	**-0.000460**	

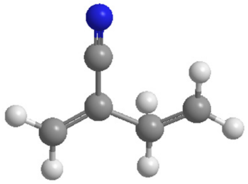
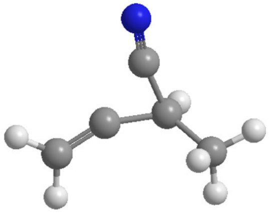
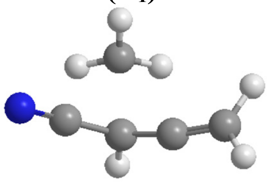
				H	-2.522862	0.267946	0.886591	
				N	2.527346	-0.830481	-0.000353	
TS B1-B2 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.088958	A	185.69365	C	-1.569340	-0.077402	0.000398	1730i, 111, 175, 271, 456, 516, 554, 565, 635, 782, 842, 853, 942, 990, 1083, 1088, 1182, 1227, 1260, 1305, 1455, 1491, 1631, 1695, 2326, 3042, 3073, 3099, 3179, 3216
	E(B3LYP+ZPE) = -248.725746	B	797.44459	C	-0.169250	0.195177	0.000487	
	E(CCSD(T)/CC-VTZ) = -248.29697415	C	960.22183	C	0.356645	1.418003	-0.000541	
				H	-0.085211	2.405769	-0.000763	
				C	0.868508	-0.925893	-0.000600	
				H	0.740621	-1.566371	0.876808	
				H	0.740607	-1.563528	-0.880078	
				C	2.209636	-0.192321	0.000499	
				H	2.804451	-0.268353	0.907865	
				H	2.809077	-0.272851	-0.903405	
				H	1.706609	1.022499	-0.002083	
				N	-2.699050	-0.323222	0.000028	
TS B1-B3 **(C$_1$)** 	ZPE(B3LYP/6-311G**) = 0.087966	A	309.79171	C	0.029808	1.745658	-0.219490	2121i, 125, 177, 224, 236, 370, 543, 566, 615, 741, 767, 830, 946, 1016, 1062, 1085, 1151, 1213, 1330, 1406, 1484, 1487, 1645, 1842, 2327, 3004, 3069, 3090, 3109, 3149
	E(B3LYP+ZPE) = -248.695248	B	690.59751	C	-0.238334	0.478736	0.081041	
	E(CCSD(T)/CC-VTZ) = -248.26477467	C	928.49478	C	-1.439053	-0.276932	0.014791	
				C	1.135801	0.030760	0.525945	
				C	1.911279	-0.953497	-0.309564	
				H	-0.529515	2.602656	-0.586601	
				H	1.260436	-0.044476	1.607226	
				H	2.952601	-1.010312	0.014500	
				H	1.478061	-1.958264	-0.219852	
				H	1.888298	-0.680348	-1.367777	
				H	1.348593	1.378736	0.204888	
				N	-2.399354	-0.919478	-0.029818	
TS B2-1 **(C$_1$)**	ZPE(B3LYP/6-311G**) = 0.085413	A	391.30673	C	-0.678955	1.808546	-0.101929	739i, 116, 163, 268, 312, 372, 426, 480, 530, 642, 729, 746, 756, 929, 940, 957, 1025, 1059, 1302, 1312, 1411, 1457, 1599, 1666, 2341, 3148, 3154, 3162, 3241, 3250
	E(B3LYP+ZPE) = -248.713376	B	522.21969	H	-1.744195	1.993550	-0.135325	
	E(CCSD(T)/CC-VTZ) = -248.28236518	C	883.11666	C	-0.181946	0.564422	-0.023646	
				C	-1.081019	-0.554966	0.022022	
				C	1.267611	0.277730	0.001326	
				H	1.517082	0.555206	1.916453	

				H	1.903705	1.153614	-0.074688	
				C	1.801676	-0.952870	-0.160097	
				H	2.873851	-1.086080	-0.225658	
				H	1.184544	-1.843543	-0.179601	
				H	-0.016145	2.665137	-0.130848	
				N	-1.783292	-1.470723	0.057659	
TS B3-1	ZPE(B3LYP/6-311G**) = 0.085351	A	391.79640	C	1.884687	-0.865815	-0.086599	945i, 142, 159, 282, 318, 397, 469, 478, 521, 637, 672, 732, 764, 898, 935, 965, 1017, 1058, 1302, 1322, 1397, 1454, 1557, 1689, 2347, 3144, 3156, 3160, 3233, 3257
(C_1)	E(B3LYP+ZPE) = -248.708704	B	516.87649	H	1.313742	-1.787271	-0.116432	
	E(CCSD(T)/CC-VTZ) = -248.27805418	C	876.44949	H	2.962624	-0.948989	-0.146746	
				C	1.297839	0.324824	0.019035	
				H	1.895139	1.231048	0.050221	
				C	-0.163446	0.555950	0.078909	
				H	-0.205196	0.517046	1.952132	
				C	-0.708038	1.784859	-0.163065	
				H	-1.777696	1.924537	-0.236633	
				H	-0.072257	2.658948	-0.227682	
				C	-1.023372	-0.602612	0.013703	
				N	-1.691768	-1.539794	-0.063824	
TS B2-B3	ZPE(B3LYP/6-311G**) = 0.088820	A	229.88853	C	-0.048048	1.635612	-0.023709	1782i, 131, 174, 283, 309, 437, 470, 584, 626, 659, 679, 781, 833, 873, 936, 1070, 1152, 1229, 1264, 1406, 1437, 1476, 1569, 2206, 2332, 3164, 3175, 3181, 3258, 3291
(C_1)	E(B3LYP+ZPE) = -248.720768	B	770.68918	H	0.785331	2.320525	0.044172	
	E(CCSD(T)/CC-VTZ) = -248.28896425	C	990.54939	H	-1.041301	2.058010	-0.095176	
				C	0.150195	0.288872	-0.038242	
				C	-0.895007	-0.715980	-0.067959	
				H	-1.508757	-0.867918	1.008460	
				H	-0.619544	-1.710724	-0.397728	
				C	-2.335754	-0.420822	-0.003229	
				H	-3.043840	-1.195812	-0.255223	
				H	-2.690617	0.569349	0.238620	
				C	1.490808	-0.223141	0.004914	
				N	2.563652	-0.651525	0.032318	
TS B3-C1	ZPE(B3LYP/6-311G**) = 0.087735	A	368.53942	C	0.174818	1.910161	0.000001	2174i, 125, 133, 202, 285, 307, 477, 513, 604, 631, 703, 967, 1016, 1038, 1051, 1072, 1120, 1220, 1392, 1428, 1458, 1470, 1725, 1836, 2324, 3008, 3075, 3077, 3081, 3174
(C_1)	E(B3LYP+ZPE) = -248.702111	B	632.12918	H	0.440431	2.425346	-0.921464	
	E(CCSD(T)/CC-VTZ) = -248.27003994	C	977.26858	H	-1.202681	1.564569	0.000000	
				H	0.440432	2.425343	0.921467	
				C	0.204908	0.404272	-0.000002	
				C	1.320755	-0.473425	-0.000001	
				C	-1.103139	0.146536	-0.000001	

				C	-2.018364	-1.016379	0.000000	
				H	-2.666684	-0.999305	0.881138	
				H	-2.666763	-0.999248	-0.881078	
				H	-1.452400	-1.955176	-0.000054	
				N	2.233400	-1.184075	0.000001	
TS C1-1 (C_1) 	ZPE(B3LYP/6-311G**) = 0.087666	A	330.63396	C	-0.559649	2.016586	0.000001	488i, 41, 68, 111, 144, 155, 340, 359, 491, 507, 527, 573, 671, 874, 1025, 1047, 1163, 1409, 1416, 1416, 1464, 1466, 2112, 2342, 3005, 3064, 3084, 3091, 3254, 3258
	E(B3LYP+ZPE) = -248.712744	B	864.02248	H	-1.119620	2.058856	0.925318	
	E(CCSD(T)/CC-VTZ) = -248.27673779	C	1171.08340	H	0.431221	2.452159	-0.000845	
				H	-1.121048	2.058504	-0.924466	
				C	-0.070364	-0.226032	-0.000011	
				C	-1.382681	-0.663355	-0.000003	
				C	1.139720	-0.452039	0.000002	
				C	2.588084	-0.400672	0.000003	
				H	2.945707	0.636318	0.000132	
				H	2.995972	-0.899253	0.884266	
				H	2.995955	-0.899030	-0.884396	
				N	-2.488406	-1.007783	0.000006	
TS C1-C2 (C_1) 	ZPE(B3LYP/6-311G**) = 0.088302	A	401.71946	C	-1.009808	1.710237	0.070238	1804i, 130, 134, 215, 247, 289, 416, 506, 586, 635, 715, 906, 982, 1035, 1054, 1141, 1192, 1238, 1408, 1460, 1478, 1489, 1599, 2164, 2286, 3023, 3054, 3073, 3120, 3185
	E(B3LYP+ZPE) = -248.700683	B	560.40321	H	-1.534146	1.760528	1.029431	
	E(CCSD(T)/CC-VTZ) = -248.26631244	C	935.62216	H	-0.344813	2.570324	-0.012782	
				H	-1.766101	1.777946	-0.718147	
				C	-0.217644	0.430033	-0.045825	
				C	-0.932399	-0.804394	-0.019209	
				C	1.118926	0.380817	-0.254822	
				C	2.186042	-0.471943	0.088263	
				H	3.079661	-0.476324	-0.527659	
				H	2.139453	0.828049	0.406202	
				H	2.095612	-1.247935	0.851075	
				N	-1.505767	-1.811585	-0.008571	
TS C1-2 (C_1)	ZPE(B3LYP/6-311G**) = 0.083991	A	356.12594	C	0.675028	1.803491	0.000004	489i, 121, 156, 204, 209, 218, 296, 377, 508, 567, 615, 700, 718, 910, 990, 1008, 1060, 1177, 1275, 1408, 1454, 1481, 1496, 2007, 2333, 3037, 3096, 3119, 3133, 3195
	E(B3LYP+ZPE) = -248.700887	B	676.10850	H	1.289859	1.993962	-0.883463	
	E(CCSD(T)/CC-VTZ) = -248.26432354	C	1008.62137	H	-0.168440	2.493133	-0.000056	
				H	1.289756	1.993988	0.883536	
				C	0.182328	0.367412	-0.000002	
				C	1.177127	-0.666671	-0.000001	
				C	-1.086919	0.031721	-0.000003	

				C	-2.339066	-0.348125	-0.000005	
				H	-2.896477	-0.439047	0.927182	
				H	-2.896472	-0.439059	-0.927193	
				H	-2.330797	-2.449088	0.000046	
				N	2.008799	-1.468694	-0.000002	
TS C2-1 **(C1)**	ZPE(B3LYP/6-311G**) = 0.084461	A	264.13148	C	-2.217177	-0.384870	-0.004707	206i, 78, 132, 178, 189, 292, 301,
	E(B3LYP+ZPE) = -248.713719	B	763.13711	H	-2.518051	0.477300	0.579670	454, 555, 592, 736, 759, 786, 942,
	E(CCSD(T)/CC-VTZ) = -248.28350499	C	970.25129	H	-2.387562	-1.529168	2.124084	956, 958, 1017, 1092, 1245, 1327,
				H	-2.997480	-1.076532	-0.296315	1432, 1455, 1642, 1673, 2338,
				C	-0.951446	-0.575057	-0.392020	3144, 3157, 3160, 3233, 3251
				H	-0.689104	-1.474159	-0.941312	
				C	0.168644	0.340637	-0.093485	
				C	0.058353	1.672443	0.040531	
				H	-0.894711	2.166524	-0.100559	
				H	0.915889	2.287880	0.278554	
				C	1.463168	-0.273104	0.031958	
				N	2.491680	-0.790305	0.123174	
TS D1-1 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.087413	A	377.50211	C	-1.598332	0.329196	0.000000	457i, 38, 53, 67, 189, 318,
	E(B3LYP+ZPE) = -248.698933	B	769.08016	C	-1.133113	-1.065836	-0.000002	358, 365, 461, 496, 573, 668, 731,
	E(CCSD(T)/CC-VTZ) = -248.26790034	C	1123.13850	H	-1.555159	-1.568586	0.877602	844, 897, 938, 974, 1248, 1333,
				H	-1.555153	-1.568581	-0.877612	1412, 1423, 1451, 2086, 2362,
				C	0.324858	-1.175484	0.000003	3025, 3053, 3089, 3249, 3262,
				C	1.528964	-0.984374	0.000001	3406
				H	2.555667	-1.271757	0.000001	
				C	2.146385	1.257050	-0.000001	
				H	2.707091	1.262812	-0.926422	
				H	1.177078	1.736664	-0.000042	
				H	2.707022	1.262830	0.926462	
				N	-1.949874	1.426186	0.000002	
TS D1-D2 **(C_1)**	ZPE(B3LYP/6-311G**) = 0.091427	A	155.13614	C	1.655216	-0.000842	0.000612	628i, 79, 125, 163, 306, 333, 395,
	E(B3LYP+ZPE) = -248.715074	B	942.36443	C	0.749357	1.162616	-0.000172	558, 766, 797, 873, 932, 1018,
	E(CCSD(T)/CC-VTZ) = -248.28410456	C	1074.46211	H	0.779431	1.769529	0.908055	1052, 1091, 1103, 1166, 1335,
				H	0.780184	1.769301	-0.908525	1401, 1433, 1481, 1489, 1777,
				C	-0.101570	-0.026302	-0.000313	2021, 3019, 3030, 3070, 3097,

				C	-1.254053	-0.652130	-0.000194	3103, 3119
				H	-1.255332	-1.741268	-0.000326	
				C	-2.605844	0.020936	0.000156	
				H	-3.181893	-0.279135	0.881679	
				H	-2.518949	1.108748	-0.001399	
				H	-3.183615	-0.281571	-0.879386	
				N	2.560220	-0.767324	-0.000090	
TS E1-1 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.084461	A	264.13148	C	-2.217177	-0.384870	-0.004707	206i, 78, 132, 178, 189, 292, 301, 454, 555, 592, 736, 759, 786, 942, 956, 958, 1017, 1092, 1245, 1327, 1432, 1455, 1642, 1673, 2338, 3144, 3157, 3160, 3233, 3251
	E(B3LYP+ZPE) = -248.713719	B	763.13711	H	-2.518051	0.477300	0.579670	
	E(CCSD(T)/CC-VTZ) = -248.28350499	C	970.25129	H	-2.387562	-1.529168	2.124084	
				H	-2.997480	-1.076532	-0.296315	
				C	-0.951446	-0.575057	-0.392020	
				H	-0.689104	-1.474159	-0.941312	
				C	0.168644	0.340637	-0.093485	
				C	0.058353	1.672443	0.040531	
				H	-0.894711	2.166524	-0.100559	
				H	0.915889	2.287880	0.278554	
				C	1.463168	-0.273104	0.031958	
				N	2.491680	-0.790305	0.123174	
TS E1-E3 **(C_1)** 	ZPE(B3LYP/6-311G**) = 0.088820	A	229.88853	C	-0.048048	1.635612	-0.023709	1782i, 131, 174, 283, 309, 437, 470, 584, 626, 659, 679, 781, 833, 873, 936, 1070, 1152, 1229, 1264, 1406, 1437, 1476, 1569, 2206, 2332, 3164, 3175, 3181, 3258, 3291
	E(B3LYP+ZPE) = -248.720768	B	770.68918	H	0.785331	2.320525	0.044172	
	E(CCSD(T)/CC-VTZ) = -248.28896425	C	990.54939	H	-1.041301	2.058010	-0.095176	
				C	0.150195	0.288872	-0.038242	
				C	-0.895007	-0.715980	-0.067959	
				H	-1.508757	-0.867918	1.008460	
				H	-0.619544	-1.710724	-0.397728	
				C	-2.335754	-0.420822	-0.003229	
				H	-3.043840	-1.195812	-0.255223	
				H	-2.690617	0.569349	0.238620	
				C	1.490808	-0.223141	0.004914	
				N	2.563652	-0.651525	0.032318	

TS E3-1 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.085413** **E(B3LYP+ZPE) = -248.713376** **E(CCSD(T)/CC-VTZ) = -248.28236518**	**A**	**391.30673**	**C**	**-0.678955**	**1.808546**	**-0.101929**	**739i, 116, 163, 268, 312, 372, 426, 480, 530, 642, 729, 746, 756, 929, 940, 957, 1025, 1059, 1302, 1312, 1411, 1457, 1599, 1666, 2341, 3148, 3154, 3162, 3241, 3250**
		B	**522.21969**	**H**	**-1.744195**	**1.993550**	**-0.135325**	
		C	**883.11666**	**C**	**-0.181946**	**0.564422**	**-0.023646**	
				C	**-1.081019**	**-0.554966**	**0.022022**	
				C	**1.267611**	**0.277730**	**0.001326**	
				H	**1.517082**	**0.555206**	**1.916453**	
				H	**1.903705**	**1.153614**	**-0.074688**	
				C	**1.801676**	**-0.952870**	**-0.160097**	
				H	**2.873851**	**-1.086080**	**-0.225658**	
				H	**1.184544**	**-1.843543**	**-0.179601**	
				H	**-0.016145**	**2.665137**	**-0.130848**	
				N	**-1.783292**	**-1.470723**	**0.057659**	
TS E2-F1 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.091046** **E(B3LYP+ZPE) = -248.714629** **E(CCSD(T)/CC-VTZ) = -248.28479123**	**A**	**423.77073**	**C**	**2.180072**	**0.013669**	**-0.136247**	**633i, 135, 183, 201, 213, 312, 397, 507, 628, 800, 819, 920, 1019, 1040, 1073, 1085, 1182, 1306, 1407, 1434, 1492, 1494, 1762, 2004, 3041, 3045, 3064, 3113, 3124, 3166**
		B	**486.61889**	**H**	**2.718660**	**0.884893**	**-0.496798**	
		C	**837.88943**	**H**	**2.760135**	**-0.901231**	**-0.001733**	
				C	**0.899919**	**0.057928**	**0.132708**	
				C	**-0.644262**	**0.886018**	**0.100826**	
				C	**-0.391414**	**-0.513056**	**0.515530**	
				H	**-0.518278**	**-0.641376**	**1.594849**	
				C	**-1.016876**	**-1.641268**	**-0.303875**	
				H	**-0.536055**	**-2.589277**	**-0.051831**	
				H	**-2.083860**	**-1.718882**	**-0.086420**	
				H	**-0.888947**	**-1.458440**	**-1.371679**	
				N	**-1.088040**	**1.943509**	**-0.205720**	
TS F1-1 **(C$_1$)** 	**ZPE(B3LYP/6-311G**) = 0.087586** **E(B3LYP+ZPE) = -248.708389** **E(CCSD(T)/CC-VTZ) = -248.27130151**	**A**	**394.75279**	**C**	**0.608891**	**2.016410**	**-0.188126**	**497i, 105, 116, 135, 157, 327, 374, 404, 557, 563, 571, 606, 826, 897, 932, 952, 979, 1098, 1333, 1419, 1424, 1444, 1938, 2345, 3076, 3086, 3138, 3148, 3245, 3252**
		B	**724.48856**	**H**	**-0.199344**	**2.620070**	**0.206269**	
		C	**1023.74757**	**H**	**1.581832**	**2.134240**	**0.273918**	
				H	**0.599007**	**1.817333**	**-1.252045**	
				C	**0.031843**	**-0.016365**	**0.612710**	
				H	**0.162679**	**0.374000**	**1.617998**	
				C	**1.164429**	**-0.716252**	**0.072612**	
				C	**-1.211272**	**-0.340048**	**0.211655**	
				C	**-2.407174**	**-0.453971**	**-0.276479**	
				H	**-3.049483**	**-1.298559**	**-0.037621**	
				H	**-2.817305**	**0.293738**	**-0.955694**	
				N	**2.086045**	**-1.268496**	**-0.349579**	

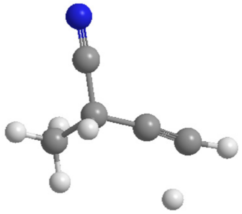
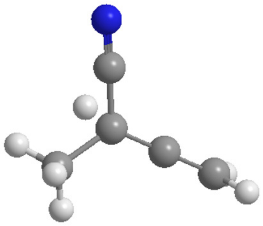
TS F1-2 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.084147** **E(B3LYP+ZPE) = -248.683799** **E(CCSD(T)/CC-VTZ) = -248.25463038**	**A** **B** **C**	**325.46342** **695.54032** **953.24801**	**C** **H** **H** **H** **C** **H** **C** **C** **C** **H** **H** **N**	**0.124276** **-0.739044** **1.036768** **0.060980** **0.132799** **0.210332** **1.319762** **-1.096271** **-2.165429** **-3.292081** **-3.014640** **2.263836**	**1.721868** **2.281918** **2.259193** **1.637244** **0.314809** **0.437541** **-0.448712** **-0.429461** **-0.917462** **0.617661** **-1.536189** **-1.020517**	**-0.182212** **0.178319** **0.080294** **-1.267136** **0.469069** **1.556673** **0.048408** **0.182125** **-0.094724** **-0.855634** **-0.260040** **-0.281212**	**537i, 43, 129, 186, 213, 232, 325, 370, 498, 572, 588, 680, 781, 790, 927, 1022, 1074, 1139, 1297, 1332, 1412, 1493, 1499, 2174, 2362, 3020, 3053, 3131, 3137, 3457**
TS F1-3 **(C_1)** 	**ZPE(B3LYP/6-311G**) = 0.084518** **E(B3LYP+ZPE) = -248.694713** **E(CCSD(T)/CC-VTZ) = -248.25873819**	**A** **B** **C**	**340.67289** **683.13708** **968.60677**	**C** **H** **H** **C** **C** **H** **C** **H** **H** **H** **C** **N**	**2.333387** **2.856334** **2.857683** **1.133104** **-0.085804** **-0.189861** **-0.365330** **-0.659248** **-1.175379** **0.528670** **-1.216389** **-2.144572**	**-0.696831** **-0.883184** **-0.945094** **-0.208347** **0.311631** **0.398074** **1.797977** **1.978119** **2.128472** **2.380143** **-0.578473** **-1.258896**	**-0.049716** **0.886865** **-0.968609** **-0.056313** **0.089953** **1.978678** **-0.115067** **-1.152508** **0.535348** **0.105991** **0.002238** **-0.087476**	**829i, 135, 172, 193, 224, 332, 443, 495, 498, 554, 606, 642, 713, 895, 985, 990, 1061, 1167, 1274, 1409, 1444, 1485, 1496, 1986, 2341, 3044, 3096, 3113, 3140, 3170**

Table A12. RRKM single-collision rate constants for all paths on the CN addition to 1-butyne and 2-butyne.

Channel	Barrier	0.0	1.0	2.0	3.0	4.0	5.0
INT B1 → INT B3	TS B1-B3	5.51E+06	1.13E+07	1.02E+07	1.35E+07	1.78E+07	2.30E+07
INT B3 → INT B1	TS B1-B3	1.04E+03	2.29E+03	2.21E+03	3.14E+03	4.41E+03	6.11E+03
INT B1 → INT B2	TS B1-B2	5.26E+10	5.73E+10	6.23E+10	6.76E+10	7.31E+10	7.89E+10
INT B2 → INT B1	TS B1-B2	4.94E+08	8.36E+08	6.28E+08	7.04E+08	7.87E+08	8.77E+08
INT B1 → INT A2	TS A2-B1	7.38E+08	2.64E+09	1.04E+09	1.22E+09	1.43E+09	1.66E+09
INT A2 → INT B1	TS A2-B1	2.74E+12	8.62E+12	3.00E+12	3.13E+12	3.26E+12	3.38E+12
INT B1 → cyanoacetylene + C_2H_5	TS B1-1	5.22E+08	2.09E+09	9.14E+08	1.19E+09	1.52E+09	1.93E+09
INT B3 → INT C1	TS B3-C1	6.96E+03	2.90E+04	1.32E+04	1.79E+04	2.40E+04	3.17E+04
INT C1 → INT B3	TS B3-C1	5.04E+06	6.68E+06	8.75E+06	1.13E+07	1.45E+07	1.84E+07
INT B2 → INT B3	TS B2-B3	2.72E+06	3.33E+06	4.04E+06	4.89E+06	5.87E+06	7.01E+06
INT B3 → INT B2	TS B2-B3	1.36E+08	2.40E+08	1.88E+08	2.19E+08	2.54E+08	2.94E+08
INT B2 → 2-cyano-1,3-butadiene + H	TS B1-1	3.20E+07	3.99E+07	4.94E+07	6.08E+07	7.44E+07	9.04E+07
INT C1 → INT 6	TS CTS	3.20E+12	9.67E+12	3.25E+12	3.28E+12	3.30E+12	3.33E+12
INT 6 → INT C1	TS CTS	8.89E+15	2.42E+16	7.32E+15	6.67E+15	6.10E+15	5.59E+15
INT C1 → 3-cyano-1,2-butadiene + H	TS C1-2	1.20E+07	1.68E+07	2.30E+07	3.12E+07	4.16E+07	5.50E+07
INT C1 → 1-cyano-prop-1-yne + CH_3	TS C1-1	1.87E+09	7.16E+09	3.02E+09	3.79E+09	4.71E+09	5.81E+09
INT B2 → 2-cyano-1,3-butadiene + H	TS B2-1	1.38E+08	2.50E+08	2.01E+08	2.41E+08	2.86E+08	3.39E+08
INT A2 → INT A1	TS A1-A2	3.42E+12	1.07E+13	3.72E+12	3.87E+12	4.02E+12	4.16E+12
INT A1 → INT A2	TS A1-A2	1.45E+08	5.24E+08	2.09E+08	2.49E+08	2.94E+08	3.45E+08
INT A1 → INT A3	TS A1-A3	1.88E+06	2.57E+06	3.47E+06	4.62E+06	6.08E+06	7.90E+06
INT A3 → INT A1	TS A1-A3	2.46E+04	1.03E+05	4.74E+04	6.43E+04	8.61E+04	1.14E+05
INT A1 → 1-cyano-1,2-butadiene + H	TS A2-2	6.49E+06	1.38E+07	1.29E+07	1.78E+07	2.41E+07	3.22E+07
INT A1 → 1-cyano-1-butyne + H	TS A2-3	4.25E+06	1.87E+07	8.99E+06	1.27E+07	1.76E+07	2.41E+07
INT A1 → cyanoallene + CH3	TS A2-1	8.00E+07	3.18E+08	1.39E+08	1.79E+08	2.29E+08	2.91E+08
INT A3 → 1-cyano-1,3-butadiene + H	TS A3-1	1.18E+08	2.12E+08	1.69E+08	2.01E+08	2.37E+08	2.79E+08

Table A13. Rate coefficients of all channels on the CN + 1,2-butadiene reaction.

Channel	Barrier	0.0	1.0	2.0	3.0	4.0	5.0
INT D1 → INT D2	TS D1-D2	2.59E+08	3.09E+08	3.67E+08	4.33E+08	5.07E+08	5.91E+08
INT D2 → INT D1	TS D1-D2	7.04E+11	7.58E+11	8.13E+11	8.70E+11	9.27E+11	9.85E+11
INT D1 → 1-cyano-prop-3-yne + CH_3	TS E1-2	3.33E+08	4.66E+08	6.42E+08	8.69E+08	1.16E+09	1.53E+09
INT E1 → INT D2	TS D2-E1	1.17E+13	1.17E+13	1.17E+13	1.18E+13	1.18E+13	1.18E+13
INT D2 → INT E1	TS D2-E1	2.76E+06	3.29E+06	3.91E+06	4.61E+06	5.42E+06	6.34E+06
INT E1 → INT E2	TS E1-E2	1.16E+06	1.40E+06	1.68E+06	2.01E+06	2.39E+06	2.83E+06
INT E2 → INT E1	TS E1-E2	1.90E+13	1.88E+13	1.85E+13	1.82E+13	1.80E+13	1.78E+13
INT E1 → 2-cyano-1,3-butadiene + H	TS E1-1	2.32E+07	2.92E+07	3.65E+07	4.53E+07	5.59E+07	6.85E+07
INT E2 → INT F1	TS E2-F1	2.47E+12	2.56E+12	2.65E+12	2.74E+12	2.83E+12	2.92E+12
INT F1 → INT E2	TS E2-F1	5.01E+08	5.94E+08	6.98E+08	8.16E+08	9.48E+08	1.10E+09
INT F1 → cyanoallene + CH_3	TS F1-1	2.08E+08	2.76E+08	3.62E+08	4.69E+08	6.00E+08	7.59E+08

Table A14. Product Branching Ratios for CN addition to centrally and terminally to 1-butyne, addition to 2-butyne, and addition with a 1:1 ratio of INT 1 (central) and INT A (terminal) to determine equal probability.

Product	Initial Adduct	0.0	1.0	2.0	3.0	4.0	5.0
1-cyano-1,3-butadiene + H	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT C1	1.2	1.3	1.4	1.4	1.5	1.6
	1:1	0.0	0.0	0.0	0.0	0.0	0.0
1-cyano-1,2-butadiene + H	INT B1	0.1	0.1	0.1	0.1	0.1	0.2
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT C1	4.2	4.6	5.0	5.5	5.9	6.4
	1:1	0.1	0.1	0.1	0.1	0.1	0.2
2-cyano-1,3-butadiene + H	INT B1	96.0	95.6	94.8	94.1	93.4	92.7
	INT A1	0.3	0.3	0.3	0.3	0.3	0.3
	INT C1	39.4	34.8	34.3	32.2	30.1	28.1
	1:1	96.0	95.6	94.8	94.1	93.4	92.7
3-cyano-1,2-butadiene + H	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	0.6	0.7	0.8	0.8	0.9	0.9
	INT C1	0.0	0.0	0.0	0.0	0.0	0.0
	1:1	0.0	0.0	0.0	0.0	0.0	0.0
cyanoacetylene + C2H5	INT B1	2.7	3.1	3.7	4.3	4.9	5.5
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT C1	1.1	1.2	1.3	1.5	1.6	1.7
	1:1	2.7	3.1	3.7	4.3	4.9	5.5
1-cyano-1-butyne + H	INT B1	0.1	0.1	0.1	0.1	0.1	0.1
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT C1	2.7	3.3	3.5	3.9	4.3	4.8
	1:1	0.1	0.1	0.1	0.1	0.1	0.1
1-cyano-prop-1-yne + CH3	INT B1	0.0	0.0	0.0	0.0	0.0	0.0
	INT A1	99.1	99.5	99.0	98.9	98.8	98.8
	INT C1	0.0	0.0	0.0	0.0	0.0	0.0
	1:1	0.0	0.0	0.0	0.0	0.0	0.0
cyanoallene + CH3	INT B1	1.1	1.2	1.3	1.3	1.4	1.5
	INT A1	0.0	0.0	0.0	0.0	0.0	0.0
	INT C1	51.4	52.9	54.4	55.5	56.5	57.5
	1:1	1.1	1.2	1.3	1.3	1.4	1.5

Table A15. Product Branching Ratios from the reaction of CN + 1,2-butadiene. The distribution of products varies based on the initial adduct that forms.

Product	**Initial Adduct**	**0.0**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
1-cyano-prop-3-ene + CH_3	INT D1	57.8	61.8	65.3	68.5	71.3	73.9
	INT D2	3.6	4.2	4.7	5.1	5.7	6.2
	INT E1	0.4	0.4	0.5	0.5	0.5	0.5
	INT E2	0.4	0.4	0.4	0.5	0.5	0.5
	INT F1	0.3	0.3	0.3	0.3	0.3	0.3
2-cyano-1,3-butadiene + H	INT D1	42.1	38.1	34.6	31.5	28.6	26.1
	INT D2	96.2	95.6	95.1	94.6	94.1	93.6
	INT E1	99.4	99.4	99.3	99.3	99.3	99.2
	INT E2	95.8	95.3	94.7	94.2	93.6	93.0
	INT F1	67.7	65.0	62.4	60.0	57.3	55.0
cyanoallene + CH_3	INT D1	0.0	0.0	0.0	0.0	0.0	0.0
	INT D2	0.2	0.2	0.2	0.2	0.2	0.2
	INT E1	0.2	0.2	0.2	0.2	0.2	0.3
	INT E2	3.8	4.3	4.9	5.4	6.0	6.5
	INT F1	32.1	34.7	37.4	40.0	42.4	44.7

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Publications:

Jamal, A.; Mebel, A. A Theoretical Investigation of the Mechanism and Product Branching Ratios of the Reactions of Cyano Radical with 1- and 2-Butynes and 1,2-Butadiene. In Submission.

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Presentations:
8th Workshop on Computational Chemistry and Molecular Spectroscopy
Poster: Formation of Aromatics in Cold Planetary Atmospheres and the Intersteller Medium: An *Ab Initio* Study
October 2012 – Punta de Tralca, Chile

American Chemical Society – Chemistry of Life
Oral: Theoretical Study of the Reaction Mechanism and Product Branching Ratios of Ethynyl and Cyano Radical with Unsaturated Hydrocarbons on Titan
March 2012 – San Diego, CA

American Chemical Society – Chemistry of Air, Space, and Water
Poster: A Theoretical Study of Cyano Radical Reactions with C_4H_6 Isomers
August 2011 – Denver, CO

Titan Workshop V – Observations, Experiments, Computations, and Modeling
Poster: An Ab Initio/RRKM Study of Ethynyl Radical and 1-butyne/2-butyne
April 2011 – Kauai, Hawai'i

Faraday Discussions 147: Chemistry of the Planets
Poster: A Theoretical Study of the Reaction of Ethynyl Radical with Unsaturated Hydrocarbons
March 2010 – Brittany, France

Titan Workshop IV – Observations, Experiments, Computations, and Modeling
Poster: A Theoretical Study of Ethynyl Radical with Allene and Methylacetylene
March 2010 – Brittany, France

Titan Workshop III – Observations, Experiments, Computations, and Modeling
Poster: An Ab Initio/RRKM Study of Cyano Radical with Diacetylene
February 2009 – San Juan, Puerto Rico