RECROSSING AND HEAVY-ATOM TUNNELING IN COMMON ORGANIC REACTIONS

A Dissertation

by

OLLIE MICHELLE JAMES

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

DOCTOR OF PHILOSOPHY

December 2011

Major Subject: Chemistry

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Approved by:

Chair of Committee,	Daniel A. Singleton
Committee Members,	David E. Bergbreiter
	Simon W. North
	Tahir Cagin
Head of Department,	David H. Russell

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ABSTRACT

Recrossing and Heavy-atom Tunneling in Common Organic Reactions.

(December 2011)

Ollie Michelle James, B.S., Trinity University

Chair of Advisory Committee: Dr. Daniel A. Singleton

Non-statistical recrossing in ketene cycloadditions with alkenes, heavy-atom tunneling and the mechanism of the decarboxylation of Mandelylthiamin is investigated in this dissertation. A combination of experimental kinetic isotope effects and theoretical models and kinetic isotope effects is utilized for this endeavor. This dissertation also describes how the use of quasiclassical dynamic trajectories, microcanonical RRKM calculations, and canonical variational transition state theory in combination with small-curvature tunneling approximations is utilized to help advance our research methodology to better understand mechanism.

In the cycloaddition of dichloroketene with cis-2-butene, significant amounts of recrossing is observed using quasiclassical dynamic trajectories. An unusual inverse ^{13}C intramolecular KIE lead us to investigate the role that heavy atoms play in non-statistical recrossing. More importantly, this discovery has uncovered a new phenomena of entropic intermediates that not only applies to ketene cycloadditions, but can also be applicable to other "concerted" reactions such as Diels-Alder reactions.

The ring-opening of cyclopropylcarbinyl radical has revealed that heavy-atom tunneling plays a major role. The intramolecular ^{13}C kinetic isotope effects for the ring-opening of cyclopropylcarbinyl radical were unprecedentedly large and in combination with theoretical predictions and multidimensional tunneling corrections, the role of tunneling in this reaction can be better understood.

The mechanism decarboxylation of mandelylthiamin has been extensively studied in the literature. However, until the use of theoretically predicted KIEs and theoretical binding motifs the rate-limiting step of this reaction has been hotly debated. In this dissertation, a discussion of how the theoretical KIEs indicate the initial C-C bond as the rate-limiting step and chelating binding motifs of pyridinium and mandelylthiamin to explain the observed catalysis is given.

DEDICATION

I dedicate this work to the ones that make me smile, my daughter Alanna, my mom, and the love of my life Henry.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Singleton, for all his guidance and assistance through this long process. I'd like to thank him for all the lengthy talks about chemistry and the world. I would not be the chemist or person I am today if he was not in my life.

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I would like to thank all of the group members for their contributions to my work, the stimulating conversations and their expert guidance. I would like to extend a special thanks to Dr. Christopher Hobbs for his friendship and for helping me get through graduate school with my sanity.

Finally, I would like to thank my mother who always believed in me and never allowed me to quit anything, my husband Henry for his patience and love and my daughter Alanna for making my life better everyday.

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CHAPTER I

INTRODUCTION

In the mid 1990's the Singleton research group developed methodology to elucidate kinetic isotope effects of ^{13}C and ^{2}H using a natural abundance approach.[1] This methodology was utilized to study common organic reaction mechanisms in the normal way. It was found that combined with a theoretical approach to predicting isotope effects, this method was highly powerful at studying reaction mechanisms.[2-9] Theoretical methods based on transition state theory (TST) in conjunction with experimental KIEs were successfully employed to gain insight into the transition state geometry and hence the mechanism of several important organic reactions.[2-6]

As physical organic chemists a fundamental goal is to understand how reactions occur. This understanding can be utilized to design new reactions and to control their rates and selectivity. Scientists currently use TST to understand reaction mechanisms.

A transition state is a hypersurface that divides starting materials from products for defining reactive trajectories. In conventional transition state theory, this hypersurface is placed perpendicular to the minimum-energy path at a potential energy saddle point. It is understood that this description is simplistic and that assumptions have been made in TST. The free energy of a transition state can be directly related to the reaction rate as seen in equation 1.1.[10]

This dissertation follows the style of the *Journal of the American Chemical Society.*

$$k = \kappa(\frac{kT}{h})e^{\frac{-\Delta G_{act}^{0}}{RT}} = \kappa(\frac{kT}{h})e^{\frac{-\Delta H_{act}^{0}}{RT}}e^{\frac{\Delta S_{act}^{0}}{R}} \tag{1.1}$$

The selectivity of products is predicted using the difference in free energy of the transition states. While catalysis is understood by lowering the free energy of the transition state compared to the uncatalyzed process. Basically, TST is used as sciences fundamental understanding of reaction rates and mechanisms.

In variational TST, the position of a coordinate-space hypersurface transverse to the minimum energy pathway (MEP) is adjusted to minimize crossing. However, variational TST can only be useful if the recrossing is statistically predictable.[11] The transmission coefficient κ, which is incorporated into TST, in general is assumed to be unity and a transition state is only useful at understanding rates and selectivity when κ does not depart to drastically from unity.

However, κ may be viewed as a correction for two complications that affect the rates of reactions, recrossing and tunneling. Tunneling allows reactive trajectories that do not adhere to the limitations of the transition state energy, leading to an underestimation of the rate, and a κ greater than unity may be incorporated as a correction. Recrossing occurs when trajectories pass through a transition state but pass back without affording product. Because such trajectories in effect lower the free-energy of activation but do not contribute to the rate, the rate is overestimated and a κ less than unity corrects for this. In variational transition state theory (VTST), the transition state hypersurface is itself repositioned to minimize the error encountered by recrossing.

Unless the system is encountering hydrogen-transfer or barrierless reactions, these complications are usually ignored with the assumption that their effect will be negligible. However, this is not always the case and such instances will be reported in this work.

During the course of rigorous application of the Singleton methodology combining isotope effects and theoretical studies, the Singleton group encountered several instances where conventional TST fails to account for experimental observations.[7-9,12] When an experimental observation cannot be accounted for within the standard theoretical framework of TST, more detailed examination of the reaction dynamics is required. Recently, our research efforts have been directed largely towards the observation and interpretation of phenomena outside of TST that affect kinetic observations in organic reactions.

1.1 Transition State Theory and Kinetic Isotope Effects

Kinetic isotope effect measurements are powerful mechanistic probes. There are two origins of the kinetic isotope effect. The first origin of kinetic isotope effects are caused by differences in the activation energy for reactions involving different isotopes due to either the reactants, the transition state, or both, having different zero point vibrational energies. Vibrational frequencies, and therefore vibrational zero point energies, depend on the reduced mass of the vibrating system.[13]

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.2}$$

Figure 1.1 is a 2D representation of the vibrational normal modes associated with the reactant and the transition state for a reaction, focusing on as an example the stretching vibration of a C- H bond. Isotopic substitution, in this case by deuterium, affects the zero-point energy (ZPE) of the vibrational normal modes of a molecule. The main origin of KIEs lies in how the ZPE is different at the stage of reactants versus the transition state. Since the transition state is more loosely bound than the reactants, the vibrational levels are more closely spaced.

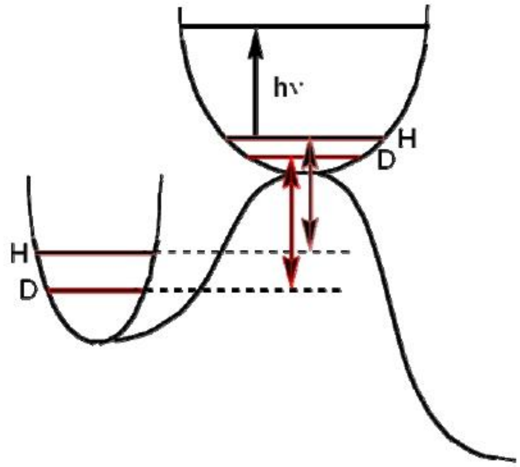


Figure 1.1. The origin of the kinetic isotope effect.

The net effect is that the activation energy is higher, and therefore reaction slower, for the heavier isotopomer (a ‘normal’ isotope effect). The maximum isotope effect is obtained when the bond involving the isotope is completely broken in the transition state, in which case the difference in activation energies is simply the difference in zero point energies of the reactants. Sometimes the normal modes are tighter at the transition state versus the starting material; this causes the ZPE to be increased at the transition state and heavier isotopes encounter a lower barrier. The resulting faster rate for the heavier isotope (($k_{\text{light}}/k_{\text{heavy}} < 1$) is an "inverse" isotope effect. Since the KIEs are intimately associated with the normal modes at the transition state, KIEs can be used to experimentally probe the transition state geometry, i.e. the extent of bond formation / bond breaking occurring as the reaction goes over the transition state.[13]

The second origin for kinetic isotope effects is quantum mechanical tunneling through the reaction potential energy barrier, is usually only important at very low temperatures and for reactions involving very light atoms. For the simplest model case of a square barrier, the probability of tunneling through the barrier is seen in equation 1.3.

$$P = \exp^{-2(\frac{2m(V_0 - E)}{\hbar^2})^{1/2} a} \tag{1.3}$$

The tunneling probability therefore depends on the particle mass m, the particle energy E and the height Vo and width a of the barrier, but is independent of temperature. At normal temperatures, tunneling makes only a small contribution to the overall reaction rate. However, since the rate of normal reaction falls off with temperature as less and less reactants have enough energy to surmount the activation barrier, at low temperatures the constant tunneling contribution can make up a significant fraction of the overall reaction. The mass dependence of the tunneling probability means that tunneling rates are significantly different for different isotopes, which can lead to large kinetic isotope effects in some cases.[13]

1.2 Experimental KIE Measurements

Since KIEs are rate differences observed when a molecule is replaced by an isotopologue, it might be thought that isotope effects may be measured by a direct measurement of rate constants. This is often done when the rate differences are large. The imprecision in the measurement of rate constants makes their use in the measurement of small KIEs impractical in most cases. As a result, small KIEs are measured in competition reactions that rely on the precise measurement of the isotopic position of either starting materials or products. These competition reactions were traditionally carried out using labeled materials. The methodology developed in the Singleton research group allows these measurements to be made at natural abundance.

The Singleton method for the determination of ^{13}C KIEs at natural abundance has been well documented in papers and dissertations,[1-6] and the discussion here will simply outline the methodology. Each individual carbon and hydrogen in an organic molecule contains at natural abundance approximately 1.1% of ^{13}C and 0.015% of ^{2}H. As a reaction progresses, the starting materials are enriched in the slower reacting isotopomers (isotopically substituted isomers) and the products in the faster reacting ones. If this isotopic enrichment at every position in a molecule can be measured, KIEs can be determined without the use of explicitly labeled substrate. The Singleton research group can use this idea in three different ways to determine ^{13}C and ^{2}H KIEs at natural abundance.

(a) *Intermolecular starting material KIEs* - The original methodology developed in the Singleton group measured KIEs by analysis of starting material recovered from reactions taken to high conversion, typically ~80%. The isotopic composition of this recovered material is determined by NMR at natural abundance and compared to that of unreacted starting material (drawn from the bottle originally used for the reaction). The enrichment (depletion) thus measured can be used to determine the KIEs based on equation 1.4, where F_1 is the fractional conversion of the lighter isotopomer and R/R_0 is the proportion of minor isotopic component in recovered starting material versus the original material.

$$\log(1-F_1)/\log[(1-F_1)(R/R_0)] \qquad (1.4)$$

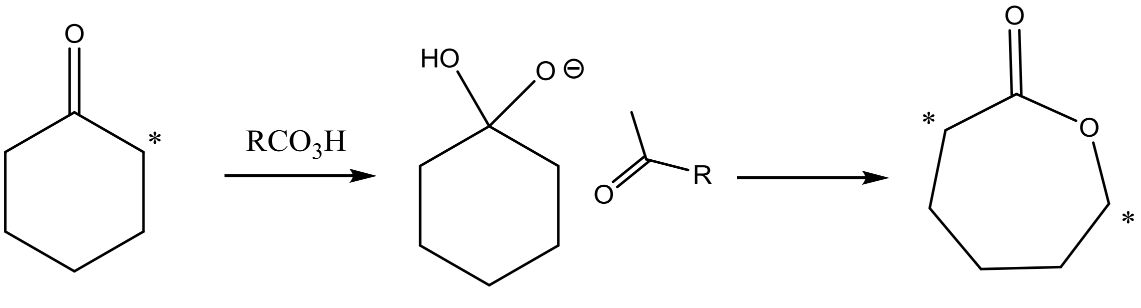
This methodology has some advantages when it can be applied. One advantage is that the precision of the KIEs obtained can exceed the precision of the analysis. Another advantage is that the KIEs are insensitive to further side reactions that the product may undergo. A disadvantage is that the methodology cannot be applied to reactants that must be used in large excess.

(b) *Intermolecular product KIEs* - An alternative process involves taking reactions to low conversion (typically ~20%) and analyzing the isolated reaction product. The isotopic composition of the product is compared to that of product isolated from a reaction taken to 100% conversion reaction. Equation 1.5 is then used to calculate the KIEs. This method is prone to two possible errors.

$$\log(1-F_1)/\log[(1-(F_1 * R_p/R_0)] \qquad (1.5)$$

Further conversion of product to form side product will adversely affect the measurement. Also, errors may arise from any inefficiency in the '100% conversion' reaction.

(c) *Intramolecular product KIEs* - While intermolecular KIEs in general relate to the *rate-limiting step* of a reaction, intramolecular KIE measurements are elegant probes that provide valuable information about intermediates and subsequent steps in a reaction. They enable one to probe the step in which the reaction becomes desymmetrized. In some cases this is not the *rate-limiting step* and this process can be used to tell you more about the mechanism besides the step that is rate-limiting. For example, in the Baeyer-Villiger oxidation of **1,** the rate determining step is the formation of the hemiperacetal **2**. When partially labeled **1** (assume * is a ^{13}C label) passes through a rate-limiting transition state and has a regiochemical choice of reactive isotopes, the product distribution (i.e. where the label actually ends up in **3**) reflects the KIE of the second step. This information can be gained by analyzing the ^{13}C composition of product isolated from this reaction.



1 **2** **3**

The intramolecular product KIE measured represents the KIE of the "product determining step" of a reaction, that is, the first step that irreversibly desymmetrizes a symmetric molecule.[14] Used in conjunction with intermolecular KIEs, intramolecular KIEs can be used to distinguish a single step from a multi-step reaction mechanism.

1.3 Theoretical Prediction of KIEs

The interpretation of experimentally measured KIEs is often aided by the development of theoretical models used to quantitatively predict the experimental KIEs. Theoretical predictions of equilibrium isotope effects and KIEs are based upon the formula proposed by Bigeleisen and Mayer.[15,16] The calculation of the KIE is represented in equation 1.6.

$$KIE_{TST} = \frac{v_1^{\ddagger}(\frac{s_2}{s_1})f_{GS}}{v_2^{\ddagger}(\frac{s_2}{s_1})f_{TS}} \tag{1.6}$$

The KIE is composed of the $(\frac{v_1^{\ddagger}}{v_2^{\ddagger}})$ term which represents the product of vibrational frequencies for the ground state and transition state. The $[(s_2 / s_1) f]$ represents the contributions from the rotational, vibrational and electronic partition functions to the KIE for the different isotopomers. At the ground state 3N-6 (for non-linear molecules where N= the number of atoms) vibrational degrees of freedom must be taken into account. The equation for the transition state however, requires 3N-7 vibrational degrees of freedom because one degree of freedom is lost along the reaction coordinate as seen in equation 1.6 and 1.7.

$$(\frac{s_2}{s_1})f_{GS} = \prod_i^{3N-6} \frac{v_{2i}}{v_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \tag{1.7}$$

$$where \longrightarrow u_i = \frac{hv_i}{kT}$$

$$(\frac{s_2}{s_1})f_{TS} = \prod_i^{3N-7} \frac{v_{2i}}{v_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \tag{1.8}$$

Calculated KIEs are representative of the semi-classical KIEs and do not account for other non-statistical phenomena such as tunneling, recrossing, variational transition state theory and other dynamic effects. The Singleton group has a long history of including a one-dimensional tunneling correction (the infinite parabola approximation) to account for any heavy-atom tunneling occurring in the reaction.[17,] However, some reactions that exhibit significant amounts of tunneling require the use of a multi-dimensional approximation and in these cases the program POLYRATE can be employed.[18-22] For other dynamic effects such as non-statistical recrossing a more intense theoretical treatment such as dynamic simulations are required.

However, for most standard reactions the predictions of KIEs are derived from theoretical models of the lowest energy ground state of the molecule and the model of the transition state of the reaction. The program QUIVER which is written in FORTRAN and developed by Saunders and Wolfsberg is utilized to extract the necessary data from a theoretical frequency calculation in Gaussian and is then used to calculate the theoretical KIE using the Bigeleisen equation.[23]

1.4 Theoretical Calculations

Computational studies can predict in complete detail the mechanisms of chemical reactions. However, it must be remembered that the computations employed in quantum chemistry are themselves only approximate models of electronic structure in reality, and systems being modeled are usually only crude models of complex reactions including solvent. As a result, the key question in computational studies is whether the results obtained are accurate depictions of the experimental chemistry.

Theoretical models also aid in our understanding of the details of a chemical reaction such as sources of catalysis, reaction stereo and regioselectivities, and steric and electronic effects of a reaction. Calculational methods employed include semi-empirical methods, density functional theory, molecular mechanics, *ab initio* methods, Monte Carlo simulations, RRKM theory, variational transition state theory, marcus theory, electron valence bond theory as well as others. The theory that is ultimately used will be determined based on the desired goal of the study. Density functional theory (DFT) is highly utilized within the Singleton research group and is known to give excellent agreement between experimental and theoretical KIEs.[3, 24-26]

The perfect theoretical model would give an exact solution to the non-relativistic Schrödinger equation or match perfect with the real world. However, in systems with many electrons an exact solution is unrealistic. Ab initio methods including Hartee-Fock (HF) and Moller-Plesset (MP) theories include a term for electron exchange which takes into account the interaction of an electron with other electrons in the system this is known as the electron correlation energy. The crux of theoretical chemists is the ability to have a calculation that can predict this energy correctly or close to reality. The electron correlation energy is defined as the difference between the actual energy of the system and the calculated energy of the system. An exact quantum mechanical result could in theory be obtained with an inclusion of all possible electronic excited states and an infinitely large number of orbitals on the system. However, this is theoretically impossible. Besides *ab initio* calculations another approach to this issue is the use of a DFT model.

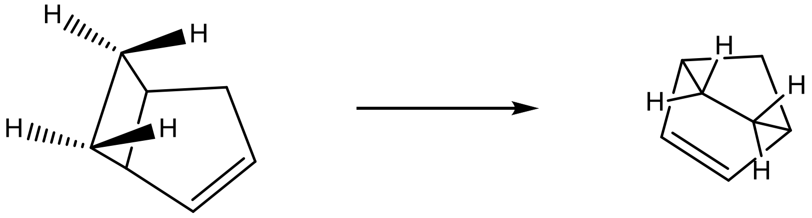
In DFT, the energy of a molecule is determined as a functional of the electron density of the system rather than the interaction of electronic wave functions as seen using *ab initio* calculations. Several functionals have been developed within DFT in order to correctly describe the energies of specific molecules. In order to decide which functional is best to use, researchers generally employ the method that best fits with experimental evidence. This is the method that is employed by the Singleton research group to decide which method is best to use. However, some systems put limitations on the method that can be employed due to the cost of computer limitations.

1.5 Dynamic Effects

Within the realm of dynamic effects there are generally six different types to consider: dynamic matching, incomplete IVR (intramolecular vibrational energy redistribution), bifurcating energy surfaces, entropic bifurcations, non-statistical recrossing, and quasiclassical corner-cutting.

Currently, transition state theory ignores any effect of a non-statistical distribution of vibrational energy may affect the outcome of a reaction.[27] In the Singleton group dynamics is understood as the study of how atomic Newtonian motion affects the outcome of a reaction.

Dynamic matching is probably the most well known of the dynamic effects as studied by Carpenter in 1984.[28-34] Carpenter studied the rearrangement of bicyclo[3.2.0]hept-2-ene **4** to bicyclo[2.2.1]hept-2-ene **5**.[28,34,35] Studying this system Carpenter showed that the in the rearrangement of **4** to **5** if the energy necessary to pass over all barriers is introduced during the breaking apart of the cyclobutane ring, and the energy is introduced into the molecule in such a way that it creates a specialized distribution, then this may allow for product formation without formation of an intermediate. Basically allowing a stepwise process to become concerted. In other words the momentum of the molecule is carrying the reaction away from the minimum energy pathway and hence this is what is considered dynamics.



4 **5**

The reasons behind transition state failure can be attributed to the assumptions that TST makes. One of those assumptions is that intramolecular vibrational energy redistribution (IVR) occurs fast on a time scale of a reaction coordinate.[36] However, IVR is not instantaneous and this can cause molecules to follow paths that are not the minimum energy pathway due to the inability to change its trajectory on the energy surface. When this happens dynamic effects can be observed.

To understand dynamics better it would be useful to discuss a reaction coordinate diagram. After a molecule proceeds through the transition state, at the col of a potential energy surface, it will continue along its path until reaching a stable product. The trajectory will follow closely to the minimum energy pathway if the energy of the system increases dramatically while proceeding along the reaction coordinate in the x-dimension. However, if there is very little increase in energy while proceeding along the x-dimension of the reaction coordinate, then the trajectories will then deviate from the minimum energy pathway and the motion inherent in the molecule may decide the outcome of the trajectories. In most cases this deviation will have little if no effect on the outcome of the trajectories, however this is not always the case.[37]

Another assumption that transition state theory makes is that only a single product can arise from a single transition state. However, this is not the case with what is known as bifurcating energy surfaces. Bifurcating energy surfaces are defined as a potential energy surface that has a singular transition state leading to two or more products (Figure 1.2).

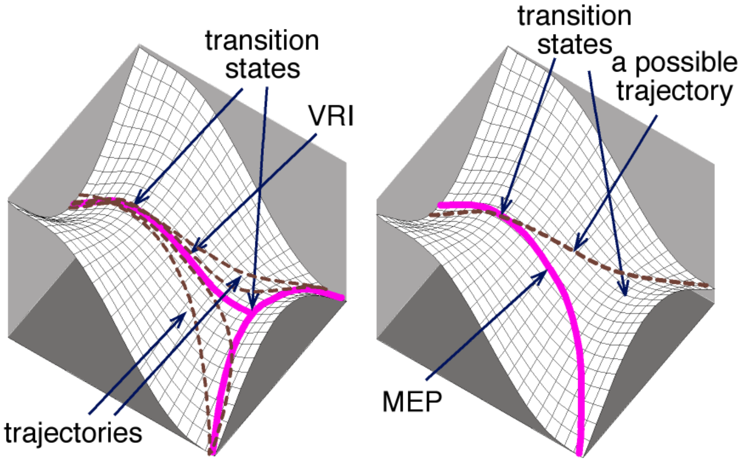


Figure 1.2. Bifurcating energy surface in which a single transition state leads to multiple products.

Theoreticians have been predicting this for many years and there are a few possible scenarios. A surface that is completely symmetrical and leads to two identical products and more interestingly an unsymmetrical surface in which dynamics would determine the preferred product.[38]

Pertaining to this dissertation recrossing is another type of dynamics in which a trajectory passes a delineated transition state however before affording product the trajectory hits some energetic all and returns to starting material. Variational transition state theory addresses the issue of recrossing to some extent and will be able to predict recrossing.[39] But in some reactions recrossing is not statistically predictable and this is known as non-statistical recrossing. Hase in particular has studied this phenomena in Sn2 reactions[40-42] and the Singleton group has further published work in this area involving the cycloaddition of ketenes with cyclopentadiene.[43] This dynamic effect will be discussed in greater detail later in the dissertation.

1.6 Tunneling

Quantum mechanical tunneling is of high interest to the scientific community, it affects the rates of barrier crossings in all chemical reactions and scientists are continually looking for reactions in which tunneling plays a significant role. Tunneling allows reactive trajectories that do not adhere to the limitations of the transition state energy, leading to an underestimation of the rate. In general, tunneling is thought to occur primarily with protons, hydrogen, or hydride.[44] Tunneling of hydrogen-transfer is well understood and many experimental techniques have been used to detect this occurrence. However, heavy atom tunneling, while thought to be trivial, plays a role, albeit small, in most reactions. A one dimensional tunneling correction (infinite parabola) is included in all predicted isotope effects of the Singleton group and this in general gets the theoretical value closer to the experimental value.[24,26,45-47] Cases in which heavy atom tunneling is seen as significant are lacking. However, the tunneling contribution can become unusually large if in fact the major motion of the transition state is from contribution of a heavy atom. When this occurs increased rates are observed, compared to theoretical rates and large KIEs are observed experimentally as will be seen later in this dissertation.

CHAPTER II

OBSERVATION, PREDICTION, AND ORIGIN OF AN ISOTOPE EFFECT ON RECROSSING. STUDY OF THE MECHANISM OF THE CYCLOADDITION OF DICHLOROKETENE AND OLEFINS

2.1 Introduction

Conventional transition state theory (TST) assumes that molecular systems passing through a dividing surface in the direction of products do not turn back and reform reactants. It was recognized from the beginning that this "no-recrossing assumption" is an approximation, and this led to the incorporation of transmission coefficients into TST.[48,49] The inaccuracy in TST engendered by recrossing can be minimized by a sagacious choice of the dividing surface, and this is the central idea in variational TST,[39] but it is understood that some recrossing occurs that is not yet predictable by statistical methods. The importance of such recrossing has been noted in a number of trajectory studies in recent years, particularly by Hase and coworkers who studied the effect of non-statistical recrossing in S_N2 reactions.[40-42,50,51] The Singleton group has also observed its impact on experimental observations.[43,52] In 2006, Ussing et. al. studied the [2+2] cycloaddition of ketenes with cyclopentadiene. They find that dynamics plays a major role in determining the product ratios of these reactions and that with understanding non-statistical recrossing the experimental evidence would not make sense. Even though much research has been performed to study this effect, recrossing remains a hidden phenomenon; little is known about its importance in ordinary reactions and there are no general experimental probes for its occurrence.

The [2 + 2] cycloaddition of ketenes was significant in the development of Woodward-Hoffmann rules.[53] According to orbital symmetry rules there is no geometric configuration that will allow for the concerted formation of a cyclobutane ring. However, researchers early on discovered that when reacting ketenes with cyclopentadiene the resulting product was not the [4 + 2] cycloaddition to give the six-membered ring it was instead the cyclobutanone product that resulted from a [2 +2] cycloaddition. Ketenes have a unique propensity for giving facile [2 + 2] cycloaddition reactions, even when other pathways are available.[54-56] This feature is of major importance in organic chemistry for the purposes of preparing cyclobutanone products usually with a high degree of stereoselectivity. A great deal of the currently available experimental and theoretical evidence suggested that many [2 + 2] cycloadditions are a concerted process. The Woodward-Hoffmann analysis of ketene cycloadditions provide a theoretical basis for understanding ketene cycloadditions. It was suggested that ketene cycloadditions with alkenes proceed by the perpendicular arrangement of the two reactants as seen in Figure 2.1, with both bonds to the alkene being formed on the same side (suprafacial), and the bonds of the two carbons of the ketene were formed on the opposite sides (antarafacial).[53] This process has been the subject of continuous debate. There is strong evidence however that many ketene cycloadditions are not concerted and can proceed through a two-step process with a zwitterionic intermediate (this will be discussed further in the next chapter). However, for the purpose of dichloroketene all experimental and computational evidence suggests that this process proceeds through a concerted process.

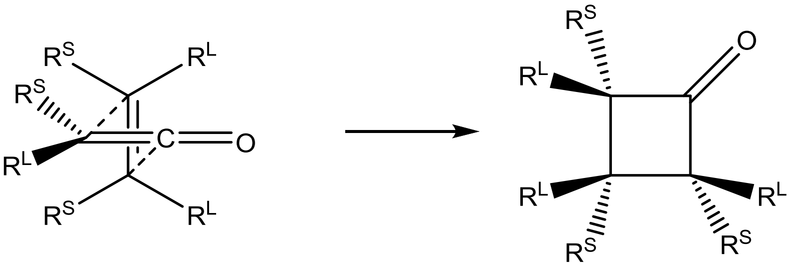
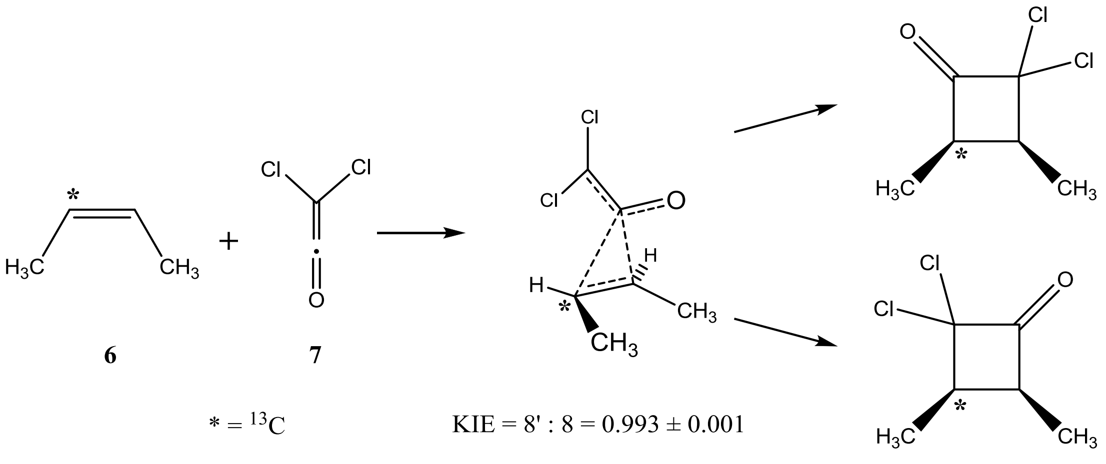


Figure 2.1. The [2 + 2] cycloaddition of ketene.

The [2 + 2] cycloaddition of dichloroketene with alkenes presents an unique opportunity to study recrossing. As mentioned before recrossing occurs when a trajectory passes a delineated transition state but hits some energetic barrier and bounces back to starting material before reaching product. The energy surfaces for these cycloadditions are described as bifurcating energy surfaces where the transition state is such that the ketene is perpendicular to the alkene to allow the initial carbon-carbon bond formation. In order for product to form the trajectory has to make a sharp turn on the potential energy surface. This makes the trajectory pre-disposed to recrossing in the sense that if the trajectory fails to make this turn it will hit the wall ahead and bounce back to starting material. Because of this geometric predisposition, the study of dichloroketene with alkenes provides a unique opportunity to study the effect of recrossing. In this chapter we explore the [2 + 2] cycloaddition of dichloroketene with cis-2-butene, cyclohexene and cis-2-heptene and examine how recrossing affects these reactions both experimentally and theoretically.

2.2 The Experimental and Theoretical Study of the [2 + 2] Cycloaddition of Dichloroketene and Cis-2-butene

Our previous work suggested that asynchronous cycloadditions are often subject to substantial recrossing of the conventional or variational transition state.[43] Because suprafacial [2 + 2] cycloadditions are formally forbidden pericyclic processes, the [2 + 2] cycloadditions of ketenes with alkenes are intrinsically highly asynchronous, and we chose the facile reaction of cis-2-butene (**6**) with dichloroketene (**7**) to afford the cyclobutanone product **8** for experimental study. As stated previously these reactions are geometrically predisposed to recrossing and the specific reaction of dichloroketene with cis-2-butene was determined to be symmetric at the transition state using a MPW1K/6-31+G** methodology. The symmetry of this reaction would suggest there to be no observable intramolecular isotope effect in the methine carbons of the cyclobutanone. This reaction was probed by the determination of the intramolecular kinetic isotope effects (KIEs) for the cis-2-butene carbons in the reaction.



8

8'

* = ^{13}C

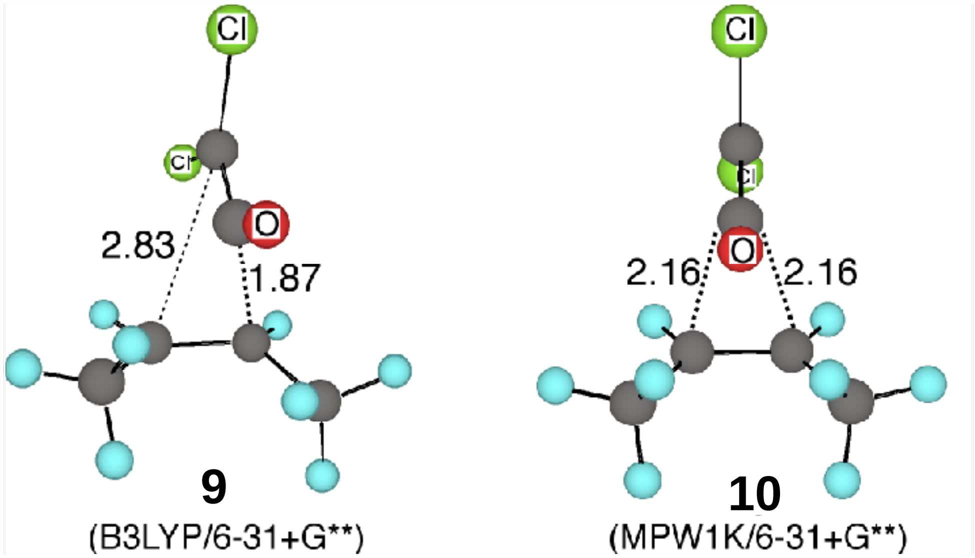
KIE = 8' : 8 = 0.993 ± 0.001

2.2.1 Experimental Intramolecular KIEs for the Cycloaddition of Cis-2-butene and Dichloroketene

As stated previously intramolecular kinetic isotope effects are useful for examining the first desymmetrizing step in a reaction when you have a symmetrical starting material. In the cycloaddition of cis-2-butene with dichloroketene the cis-2-butene is symmetrical and so examining the methine or methyl carbons of **8** can be used to determine the intramolecular KIE of this reaction. When a ^{13}C is present in cis-2-butene, the otherwise equivalent cyclobutanone products become isotopomeric and distinguishable, The ratio of the products constitutes an intramolecular KIE, and two such KIEs may be observed depending on whether the ^{13}C was in the olefinic or methyl carbons of cis-2-butene. These KIEs were readily determined at natural abundance by NMR methodology.[14,57,58] A total of 24 KIE measurements were made on samples of **8** obtained from three independent reactions at 25 °C. The methyl-carbon KIE was 1.000 ± 0.001. The more interesting olefinic-carbon results are 0.993 ± 0.001. The unusual observation here is that more ^{13}C is found in the methine position adjacent to the carbonyl (as in **8**) than in the methine distal from the carbonyl (as in **8'**). If the cycloaddition is viewed in qualitative terms as an electrophilic attack of the carbonyl carbon of the ketene on the olefinic carbons, then one would generally expect that the carbonyl carbon would preferentially end up attached to ^{12}C.

2.2.2 Theoretical KIEs for the Cycloaddition of Cis-2-butene and Dichloroketene

In order to study this system more fully the theoretical KIEs were predicted using a variety of different methods. In keeping with this idea, KIEs (defined as **8'**/**8**) calculated based on ordinary asynchronous transition structures such as the B3LYP/6-31+G** structure **9** (Figure 2.2) are generally in the 1.01 to 1.02 range, as seen in Table 2.1. The experimental "inverse"[59] intramolecular KIE shows that such calculated structures are qualitatively incorrect.



9
(B3LYP/6-31+G**)

10
(MPW1K/6-31+G**)

Figure 2.2. Theoretical structures for the cycloaddition of dichloroketene and cis-2-butene.

Table 2.1. Predicted isotope effects for the asynchronous transition states of the cycloaddition of cis-2-butene and dichloroketene.

Method/Basis set	KIE predicted	Bond Distance 1[a]	Bond Distance 2[a]
HF/3-21	1.004	1.698	2.126
HF/6-31+G**	1.001	1.695	2.052
HF/6-31+G** PCM	1.016	1.814	2.063
Becke/6-31+G*	1.019	1.847	2.136
Becke/6-31+G* PCM	1.014	1.989	2.111
M05/6-31+G**	1.006	2.198	2.254
MPW3LYP/6-31+G**	1.018	1.849	2.130

[a] Bond Distances seen in Figure 2.3.

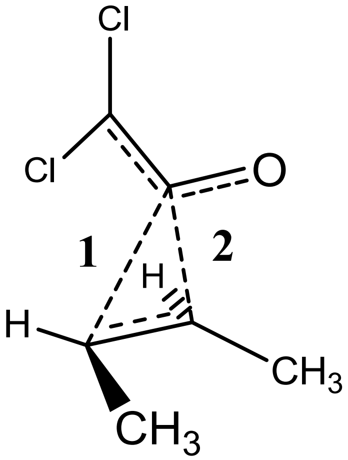


Figure 2.3. Transition state for the cycloaddition of dichloroketene and cis-2-butene and the corresponding bond distances of interest.

Other calculational methods support a different picture of the reaction. In M06, MPW1K, MP2, and other calculations, the lowest-energy approach of the two molecules places the axis of the ketene orthogonal to the π-bond of the alkene and the cycloaddition transition structure has C_s-symmetry, e.g. the MPW1K/6-31+G** structure **10**. This predicts the isotope effect be zero or 1.000 in most cases, as seen in Table 2.2.

Table 2.2. Predicted isotope effects for the symmetrical transition states of the cycloaddition of cis-2-butene and dichloroketene.

Method/Basis set	KIE predicted	Bond Distance 1[a]	Bond Distance 2[a]
MPW1K/6-31+G**	1.000	2.165	2.165
M05-2x/6-31+G**	1.000	2.387	2.437
M06/6-31+G**	1.000	2.140	2.139
MP2	1.000	2.014	2.014
M06-2x/6-31+G** PCM	1.001	2.437	2.486

[a] Bond Distances seen in Figure 2.3.

The Cs-symmetry is supported by CCSD(T)/6-311++G**/PCM(CH2Cl2) single-point energies on a grid of M06-2X/6-31+G** geometries. The qualitative picture of the energy surface obtained in these calculations is shown in Figure 2.4. This is a "bifurcating energy surface" in which there is a continual downhill path from the transition structure to two product wells. On this surface, the formation of the second new C-C bond in the cycloaddition is not set up to occur by a continuation of motion through the TS. Rather, trajectories crossing the saddle point must make a sharp "turn" to get to either of two equivalent cyclobutanone products **8** / **8'**. A second saddle point on this surface, **11**, is formally the transition structure for the interconversion of the two products. Conventional TST provides no prediction of the intramolecular isotope effect on such bifurcating surfaces, and we turned to trajectories to gain insight into the unusual KIE.

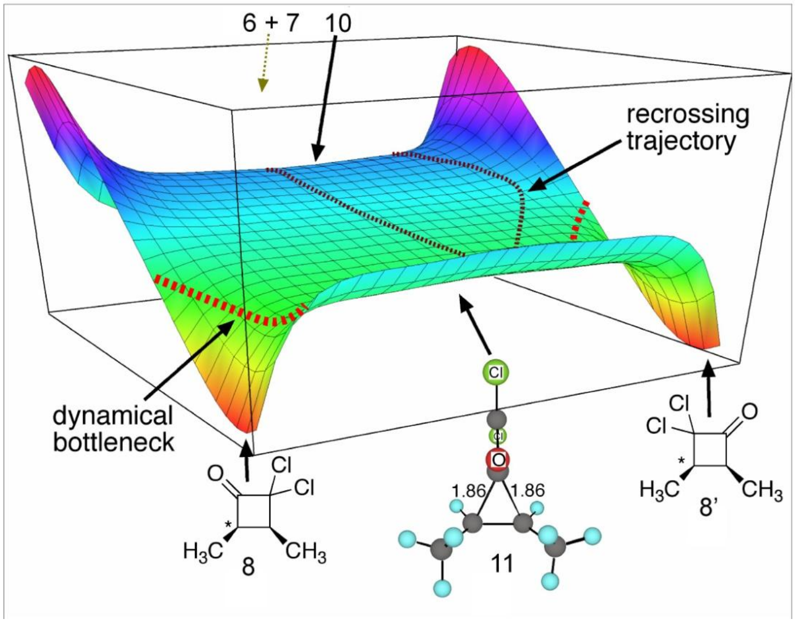


Figure 2.4. A qualitative depiction of the symmetrical energy surface for the [2 + 2] cycloaddition of dichloroketene with cis-2-butene.

2.2.3 Dynamic Trajectories for the Cycloaddition of Dichloroketene and Cis-2-butene

Dynamic trajectories as stated previously can be used to help explain experimental observations that normal transition state theory is unable to explain. The closet energy surface to reality would be the idea surface to use for dynamic trajectories. A good way to measure reality is to use high-level theoretical calculations such as CCSD(T). Because of the high cost of these calculations dynamic trajectory studies with this surface would be impossible. However, we can instead use a method that closely resembles this surface which would be the MPW1K/6-31+G** energy surface. Structure **10** was used as the starting point for quasiclassical direct dynamic trajectories. These trajectories were initiated based on the idea that at the transition state there should be a random distribution of states with respect to degrees of freedom not associated with the imaginary frequency.[37] Therefore, to mimic the random distribution of Newtonian motion, the starting atomic position on the potential energy ridge in the area of the transition structures were randomized. This was accomplished using a linear sampling of possible harmonic classical displacements for each normal mode, adjusting the kinetic energy for each mode accordingly. Each mode was given a random sign for its initial velocity, and a total energy based on a random Boltzmann sampling of vibrational levels appropriate for the temperature, including zero-point energies. The mode associated with the imaginary frequency was treated as a translation and given a Boltzmann sampling of translational energy forward (toward products) over the col.

Newton's laws govern the motion of classical particles. While equation 2.1 dives position in a trajectory if force is constant, it fails when force is variable. However, the future position of a particle may be estimated from equation 2.2 so long as the time t is very short compared to the change of F. A better estimation for a longer t comes from the Verlet algorithm as seen in equation 2.3.[60] The Verlet algorithm can be used to determine the next position in a trajectory without using a Taylor expansion. All the algorithm needs to be successful is the current position, the previous position, and the forces acting on the particle at the current position.

$$x = x_0 + vt + (F/2m)t^2 \tag{2.1}$$

$$x(t_0 + \Delta t) = x(t_0) + v_0\Delta t + (F/2m)\,\Delta t^2 \tag{2.2}$$

$$x(t_0 + \Delta t) = 2x(t_0) - x(t_0 - \Delta t) + (F/m)\,\Delta t^2 \tag{2.3}$$

The Verlet algorithm was used to generate the position of all points successive to initialization. The forces used in the Verlet algorithm were calculated using either Gaussian03[61] or Gaussian09.[62] Trajectories were propagated in this manner until either products or starting material were formed based on the parameters that were programmed. The trajectories were allowed to propagate for a maximum time of 500 fs which translates to 500 points.

Due to the impractical number of trajectories required for statistically significant predictions of small KIEs, we applied our previously described trick of using, *in silico*, superheavy isotopes of carbon.[63] Quasiclassical direct-dynamics trajectories on an MPW1K/6-31G* energy surface[64] (chosen because it models well the CCSD(T)/6-311++G**/PCM(CH_2Cl_2) surface) were initiated from isotopologues of **10** containing a single ^{28}C, ^{44}C, ^{76}C, or ^{140}C ($12 + 2^N$ amu, N=4, 5, 6, or 7). Each normal mode in **10** was given its ZPE plus a Boltzmann sampling of additional energy appropriate for 25 °C, with a random phase and sign for its initial velocity. As will be discussed later, the sign of the velocity in a particular normal mode, "mode 3", has a dominant effect of the trajectory outcome, and an equal number of trajectories were started with the sign of the mode 3 velocity being positive versus negative. The transition vector was given a Boltzmann sampling of energy 'forward' from the col. Employing a Verlet algorithm, 1-fs steps were taken until either the product was formed or separate starting materials were reformed, and the trajectories affording **8**, **8'** or recrossing were counted (Table 2.3).

Table 2.3. Dynamic trajectory results for the ^{28}C, ^{44}C, ^{76}C, or ^{140}C isotopes and the resulting KIE.

isotope	total runs	mode 3 positive **8'** : **8** : recrossed[a]	mode 3 negative **8'** : **8** : recrossed[a]	**8'/ 8**
^{140}C	11092	39.3 : 1.3 : 59.5	1.3 : 48.2 : 50.5	0.820(5)
^{76}C	7112	40.5 : 1.0 : 58.5	0.6 : 47.3 : 52.1	0.852(6)
^{44}C	5860	40.2 : 0.6 : 59.1	0.7 : 45.3 : 54.1	0.889(6)
^{28}C	10366	40.1 : 0.8 : 59.1	0.5 : 43.4: 56.1	0.915(5)
			extrapolated to ^{13}C:	0.990(3)

[a] Recrossing separated based on the direction on mode 3.

The trajectories results provide a number of interesting observations. The first is that they account for the experimentally observed isotope effect. Superheavy olefinic carbons in **6** preferentially end up adjacent to the carbonyl carbon in the product (**8'** < **8**), and the preference increases with increasing mass. Extrapolation of the results to ^{13}C leads to a predicted KIE of 0.990 ±0.003. The consistency with the unusual experimental KIE supports the idea that the underlying physics leading to the KIEs with the superheavy carbons is the same as with ^{13}C experimentally.

The process for extrapolation of the trajectory results to ^{13}C starts with the assumption that the additional isotope effect per additional mass unit decreases as the mass grows. For example, the effect of going from ^{13}C to ^{14}C would be larger than the effect of going from ^{140}C to ^{141}C. We further assumed that this decrease with mass is nonlinear with a decreasing slope, that is, that a plot of the additional isotope effect per additional mass versus mass would have a greater slope at low masses (e.g., ^{13}C to ^{14}C) than at high masses (e.g. ^{140}C to ^{141}C). These simple assumptions exclude some extrapolation processes that would lead to physically unreasonable isotope effects at both high masses and at ^{13}C. Table 2.4 and the Figure 2.5 show the data used in the extrapolation, the extrapolated results, and the complete linear regression analysis and statistics. The Nominal KIEs come from the dynamic simulations previously described in the previous paragraph. The "additional mass" is defined as the mass beyond 12 amu. The "isotope effect per mass" is defined as the geometric average (eq 2.4).

$$\text{isotope effect per mass} = (\text{Nominal KIE})^{(1/\text{additional mass})} \qquad (2.4)$$

The extrapolation was then carried out by assuming a linear relationship between the log of the additional mass (the base is arbitrary but set conveniently here as 2) versus the isotope effect per mass. The extrapolation process used the Regression tool in Microsoft Excel 2004 for Mac, Version 11.3.3. The reported standard deviations and confidence limits are based on that analysis and the uncertainties are based on the fit of the points to the regression line.

Table 2.4 Data used in the extrapolation of the kinetic isotope effect.

Mass	Additional Mass	log2	Nominal KIE	Isotope Effect /per mass
140	128	7	0.820	0.998
76	64	6	0.852	0.998
44	32	5	0.889	0.996
28	16	4	0.916	0.995
13	1	0		0.990

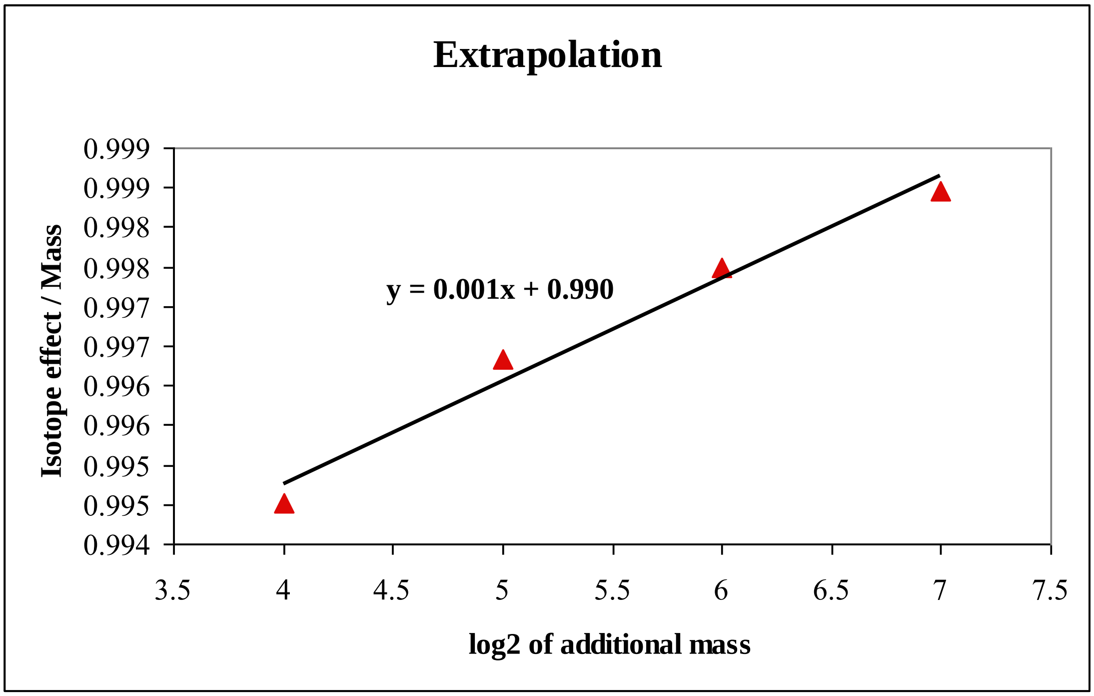


Figure 2.5. Extrapolation of the KIE for the cycloaddition of dichloroketene and cis-2-butene.

The second observation is that the product outcome of the trajectories is essentially completely predetermined by the sign of the velocity of a normal mode at the TS. Motion in the low-energy (74 cm^{-1}) mode 3, depicted in Figure 2.6, desymmetrizes the transition structure in such a way that the combination of motion in this mode and motion along the transition vector morphs the transition structure toward the product geometries. When the trajectories have an initial positive sign for the mode 3 velocity (defining positive as the sign that moves the carbonyl carbon away from the labeled olefinic carbon), then ≈98% of the product formed is **8'**. When mode 3 is negative, ≈98% of the product formed is **8**. The small amount of crossover process occurs equally in each direction. This correspondence of selectivity to motion through an initial TS is a form of dynamic matching.[28-34] The mode 3 motion defines a "ridge" in the TS hypersurface. Trajectories cross the ridge at a variety of positions but the location of the crossing point is interestingly irrelevant to the product outcome; only the direction of mode 3 motion and not its displacement controls which product is formed. Since the mode 3 velocity determines the product and since an equal number of trajectories must have positive versus negative velocities in this mode, how it is possible for product selectivity to occur in the reaction?

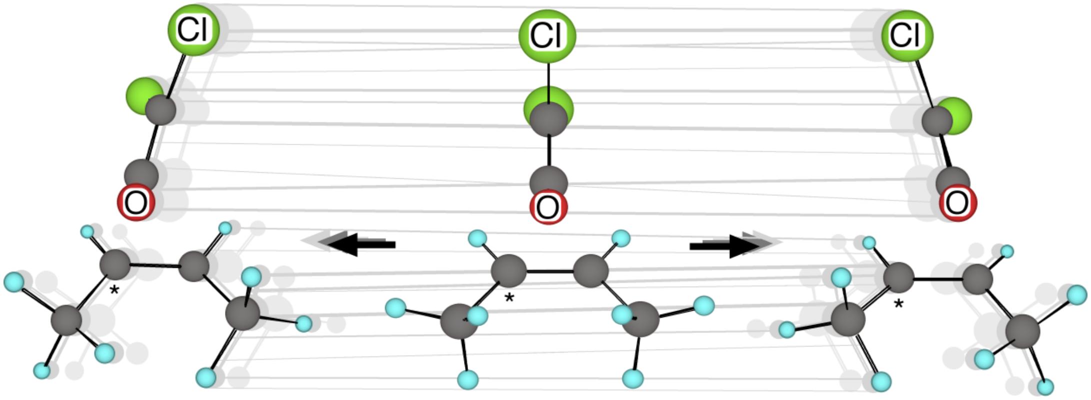


Figure 2.6. Motion associated with "mode 3" in the cycloaddition saddle point. With "*" designating a heavier isotope, a positive velocity is defined as motion toward the right.

The answer lies in the most interesting observation from the trajectories: most trajectories recross the TS and reform the starting materials and the propensity for recrossing depends on isotopic mass. The trajectories that recross the conventional TS are not trivial[65] and they are not associated with the canonical variational TS near **10**‡. Rather, the recrossing trajectories proceed into the area of **11** and beyond; the average closest approach of the carbonyl carbon to the olefinic carbons is 1.69 Å. In the parent isotopologue (all carbons ^{12}C), only 39% of the trajectories crossing the conventional TS proceed to products, while 61% recross, and the average time from crossing the TS to recrossing it (defined by C-C distances > 2.2 Å) is 183 fs. When the mass of both of the olefinic carbons is increased to ^{140}C, the recrossing is decreased to 54%. With one isotopically labeled carbon, the recrossing depends on the sign of mode 3; trajectories with the ketene carbonyl carbon moving away from the label are unaffected in their recrossing, but the trajectories with the ketene carbonyl carbon moving toward the label recross less and less as the mass is increased. It is this decrease in recrossing with increasing mass that leads to the observed KIE.

We analyzed the origin of this mass effect on recrossing from both a dynamical perspective and a statistical perspective. From a dynamical perspective, a number of observations appear pertinent. First, the major product is not correctly predicted by the IRC, that is, the steepest-descent path in mass-weighted coordinates starting from **10** leads to **8'**, not the major **8**. This suggests that the observed KIE is not analogous to the "Newtonian" KIEs that were described in the dimerization of cyclopentadiene performed earlier by Singleton.[63] The second observation is that the experimental isotope effect is also approximately accounted for by fully classical trajectories. Classical trajectories are defined by trajectories in which all zero-point energy is removed from the calculations leading to a energy surface that only accounts for the potential energy of the system. In other words the trajectories will no longer follow the laws of quantum mechanics but instead only follow Newtonian motion. The classical trajectories that were run are summarized in Table 2.5. As the table demonstrates, most if not all of the isotope effect can be accounted for by the classical trajectories with an extrapolated isotope effect of 0.992. The suggestion from this observation is that zero-point energy effects are at most a minor contributor to the isotope effect.

Table 2.5. Classical Trajectory results with the extrapolation to the ^{13}C KIE.

isotope	Total Runs	mode 3 positive **8'** : **8** : recrossed	mode 3 negative **8'** : **8** : recrossed	**8'**/ **8**
^{140}C	2136	41.6 : 0.4 : 58.0	47.4 : 0.4 : 52.3	0.880
^{28}C	17088	40.1 : 0.8 : 59.1	0.8 : 43.4: 56.1	0.939
			extrapolated to ^{13}C:	0.992

Third, increasing isotopic mass increases the time required for both product-forming and recrossing trajectories. With all carbons as ^{12}C, the average times taken for product formation and recrossing were 195 fs and 163 fs,[66] respectively, while with both olefinic carbons as ^{140}C, these times were increased to 245 fs and 238 fs, respectively. When there is a single heavy isotope in the olefin, the effect on the trajectory times depends on whether mode 3 is positive or negative. When mode 3 is negative, with the carbonyl carbon approaching the heavy olefinic carbon, the longer-lived trajectories that might have recrossed get "pruned" by relatively fast product formation (which requires little motion of the heavy isotope). Because of this pruning, the average lifetime of the mode-3-negative recrossing trajectories (203 fs) is increased less (versus all ^{12}C) than that of mode-3-positive trajectories (218 fs) and few trajectories recross. This picture, summarized in Figure 2.7, is a gross simplification of the effect of mass on the complex ensemble of trajectories but it qualitatively accounts for the trajectory and experimental observations. A more detailed explanation of the reaction times can be seen in Table 2.6.

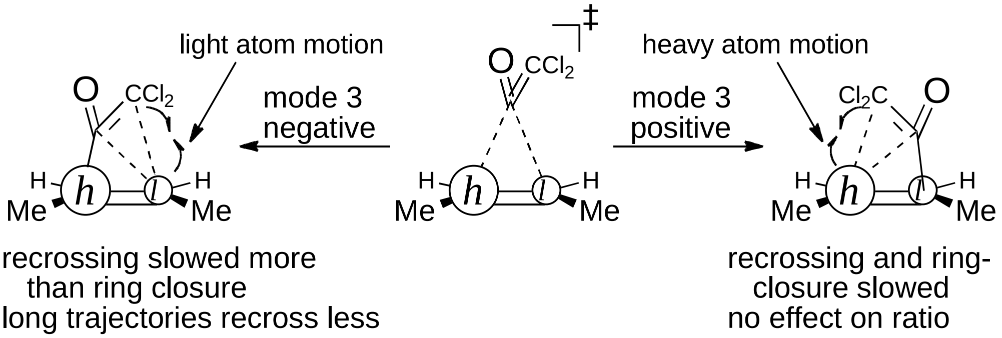


Figure 2.7. A cartoon depicting the effect of a heavy isotope on trajectories. Fewer trajectories recross at left because the ring closure, involving mainly light-atom motion, is slowed less than the recrossing is by the presence of a heavy isotope.

Table 2.6. Trajectory times for dynamic simulations including recrossing and product formation trajectories.

Mass	Recross Time		Product Formation Time	
	Mode 3 (+)	Mode 3 (-)	Mode 3 (+)	Mode 3 (-)
140	218	203		
76	203	193	215	218
44			213	213
28				
12-12	163		195	
140-140	238		245	

2.2.4 Statistical Method for Analyzing the KIE from the Cycloaddition of Dichloroketene and Cis-2-butene

A statistical approach to understanding the isotope effect is made possible by the presence of "hidden" dynamical bottlenecks for product formation. This bottleneck may be understood by viewing the asynchronous cycloaddition process as occurring in two stages, corresponding to the formation of a first C-C bond (between the carbonyl and an olefinic carbon) and a second C-C bond (between the CCl_2 carbon and the other olefinic carbon). As the second stage starts, the atoms involved the bond formation are restricted in their motions, the vibrational frequencies increase, and the entropy decreases. While there is no barrier between **10** and the products on either the potential energy surface or a surface including the ZPE, above 100 K a barrier appears on the canonical free-energy surface. The free energy profile for the reaction after the valley-ridge inflection point (VRI) at 298.15 K can be seen in Figure 2.8. The formal consideration of the effect of this entropy change requires defined reaction paths between **10** and the two products, and we adopted the procedure of Lluch for defining such paths on bifurcating energy surfaces.[67] On these paths there is no barrier between **10** and the products in either potential energy or energy including ZPE. However, above 100 K a barrier appears in the free-energy (if the energy distribution were a canonical Boltzmann distribution) and at 298 K this later barrier is 1.3 kcal/mol above that of **10**! In other words, trajectories must pass through two TSs to afford the products, the first being associated with **10** and the second being a rate-limiting variational TS associated with forming the second C–C bond. The short-lived species in between the TSs would, perforce, be an *intermediate*.

In this statistical view the cycloaddition is a stepwise process, and this has an experimental consequence in the isotope effect. The intermediate itself is delineated by an entropic barrier and has no focal structure; it would not be located in a standard computational mechanistic exploration, no matter how accurate the potential energy surface employed. To imagine this surface further a flow chart can be seen in Figure 2.9.

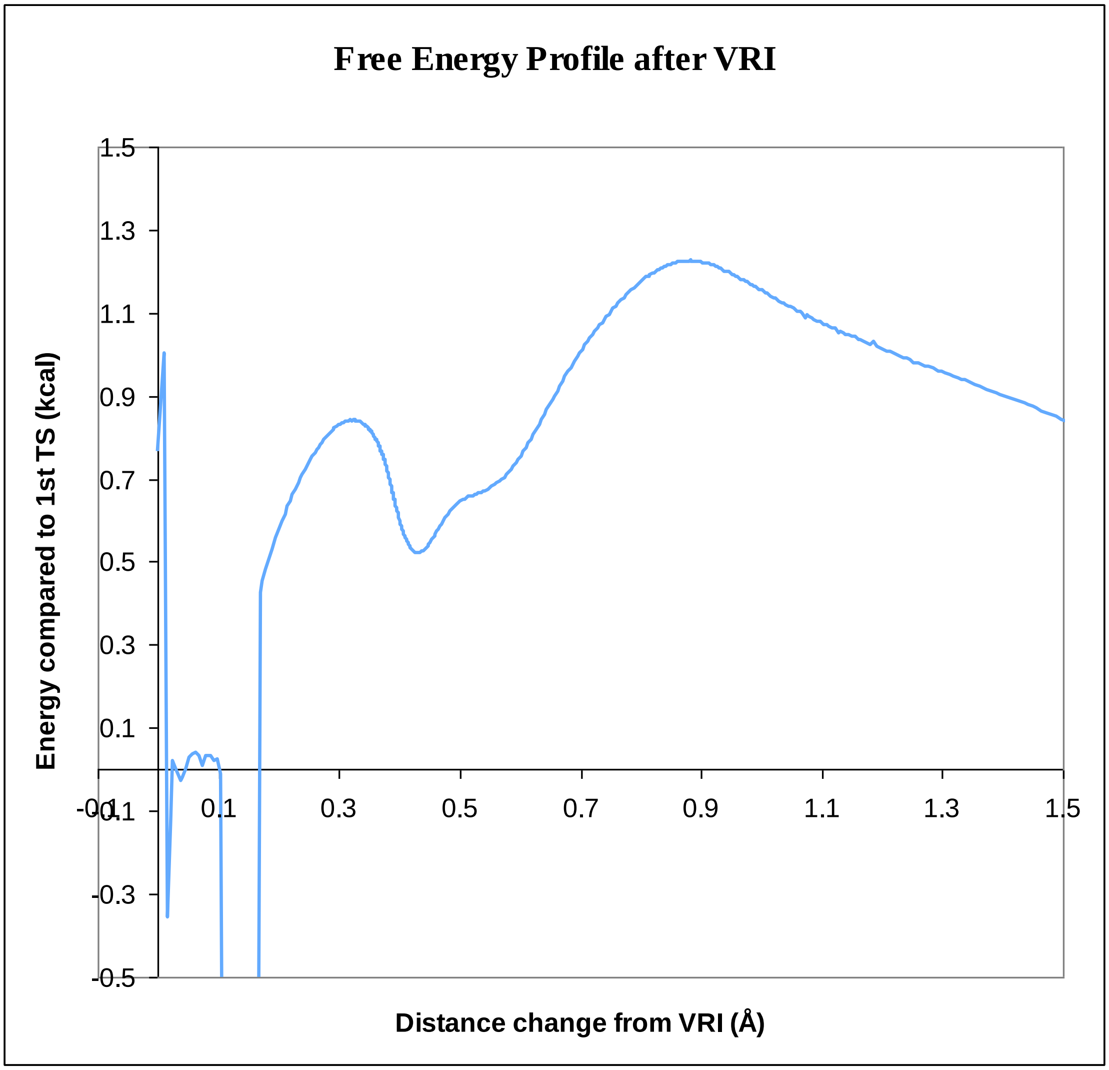


Figure 2.8. Free energy profile for reaction after the valley-ridge inflection point (VRI).

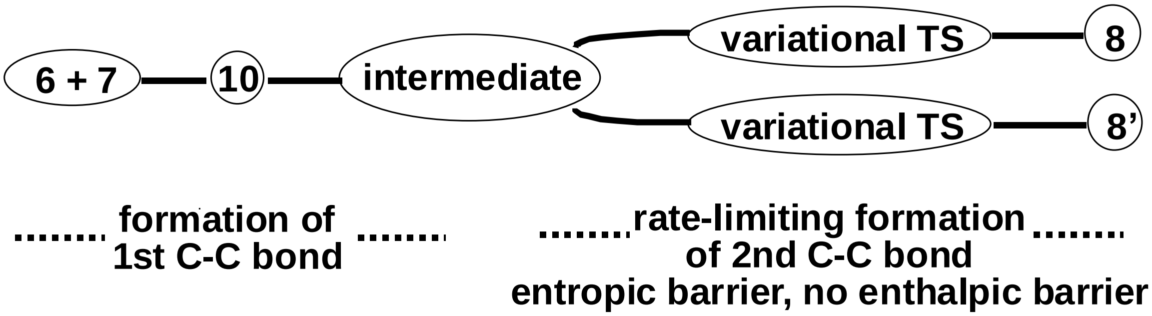


Figure 2.9. Flow chart depiction of Free energy surface for [2 + 2] cycloaddition of cis-2-butene and dichloroketene.

In 2009, Truhlar published a paper that described a nonstatistical approach to predicting branching ratios of chemical reactions when a branching of the reaction path occurs after the dynamical bottleneck, including the case where it occurs after an intermediate.[68] The model is based on combining nonstatistical phase space theory for the direct component of a reaction with variational transition-state theory for an indirect component of reaction. The competition between direct and indirect processes is treated by an extension of the unified statistical model. This new method provides a way to understand the factors that control this kind of chemical reaction and to perform calculations using high-level electronic structure methods for complex systems. The model is based on quantized energy levels of transition states and products, and it involves the same information as required for calculating transition-state rate constants and equilibrium constants plus a phenomenological relaxation time, which was taken from previous work. The model reaction that was studied in this article was the hydroboration of propene using BH_3. This approach can be applied to the cycloaddition of cis-2-butene with dichloroketene and the resulting EIE is predicted to be 1.002 which is in the opposite direction of the observed isotope effect. Even though this theory cannot accurately predict the experimental isotope effect, other statistical methods were investigated to further study this reaction.

Other possible theoretical approaches that have been used in the literature to explain experimental KIEs were examined. In predicting a KIE from the Lluch statistical perspective, a problem is that the energy distribution after passing through the first transition state would not be canonical. To allow for this, we have extended the canonical variational TST procedure employed by Lluch to a microcanonical variational RRKM procedure. The key assumptions in our model are that the total molecular energy is conserved over the time course of the reaction coordinate past the initial transition state, and that the energy is statistically distributed. For each energy slice out of a canonical energy distribution for 25 °C in **10** (including one ^{13}C in an olefinic position), the RRKM rate constant was calculated at each point along the paths to **8** and **8'**. At each energy the RRKM transition state was defined by the point at which the RRKM rate constant was a minimum, and total rate constants were obtained by integrating over the initial energy distribution. The predicted amount of recrossing, based on the relative rate constants for product formation versus crossing the initial barrier, is 86%. The predicted KIE, calculated from the ratio of the total rate constants for formation of **8'** versus **8**, is 0.9955. The structure of the VRI is shown in Figure 2.10 and the geometry of the structure is shown later in the theoretical section. The detailed rates and weighted distribution can be seen in Table 2.7.

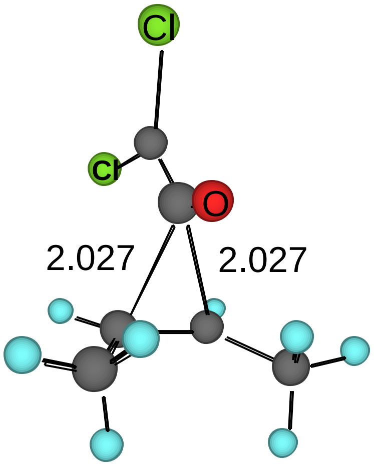


Figure 2.10. Structure of the valley-ridge inflection point from the MPW1K/6-31+G** surface.

Table 2.7. RRKM rate constants for the various energy levels based on the threshold of the reaction along with weighted KIEs based on a Boltzman distribution of the energies for this reaction.

energy level	position of VTS for attack of Light C	rate constant for attack of Light C	position of VTS for attack of Heavy C	rate constant for attack of Heavy C	Predicted KIE	Count	Weighting (= count / total count)	KIE contribution Weighted KIE 0.996
7.80	78.97	1.20E+00	76.91	1.18E+00	1*	0	0.0000	0.000
7.90	77.11	2.05E+00	76.09	2.00E+00	1*	1	0.0000	0.000
8.00	77.70	3.58E+00	76.69	3.48E+00	1*	2	0.0001	0.000
8.10	78.22	5.89E+00	77.43	5.81E+00	1*	4	0.0002	0.000
8.20	77.85	7.68E+00	76.38	7.57E+00	1*	7	0.0003	0.000
8.30	78.15	1.09E+01	76.66	1.08E+01	1*	11	0.0005	0.000
8.40	78.05	1.49E+01	77.00	1.47E+01	1*	15	0.0006	0.001
8.50	77.96	1.95E+01	75.97	1.92E+01	1*	16	0.0007	0.001
8.60	78.12	2.45E+01	76.61	2.40E+01	1*	21	0.0009	0.001
8.70	78.14	3.13E+01	76.56	3.07E+01	1*	31	0.0013	0.001
8.80	78.10	3.83E+01	76.42	3.78E+01	1*	32	0.0013	0.001
8.90	321.40	4.57E+01	349.47	4.61E+01	1.009	35	0.0015	0.001
9.00	322.30	5.34E+01	353.51	5.39E+01	1.009	62	0.0026	0.003
9.10	321.63	6.16E+01	349.59	6.22E+01	1.010	68	0.0028	0.003
9.20	326.41	7.09E+01	354.13	7.16E+01	1.010	84	0.0035	0.004
9.30	327.08	8.15E+01	357.75	8.22E+01	1.009	75	0.0031	0.003
9.40	327.72	9.16E+01	358.11	9.25E+01	1.009	103	0.0043	0.004
9.50	328.88	1.04E+02	359.03	1.05E+02	1.008	98	0.0041	0.004
9.60	329.93	1.17E+02	359.19	1.18E+02	1.008	105	0.0044	0.004
9.70	331.90	1.30E+02	359.85	1.31E+02	1.008	172	0.0071	0.007

***Table 2.7.* Continued.**

energy level	position of VTS for attack of Light C	rate constant for attack of Light C	position of VTS for attack of Heavy C	rate constant for attack of Heavy C	Predicted KIE	Count	Weighting (= count / total count)	KIE contribution Weighted KIE 0.996
9.80	332.37	1.45E+02	360.23	1.46E+02	1.008	159	0.0066	0.007
9.90	332.92	1.60E+02	360.60	1.61E+02	1.008	179	0.0074	0.007
10.00	333.57	1.77E+02	361.11	1.78E+02	1.007	155	0.0064	0.006
10.10	334.03	1.95E+02	361.33	1.96E+02	1.007	191	0.0079	0.008
10.20	334.55	2.13E+02	361.72	2.15E+02	1.008	203	0.0084	0.008
10.30	334.99	2.33E+02	362.09	2.35E+02	1.008	241	0.0100	0.010
10.40	335.42	2.53E+02	362.45	2.55E+02	1.008	264	0.0109	0.011
10.50	337.65	2.75E+02	362.85	2.77E+02	1.008	258	0.0107	0.011
10.60	338.07	2.98E+02	363.42	3.00E+02	1.009	259	0.0107	0.011
10.70	338.46	3.21E+02	363.86	3.25E+02	1.010	265	0.0110	0.011
10.80	338.79	3.46E+02	368.14	3.50E+02	1.010	308	0.0128	0.013
10.90	339.17	3.72E+02	368.92	3.76E+02	1.010	314	0.0130	0.013
11.00	339.47	3.99E+02	369.45	4.03E+02	1.010	304	0.0126	0.013
11.10	339.88	4.27E+02	373.13	4.31E+02	1.009	349	0.0145	0.015
11.20	340.16	4.57E+02	373.42	4.61E+02	1.009	345	0.0143	0.014
11.30	340.48	4.87E+02	373.78	4.91E+02	1.009	361	0.0150	0.015
11.40	340.78	5.18E+02	374.07	5.22E+02	1.008	342	0.0142	0.014
11.50	341.06	5.51E+02	374.35	5.55E+02	1.008	395	0.0164	0.017
11.60	341.41	5.85E+02	374.73	5.89E+02	1.007	372	0.0154	0.016
11.70	341.66	6.19E+02	375.01	6.23E+02	1.007	398	0.0165	0.017
11.80	341.95	6.55E+02	375.31	6.59E+02	1.006	410	0.0170	0.017
11.90	342.55	6.93E+02	376.05	6.96E+02	1.005	386	0.0160	0.016
12.00	342.87	7.31E+02	376.31	7.34E+02	1.004	395	0.0164	0.016
12.10	343.28	7.70E+02	376.58	7.73E+02	1.004	441	0.0183	0.018
12.20	343.58	8.11E+02	376.81	8.14E+02	1.004	388	0.0161	0.016
12.30	343.90	8.52E+02	377.03	8.55E+02	1.003	446	0.0185	0.019
12.40	346.94	8.95E+02	377.23	8.97E+02	1.003	412	0.0171	0.017
12.50	347.27	9.38E+02	378.01	9.41E+02	1.003	429	0.0178	0.018
12.60	347.57	9.83E+02	378.19	9.85E+02	1.003	427	0.0177	0.018
12.70	347.86	1.03E+03	378.42	1.03E+03	1.003	429	0.0178	0.018
12.80	348.25	1.08E+03	378.53	1.08E+03	1.002	430	0.0178	0.018
12.90	348.51	1.12E+03	378.77	1.13E+03	1.002	426	0.0177	0.018
13.00	348.81	1.17E+03	378.94	1.17E+03	1.002	434	0.0180	0.018
13.10	349.01	1.22E+03	379.10	1.22E+03	1.002	429	0.0178	0.018
13.20	349.28	1.27E+03	379.30	1.28E+03	1.002	396	0.0164	0.016
13.30	349.60	1.33E+03	379.48	1.33E+03	1.002	411	0.0170	0.017
13.40	351.51	1.38E+03	379.66	1.38E+03	1.002	431	0.0179	0.018
13.50	351.68	1.43E+03	379.81	1.44E+03	1.002	395	0.0164	0.016
13.60	351.90	1.49E+03	379.99	1.49E+03	1.002	401	0.0166	0.017
13.70	352.16	1.54E+03	380.15	1.55E+03	1.002	358	0.0148	0.015
13.80	352.40	1.60E+03	380.31	1.60E+03	1.002	340	0.0141	0.014
13.90	352.57	1.66E+03	380.47	1.66E+03	1.002	355	0.0147	0.015
14.00	352.82	1.72E+03	380.60	1.72E+03	1.002	340	0.0141	0.014
14.10	353.00	1.78E+03	380.72	1.78E+03	1.002	318	0.0132	0.013
14.20	353.21	1.84E+03	380.90	1.84E+03	1.002	369	0.0153	0.015
14.30	353.43	1.90E+03	381.04	1.91E+03	1.002	324	0.0134	0.013
14.40	353.61	1.97E+03	381.17	1.97E+03	1.002	320	0.0133	0.013
14.50	353.76	2.03E+03	381.32	2.04E+03	1.002	296	0.0123	0.012
14.60	353.98	2.10E+03	381.48	2.10E+03	1.002	309	0.0128	0.013
14.70	354.17	2.16E+03	381.60	2.17E+03	1.002	279	0.0116	0.012

Table 2.7. **Continued.**

energy level	position of VTS for attack of Light C	rate constant for attack of Light C	position of VTS for attack of Heavy C	rate constant for attack of Heavy C	Predicted KIE	Count	Weighting (= count / total count)	KIE contribution Weighted KIE 0.996
14.80	354.35	2.23E+03	381.74	2.24E+03	1.002	267	0.0111	0.011
14.90	354.49	2.30E+03	381.89	2.30E+03	1.003	275	0.0114	0.011
15.00	354.71	2.37E+03	382.04	2.37E+03	1.003	260	0.0108	0.011
15.10	354.86	2.44E+03	382.16	2.45E+03	1.003	254	0.0105	0.011
15.20	355.04	2.51E+03	382.27	2.52E+03	1.003	226	0.0094	0.009
15.30	355.25	2.58E+03	381.38	2.59E+03	1.003	251	0.0104	0.010
15.40	355.34	2.66E+03	381.52	2.66E+03	1.003	209	0.0087	0.009
15.50	355.52	2.73E+03	381.65	2.74E+03	1.003	200	0.0083	0.008
15.60	355.70	2.80E+03	381.77	2.81E+03	1.003	210	0.0087	0.009
15.70	355.86	2.88E+03	381.92	2.89E+03	1.003	194	0.0080	0.008
15.80	355.98	2.96E+03	383.47	2.97E+03	1.003	210	0.0087	0.009
15.90	356.14	3.04E+03	383.63	3.05E+03	1.004	168	0.0070	0.007
16.00	356.28	3.11E+03	383.78	3.13E+03	1.004	166	0.0069	0.007
16.10	356.44	3.19E+03	383.93	3.21E+03	1.003	184	0.0076	0.008
16.20	356.58	3.28E+03	384.08	3.29E+03	1.004	172	0.0071	0.007
16.30	356.69	3.36E+03	384.22	3.37E+03	1.004	160	0.0066	0.007
16.40	356.81	3.44E+03	384.35	3.45E+03	1.004	156	0.0065	0.006
16.50	356.96	3.52E+03	384.46	3.53E+03	1.004	143	0.0059	0.006
16.60	361.63	3.61E+03	384.62	3.62E+03	1.003	141	0.0058	0.006
16.70	361.90	3.69E+03	384.76	3.70E+03	1.003	121	0.0050	0.005
16.80	362.20	3.78E+03	384.90	3.79E+03	1.004	115	0.0048	0.005
16.90	362.45	3.86E+03	385.02	3.88E+03	1.004	99	0.0041	0.004
17.00	362.66	3.95E+03	385.18	3.97E+03	1.004	112	0.0046	0.005
17.10	362.94	4.04E+03	385.32	4.05E+03	1.004	112	0.0046	0.005
17.20	363.19	4.13E+03	385.45	4.14E+03	1.004	97	0.0040	0.004
17.30	363.42	4.22E+03	385.57	4.24E+03	1.004	100	0.0041	0.004
17.40	363.62	4.31E+03	385.71	4.33E+03	1.005	92	0.0038	0.004
17.50	363.90	4.40E+03	385.84	4.42E+03	1.005	113	0.0047	0.005
17.60	363.21	4.49E+03	385.96	4.51E+03	1.005	78	0.0032	0.003
17.70	363.46	4.58E+03	395.20	4.61E+03	1.005	62	0.0026	0.003
17.80	363.73	4.68E+03	395.33	4.70E+03	1.005	71	0.0029	0.003
17.90	364.99	4.77E+03	395.46	4.79E+03	1.005	74	0.0031	0.003
18.00	365.21	4.87E+03	395.61	4.89E+03	1.005	64	0.0027	0.003
18.10	365.41	4.96E+03	395.72	4.98E+03	1.005	65	0.0027	0.003
18.20	365.61	5.06E+03	395.84	5.08E+03	1.004	49	0.0020	0.002
18.30	365.80	5.15E+03	395.96	5.18E+03	1.004	52	0.0022	0.002
18.40	366.01	5.25E+03	396.10	5.27E+03	1.004	63	0.0026	0.003
18.50	366.20	5.35E+03	396.22	5.37E+03	1.004	40	0.0017	0.002
18.60	366.41	5.45E+03	396.35	5.47E+03	1.004	47	0.0019	0.002
18.70	366.59	5.55E+03	396.45	5.57E+03	1.004	50	0.0021	0.002
18.80	366.81	5.65E+03	396.59	5.67E+03	1.004	36	0.0015	0.001
18.90	368.18	5.75E+03	396.69	5.78E+03	1.004	47	0.0019	0.002
19.00	368.36	5.85E+03	396.79	5.88E+03	1.004	26	0.0011	0.001
19.10	370.43	5.96E+03	396.93	5.98E+03	1.004	33	0.0014	0.001
19.20	370.56	6.06E+03	397.02	6.08E+03	1.004	35	0.0015	0.001
19.30	370.70	6.16E+03	397.13	6.19E+03	1.004	29	0.0012	0.001
19.40	370.84	6.27E+03	397.26	6.29E+03	1.004	24	0.0010	0.001
19.50	370.96	6.37E+03	397.36	6.40E+03	1.004	17	0.0007	0.001
19.60	371.08	6.48E+03	397.48	6.50E+03	1.004	21	0.0009	0.001
19.70	371.21	6.59E+03	397.56	6.61E+03	1.004	23	0.0010	0.001

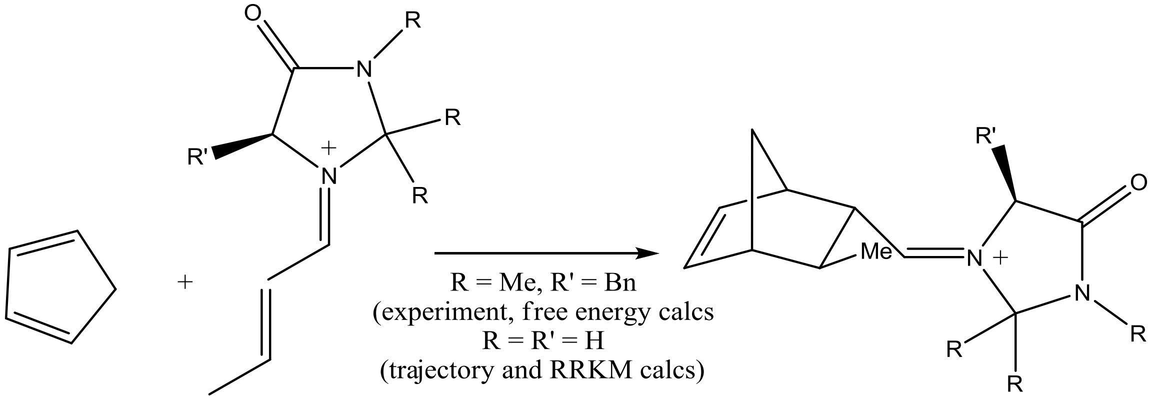
Table 2.7. **Continued.**

energy level	position of VTS for attack of Light C	rate constant for attack of Light C	position of VTS for attack of Heavy C	rate constant for attack of Heavy C	Predicted KIE	Count	Weighting (= count / total count)	KIE contribution Weighted KIE 0.996
19.80	371.34	6.69E+03	397.67	6.72E+03	1.004	22	0.0009	0.001
19.90	371.46	6.80E+03	397.77	6.83E+03	1.004	15	0.0006	0.001
20.00	371.02	6.91E+03	397.88	6.94E+03	1.004	17	0.0007	0.001
20.10	371.15	7.02E+03	398.00	7.05E+03	1.004	11	0.0005	0.000
20.20	371.27	7.13E+03	398.07	7.16E+03	1.004	11	0.0005	0.000
20.30	371.40	7.24E+03	398.18	7.27E+03	1.004	13	0.0005	0.001
20.40	371.50	7.35E+03	398.27	7.38E+03	1.004	19	0.0008	0.001
20.50	371.61	7.46E+03	398.38	7.49E+03	1.004	15	0.0006	0.001
20.60	371.72	7.57E+03	398.46	7.60E+03	1.004	13	0.0005	0.001
20.70	371.85	7.68E+03	398.57	7.72E+03	1.004	10	0.0004	0.000
20.80	371.94	7.80E+03	398.66	7.83E+03	1.004	15	0.0006	0.001
20.90	372.65	7.91E+03	398.76	7.94E+03	1.004	13	0.0005	0.001

The success of the statistical model in predicting the KIE is at once enlightening and unconvincing. It is enlightening in that it suggests that the observed selectivity arises ultimately from the normal factors considered by statistical rate theory, i.e. in thermodynamic parlance the enthalpy and entropy associated with dynamic bottlenecks. The success is unconvincing because it is difficult to completely reconcile the statistical picture with the trajectory observations. Most notably, the intermediate in the statistical model is presumed to make a statistical choice between product formation and recrossing, but the predetermination of the product by the sign of mode 3 shows that the intermediate in no way makes a statistical choice between the two product-forming pathways. It is also notable that the amount of recrossing in the statistical model is significantly higher than that seen in the trajectories, suggesting that the formation of product, as opposed to recrossing, may be favored by non-statistical dynamics in the system. This intriguing trend is seen again in the example in the next section.

2.2.5 Hidden Rate-limiting Steps in Concerted Reactions. Examination of the Diels-Alder Reaction of the MacMillan Vinyliminium Ion and Cyclopentadiene

Despite our incomplete understanding of them, the mechanistic complications of recrossing, entropically delineated intermediates and hidden transition states may be broadly relevant to asynchronous cycloadditions. A suggestive example is the Diels-Alder reaction of the vinyliminium ion **12** with cyclopentadiene. This reaction is the prototypical organocatalyzed Diels-Alder reaction from MacMillan,[69] and a standard computational study of its mechanism and stereochemistry has been reported by Houk.[70] On the B3LYP/6-31G* surface this reaction has a single potential energy saddle point for each stereochemical mode of approach, e.g. **13**‡, giving the appearance of a simple concerted cycloaddition.



12

This misses much. When quasiclassical trajectories are started from the cycloaddition saddle point (with R = R' = H), 45% (142 out of 315) fully form one C–C bond (with an average C–C minimum distance of 1.62 Å before recrossing to starting materials. Treating the energy distribution as canonical for 25 °C in the full system (R =

Me, R' = Bn), there are two variational TSs along the IRC, the first being associated with **13**‡ and the second, **14**‡, near the start of a stage forming the second C–C bond (Figure 2.11).

The latter is highest in free energy and represents a hidden rate-limiting step in the reaction. To allow for a non-canonical distribution of energy in the area past **13**‡, we employed the microcanonical variational RRKM model described above, calculating TS positions and rate constants for each energy slice of a canonical distribution passing through **13**‡. Based on the rate constants along the IRC, 94% of the energy distribution passing through **13**‡ faces its tightest bottleneck (lowest k) in the area of **14**‡ (the exact position depending on the energy). At an average energy the rate constant through the second bottleneck is half that through the first. It should be noted that the frequencies along the IRC were corrected for free energy by removing the lowest energy mode, which is an approximation of the free energy along the IRC. While slight errors might occur using this approach, the general concept of forming an entropic intermediate to shift a concerted process to a stepwise process remains intact. Within either statistical model, the cycloaddition is stepwise and its reactivity, selectivity, substituent effects, solvent effects, isotope effects, and activation parameters would be mainly determined at a geometry that is far from the conventional TS.

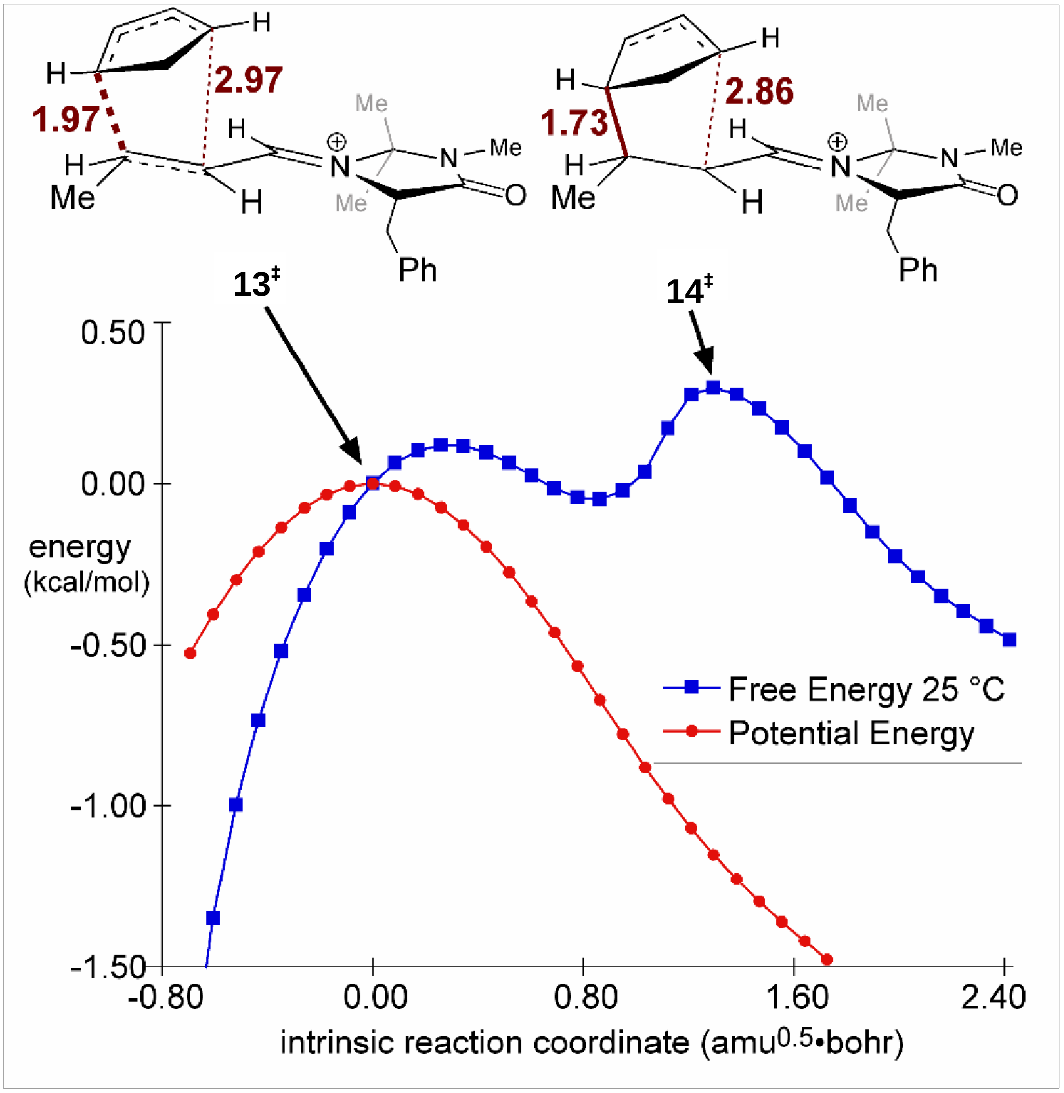
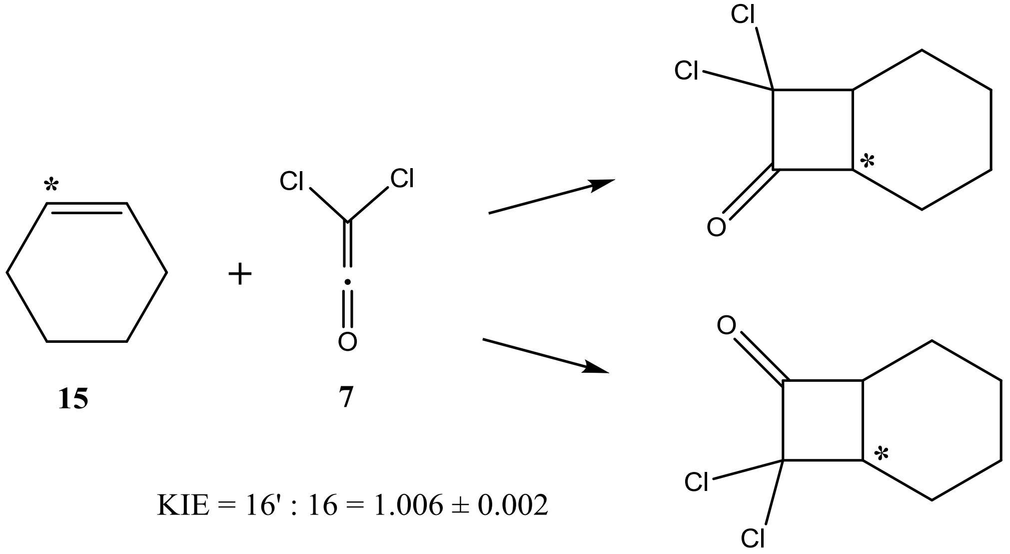


Figure 2.11. Potential energy and free energy at 25 °C along the IRC through TS **13**‡. The TS is taken as the zero of energy.

2.3 KIE and Dynamic Effects in the Cycloaddition of Cyclohexene and Dichloroketene

As in the case of cis-2-butene, the cycloaddition of dichloroketene and cyclohexene represents another example in which intramolecular KIE can be employed to study the reaction. To further explore the idea of recrossing in the cycloaddition of ketenes and alkenes this reaction was studied using the Singleton methodology of ^{13}C NMR and theoretical predictions.



15 **7** **16** **16'**

KIE = 16' : 16 = 1.006 ± 0.002

Intramolecular kinetic isotope effects are useful for examining the first desymmetrizing step in a reaction when you have a symmetrical starting material. In the cycloaddition of cyclohexene (**15**) with dichloroketene (**7**), **15** is symmetrical and so examining the third and fourth position of the cyclobutanone ring of **16** can be used to determine the intramolecular KIE of this reaction.

When a ^{13}C is present in cyclohexene, the otherwise equivalent cyclobutanone products become isotopomeric and distinguishable, The ratio of the products constitutes an intramolecular KIE, and two such KIEs may be observed. These KIEs were readily determined at natural abundance by NMR methodology. A total of 18 KIE measurements were made on samples of **16** obtained from three independent reactions at 25 °C. The olefinic-carbon results are 1.006 ± 0.002 placing more ^{13}C in the initial attack position of the cyclobutanone ring. These results are in fact opposite from that which was observed in the cis-2-butene case. We turn to theory and dynamic trajectories to find an explanation of the experimental observations.

Using our computational approach of optimizing the transition states and ground state structures using either DFT or ab initio techniques and then applying the Bigeleisen equation to predicted the isotope effects from transition state theory. Using a B3LYP/6-31G* and MPW1K/6-31+G** level of theories were determined in this way and the predicted isotope effects from these calculations were predicted to be 1.002 and 1.001. The transition state corresponding to the MPW1K/6-31+G** is seen in Figure 2.12.

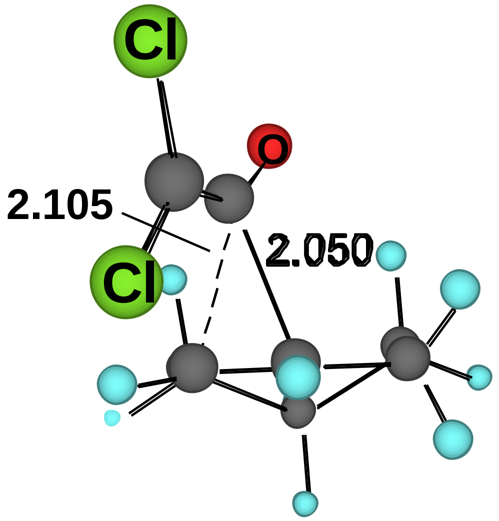


Figure 2.12. MPW1K/6-31+G** transition state for the cycloaddition of dichloroketene and cyclohexene.

As can be seen in Figure 2.12. the transition state for the cycloaddition of dichloroketene and cyclohexene is not completely symmetrical however the difference between the two olefinic carbon bond distances are less than 0.05 Å. This is related in the insignificant isotope effect predicted from these structures. However, experimentally the isotope effect observed is 0.5 % larger. In hopes of further exploring this reaction, dynamic trajectories were performed in the same manner as the cis-2-butene reaction. As seen in Table 2.8 there is about 49 % recrossing occurring in this reaction. However, unlike the cis-2-butene case there is a bias between attack of one carbon versus the other (event in the Up product formed versus Down product formed, Figure 2.13) which makes using the heavy isotope method of replacing one carbon with a 140 C more difficult to perform.

Table 2.8. Recrossing Trajectories for the cycloaddition of dichloroketene and cyclohexene.

Total runs	Total recrossing	Up product Formed	Down product Formed
81	40	35	6

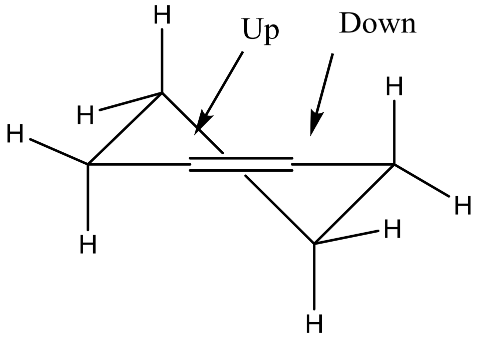
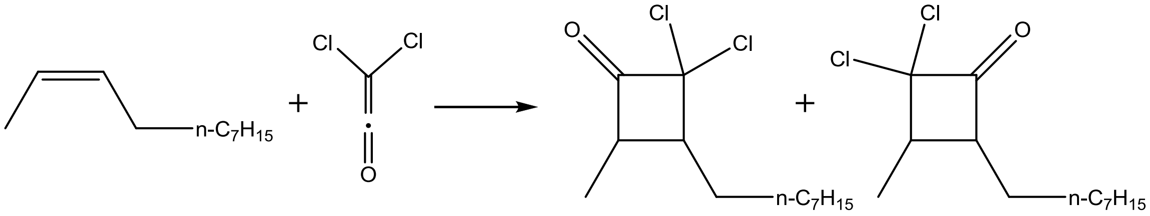


Figure 2.13. Cyclohexene conformation for initial attack of dichloroketene.

The cycloaddition of dichloroketene with cyclohexene appears to be a case in which dynamics are controlling the reaction however, there is not theoretical method to predict the experimental isotope effect.

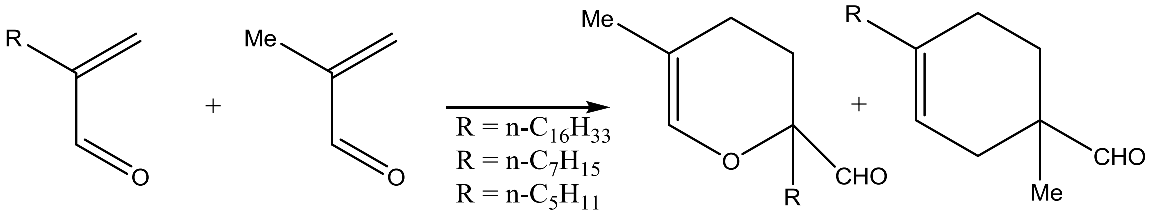
2.4 KIE and Dynamic Effects in the Cycloaddition of Cis-2-heptene and Dichloroketene

An extension of the study of selectivity of the heavy carbons versus light carbons is the study of regioselectivity in unsymmetrical reactions. No significant regioselectivity is normally expected in additions to internal disubstituted alkenes, for example additions to cis-2-undecene (**17**). The explanation for this routine experience is subtly built on transition state theory. The size of the groups makes no difference in the barriers for reactions, and when two reactions face an equal free-energy barrier for passage through their competitive transition states, the two occur at the same rate.



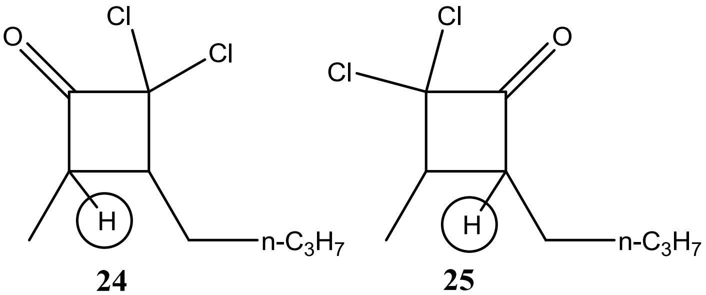
17 **7** **18** **19**

There are many similar situations, for example the Diels-Alder cycloaddition of methacrolein and analogous enones. For these reactions little selectivity might be expected among the products **22** and **23** from the reaction of **20** and **21**, no matter the size of the chain in **20**. But in actuality the selectivity of the reaction would not be controlled by transition state energies.[71] This reaction instead involves a bifurcating energy surface and would be controlled by dynamics. The addition of dichloroketene to unsymmetrical cis-2-alkenes like **17** would also involve a bifurcating energy surface along with significant amounts of recrossing (as seen earlier in this chapter). Because dynamics controls these reactions instead of TST the standard rules of selectivity no longer apply.



20 **21** **22** **23**

Similar experiments could be carried out in the additions of dichloroketene to unsymmetrical cis-2-alkenes as done with cis-2-butene to test whether group size on the alkene has the same effect on recrossing that is seen from an isotopic substitution in inertial isotope effects. The alkene studied for this experiment was cis-2-heptene and the resulting product ratios were measured by looking at a ^{1}H NMR of a completed reaction and looking at the protons beta to the carbonyl for each product (Figure 2.14).



24 **25**

Figure 2.14. Protons that were used to determine product ratios in the ^{1}H NMR. Proton for **24** was at a frequency of 3.0 ppm and proton for **25** was at a frequency of 2.9 ppm.

The full spectra can be seen in the experimental chapter and the protons were assigned based literature values for 2,2-dichlorocyclobutanones which arise in the 3.0 ppm region. The assignment for the proton of **24** versus **25** was done based on coupling constants. Because the proton of **24** is coupled by 4 other protons while the proton from **25** is coupled by only 3 other protons, the proton for **24** should have a larger total coupling constant associated with its spectral peak. Integrations of these peaks give an relative ratio of 46.5 % for **24** and 53.5 % for **25.** While the product ratio difference is not large there is still a slight preference for the dichloroketene to attack the side with the longer chain over the side with the methyl group. This correlates well with the isotopic observation of cis-2-butene where there was a preference for the dichloroketene to attack the heavier atom. As explained earlier this could be due to the preference to form the second bond to be associated with a lighter atom or in this case a smaller chain.

In order to further study these experimental results we turn to theoretical calculations. The transition state and starting materials were optimized with a MPW1K/6-31+G** level of theory for the cycloaddition of dichloroketene and cis-2-undecene (the optimized transition state can be seen in Figure 2.15). Cis-2-undecene was chosen to study theoretically instead of cis-2-heptene for hopes to enhance the recrossing effect that we predict as the cause of the product ratio difference observed experimentally.

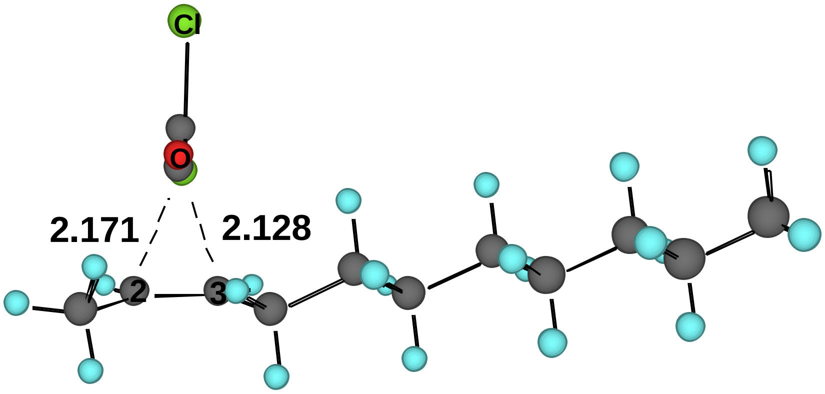


Figure 2.15. Transition state for the cycloaddition of dichloroketene and cis-2-undecene with a MPW1K/6-31+G** level of theory.

The associated bond distance for the ketene olefin C-C distance is 2.171 Å and 2.128 Å for the C2 and C3 carbon respectively. Showing a slight preference for the attack on the C3 carbon. Instead of two separate transition state structures to afford the two products there is one transition state on a bifurcating energy surface leading to the two products. In order to examine the product ratios from a theoretical perspective dynamic trajectories were employed in much the same way as with the cis-2-butene and cyclohexene studies. The trajectory studies are summarized in Table 2.9.

Table 2.9. Trajectory results for the cycloaddition of dichloroketene and cis-2-undecene from a MPW1K/6-31G* energy surface.

Total runs	Total recrossing	Product 15	Product 16
231	158	47	26

As can be seen in the table the trajectory study predicts the opposite effect that is seen experimentally. While the amount of recrossing reaches an astounding 68 % of the trajectories, the dynamic runs show a 1.8 : 1 preference for formation of product **24**. While we would predict based on the previous results of cis-2-butene and the experimental evidence that the trajectories would favor the formation of **25**, the theoretical results tell a different story. Clearly the theory used in this case does not encompass the true nature of this reaction. As to the reasoning why the theory fails in this case there are many possible explanation and the true nature of the erroneous prediction will never truly be understood. However, it is possible that a different method or basis set could give a more accurate description of the energy surface and ultimately correct this discrepancy. Further investigation will need to be done to in order to obtain a better understanding of this system.

2.5 Experimental Procedures

2.5.1 General

Oven-dried glassware was cooled under a stream of nitrogen prior to use, and standard syringe-and-septa techniques were employed in all cases. The reaction apparatus was a 500 mL three-necked round-bottomed flask equipped with dry ice condenser (using dry ice and acetone) and an addition funnel. The system was purged with nitrogen prior to use.

2.5.2 Formation and Purification of 2,2-Dichloro-3,4-dimethylcyclobutanone from the Cycloaddition of Dichloroketene and Cis-2-butene, Example Procedure

To 100 mL (1233 mmol) of dry tetrahydrofuran (THF) at 25 °C was added 5 g (76 mmol) of activated zinc-copper complex. While stirring the solution, 3.4 g (60 mmol) of cis-2-butene was added to the reaction mixture using a balloon. Using a addition funnel, 7 mL (11.3 g, 62 mmol) of trichloroacetyl chloride in 100 mL (1233 mmol) of THF was added to the solution over a four hour period and the temperature maintained at 25 °C. The reaction was allowed to stir for 16 hours. Aliquots of 0.5 mL of the reaction mixture were analyzed directly by ^{1}H NMR to insure completion of the reaction. The reaction mixture was then filtered over celite to remove any zinc. Pentane was then used to crystallize the salts in the solution which were then filtered off. The remaining solution was then concentrated under reduced pressure and washed with pentane once more. The process of washing with pentanes, filtering the salts and condensation was repeated until no more salts resulted from addition of pentane to the solution. The final concentrated crude is subjected to a silica plug using 1% ethyl acetate and hexanes. Collection of the purified material followed by further concentration under reduced pressure, lead to vacuum distillation where 2,2-Dichloro-3,4-dimethylcyclobutanone is collected at 40 °C at 0.1 mm Hg. The product is a clear viscous oil. About 600 mg of pure 2,2-Dichloro-3,4-ube to reach a height of 5 cm. This is the general procedure used for all KIE measurements of 2,2-Dichloro-3,4-dimethylcyclobutanone.

2.5.3 NMR Measurements of 2,2-Dichloro-3,4-dimethylcyclobutanone

All NMR samples were prepared in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 160 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 347 224 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half height. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction is ever applied. Six spectra were recorded for each sample. The complete results from the NMR measurements and the details of the calculation of the ^{13}C ratios and KIEs are given in the next section.

2.5.4 Formation and Purification of 8,8-Dichloro-bicyclo[4.2.0]octan-7-one from the Cycloaddition of Dichloroketene and Cyclohexene, Example Procedure

To 100 mL (1233 mmol) of dry tetrahydrofuran (THF) at 25 °C was added 5 g (76 mmol) of activated zinc-copper complex. While stirring the solution, 6.1 mL (4.93 g, 60 mmol) of cyclohexene was added to the reaction mixture using a syringe. Using a addition funnel, 7 mL (11.3 g, 62 mmol) of trichloroacetyl chloride in 100 mL (1233 mmol) of THF was added to the solution over a four hour period and the temperature maintained at 25 °C. The reaction was allowed to stir for 16 hours. Aliquots of 0.5 mL of the reaction mixture were analyzed directly by ^{1}H NMR to insure completion of the reaction. The reaction mixture was then filtered over celite to remove any zinc. Pentane was then used to crystallize the salts in the solution which were then filtered off. The remaining solution was then concentrated under reduced pressure and washed with pentane once more. The process of washing with pentanes, filtering the salts and condensation was repeated until no more salts resulted from addition of pentane to the solution. The final concentrated crude is subjected to a silica plug using 1% ethyl acetate and hexanes. Collection of the purified material followed by further concentration under reduced pressure, lead to vacuum distillation where 8,8-Dichloro-bicyclo[4.2.0]octan-7-one is collected at 50 °C at 0.1 mm Hg. The product is a clear viscous oil. About 600 mg of pure 8,8-Dichloro-bicyclo[4.2.0]octan-7-one to reach a height of 5 cm. This is the general procedure used for all KIE measurements of 8,8-Dichloro-bicyclo[4.2.0]octan-7-one.

2.5.5 NMR Measurements of 8,8-Dichloro-bicyclo[4.2.0]octan-7-one

The same procedure is followed as seen in Section 2.5.3.

2.5.6 Formation and Identification of 4-Butyl-2,2-dichloro-3-methylcyclobutanone and 3-Butyl-2,2-dichloro-4-methylcyclobutanone from the Cycloaddition of Dichloroketene and Cis-2-heptene, Example Procedure

To 60 mL (740 mmol) of dry tetrahydrofuran (THF) at 25 °C was added 2.5 g (38 mmol) of activated zinc-copper complex. While stirring the solution, 2.8 mL (1.96 g, 20 mmol) of cis-2-heptene was added to the reaction mixture using a syringe. Using a addition funnel, 2.23 mL (3.64 g, 20 mmol) of trichloroacetyl chloride in 60 mL (740 mmol) of THF was added to the solution over a four hour period and the temperature maintained at 25 °C. The reaction was allowed to stir for 16 hours. Aliquots of 0.5 mL of the reaction mixture were analyzed directly by ^{1}H NMR to insure completion of the reaction. The reaction mixture was then filtered over celite to remove any zinc. Pentane was then used to crystallize the salts in the solution which were then filtered off. The remaining solution was then concentrated under reduced pressure and washed with pentane once more. The process of washing with pentanes, filtering the salts and condensation was repeated until no more salts resulted from addition of pentane to the solution. The resulting mixture was then analyzed using ^{1}H NMR to obtain the product ratio.

2.6 Summary

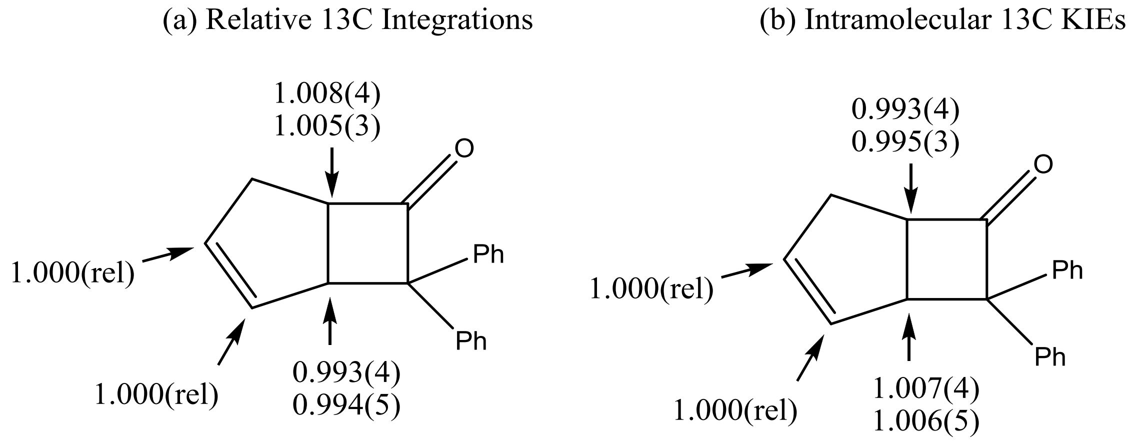
It is of course well understood that conventional TST is an approximation. Due to the complications of recrossing and tunneling, the understanding of the rates and selectivities of reactions using conventional TST is subject to some inaccuracy. That inaccuracy is often negligible, but in pernicious examples such as barrierless reactions and high-tunneling regimes, TST can fail at a qualitative level. In this regard the results here have simply demonstrated another, arguably relatively minor, inaccuracy. However, our results demonstrate that hidden dynamical bottlenecks in cycloadditions can affect experimental observations and affect the qualitative understanding of their mechanism. Even though some of the experimental findings here can not yet be understood, it is still important to note that traditional transition state theory is unable to explain our findings , indicating that more than likely dynamics are playing a role in this reaction. In turn, the unusual experimentally observed isotope effects arising from recrossing should be useful as probes of hidden intermediates and transition states in seemingly simple reactions.

CHAPTER III

TRAPPING OF AN INTERMEDIATE IN A CYCLOADDITION

3.1 Introduction

While not very prominent in literature, non-statistical recrossing has been discussed in literature since 1990 by Hase's discussion of S_N2 reactions. [40-42,50,51] As discussed earlier NSR is the non-predictable recrossing that can occur when a reaction having passed the transition state and made progress towards product formation, the trajectory hits an energetic wall and returns to starting materials. It has been later shown by the Singleton group that the cycloaddition of diphenylketene with cyclopentadiene NSR plays a significant role in determining the experimental KIEs (Figure 3.1).[43] The experimental KIEs observed did not correlate to the predicted KIEs using TST. However, once dynamic trajectories were run on this system it became obvious that NSR was playing a significant role in this reaction. Once NSR was considered the experimental evidence began to make sense. Since the transition state for the cycloaddition did not determine the products it could not accurately predict the KIE. However, the KIE represent the point at when the molecule decides to go to product and this is when it decides to recross or to go to product.



(a) Relative 13C Integrations

(b) Intramolecular 13C KIEs

Figure 3.1. Isotope effects measured for the cycloaddition of diphenylketene and cyclopentadiene.[43]

After this scientific finding, we decided to investigate further into the role that non-statistical recrossing plays in the cycloaddition of ketenes with alkenes. In particular, the Singleton group was interested in the [2 + 2] cycloaddition of dimethylketene with alkenes. Because dimethylketene is a less reactive ketene the well after the transition state is shallower or one could say less steep going towards products, this shape appears to be highly conducive for extensive recrossing and led our group to further investigate the role in which NSR plays in these reactions.

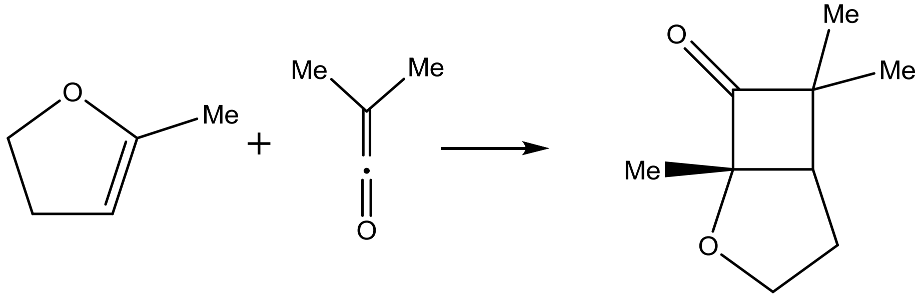
Ketene [2 +2] cycloadditions have been noted in the literature as proceeding in a concerted fashion, even though the Woodward-Hoffmann rules would suggest otherwise,[53] dynamics would support this concerted view of these cycloadditions. However, this view has evolved to a more complex view of ketene reactions, from fully synchronous and concerted transformations to highly asynchronous or even stepwise mechanisms involving biradicals or zwitterionic intermediates.[72-82]

In this chapter we will describe the experimental and theoretical study of the "cycloaddition" of dimethylketene and 2,3-dihydro-5-methylfuran and how a stepwise mechanism my be a more appropriate explanation for our experimental findings.

3.2 Experimental Results for the Reaction of Dimethylketene and 2,3-Dihydro-5-methyfuran

Many of the experimental criteria that have been applied to the differentiation of concerted and stepwise reaction pathways for ketene cycloadditions are ambiguous, as an unsymmetrical concerted process and a stepwise process have many of the same features. In cases where there is a loss of stereochemical homogeneity in the alkene or where there is isolation, spectroscopic detection, or interception of an intermediate that lies on the cycloaddition pathway, there is unequivocal evidence for a stepwise process. Such intermediates have indeed been detected in a number of cycloaddition reactions of ketenes and because of this intermediate these reactions can be considered stepwise processes.[83-85]

The types of evidence available regarding the mechanism of ketene [2 + 2] cycloadditions include theoretical analysis, stereochemistry, isotope effects, subsistent effects, solvent effects, pressure effects and activation parameters. In this chapter we utilize a combination of theoretical analysis, isotope effects, solvent effects and base effects to study the mechanism of this reaction. The reaction of interest illustrates the cyclobutanone product that is formed form this addition.



26 **27** **28**

3.2.1 Intermolecular Starting Material KIEs for the Cycloaddition of Dimethylketene and 2,3-Dihydro-5-methyl-furan

As discussed in Chapter I, intermolecular KIEs can be useful for obtaining the isotope effect on each individual carbon. Starting material KIEs were obtained for this system by taking the system to about 80 % conversion and recovering starting material **26**. The Singleton groups NMR methodology can then be applied to obtain the isotope effects for each position of the furan starting material. There are several ways to make dimethylketene in the literature.[87-91] However, the most facile approach to forming dimethylketene in situ was using isobutyryl chloride and triethylamine.[87] The observed isotope effects can be seen in Figure 3.2 below.

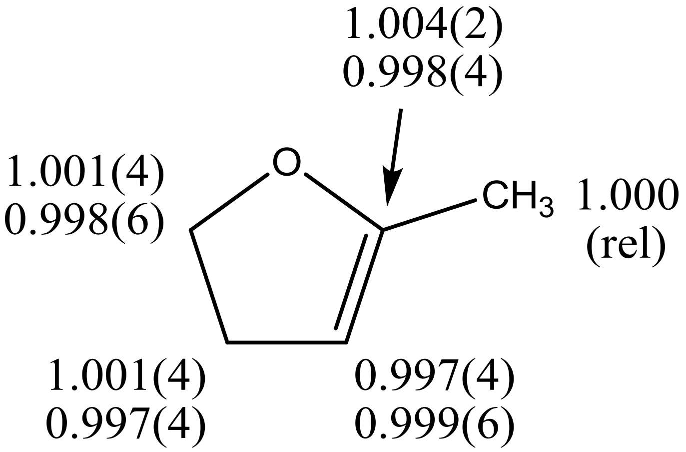
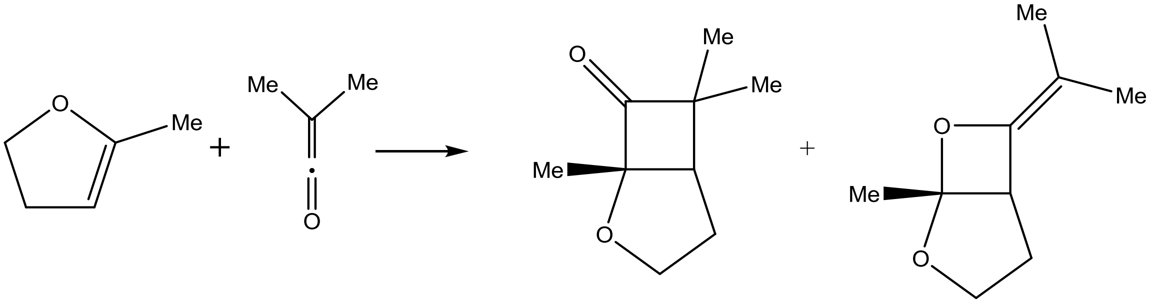


Figure 3.2. Intermolecular Starting Material KIEs for the cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran.

What is highly notable about the isotope effects above is that there is no significant isotope effect associated with any of the carbons. In order to understand these experimental observations further experimental examinations were investigated.

3.2.2 Solvent and Base Studies for the Cycloaddition of Dimethylketene and 2,3-Dihydro-5-methylfuran

After further examination of these reactions the ^1H NMR reveals that not only is cyclobutanone product **28** being formed but the oxetane product **29** can also be detected.



26 **27** **28** **29**

The formation of the second product could indicate a second transition state however from a dynamic perspective a bifurcating energy surface could be the culprit of the second product. However, this idea will be examined further in the theoretical section. This reaction was originally preformed in o-dichlorobenzene and the ratio based on ^{1}H NMR of **28** to **29** is 66 to 34 percent. However, by changing the solvent to dichloromethane the ratio of products change to 28 to 72 percent. This observed difference gives no indication of whether this reaction proceeds through a concerted process with two transition states or a bifurcating energy surface in which a stepwise process might be the pathway. A detailed examination of base and solvent effects was done and the results can be seen in Table 3.1.

Table 3.1. Solvent and Base studies for the cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran and the associated product ratios of **28** and **29**.

Base	**Solvent**	**28**	**29**
triethylamine	DCM[a]	28	72
triethylamine	ODCB[b]	66	34
Hunig's base	DCM[a]	product formed unable to determine ratio	
Hunig's base	ODCB[b]	43	57
tributylamine	DCM[a]	product formed unable to determine ratio	
tributylamine	ODCB[b]	48	52
Et2MeN	DCM[a]	product formed unable to determine ratio	
Et2MeN	ODCB[b]	67	33

[a]DCM (dichloromethane). [b]ODCB (o-dichlorobenzene).

The information that can be gathered from this table is that there is difference in product ratios based on the base that is used in this reaction. This indicates that the base is somehow involved in the rate-limiting step of this reaction. This might include some form of catalysis and will be examined in the next section.

3.3 Theoretical Results and Dynamic Simulations for the Reaction of Dimethylketene and 2,3-Dihydro-5-methyfuran

3.3.1 Predicted Isotope Effects for the Reaction of Dimethylketene and 2,3-Dihydro-5-methyfuran

A standard calculational exploration of this reaction was performed utilizing a gas-phase MPW1K calculation with a 6-31+G** basis set. The QUIVER program was then utilized to predict to KIE for this reaction. The transition structure used for this was done at a MPW1K/6-31+G** method and basis set and can be seen in Figure 3.3.

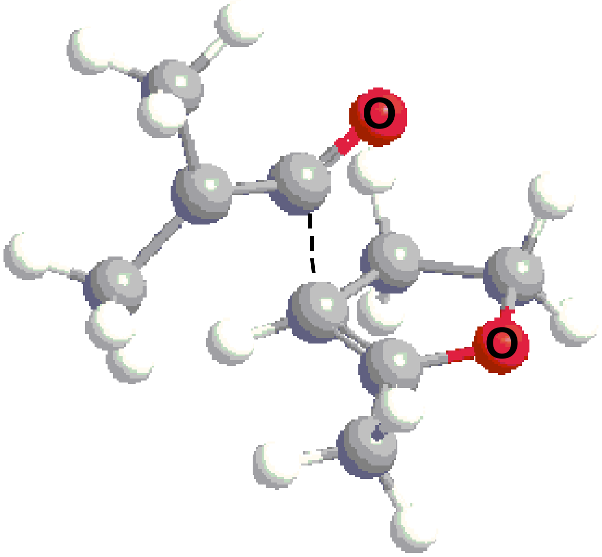


Figure 3.3. Transition State structure for the cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran using a MPW1K/6-31+G** method and basis set.

The predicted isotope effects for this transition state can be seen in Figure 3.4 below. These isotope effects indicate that there should be a significant isotope effect located at the 4 position of the furan. However, no such isotope effect is observed experimentally. This appears to be a case in which simple transition state theory cannot explain our experimental observations and so we turn to dynamics for further investigation into thus reaction.

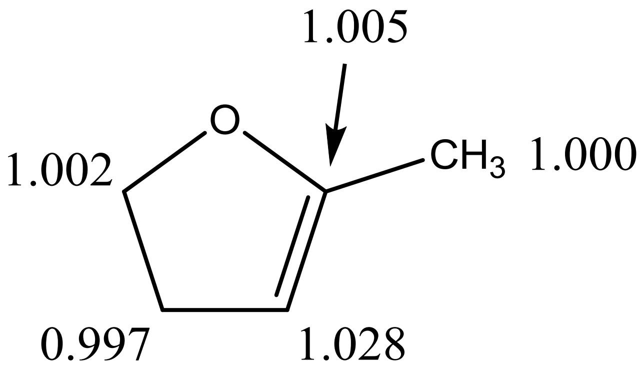


Figure 3.4. Theoretically predicted isotope effects for the cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran using a MPW1K/6-31+G** method and basis set.

3.3.2 Dynamic Studies for the Reaction of Dimethylketene and 2,3-Dihydro-5-methyfuran

Using the procedure previously employed in Chapter II for dynamics, the transition structure from Figure 3.3 was used as the starting point for quasiclassical direct dynamics trajectories on the MPW1K/6-31+G** surface. Trajectories were followed until either the cyclobutanone product **28** or oxetane product **29** were formed or recrossing occurred to afford the starting materials (defined by a C1-Ca and C2-Cb bond distance > 2.2 Å refer to Figure 3.5 for bond definition) up to a maximum of 500 fs. The results can be seen in Table 3.2.

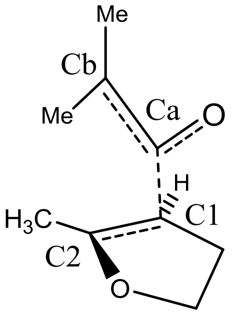


Figure 3.5. Bond definitions for the cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran.

Table 3.2. Results from Quasiclassical Trajectories Staring from MPW1K/6-31+G** transition state structure.

Total Trajectories	**Recrossed to S.M.**	**Product 28 Formed**	**Product 29 Formed**
196	179	15	2

There are several striking observations from these trajectory results. The first is the high amount of recrossing that this system exhibits, which amounts to 91 % of the trajectories. This implies that non-statistical recrossing plays a major role in this system. The second observation is that both the cyclobutanone product **28** and the oxetane product **29** are formed from this one transition state structure. This indicates that the energy surface is bifurcating for this system. However, it should also be noted that the ratio of products does not fit with our experimental observations. The experimental evidence suggests that the solvent plays are role in the product ratios and because of this it would be prudent to investigate this reaction utilizing a solvent model in our Gaussian calculations. Utilizing a MPW1K/6-31G* pcm(dichloromethane) energy surface, quasiclassical dynamic trajectories were performed. The results can be seen in Table 3.3.

Table 3.3. Results from Quasiclassical Trajectories Staring from MPW1K/6-31G* pcm(dichloromethane) transition state structure.

Total Trajectories	Recrossed to S.M.	Product 28 Formed	Product 29 Formed	Too Many Points
25	12	0	2	12

While only 25 total trajectories were completed a few striking observations can be seen from this data. First is that the oxetane product **29** appears to be favored of the cyclobutanone product (if more trajectories were run product **28** might have formed but with such few trajectories it is hard to be certain). This would fit well with our experimental observations in dichloromethane in which the oxetane product **29** is favored over the cyclobutanone product **28**. The second observation is that recrossing still seems to play an important role in this reaction with a recrossing rate of 85 % for reactive trajectories. However, the most note worthy observation from this table is the significant amount of trajectories with too many points. This would indicate that there is potentially an intermediate in the system and would make this system no longer be a concerted process. To further investigate this idea, standard calculational procedures were employed to search for the intermediate in this region along with the second transition states to be associated with the product formation. A intermediate and two transition states leading to products **28** and **29** were located on the MPW1K/6-31G* pcm(dichloromethane) energy surface. The associated reaction coordinate can be seen in Figure 3.6. The initial transition state is 25.6 kcal above the starting materials, while the intermediate is located 3.1 kcal below the first transition state. The subsequent transition states leading to the two products are located 2.9 kcal (cyclobutanone **28**) and 1.9 kcal (oxetane **29**) above the intermediate. However, both second transition states are lower in energy than the first transition state, which would make the first T.S. the rate-limiting step.

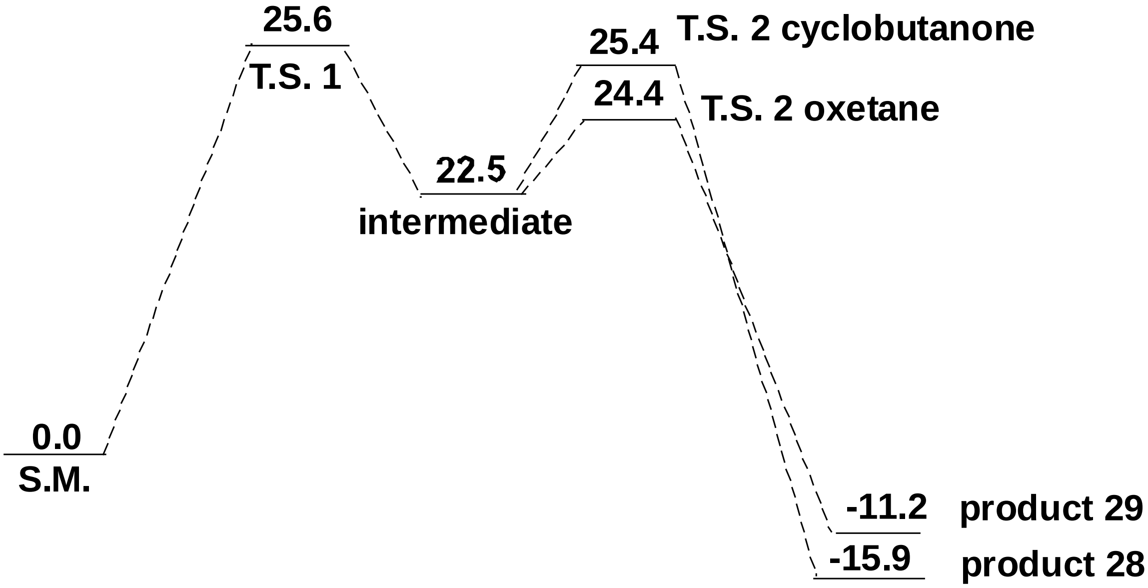
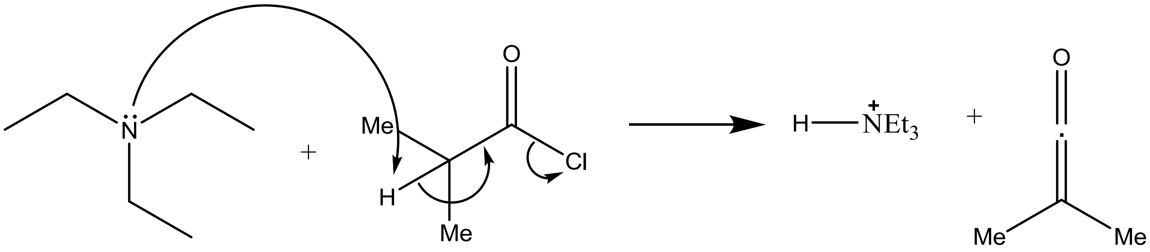


Figure 3.6. Reaction Coordinate for the addition of dimethylketene and 2,3-dihydro-5-methylfuran for the MPW1K/6-31G* pcm(dichloromethane) energy surface. Energies above lines represented in kcal.

While this explanation of a stepwise process helps one to understand the product ratios in dichloromethane, it does not explain the observed isotope effect nor does the reaction coordinate explain the differences in product ratios based on the base that was used.

To deal with this discrepancy of the bases, catalysis was examined computationally to determine the effect of a protonated amine on the reaction. What should be understood about the reaction conditions is that the formation of the ketene proceeds through acid-base chemistry. In which, the base (triethylamine) deprotonates the isobutyryl chloride which in turn kicks off the alpha chloride to form the dimethylketene. This reaction is simplified into a concerted process, however, it might be more appropriate to examine this reaction as a stepwise process of deprotonation of the isobutyryl chloride, formation of a salt complex, then elimination of the chloride to result in the formation of the ketene.



What this process implies is that over time the amount of ammonium ion will increase as more ketene is being formed and the effects of this ion on the reaction is not yet known. Using a M06-2x/6-31+G** pcm(dichloromethane) level of theory the catalyzed transition states and intermediates were located. The resulting reaction coordinate can be seen in Figure 3.7 below.

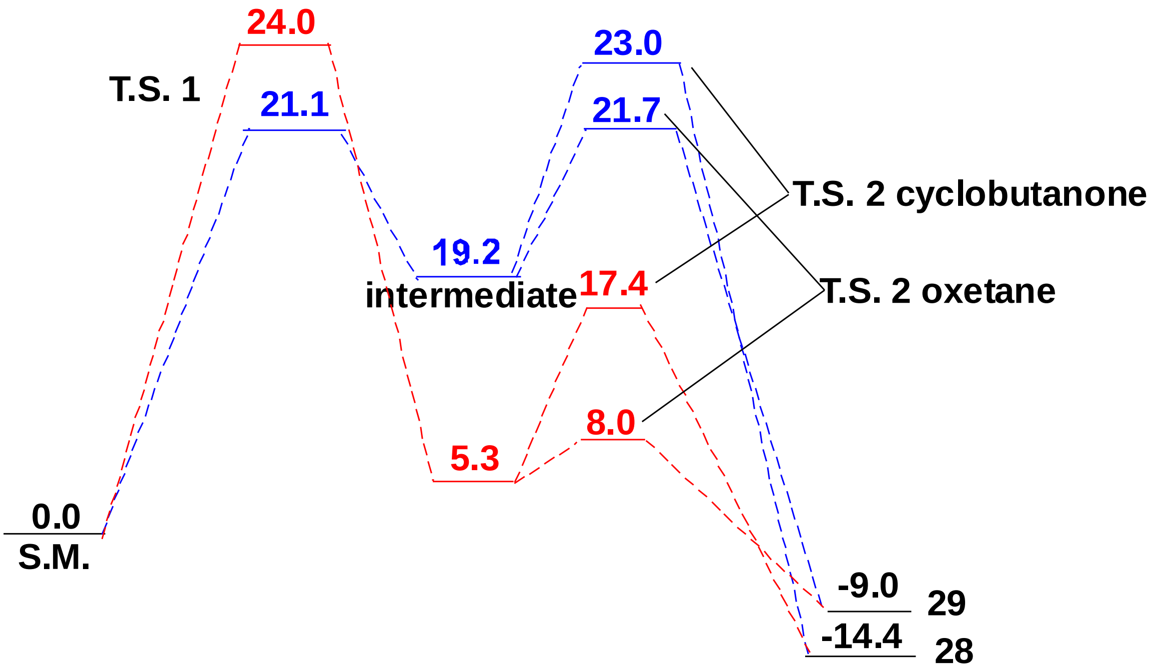
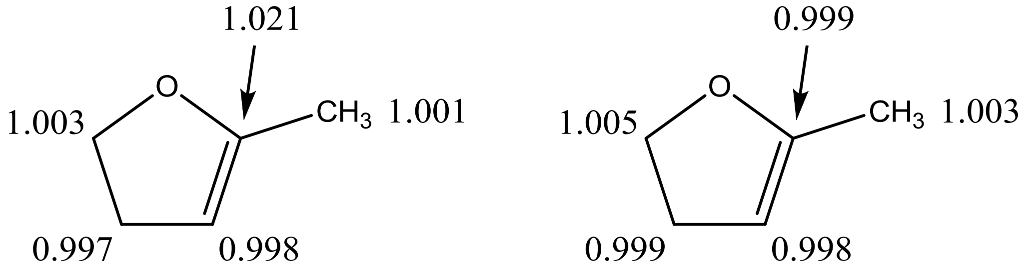


Figure 3.7. Reaction Coordinate Diagram for the catalyzed and uncatalyzed addition of dimethylketene and 2,3-dihydro-5-methylfuran for the M06-2x/6-31+G** pcm(dichloromethane) energy surface. (Red represents catalyzed process, Blue represents uncatalyzed process).

A few striking observations can be noted from Figure 3.7. Firstly, is that in the M06-2X/6-31+G** pcm(dichloromethane) energy surface the rate-limiting step is now the second transition state. This indicates that if the reaction were to proceed from a non-catalyzed process then KIE should result from a weighted average (based on the difference in energy pathway) of the two different transition states leading to product **28** and **29**. The isotope effects for the resulting transition states can be seen in Figure 3.8.

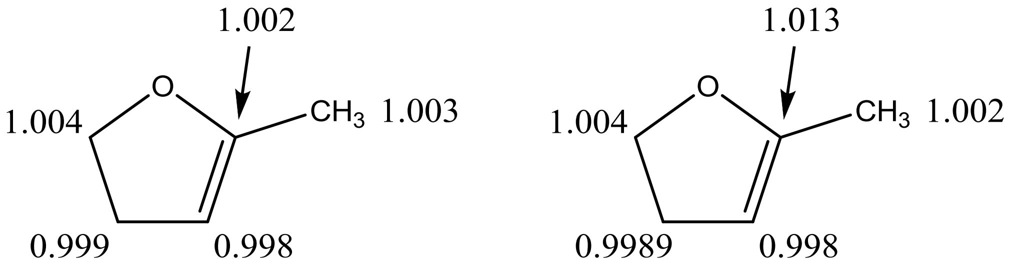


TS2 cyclobutanone **28**
product formation

TS2 oxetane **29**
product formation

Figure 3.8. Predicted KIEs for uncatalyzed TS2 for the M06-2X/6-31+G** pcm(dichloromethane) level of theory.

From these predicted KIEs what is interesting is the low isotope effects that are predicted from the transition state leading to oxetane product **29**. However, for transition state that leads to the cyclobutanone product **28**, theory predicts that there should be a significant isotope effect at the 5 position of the furan. However, no such isotope effect is observed experimentally. If this process followed "normal" transition state theory then the resulting isotope effect should result from a weighted average of the isotope effects. Based on the theoretical and experimental ratios of products the resulting weighted isotope effects can be seen in Figure 3.9.



KIE based on weighted average for theoretical product ratios

KIE based on weighted average for experimental product ratios

Figure 3.9. Weighted KIEs from the second T.S. based on theoretically predicted ratios and experimentally observed ratios.

The weighted isotope effects from the predicted ratios fit well with the experimentally observed KIEs, however using the experimental product ratios the weighted KIE depicts a significant figure at the 5 position of the olefin. What is disconcerting about the data is the discrepancy of the product ratios from theory to the experimentally observed product ratios. Looking further at Figure 3.7, a second observation is the change in the rate-limiting step when the reaction is catalyzed by the ammonium cation. While the first step in the catalyzed reaction is in fact higher in energy, complexation of the uncoordinated intermediate to the ammonium stabilizes the structure by almost 14 kcal/mol! This indicates that as more catalyst becomes available in solution the intermediate is being trapped by ammonium which will prevent the reaction from reversing to starting material and therefore the rate-limiting step is the trapping of the intermediate with the ammonium cation. This new development would explain the observed KIE that exhibits no significant effect at any carbon. However, there still appears to be a discrepancy in the theoretical product ratios with our experimentally observed product ratios. The story in this case does not appear to be clear and therefore no conclusion can be reached. However, what can be said is that this so called "concerted" process appears to be a stepwise process and the reaction mechanism appears to be enhanced through a catalytic process.

3.4 Experimental Procedures

3.4.1 General

Oven-dried glassware was cooled under a stream of nitrogen prior to use, and standard syringe-and-septa techniques were employed in all cases. The reaction apparatus was a 100 mL round-bottomed flask equipped with stir bar, septa, and positive pressure nitrogen line. The system was purged with nitrogen prior to use.

3.4.2 Formation and Purification of 2,3-Dihydro-5-methylfuran, Example Procedure

The apparatus for the formation of starting material was altered slightly have a vigreaux column attached to a distillation short path connected to a collection flask. The vigoreaux column was wrapped in heat tape and the tape was maintained at a temperature between 80 - 90 ºC. A neat mixture of 25 mL (0.25 mol) of 5-hydroxy-2-pentanone was placed in a round bottom flask. To the flask 0.375 mL of 0.1 M H_3PO_4 was added. The mixture was heated between 180 - 190 ºC with continuous stirring. The resulting distillate was a two layered mixture of water and the product 2,3-dihydro-5-methylfuran. The water was separated from the organic phase and the resulting liquid was distilled at a lower temperature to afford pure product: b.p. 82 ºC.

3.4.3 Intermolecular Kinetic Isotope Effects in the Cycloaddition of Dimethylketene and 2,3-Dihydro-5-methylfuran. Example Procedure

To 40 mL (355 mmol) of o-dichlorobenzene (ODCB) at 25 °C was added 9.4 mL (67 mmol) of triethylamine. While stirring the solution, 6 mL (66 mmol) of 2,3-dihydro-5-methylfuran was added to the reaction mixture. Using a syringe, 6.2 mL (59 mmol) of isobutyryl chloride was added to the solution slowly. The reaction was allowed to stir for 24 hours. Aliquots of 0.5 mL of the reaction mixture were analyzed directly by ^{1}H NMR to determine percent conversion of the mixture. The samples taken were from reactions taken to 85.5 and 92.2 % conversion. The reaction mixture was then washed with a NaHCO3 water wash three times and the resulting organic layer was then distilled to recover the unreacted 2,3-dihydro-5-methylfuran. About 226 mg and 194 mg of pure 2,3-dihydro-5-methylfuran was collected from two different reactions for the sample NMR and placed in a tube with C_6D_6 to reach a height of 5 cm. The standard samples were made based on the amounts of unreacted starting material recovered from the reactions.

3.4.4 NMR Measurements of 2,3-Dihydro-5-Methylfuran

All NMR samples were prepared in 5 mm NMR tubes filled to a constant height of 5 cm with C_6D_6. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 160 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 347 224 points. Integrations were numerically determined using a constant integration region for the same peak of each spectra (i.e. sample and standard) that was a constant multiple of the peak widths at half height. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction is ever applied. Six spectra were recorded for each sample and standard. The complete results from the NMR measurements and the details of the calculation of the ^{13}C ratios and KIEs are given in Appendix A.

3.5 Summary

The nature of the cycloaddition of dimethylketene with 2,3-dihydro-5-methylfuran was investigated using a combination of intermolecular starting material KIEs and theoretical models. The lack of a significant experimental isotope effect indicates the possibility of dynamics playing a major role in this reaction. However, after extensive solvent and base studies it appears that a complex catalytic process might be controlling the product selectivity of **28** and **29**. Though there is still the discrepancy of the theoretical product ratios not correlating with the experimentally observed ratios. This inconsistency confounds us and it appears that this mystery might never be solved.

CHAPTER IV

HEAVY-ATOM TUNNELING IN THE RING OPENING OF CYCLOPROPYLCARBINYL RADICAL[*]

4.1 Introduction

Tunneling is a fundamental physical phenomenon that affects the rates of barrier crossings in all chemical reactions. In most reactions, the effects of tunneling are subtle and the impact of tunneling on experimental observations is not readily recognizable. Quantum mechanical tunneling often plays an important role in which a hydrogen atom, proton, or hydride atom is transferred.[44] The 12 times larger mass of carbon, compared to hydrogen, is expected to make carbon tunneling much less likely. In most organic reactions, motion of carbon is part of the reaction coordinate, and the kinetic isotope effects are consistent with a contribution from carbon motion. However, evidence for tunneling in reactions that are dominated by carbon motion is rare, while the theoretical support for heavy-atom tunneling is unquestioned, its experimental manifestations are less obvious.

Reactions in which carbon tunneling is known to play an important role include π bond shifting in 1,3-cyclobutadiene and the ring expansion of 1-methylcyclobutylfluorocarbene.[92-100]

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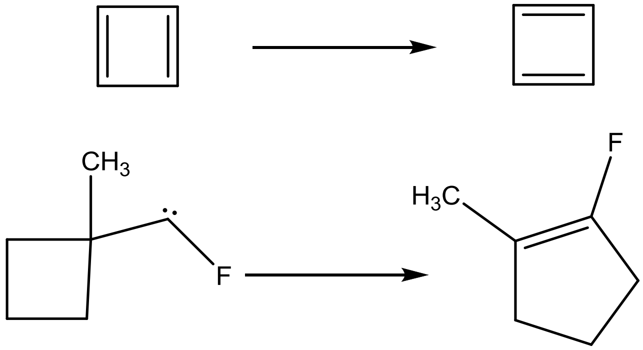
[*] Reproduced in part with permission from " Experimental Evidence for Heavy-Atom Tunneling in the Ring-Opening of Cyclopropylcarbinyl Radical from Intramolecular ^{12}C/ ^{13}C Kinetic Isotope Effects " by Gonzalez-James O. M.; Zhang, X.; Datta, A.; Hrovat, D. A.; Borden, W. T.; Singleton, D. A. *J. Am. Chem. Soc.* **2010,** *132*, 12548–12549. Copyright 2010 American Chemical Society.

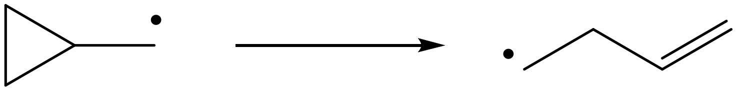


The most common evidence for heavy-atom tunneling has been the observation of reactions that occur at cryogenic temperatures, where there is insufficient thermal energy to allow passage over the reaction barrier.[92-101] The occurrence of tunneling in these reactions has been supported by calculations, which have shown that passage over the barrier is much too slow to account for the measured reaction rates, but that inclusion of tunneling provides rate constants that are in good agreement with those that have been measured.

Accurate theoretical calculations can be used to predict the contribution of tunneling to a reaction at any temperature. However, for reactions that are carried out at non-cryogenic temperatures, the question of what experimental observations, by themselves, reliably implicate heavy-atom tunneling remains open.

In 1988 Newcomb experimentally determined the rate of the radical rearrangement of cyclopropylcarbinyl radical to 3-buten-1-yl radical to be a value of $k = 1.0 * 10^8\ s^{-1}$.[102] In 2008 Borden published the theoretical calculations of this ring opening.[103] These calculations were carried out with GAUSSRATE, which the interface between Gaussian 03 and POLYRATE. Canonical variational transition state theory (CVT) calculated the rate of the ring opening at 298 K to be $k(\text{CVT}) = 1.79 * 10^7\ s^{-1}$.

When a tunneling correction was included the rate constant was calculated to be 50% higher at k(CVT+SCT) = 2.82 *10^7 s^{-1}. Borden also calculated that at low temperatures a independence of temperature is seen for the Arrhenius plot. Borden concluded that based on his computational evidence that this radical ring-opening should be another rare example of carbon tunneling to play a significant role in the reaction.



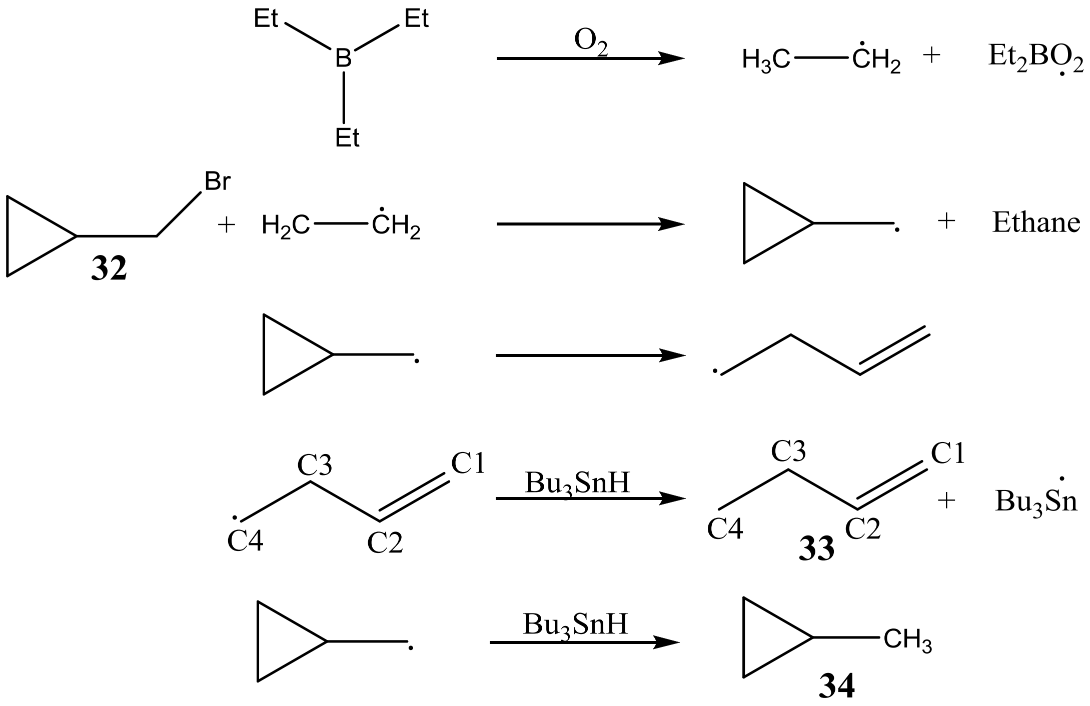
30 **31**

We describe here an experimental study of the intramolecular ^{13}C kinetic isotope effect (KIE) for the ring-opening of the cyclopropylcarbinyl radical . The results demonstrate an unprecedentedly large ^{13}C KIE and confirm recent predictions of an important role for tunneling in this reaction. A careful scrutiny of the temperature dependence of the KIE reveals an experimental diagnostic of heavy-atom tunneling in the ring opening of **30** that does not depend on a comparison between predicted and measured rate constants.

4.2 Results

Datta, Hrovat, and Borden have recently predicted that tunneling should make the ring-opening of **30** fast at 20 K.[103] A narrow reaction barrier is calculated to allow tunneling to occur rapidly, without any thermal activation, from the molecule's vibrational ground state. We sought to determine if tunneling in the ring opening of **30** would be apparent in experimental observations made at higher and more routinely accessible temperatures in solution.

Toward that end, we studied the intramolecular ^{13}C KIE for the ring opening of **30**. As probes for tunneling, intramolecular KIEs have significant advantages over absolute rate measurements; intramolecular KIEs reflect only the first irreversibly desymmetrizing step in a mechanism and they can be readily determined precisely at a broad range of temperatures. Although H/D KIEs are frequently used to investigate tunneling by hydrogen, this is the first application of $^{12}C/^{13}C$ KIEs to establishing that heavy-atom tunneling is occurring. To measure the intramolecular KIEs in the ring opening of **30**, samples of bromomethylcyclopropane (**32**) at natural abundance were reduced at temperatures ranging from -100 °C to 80 °C under free-radical chain conditions, employing tributyltin hydride as the reductant and triethylborane / O_2 as the initiator. This reduction affords 1-butene (**33**) as the major product, arising from the ring-opening of **30**, along with small amounts of methylcyclopropane (**34**), formed by the reduction of **30** before ring-opening. Under the conditions employed, the ring-opening of **30** should be irreversible (see Subsection **4.4** of this chapter for further discussion).



4.2.1 Experimental Kinetic Isotope Effect Results

The relative ^{13}C content in the C-3 versus C-4 positions of **33** was analyzed by NMR.[14,57] In all cases, less ^{13}C was observed at the C-4 position of the 1-butene than at C-3, reflecting a preference for cleavage of the ring bond to the lighter isotope of carbon. Preferential cleavage of the bond to the lighter isotope places excess ^{12}C at C-4 and excess ^{13}C at C-3 of ring-opened radical **31**. The intramolecular KIEs that are defined by the ratios of ^{13}C at C-3 and C-4 are summarized in Table 4.1.

The KIEs in Table 4.1 are strikingly large. Even at 80 °C, the ^{13}C isotope effect is over 6%, and the ^{13}C KIE ultimately increases to 16% at -100 °C. Larger ^{13}C magnetic isotope effects are known,[104,105] but among conventional ^{13}C KIEs, those in Table 4.1 are the largest known at each temperature.

Table 4.1. Intramolecular KIEs measures at various temperatures.

temperature (° C)	Experimental KIE[a,b,c]
80	1.062 ± 0.003
22	1.079 ± 0.002
0	1.085 ± 0.003
-78	1.131 ± 0.002
-100	1.163 ± 0.004

[a] Defined as k_{12C}/k_{13C}(for C-4)/k_{12C}/k_{13C}(for C-3). [b] Uncertainties are 95% confidence ranges, based on 12 measurements at 80, 22, and 0 °C, 18 measurements at -78 °C, and 6 measurements at -100 °C. [c] The reactions at 80, 22, and 0 °C were conducted in *o*-dichlorobenzene and those at -78 and -100 °C in methylcyclohexane.

4.2.2 Predicted Isotope Effects

In order to investigate the role that tunneling plays in the ^{13}C KIEs in Table 4.1, the KIEs were computed both with and without inclusion of tunneling. Canonical variational transition state theory (CVT)[106] was used to calculate the semi-classical, rate constants without tunneling; and the effect of multidimensional tunneling on the reaction dynamics was computed using the small-curvature tunneling (SCT)[107] approximation. These direct-dynamics calculations were carried out on the UB3LYP/6-31G* potential energy surface using GAUSSRATE.[108] as the interface between POLYRATE[109] and Gaussian03.[61]

Table 4.2. Predicted KIE for the ring-opening of cyclopropylcarbinyl radical.

temperature (° C)	predicted KIE[a] without tunneling	with tunneling
80	1.048	1.057
22	1.058	1.073
0	1.064	1.082
-78	1.093	1.138
-100	1.106	1.169

[a] KIE predictions without and with tunneling are based on CVT and CVT / SCT rate constants, respectively, on the UB3LYP/6-31G* potential energy surface.

As shown in Table 4.2, the theoretical KIEs without allowance for tunneling drastically underpredict the size of the observed values. The error in these predictions grows larger as the temperature decreases, rising to as large as 6%, but the error is still substantial at the high end of the temperature range. In contrast, the predicted KIEs including tunneling match well with experiment throughout the broad temperature range, with the error never exceeding 0.7%.

The contribution of tunneling to the absolute rate of the ring opening of **30**, calculated from the ratio of CVT versus CVT / SCT rate constants, varies from a factor of 1.3 at 80 °C to a factor of about four at -100 °C. With this modest level of calculated rate acceleration, in this temperature range the experimental rate constants[102] do not unequivocally implicate heavy-atom tunneling, even when compared to the results of high-quality rate calculations.[103] Other methods are needed to determine the importance of heavy-atom tunneling aside from rate constants alone.

4.3 Arrhenius Plot and Entropy Factors

Is it possible, then, to use the measured KIEs, in order to infer that tunneling is important in the ring opening of **30**, *without* recourse to comparing the measured KIEs to calculated? The contribution of tunneling to the KIE grows from approximately 1% at 80 °C to 6% at -100 °C, the latter being over a third of the total isotope effect. As a result, the experimental KIE grows much faster than semi-classical expectations as the temperature is decreased. This fact is recognizable in the curvature in the Arrhenius plot of ln KIE versus 1/T, shown in Figure 4.1.

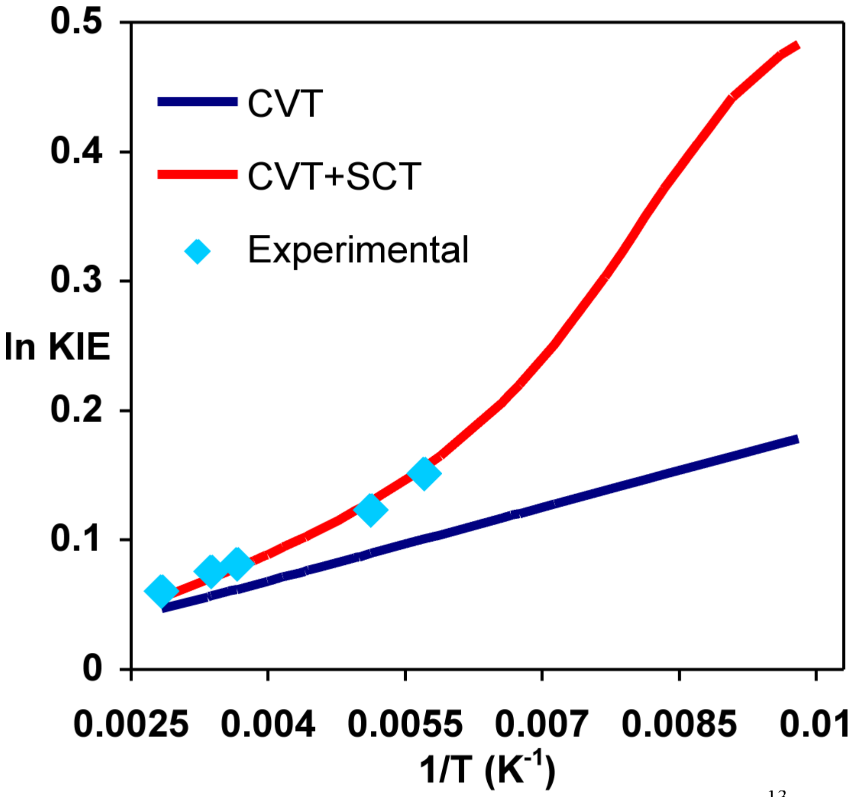


Figure 4.1. Arrhenius plot of the CVT, CVT + SCT, and experimental ^{13}C KIEs for the ring-opening of **30** from 100 to 353 K .

The Arrhenius plot of the experimental rate constants across the full temperature range of our study shows such modest curvature that it was apparently not recognized until very recently, when it was pointed out that both the E_a and A values, measured at low temperatures,[110] are smaller than the high-temperature values.[102] A least squares fit to the three high-temperature points gives Ea(^{13}C) - Ea(^{12}C) = 52 cal/mol and A(^{12}C)/A(^{13}C) = 0.987. For comparison, the two low-temperature points give Ea(^{13}C) - Ea(^{12}C) = 85 cal/mol and A(^{12}C)/A(^{13}C) = 0.908. Thermally activated tunneling by the lighter isotope increases the difference in the Ea values between ^{13}C and ^{12}C; and the effect of tunneling on lowering A values makes A(^{12}C)/A(^{13}C) << 1.0, as the importance of tunneling for the lighter isotope increases. At temperatures low enough that both the light and heavy isotopes cross the reaction barrier by tunneling, the difference between their *E*a values decreases until it becomes zero when tunneling occurs only from the lowest vibrational levels. As the difference in Ea values approaches zero, the greater efficiency of tunneling by the lighter isotope makes *A*(^{12}C)/*A*(^{13}C) > 1.0.[111]

A_{12}/A_{13} of all five data points (which equals eΔΔS‡/R), is substantially less than unity at 0.972 ± 0.008. The consideration of the isotopic Arrhenius prefactor A_{12}/A_{13} emulates a long history of the study of A_H/A_D as an indicator of hydrogen tunneling.[17,112-115]

This raises the difficult problem of defining what A_{12}/A_{13} values would be indicative of substantial tunneling. Applying the non-exact model for A_H/A_D developed by Bell,[116] A_{12}/A_{13} could conceivably fall within a range from 0.92 to 1.04 without tunneling. Using "exact" semi-classical calculations, Schneider and Stern found that a broad range of values is possible for A_H/A_D without tunneling and that there is probably no strictly defined semi-classical lower limit.[117] Such analyses do not encourage the use of A_{12}/A_{13} to suggest tunneling; however, they are only establishing theoretical possibilities for the range of possible isotopic Arrhenius prefactors and not the likelihood of unusual values. The different approach taken here[118] attempts to define the range of A_{12}/A_{13} values that may be realistically expected at ordinary temperatures in the absence of tunneling.

To evaluate semiclassical expectations, 201 sets of exact semi-classical primary ^{13}C KIEs were calculated at temperatures ranging from -100 °C to 80 °C. This was accomplished by first optimizing ground-state and transition structures for a diverse series of reactions in B3LYP/6-31G* calculations, then calculating the isotope effects from the harmonic frequencies. The derived A_{12}/A_{13} values varied little over this temperature range, and we focused on the values defined by the complete -100 °C / 80 °C range.

A histogram of the semi-classical A_{12}/A_{13} values obtained is summarized in Figure 4.2. For comparison, we also calculated the isotope effects including a tunneling correction based on a simple one-dimension truncated parabola model. Figure 2 shows the differing distribution of A_{12}/A_{13} values when this tunneling estimate is included. The semi-classical A_{12}/A_{13} values are tightly bunched around unity, with an average of 1.005, a standard deviation of 0.008, and a total range of 0.986 to 1.025. On the assumption that our limited set of model reactions is representative of the universe of organic reactions, A_{12}/A_{13} values outside of this range would be strong evidence for an involvement of substantial tunneling. The inclusion of the tunneling correction leaves most A_{12}/A_{13} values within this range; this is in line with the expectation that in most reactions heavy-atom tunneling plays a minimal role. However, the distribution of A_{12}/A_{13} including the tunneling correction is skewed downward and predicted values as low as 0.79 were obtained. A detailed table of the reactions studied is given in the theoretical section of this chapter. In the light of the contrasting semi-classical and tunneling-inclusive distributions, the experimental A_{12}/A_{13} of 0.972 ± 0.008 for the cyclopropylcarbinyl ring opening is readily interpreted as indicative of substantial heavy-atom tunneling.

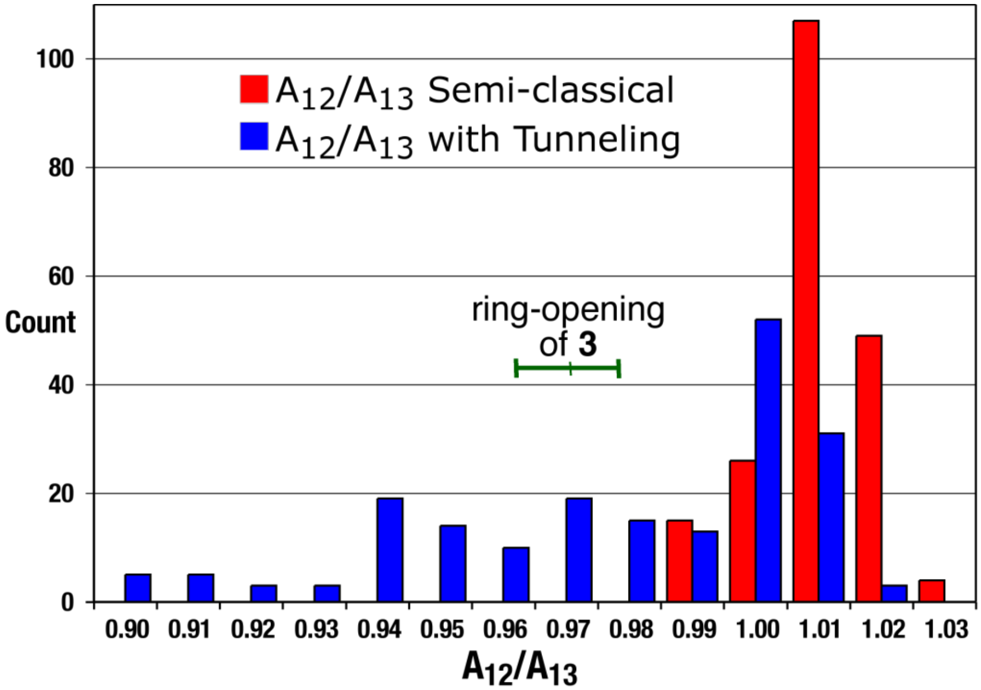


Figure 4.2. Histogram of calculated A_{12}/A_{13} values over a temperature range of -100 °C to 80 °C for 201 sets of primary ^{13}C KIEs. The red bars are derived from semi-classical KIEs while the blue bars are derived from KIEs including a tunneling correction. The histogram bins are ±0.005 from the center-point numbers shown on the abscissa.

4.4 Notes on the Irreversibility of the Ring-opening of Cyclopropylcarbinyl Radical

The experimental rate constant of the reversible process (k_r) is 4.9 x 10^3 s^{-1} at 25 °C.[119] The competing rate constant of the hydrogen abstraction from the tributyltin hydride (k_H) is known to be 2.4 x 10^6 M^{-1} s^{-1} at 25 °C from the literature.[120] Although the tributyltin hydride is added slowly as a precaution, the oxygen-initiation of the reaction occurred with the tributyltin hydride concentration at 1.3 M, making the pseudo-first order rate constant of k_H 3.1 x 10^6 s^{-1} at 25 °C,1000 times faster than k_r.

If there were any significant reversibility of the ring opening, then the isotope effect observed would start to reflect the step transferring a hydrogen from the tin hydride to the butenyl radical. The predicted carbon isotope effect for this step at 25 °C is 1.032. Because the observed isotope effects are much higher, and agree with predictions for the ring-opening step but not the hydrogen transfer step, this weighs against significant reversibility in the reaction.

4.5 Experimental Procedures

4.5.1 General

Oven-dried or flame-dried glassware was cooled under a stream of nitrogen prior to use, and standard syringe-and-septa techniques were employed in all cases. The reaction apparatus was a 100 mL three-necked round-bottomed flask equipped with an internal thermometer and a Vigreaux column connected to a distillation apparatus and Schlenck receiver flask (cooled in a -42 °C bath during the distillation). The system was purged with nitrogen prior to use.

4.5.2 Formation and Distillation of 1-Butene from the Ring-opening of Cyclopropylcarbinyl Radical, Example Procedure

To 5 mL (44 mmol) of 1,2-dichlorobenzene at 22 °C was added 0.97 mL (1.35 g, 10 mmol) of (bromomethyl)cyclopropane by syringe. While stirring the solution, 0.2 mL (0.14 g, 1.4 mmol) of triethylborane was added dropwise to the reaction mixture. Using a syringe pump, 3.25 mL (3.52 g, 12 mmol) of tributyltin hydride was added to the solution over a 1-h period. In order to initiate the reaction, 60 mL of air was bubbled into the solution using a syringe pump over a 1-h period. Until the reaction was complete, the addition of several air bubbles at once led to an increase in the internal reaction temperature, and this temperature change was used to judge whether the reaction was complete. In addition, 0.5 mL aliquots of the reaction mixture were analyzed directly by ^{1}H NMR (applicable only to reactions at or above ambient temperature). The reactions at 22 °C were judged to be complete after the 1-h period. The reaction mixture was then distilled to afford the 1-butene. Deuterated chloroform (approximately 0.5 mL) was then added to the 1-butene and the resulting mixture was sealed in an NMR tube.

Closely analogous processes and reagent amounts were employed in procedures at 80 °C, 0 °C, -78 °C and -100 °C and in replicate procedures. For reactions performed at -78 °C and -100 °C, 5 mL (39 mmol) of methylcyclohexane was used as the solvent in place of the 1,2-dichlorobenzene that was used in the higher temperature reactions. Longer reaction times (2-3 h) were employed for the reactions at -78 °C and -100 °C.

4.5.3 NMR Measurements

All NMR samples were prepared in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 160 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 347 224 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half height. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction is ever applied. Six spectra were recorded for each sample. The complete results from the NMR measurements and the details of the calculation of the ^{13}C ratios and KIEs are given in the next section.

4.6 Summary

The extraordinarily large ^{13}C KIEs seen in Table 4.1, curvature in the Arrhenius plot and the unusual isotopic Arrhenius prefactor observed here as experimental indicators of heavy-atom tunneling are still arguably subtle effects that can only be observed with careful study. Correlation with theoretical isotope effects is only accomplished when tunneling is included in the prediction, further supporting the importance for heavy-atom tunneling in this reaction. However, the heavy-atom tunneling itself has a larger if less recognizable effect on the overall outcome of the reaction. For example, under our conditions at -100 °C the reduction of cyclopropylcarbinyl radical produces mainly 1-butene plus 38% of non-ring-opened methylcyclopropane, but without the rate acceleration provided by heavy-atom tunneling the 1-butene would be a minor product. A full understanding of observations will require allowance for the role of heavy-atom tunneling.

CHAPTER V

ISOTOPE EFFECT, MECHANISM, AND ORIGIN OF CATALYSIS IN THE DECARBOXYLATION OF MANDELYLTHIAMIN[*]

5.1 Introduction

Mandelylthiamin (MTh) is formally the conjugate of thiamin and benzoylformate.[121] It is the simplified analogue of the first covalent intermediate in benzoylformate decarboxylase.[122] Although MTh is the functional equivalent of the enzymatic intermediate, the decarboxylation is 10^6-fold less reactive.[121] Thiamin diphosphate (TDP)-dependent enzymes catalyze reactions through protein-bound covalent intermediates derived from the substrate and cofactor.[122] The reactivity of synthesized conjugates of thiamin that parallel these intermediates provides a quantitative basis for evaluating the specific role of proteins in the enzymatic reactions as well as giving insights into the detailed mechanism associated with the cofactor.[124,125] Spectroscopic and crystallographic studies have shown that these intermediates can be observed and quantified on enzymes.[126-132] Because of this, Kluger investigated the reactivity of the intermediates in the conversion of benzoylformate to benzaldehyde and carbon dioxide.[133] The enzymatic process resembles the decarboxylation of pyruvate and is specifically catalyzed by benzoylformate decarboxylase (BFD). The enzyme adds thiamin diphosphate to the carbonyl group of benzoylformate to form the enzyme-

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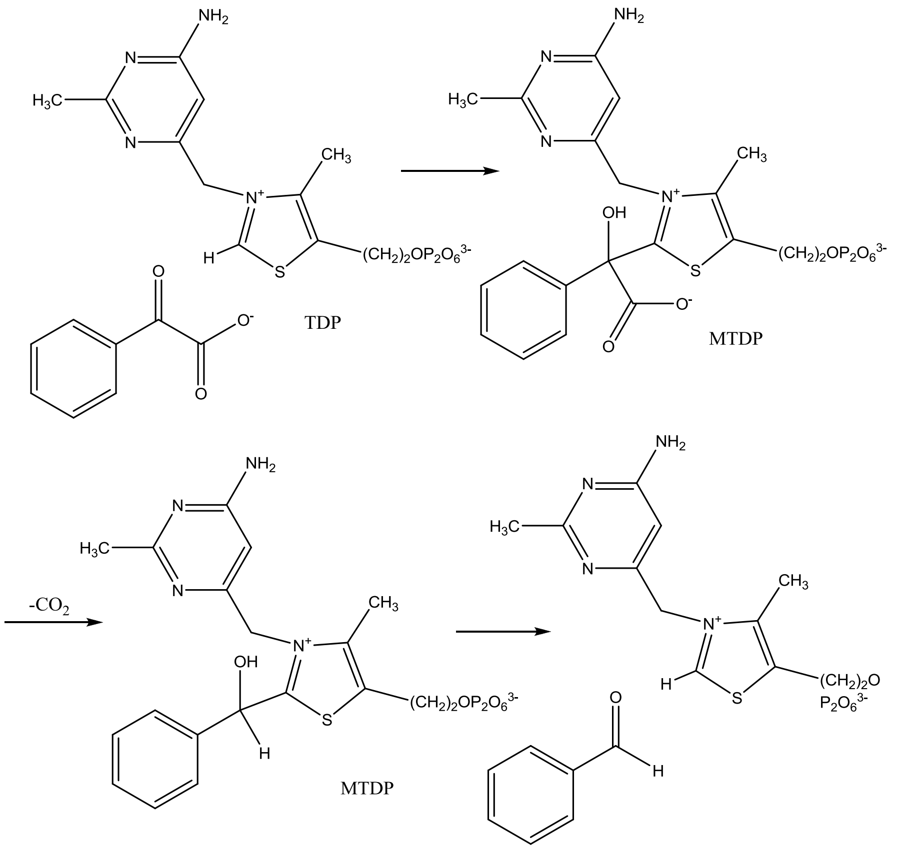
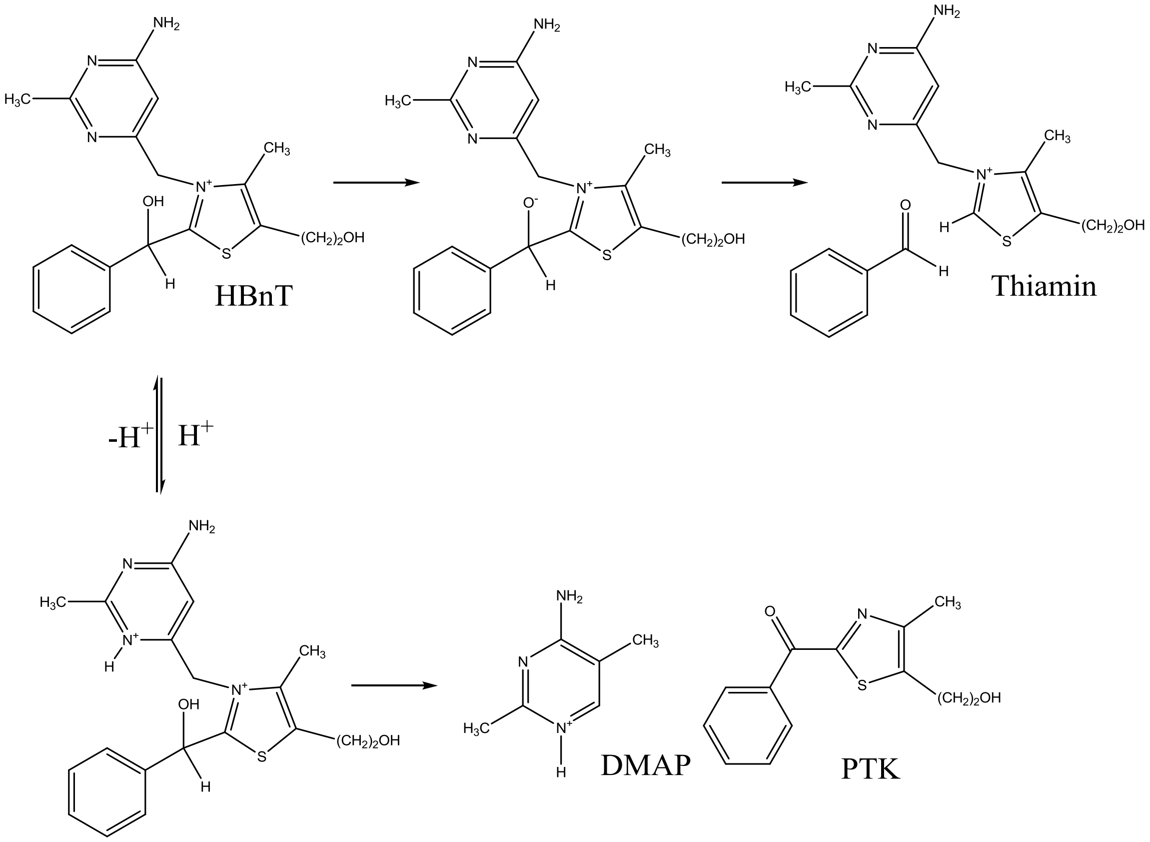
bound 2-(2-mandelyl)TDP (MTDP). Loss of carbon dioxide from MTDP is followed by protonation of the resulting carbanion to yield 2-(1-hydroxybenzyl)TDP (HBnTDP) precursor to benzaldehyde. Then breakdown of HBnTDP through the initial formation of its C2α-alkoxide, releases benzaldehyde and TDP. The simplified but chemically correct analogue of MTDP is 2-(2-mandelyl)thiamin (MTh) and undergoes decarboxylation at a relatively rapid rate compared to most carboxylic acids.



However, the rate constants for the decarboxylation of MTh is much smaller compared to the enzymatic process by about a factor of 10^6. Moreover, another divergence from the enzymatic reaction is the observation that the product of the decarboxylation of MTh, the conjugate base of 2-(1-hydroxbenzyl)thiamin (HBnT), undergoes a fast fragmentation reaction that cleaves the thiamin-derived portion of the conjugate base of HBnT. Protonation of the carbanion at the C2α position competes with the fragmentation process. While studying the intricacies of this mechanism as compared to the enzymatic process Kluger noted that the decarboxylation was pH dependent as well as the fragmentation process.[133]



Kluger achieved the synthesis of MTh from addition of benzoylformate and thiamin by condensation of the C2-conjugate base of thiamin with ethyl benzoylformate in ethanol in the presence of magnesium chloride. Hydrolysis of the ester in concentrated acid occurs without decarboxylation of the product. Kluger performed a pH-rate profile and product distribution for the decarboxylation of MTh to provide a comparison with the enzymatic reaction.[133] The profile that was performed in shown in Figure 5.1.

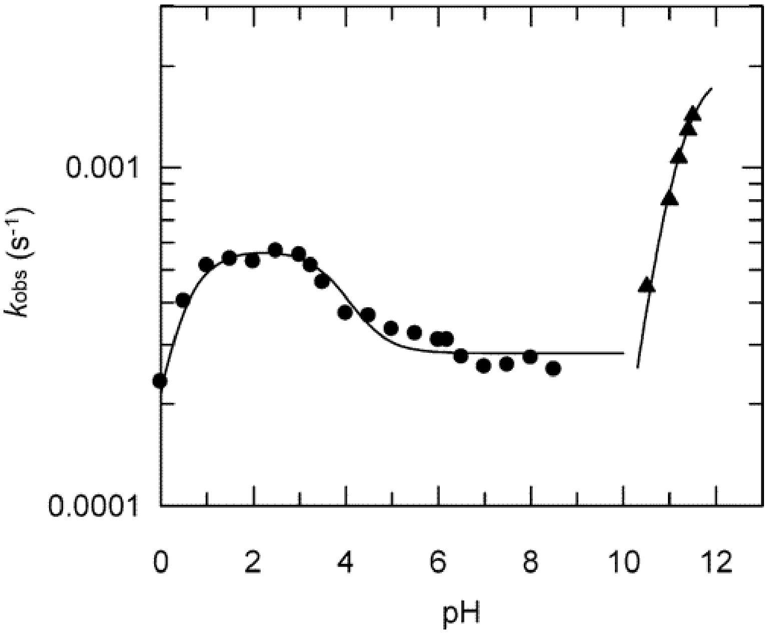


Figure 5.1. Observed first-order rate constants for decarboxylation of MTh (●) and elimination of benzoylformate from MTh(▲) as a function of pH. The data were fit to eq. 5.1 for the decarboxylation reaction and eq. 5.2 for the elimination reaction.[133]

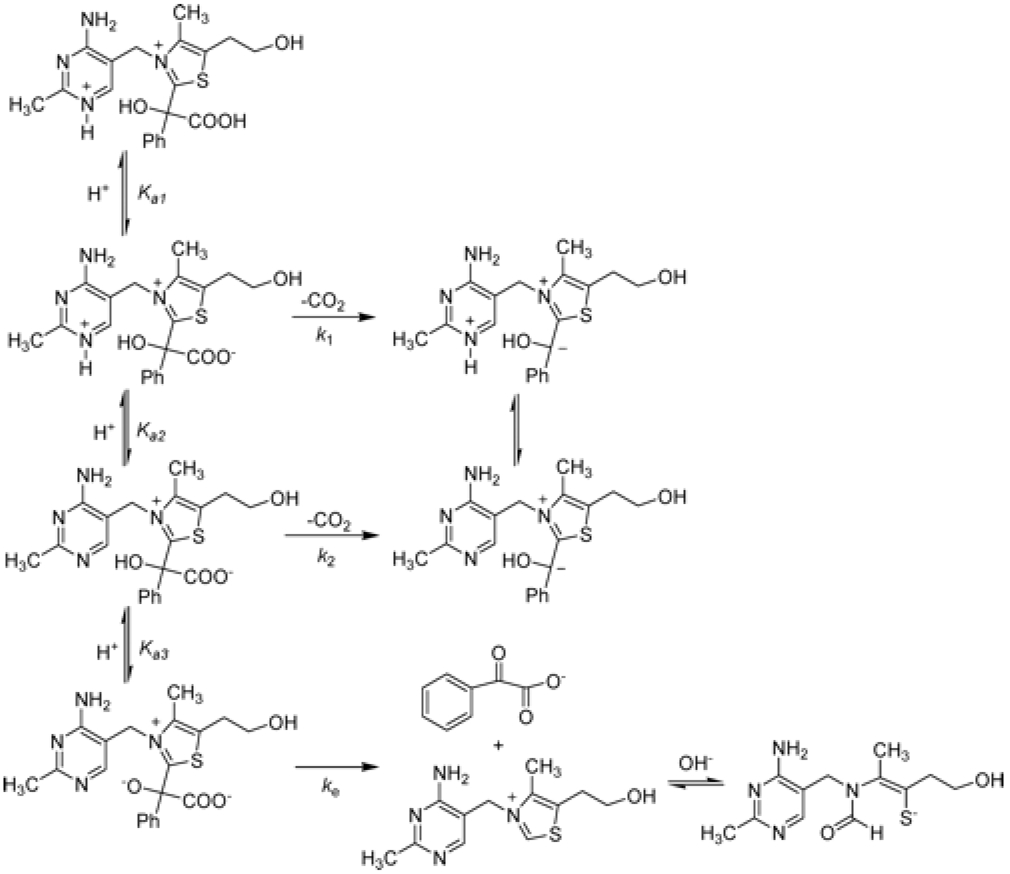
The profile shows distinct features that relate to the structure and reactions of MTh. The loss of carbon dioxide requires that the carboxyl group is not protonated, hence the increase from the highly acid region toward 0.01 M acid, leveling at pH 3. Throughout this acidic region the data fit a line generated by eq. 5.1.[133]

$$k_{obsd} = \frac{K_{a1} \cdot K_{a2} \cdot k_2 + K_{a1} \cdot k_1 \cdot [H^+]}{K_{a1} \cdot K_{a2} + K_{a1} \cdot [H^+] + [H^+]^2} \qquad (5.1)$$

The elimination of benzoylformate from MT is specific base catalyzed as seen in represented by eq. 5.2.

$$k_{obsd} = \frac{k_e \cdot [OH^-]}{K_w / K_{a3} + [OH^-]} \tag{5.2}$$

MTh has three distinct protonation states, each with its own apparent rate of decarboxylation. If the solution is more acidic than 0.03 M HCl, both the N1' and the carboxyl group are protonated. This form is unreactive towards decarboxylation. From 0.03 M to pH 4, only the N1' of the pyrimidine is protonated, while the carboxyl is ionized. This is the region in which the decarboxylation is the most rapid. From pH 4 to pH 8.5, N1' is not protonated along with the carboxyl group and the MTh decarboxylates some what more slowly. This reduced reactivity can be explained by the reduced inductive effect that would stabilize the anionic portion of the transition state of the neutral pyrimidine. At higher pH than 8.5, retrograde elimination of benzoylformate, followed by ring-opening of the resulting thiamin through addition of hydroxide, is the fastest process. This is described by eq. 5.2. From fitting the observed rate constant to this equation, k_e for elimination is 0.5 M^{-1} s^{-1}.[133]



The apparent pKa = 0.2 (from K_{a1}) that fits the data for the carboxyl group is very low but similar to other compounds of this type. The acid form overall is a dication due to the thiazolium and protonated pyrimidine. The second pK_a (= 3.9 from K_{a2}) is as expected for the conjugate acid of the pyrimidine. The decarboxylation rate constants are $(5.6 \pm 0.4) \times 10^{-4}$ s^{-1} (low pH) and $(3.0 \pm 0.4) \times 10^{-4}$ s^{-1} (neutral solution), corresponding to the forms on either side of the pK_a of the pyrimidine.[133]

As expected from the structure of MTh and the likely transition state for decarboxylation, most buffers had no effect on the rate of the decarboxylation of MTh. However, because the immediate product is subject to fragmentation, increasing concentrations of Brønsted acids, in general, divert the initial products formed upon loss of carbon dioxide from fragmentation (PTK and DMAP) to HBnT. Thus, protonation of the conjugate base of HBnT from the decarboxylation of MT is general acid catalyzed, consistent with the general base catalysis mechanism of C2α deprotonation of HBnT. The effect of concentration of the acid component of the buffer on the product distribution gives information needed to calculate the specific rate constant for fragmentation and protonation based on the estimated pK_a for dissociation of the C2α proton. Based on this observation Kluger was surprised by the catalysis of this reaction from pyridinium.[133]

5.2 Catalysis of the Decarboxylation of Mandelylthiamin

While the decarboxylation of MTh is relatively faster than most decarboxylations, the non enzymatic decarboxylation itself is 10^6 times slower than the enzymatic process and the formation of the benzaldehyde and thiamin does not occur, instead one observes the fragmentation of the conjugate acid of HBnT to form DMAP and PTK. Kluger study possible catalysis of this reaction in acidic medium and noted that this reaction was catalyzed by the conjugate acid of pyridine, pyridinium.

In the course of examining the reactivity patterns of MTh, Kluger discovered that its decarboxylation is accelerated by certain buffers.[134] The data in Figure 5.2 show that the decarboxylation of MTh is accelerated by buffers containing pyridine or 4-picoline and slightly accelerated by N-ethylpyridinium. Kluger used solutions at pH = p*K*a (pH 4.6- Kluger tested whether the acceleration from pyridine and 4-picoline arises from their effect on solvent polarity. Kluger used ethanol as an additive with a dielectric constant similar to that of pyridine. The addition of ethanol (0.1- 0.8 M) to 0.1 M phosphate buffer does not change significantly the observed rate coefficient for decarboxylation.[134]

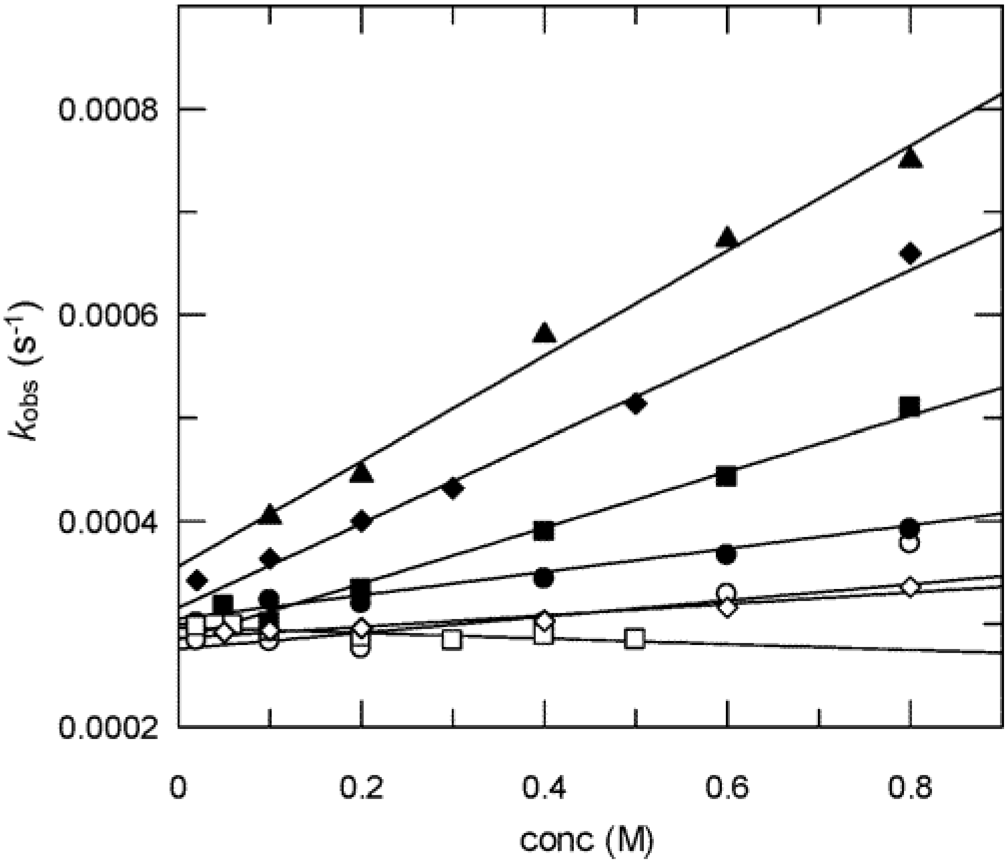


Figure 5.2. MTh decarboxylation in acetate (○), bis-tris (●), phosphate (□), pyridine (▲), and 4-picoline (♦) buffers, pH = pK_a of each buffer (acetate at pH 4.6, bis-tris at pH 6.7, phosphate at pH 6.5, 4-picoline at pH 6.0, and pyridine at pH 5.4). In the case of ethanol (◊), 0.1 M phosphate at pH 6.5 was used as buffer, and ethanol was added as a solvent component. In the case of ethyl pyridinium (■), 0.1 M phosphate at pH 6.5 was used as buffer, and ethyl pyridinium chloride was added as a component for maintenance of ionic strength.[134]

It should be noted that in 2006 Kluger studied the catalysis again and reports no acceleration in decarboxylation with the use of N-ethylpyridinium as seen in Figure 5.3.[133]

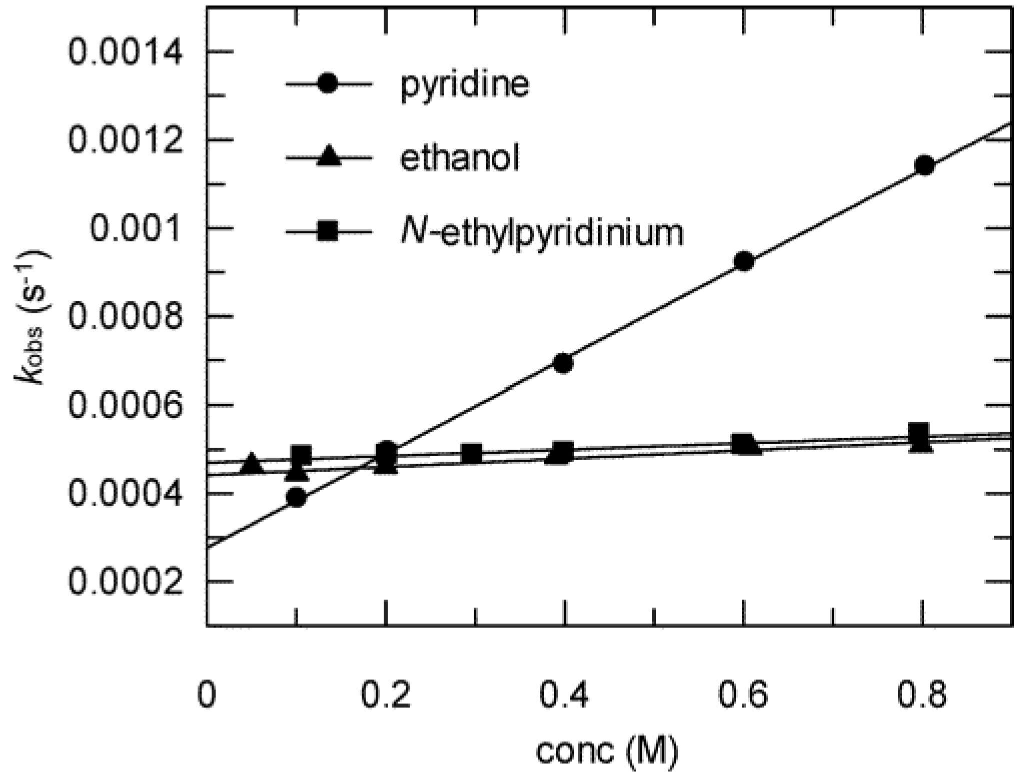


Figure 5.3. Observed first-order rate constants for decarboxylation of MT as a function of concentrations of pyridine, ethanol, and *N*-ethylpyridinium chloride in 0.2 M pyridine buffered solution at pH = pK_a‘, I = 1.0, 25 °C. The second-order rate constants from the slopes of the plots: pyridine, $k = (1.1 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1}; ethanol, $k = (9.3 \pm 1.2) \times 10^{-5}$ M^{-1} s^{-1}; *N*-ethylpyridinium chloride, $k = (7.3 \pm 1.1) \times 10^{-5}$ M^{-1} s^{-1}.[133]

Kluger also studied the variation of the pyridine acid/base buffer ratio to determine the catalytically active component. The total concentration of buffer was less than 0.8 M. A plot of the second-order rate coefficient for decarboxylation of MT as a function of the mole fraction of the acid component indicates that this is the catalytic component (Figure 5.4).[133]

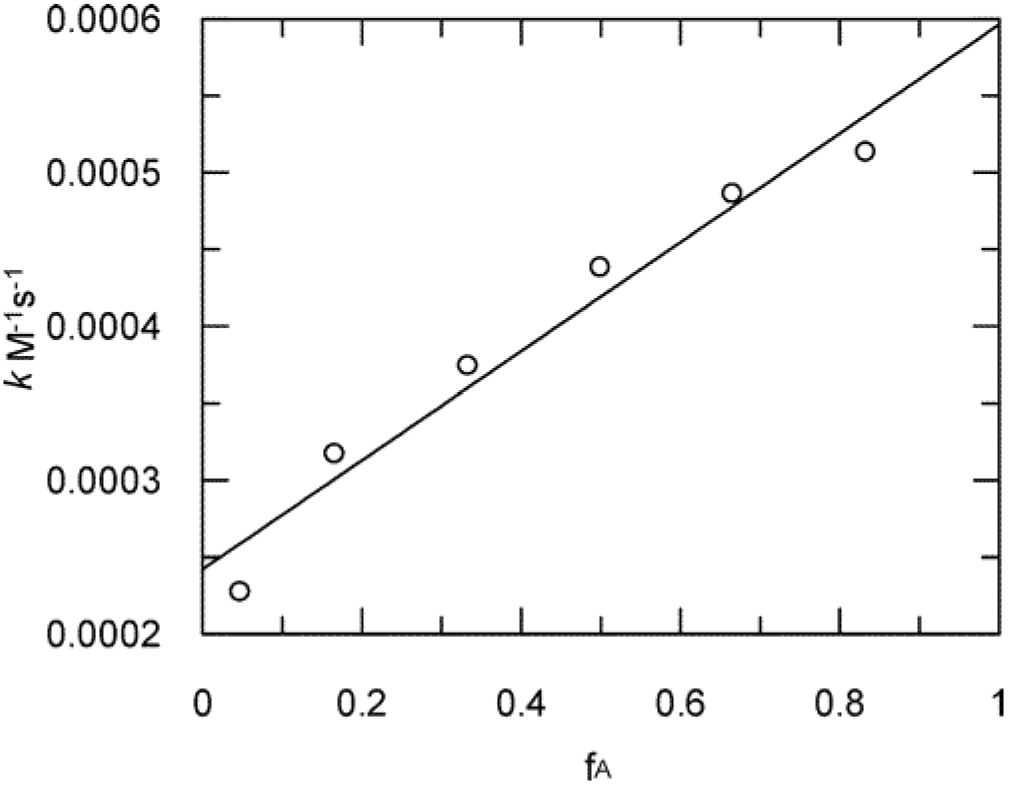


Figure 5.4. Second-order rate coefficient for decarboxylation of MT in pyridine buffer vs the acid fraction (f_A) of the pyridine buffer (acid component/total buffer). pH = pK_a‘, I = 1.0, 25 °C.[133]

C-Alkyl pyridines (2,4,6-collidine, 2,6,-lutidine, Figure 5.5) as well as 2-picoline and 4-picoline are effective catalysts, but other nitrogen-containing heterocyclic bases are not effective, as exemplified by morpholine and imidazole (Figure 5.6).[133]

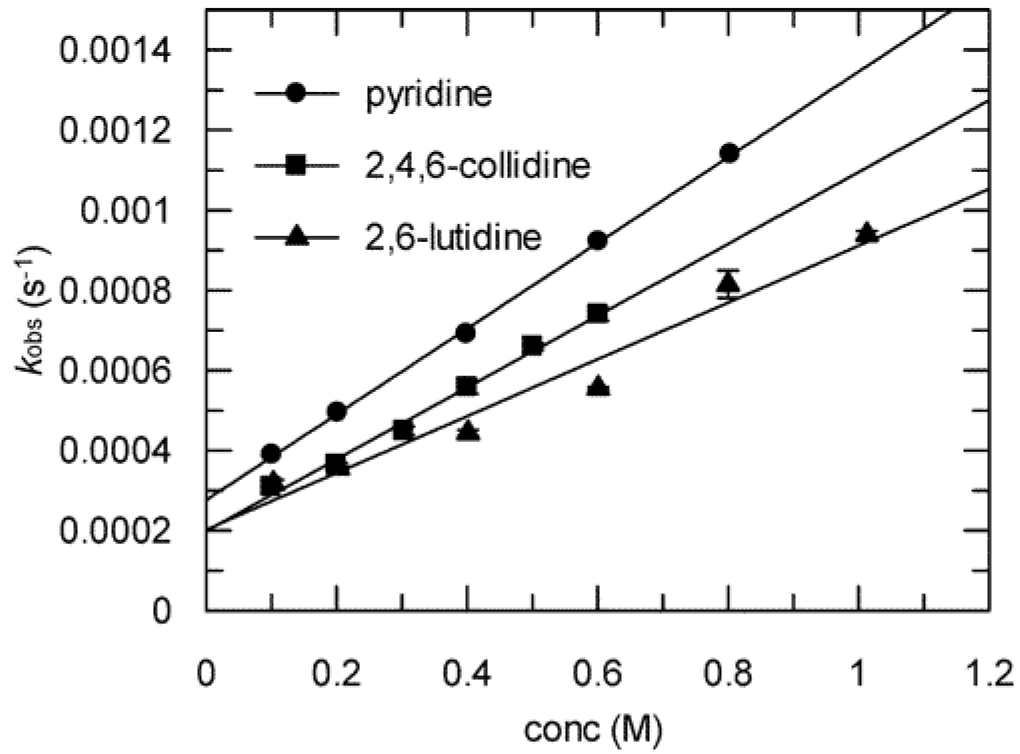


Figure 5.5. Dependence of the observed first-order rate constant for decarboxylation of MT on (substituted) pyridine buffer concentration. pH = pK_a‘, I = 1.0, 25 °C.[133]

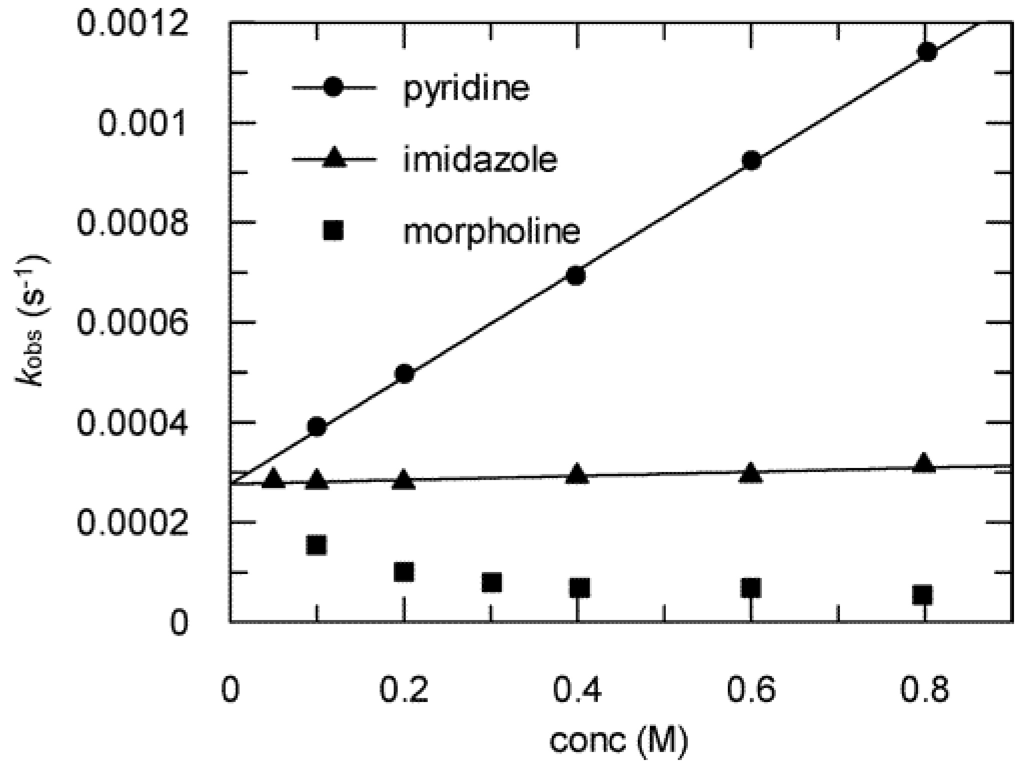
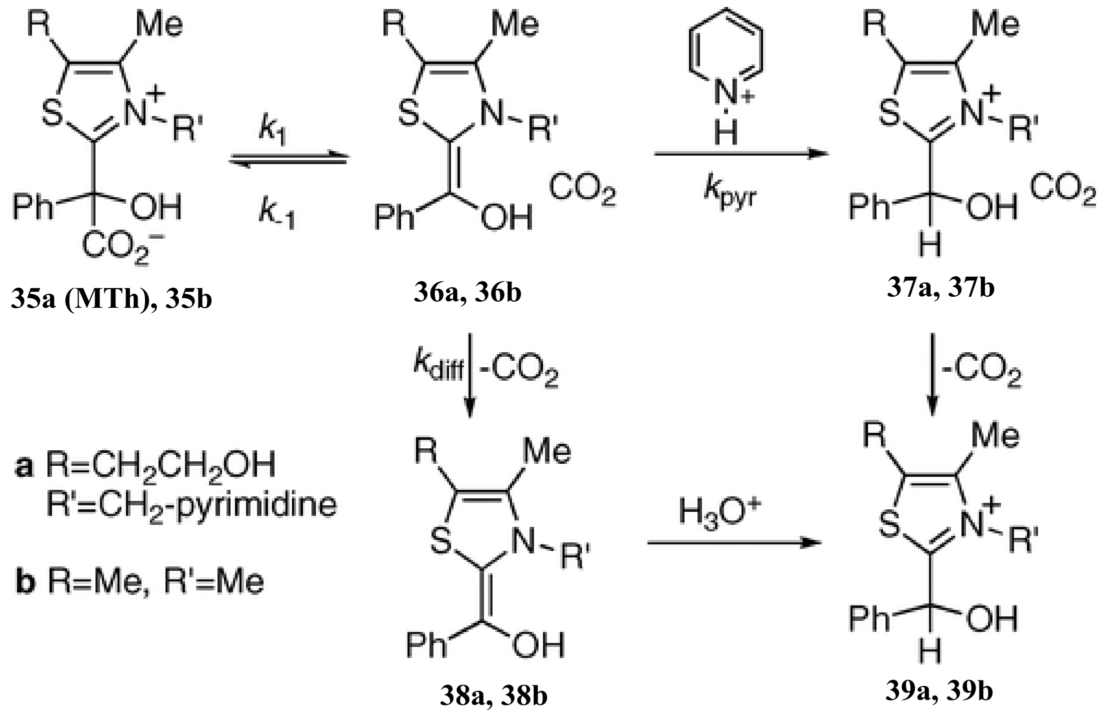


Figure 5.6. Contrasting dependence of the observed first-order rate constant on pyridine, imidazole, and morpholine buffer concentrations. pH = pK_a‘, I = 1.0, 25 °C.[133]

A key set of observations in the Kluger study is that pyridinium and C-alkyl-pyridiniums increase the rate of decarboxylation of MT while other Brønsted acids and N-alkyl-pyridiniums do not. Kluger also shows that catalysis by pyridine-derived acids is not due to their solvent effect. This leads Kluger to infer that instead of a normal binding interaction to catalyze the reaction, the reaction is catalyzed by inhibition of the recombination of the CO_2 and thiamin derivative and therefore the rate limiting step is the diffusion of the CO_2.[133] Kluger in 2009 studies the ^{13}C kinetic isotope effects of this reaction to further study this proposed idea.[135]



5.3 Experimental Kinetic Isotope Effects and Mechanism

Kinetic isotope effects have a long history of being used to determine the rate limiting step of a mechanism. They are in a since a spectroscopy of a molecules transition state of the rate limiting step. Because of this $^{12}C/^{13}C$ kinetic isotope effects (KIEs) would be useful in elucidating the mechanism of the decarboxylation of mandelylthiamin. Much debate has been encountered when discussing this mechanism. The initial carbon-carbon bond cleavage is proposed to be reversible and due to the catalytic ability of pyridinium and C-alkylated pyridinium Kluger proposed that because of this reversibility the rate limiting step was diffusion of CO_2 from the thiamin precursor and that the pyridinium is inhibiting the reverse process.[133-135] Examining the ^{13}C KIEs would be useful to examine this proposed mechanism. In 2009 Kluger studied the ^{13}C KIEs for the decarboxylation and from his study he observed the ^{13}C KIE of the uncatalyzed reaction to be 1.058 ± 0.0005 and 1.060 ± 0.0005 for the catalyzed process.[135] The significantly large isotope however did not persuade Kluger to reexamine his proposed mechanism. However, normally a isotope effect of 6 % would normally indicate a carbon-carbon cleavage to be the rate limiting step, further examination theoretically was done to study this mechanism further.

5.4 Results

Catalysis is normally understood as resulting from the reduction of activation barriers. Within this idea, the impact of a mechanistic step's catalysis is limited by the degree to which the step is rate limiting and by the size of the barrier before catalysis. A series of recent papers on biomimetic decarboxylations by Kluger and co-workers appears to expand this view of catalysis, as the proposed catalyzed step is the diffusion apart of two neutral simple molecules, normally a nearly barrierless process. By extension, this same phenomenon was suggested to be important in enzymatic catalysis. We find here that the experimental observations in the decarboxylation studied are not consistent with the mechanism and nature of catalysis previously proposed, and we present a more mundane alternative mechanism.

Mandelylthiamin (MTh) undergoes decarboxylation in water at pH 5 to 7 with a rate constant of 3×10^{-4} s^{-1}.[133] This decarboxylation is accelerated, up to a factor of 4, in the presence of pyridinium ions. Notably, *N*-ethylpyridinium ions and neutral protic acids provide no catalysis. To explain these observations, Kluger and co-workers proposed that the decarboxylation step affording the intermediate enol/CO_2 cage is reversible and “overwhelmingly reverts to the carboxylate” in the absence of catalyst, i.e. $k_{-1} \gg k_{\mathrm{diff}}$. Within this proposal, preassociated pyridinium ions would catalyze the reaction by trapping **36a**, preventing reversion to MTh.

This mechanism requires that the reaction of the two adjacent but neutral closed-shell molecules in **36a** be faster than their diffusional separation. However, from known CO_2 diffusion constants[136] and Einsteinian diffusion theory,[137] a free CO_2 molecule in water diffuses on average 5 Å in ~20 ps or 10 Å in ~80 ps. Moreover, the reformation of MTh from **36a** should not be barrierless; M06-2x/6-31+G**/PCM(water)[138] calculations place the enthalpic and free-energy barriers for formation of model **35b** from complex **36b** at 6.3 and 8.5 kcal/mol,[139] leading to a predicted k_{-1} of 4×10^6 s^{-1}. This suggests that reformation of MTh should be on the order of 10 000 times slower than diffusion, precluding the proposed catalytic mechanism.

The experimental ^{13}C kinetic isotope effect (KIE) of 1.058 for the uncatalyzed reaction[135] of MTh at 25 °C provides more direct evidence against the literature mechanism. We investigated the MTh decarboxylation as well as the mechanism of three contrasting decarboxylations in water (4-pyridylacetic acid,[140,141] trichloroacetate,[142] and 5-nitro-3-carboxybenzisoxazole[143]) by our standard process in which KIE predictions for mechanistic possibilities are compared with the experimental values.

5.4.1 Theoretical Kinetic Isotope Effects

Predicted KIEs for fully rate-limiting decarboxylation steps in these reactions were based on transition structures located in M06-2x/PCM calculations. If subsequent diffusional separation of the CO_2 from **36b** (or analogous intermediates for the other molecules) were fully rate limiting, the KIE would be the equilibrium isotope effect for the formation of the intermediate times the KIE for the diffusion step. The necessary equilibrium isotope effects for the four reactions were based on calculated structures and were in a range from 0.989 to 1.003; this corresponds perfectly with known equilibrium ^{13}C isotope effects for typical decarboxylations in water.[144] A KIE for the diffusion step of 1.0007 was assumed based on the experimental effect on the diffusion coefficient for $^{12}CO_2/^{13}CO_2$ in water.[145]

The results are summarized in Table 5.1. The experimental KIEs do not fit at all with those predicted for rate-limiting diffusion, but the KIE predictions based on fully rate-limiting decarboxylation steps are strikingly accurate. Across the board, these results exclude significant reversibility of the decarboxylation step.

Table 5.1. Experimental versus M06-2x/6-31+G**/PCM-predicted 13C KIEs (12*k*/13*k*) for Decarboxylations in Water.

system and mechanistic assumption	predicted KIE	experimental KIE
4-Pyridylacetic Acid, 25 °C		
rate limiting decarboxylation	1.054	1.057
rate limiting diffusion	0.998	
Trichloroacetate, 70.4 °C		
rate limiting decarboxylation	1.034[a]	1.034
rate limiting diffusion	0.990	
5-Nitro-3-carboxybenzisoxazole, 20 °C		
rate limiting decarboxylation	1.049	1.046
rate limiting diffusion	0.998	
MTh, 25 °C		
k_1 fully rate limiting	1.058	1.058
k_{diff} fully rate limiting	1.004	
$k_{-1} \geq 3 \times k_{diff}$	$\leq$1.018	

[a] Based on the canonical variational transition state at 70.4 °C.

For the MTh decarboxylation, one must consider an intermediate case in which the decarboxylation step and the subsequent diffusion/pyridinium trapping steps are each partially rate limiting. Assuming propositionally the literature mechanism, the observed rate constant k_{obs} would be governed by eq 5.3. The right-hand side of eq 5.3 can never exceed k_1, so the maximum possible acceleration by pyridinium catalysis, $k_{\mathrm{max}}/k_{\mathrm{uncat}}$, is limited by eq 5.4. No catalysis is possible if $k_{\mathrm{diff}} \gg k_{-1}$. The experimentally observed acceleration of at least a factor of 4 would imply that $k_{-1} \geq 3 \times k_{\mathrm{diff}}$. This leads to a maximum predicted KIE of 1.018. No realistic combination of alternative assumptions (i.e., among precedented KIEs for decarboxylation or diffusion or reasonable equilibrium isotope effects for formation of **36a**) would lead to a ^{13}C KIE approaching 1.058. In other words, the experimental ^{13}C KIE for the uncatalyzed reaction unambiguously precludes sufficient reversibility in the decarboxylation step to allow any significant catalysis by pyridinium trapping of the intermediate. The catalysis must be explained in another way, and no other evidence discretely implicates reversibility.

$$k_{obsd} = k_1 \frac{k_{diff} + k_{pyr}[PyrH^+]}{k_{-1} + k_{diff} + k_{pyr}[PyrH^+]} \tag{5.3}$$

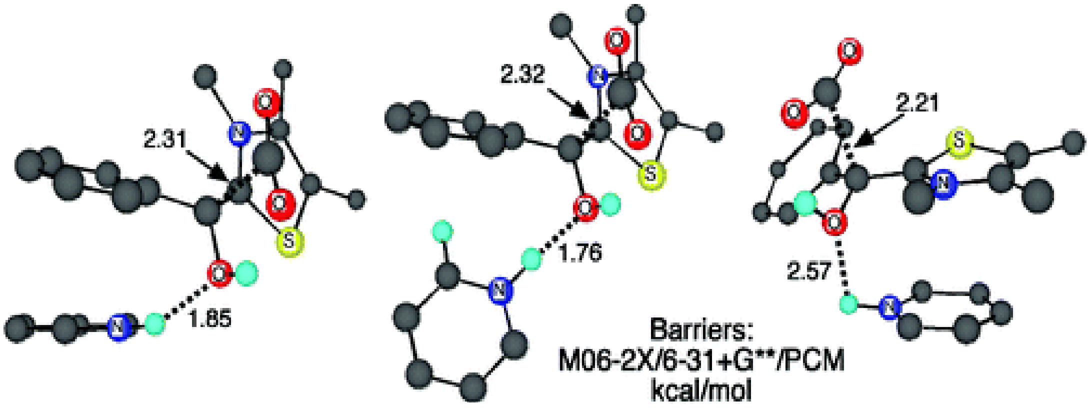
$$k_{\max} / k_{uncat} = \frac{k_{-1} + k_{diff}}{k_{diff}} \tag{5.4}$$

5.4.2 Theoretical Explanation of Catalysis

The careful work of Kluger and co-workers excluded a number of alternative mechanisms, and one is left to conclude that the pyridinium ions catalyze the reaction by directly affecting the decarboxylation step itself. How? The cation/π interaction of pyridinium ions with arenes is strong in the gas phase,[146,147] and it remains significant in aqueous solution.[148] In passing from starting MTh to transition state, the phenyl group should become more electron rich and the thiaminium cation evolves into a neutral methylenedihydrothiazol. Both changes favor coordination. We supposed that the pyridinium could coordinate with either the phenyl group or the incipient methylenedihydrothiazol at the transition state. In support of the latter possibility, strong T-shaped and face−face stacked complexes of pyridinium with methylenedihydrothiazol were located, involving interaction energies (MP2/6-311G** + zpe) of 19.7 and 18.1 kcal/mol, respectively.

To explore the potential of a cation/π interaction to catalyze the decarboxylation of MTh, M06-2x/6-31+G**/PCM(water) calculations were employed to locate transition structures for decarboxylation of **35b** complexed with pyridinium. Eighteen such structures were located with pyridinium in various positions and orientations, and eight of these had calculated formal transition state binding enthalpies (defined by the harmonic enthalpy versus that of the uncatalyzed transition structure and separate pyridinium) greater than 6 kcal/mol. The three lowest-enthalpy structures, **40-42**, are shown (Figure 5.7); others are given in later in the chapter. Structures **40** and **41** were lowest in the M06-2X calculations; structures **40** and **42** were lowest in MP2/6-311+G** single-point energies.

The predicted free-energy barrier for decarboxylation via **40**, obtained by including harmonic entropy estimates at a 1 M standard state with the M06-2x/PCM enthalpies, is 1.8 kcal/mol below that of the uncatalyzed reaction. At an experimental pyridinium concentration of 0.4 M, the catalyzed reaction would be predicted to occur about 8 times faster than the uncatalyzed. When the difficulty of the calculation and particularly the simplification of the entropy estimate are considered, this striking agreement with experiment (within 0.4 kcal/mol) is to some degree fortuitous. Nonetheless, the calculated energetics are clearly consistent with an origin of the observed catalysis in pyridinium binding to the transition state.



40 $\Delta H^{\ddagger} = 8.8$ **41** $\Delta H^{\ddagger} = 9.2$ **42** $\Delta H^{\ddagger} = 10.7$

Figure 5.7. The three lowest-enthalpy structures of pyridinium bound MTh.

An intriguing feature of the lowest-energy catalyzed transition structures is that they combine a cation/π face−face or T-shaped interaction with hydrogen bonding to the hydroxyl group. This chelating combination appears critical to the catalysis; the formal transition state binding is unsurprisingly much weaker in the many decarboxylation transition structures exhibiting only one of the interactions. This fits well with the observation that *N*-ethylpyridinium ions and neutral protic acids provide no catalysis. This simple catalysis by transition state binding is also consistent with the observation that the H/D solvent isotope effect on the catalysis is near unity.[149]

5.5 Theoretical Procedures

5.5.1 General Calculational Procedures

The M06-2X/6-31+G**/PCM minima and transition structures were obtained using Gaussian® 09.[62] The early stages of this project involving exploratory calculations using other methods, as will be listed, were performed with Gaussian® 03,[61] and unless otherwise noted all of the calculations except the M06-2X/6-31+G**/PCM were done with Gaussian® 03. Default procedures were employed unless otherwise noted. This means that the Gaussian® 09 PCM calculations used UFF radii, while the Gaussian® 03 PCM calculations used UA0 radii. Care was taken not to mix Gaussian® 03 and Gaussian® 09 results for any energy calculation.

While PCM optimizations of complex molecules in Gaussian® 03 were recalcitrant, the Gaussian® 09 PCM optimizations are generally successful. However, a problem arose with one of the conformers of MTh and two of the conformers of pyridinium-complexed decarboxylation transition structures in which an extra imaginary frequency was obtained from the frequency calculation (despite our normal process of repeatedly reoptimizing the structure after such an event). In the former case, numerical stepping along the putative imaginary frequency led to a rise in the energy. Because of this, this minor conformer is included here despite having the extra imaginary frequency in the analytical frequency calculation. In the latter cases, the structures were luckily higher in energy and their M06-2X/6-31+G**/PCM structures are not reported here. However, for the sake of illustrating the complete range of structures explored, we do provide M05-2X/6-31+G**/PCM geometries and energies for these structures, as well as some other transition structure conformers which were locatable in M05-2X calculations but not in M06-2X calculations.

5.5.2 Calculation of Isotope Effects

Kinetic isotope effects for decarboxylation transition structures were calculated based on the harmonic frequencies by the method of Bigeleisen and Mayer,[15] employing a locally modified version of the program QUIVER.[23] For the reactions of MTh, 4-pyridylacetic acid, and 5-nitro-3-carboxybenzisoxazole, tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[17] Such KIE predictions have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry.[3,6,24,25,26,] No tunneling correction was applied for the reaction of trichloroacetate since there is no energy barrier associated with the variational transition state. The temperature for each calculation was set to match the experimental temperature, i.e. 298.15, 298.15, 293.15, and 343.55 for MTh, 4-pyridylacetic acid, 5-nitro-3-carboxybenzisoxazole, and trichloroacetate, respectively.

Frequencies were scaled by 0.98. For most ^{13}C isotope effect calculations, the choice of scaling factor within a reasonable range of 0.96 to 1.00 makes no difference outside of round-off error, but for the relatively large KIEs here the difference between using a scaling factor of 0.96 and 0.98 is approximately 0.001. The unpublished zpe scaling factor for M06-2X is 0.970 (http://comp.chem.umn.edu/Truhlar/freq_scale.htm) but it should be recognized that the most appropriate scaling factor for the high frequencies (X-H stretches) that contribute most to zpe is generally lower (i.e., greater scaling, further from unity) than that for the lower frequencies important in ^{13}C isotope effects.[150] The choice of 0.98 is as an upper-middle range value that appears to give good agreement with experiment when applied retrospectively to our previously published cases.

For the MTh reaction, three low-energy conformations of the model starting material **35b** were located. These conformations have slightly different (varying by <0.002) reduced isotopic partition functions. For the purpose of calculating the isotope effect, the reduced isotopic partition functions were Boltzmann-weighted based on the calculated free energy at 25 °C.

For the 4-pyridylacetic acid reaction, the predicted isotope effect depends on the choice of tautomeric starting material reference, as found previously by Truhlar and Paneth.[141] The correct procedure in this case is to weight the potential starting materials based on their actual amounts present in solution. Based on the experimental pH of

4.0[140] and discussions of the tautomeric equilibria in the literature,[151] the tautomeric equilibria were weighted as 90% zwitterion, 9.1% protonated, and 0.9% neutral pyridylacetic acid.

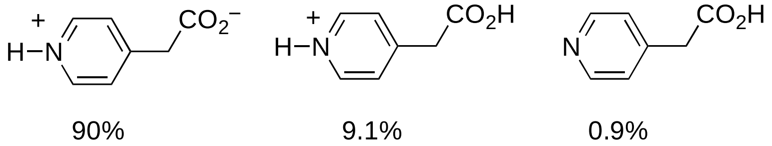
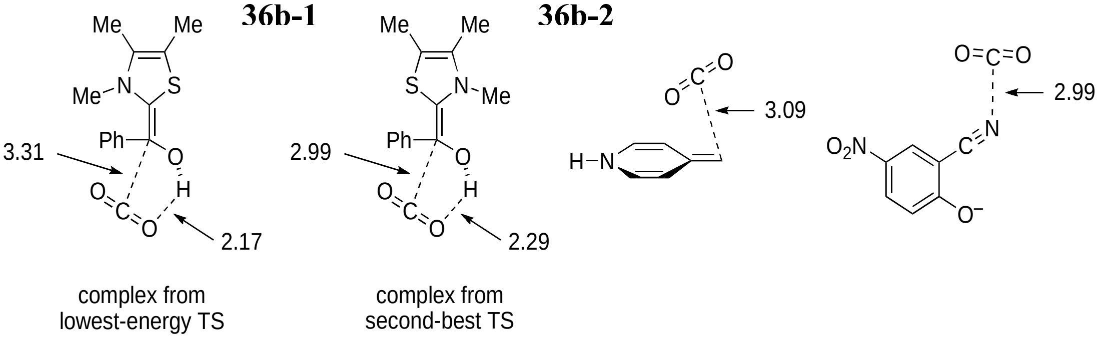


Figure 5.8. Potential starting materials for 4-pyridylacetic acid.

For the reactions of MTh, 4-pyridylacetic acid, and 5-nitro-3-carboxybenzisoxazole, the prediction of the KIEs for a mechanism involving rate-limiting diffusional separation of CO_2 started with a calculation of the equilibrium isotope effect for formation of the loose CO_2 / product complex (Figure 5.9). The choice of such complexes as opposed to free CO_2 makes a difference of 0.0029 (i.e., the isotope effects would be 0.0029 smaller versus free CO2). The equilibrium isotope effects (as $^{12}K/^{13}K$) obtained were 1.0034, 0.9977, and 0.9977, for MTh, 4-pyridylacetic acid, and 5-nitro-3-carboxybenzisoxazole, respectively. To get the final KIEs for rate-limiting diffusional separation of CO_2, these values were multiplied by 1.0007 based on the known isotope effect for diffusion and rounded to get the numbers in Table 5.1.


36b-1 **36b-2**

complex from lowest-energy TS

complex from second-best TS

Figure 5.9. Complexes used in the calculation of equilibrium isotope effects. Full geometries are given in a later section.

For the reaction of trichloroacetate, there is no potential energy barrier for reaction of a trichloromethyl anion with CO_2 so no complex could be used to calculate the equilibrium isotope effect. Instead, the equilibrium isotope effect versus free CO_2 was calculated (as 0.9891). This has the effect of throwing off the prediction for the trichloroacetate reaction by about 0.003 based on our observations above in the other systems, and it could be argued that the isotope effect prediction for trichloroacetate should be corrected upward by 0.003, but this error was considered negligible for purposes of the main text. The equilibrium isotope effect obtained was 0.9891, which was multiplied by 1.0007 to get the number in Table 5.1.

The change in the predicted isotope effects for differing calculational methods was explored. Table 5.2 below shows how much the predicted KIE changes from that predicted for the M06-2X/6-31+G**/PCM calculation; the changes are presented this way because the exploration only considered a single starting material conformer and transition state conformer. All of the calculations are PCM in water, though all but the last row use Gaussian® 03 default radii while the last uses Gaussian® 09 default radii.

Table 5.2. KIE differences from M06-2X for different levels of theory

Method/Basis set	KIE difference vs M06-2X
B3LYP/6-31+G*	0.000
B3LYP/6-31+G**	0.000
MPW3LYP/6-31+G*	0.000
MPW3LYP/6-31+G**	0.001
M05-2x/6-31+G**	0.004

5.5.3. Calculation of the KIE with Partially Rate-Limiting Steps and with Extreme Assumptions

As discussed previously, the experimentally observed acceleration of at least a factor of 4 would imply that $k_{-1} \geq 3 \text{ x } k_{\text{diff}}$. To calculate the KIE for this situation, we started with eq 5.5. Filling into eq 5.5 that $k_{-1} = 3 \text{ x } k_{\text{diff}}$ gives us that $k_{obs} = 0.25 * k_1$. This was taken as the rate constant for reaction of ^{12}C. The rate constant for reaction of ^{13}C was then calculated by putting into eq 5.5 the isotopic rate constants $^{13}k_1 = k_1 / 1.058$, $^{13}k_{diff} = k_{diff} / 1.0007$, and $^{13}k_{-1} = (3 \text{ x } k_{\text{diff}}) / (1.058/1.0034)$, where the numbers 1.058, 1.0034, and 1.0007 are the isotope effects for the forward reaction, the equilibrium isotope effect, and the isotope effect for diffusion, respectively. The result, as given in the main text, is a $^{12}k/^{13}k$ of 1.018.

$$k_{obs} = k_1 \frac{k_{diff}}{k_{-1} + k_{diff}} \tag{5.5}$$

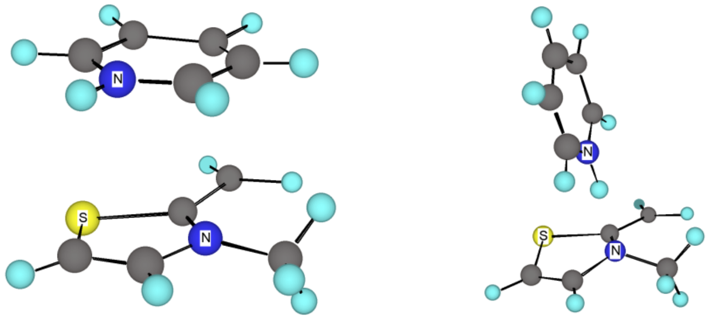
How far off could this calculation be? To gauge this, the calculated and literature diffusion isotope effects will be ignored, and the isotope effects will be assumed to have values most favorable to the literature mechanism. This would maximize the isotope effect for the forward reaction, the equilibrium isotope effect, and the isotope effect for diffusion. We are unaware of any normal ambient ^{13}C isotope effect over 1.08, so we will assume this for the isotope effects for the forward reaction. The largest equilibrium isotope effect for a decarboxylation comes from that for bicarbonate, at 1.011.[144] In the gas phase the diffusion of molecule goes with the square-root of the molecular mass (45 vs 44) so the diffusion rate difference in the gas phase would only be about 1.1%. Together, these assumptions lead to a maximum predicted isotope effect of 1.037, which is still far from the experimental isotope effect.

5.5.4. Location of the Canonical Variational Transition Structure for Decarboxylation of Trichloroacetate

The procedure used for the location of the variational transition structure for decarboxylation of trichloroacetate was adapted from the "no saddle" procedure in the program POLYRATE,[109] used first by Truhlar for the reaction of O with OH.[152] The starting point fixed the carbon-carbon distance at 3.0 Å, optimizing all other coordinates. From this structure, a steepest-descent path in mass-weighted coordinates was followed.[12] At regular intervals along the steepest-descent path, frequency calculations were carried out and free energies were calculated using the harmonic approximation without scaling. The structure reported was the free energy maximum along this path.

5.5.5 Complexes of Pyridinium with Methylenedihydrothiazol

Figure 5.10 shows face-face stacked and T-shaped complexes of pyridinium with methylenedihydrothiazol, calculated in MP2/6-311G** gas-phase calculations. (The names below the structures refer to names given in a later section for the full geometries.) It is exothermic to transfer a proton from pyridinium to methylenedihydrothiazol, so there is no implication here that the complexes would be stable or observable. Rather, the point is that the complexation is relatively strong. The complexation energies (E + zpe) for the stacked and T-shaped structures are 18.1 and 19.7 kcal/mol, respectively. For comparison, the same level of calculation places the stacked and T-shaped structures of pyridinium with benzene with complexation energies of 11.2 and 16.7 kcal/mol, respectively.

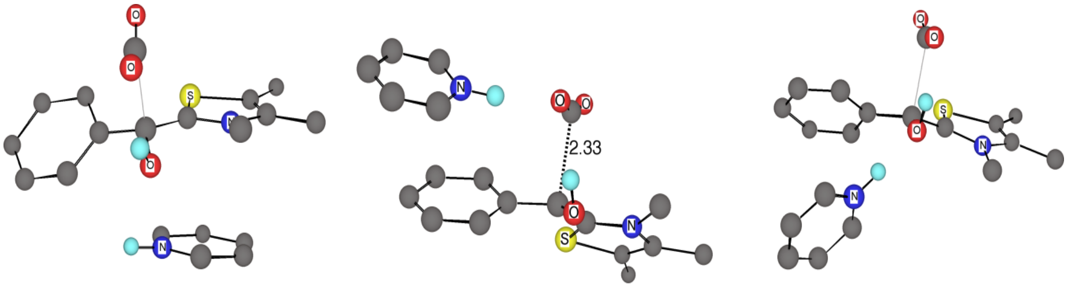


thiaminepyridinium2MP2 thiaminepyridinium3MP2

Figure 5.10. Face-face stacked and T-shaped complexes of pyridinium with methylenedihydrothiazol, calculated in MP2/6-311G** gas-phase calculations.

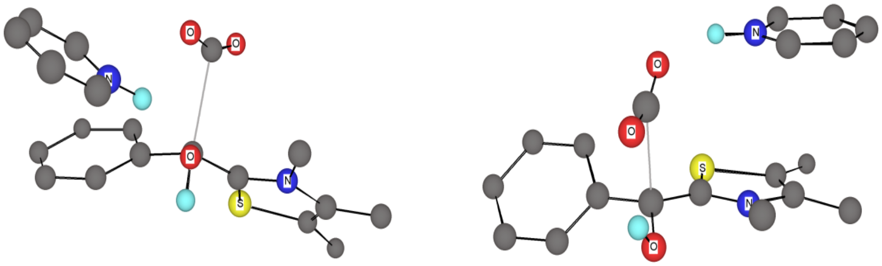
5.5.6 Motifs for Binding of Pyridinium with the Decarboxylation Transition State

Figure 5.11 shows some motifs for binding of the pyridinium ion with the decarboxylation transition state. (The names below the structures refer to names given in a later section for the full geometries.) PyridiniumTSI3 has the pyridinium anti to the leaving CO_2 and is stacked with the methylenedihydrothiazol. PyridiniumTSU1 has the pyridinium syn to the leaving CO_2 and is stacked with the phenyl group. PyridiniumTSV1, like structure **40**, has the pyridinium anti to the leaving CO_2 and is stacked with the phenyl group. PyridiniumTSJ5 has the pyridinium syn to the leaving CO_2 and is stacked with the methylenedihydrothiazol. PyridiniumTSQ1 is different from the others in that it has the pyridinium hydrogen bonded with the carboxylate and hydroxyl, but is not significantly stacked with the arenes. Within most motifs, the pyridine can be rotated by 60°, 120°, 180°, etc., to get to a new structure which on optimization may be a stationary point or may rotate back to the original structure, and the various structures given in a later section may be viewed as resulting from such rotations. The most favorable geometry in each motif tends to have the pyridinium nitrogen oriented toward the carboxylate or hydroxyl group, as shown in the structures of Figure 5.10.



pyridiniumTSI3 (**8**) pyridiniumTSU1 pyridiniumTSV1

41



pyridiniumTSQ1 pyridiniumTSJ5

Figure 5.11. Motifs for binding of the pyridinium ion with the decarboxylation transition state.

5.6 Technical Comments

5.6.1 Note on Terminology and the Description of Steps as Decarboxylation and Diffusional Separation

We refer to the kinetic step in which the carbon-carbon bond is broken to the carboxylate carbon as "the decarboxylation step" or more simply "decarboxylation." If we propositionally assume the literature mechanism in which the decarboxylation step is reversible or partially reversible in the absence of catalyst, then some subsequent step in the mechanism would necessarily be irreversible and kinetically important. We discuss this subsequent step as "diffusional separation" or "the diffusion step." *In* *principle*, the subsequent irreversible step would not have to be diffusion. However, any process slower than diffusional separation (such as trapping the intermediate by the water solvent) will not be kinetically relevant for the question here of whether the decarboxylation step is reversible. On the other hand, if the subsequent irreversible step is one that is faster than diffusion (such as, in principle, thermal relaxation or solvent relaxation) then the importance of such a step would strengthen the argument of the main text that the decarboxylation step should not be reversible. This explains our focus on the diffusion step in analyzing the prospects for reversible decarboxylation. (It should be noted that because the lifetime of the intermediate enol is limited, we agree with Kluger and coworkers that diffusional separation should be irreversible. Anyway, if it were not irreversible then the observed KIE would approach the small equilibrium KIE.)

5.6.2 On the Nature of the Enol in 36a. Enol, Zwitterion, or Carbanion?

The enol resulting from decarboxylation of MTh has been routinely referred to as a "carbanion" in the series of papers by Kluger,[133-135] and its reactivity has been assumed to be analogous to that of true carbanions. Overall, its charge is neutral (ignoring the unimportant complication of the possible protonation of the pyrimidyl ring), but of course a zwitterionic resonance structure would normally be considered to be contributing by organic chemists. It is of interest to examine here what is the best description of this molecule.

One way to look at this issue is to consider the bond length for the bond from the thiamin ring to the central hydroxymethylene carbon (Figure 5.12). Does this look like a single bond or a double bond? The M06-2X/6-31+G**/PCM(water) calculations get a distance of 1.352 Å for this bond. For comparison, the double bond in styrene has a distance of 1.337 and the central single bond of 1,3-butadiene (as a model for an sp^2-sp^2 bond with much less double bond character) has a distance of 1.464 Å using the same calculations. Clearly, the distance is much closer to that expected for a double bond.

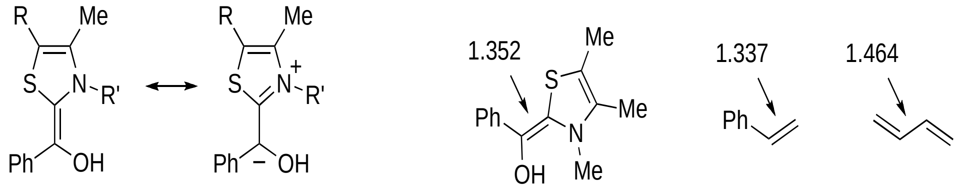


Figure 5.12. Bond length depiction of the Thiamin Ring.

Another way to look at this issue is to calculate the charges on the atoms (Figure 5.13). The NPA charges shown below suggest that there is no substantial negative charge on the central carbon. (All charge calculations should be treated skeptically but they should exhibit gross trends. An ESP charge calculation places a +0.14 charge in the central HOC group, but our experience is that the NPA charges are internally more self consistent.) Due to the ability of the heterocycle to accept a positive charge on reaction of the enol with electrophiles, the central carbon of the enol is certainly nucleophilic and its thermodynamic basicity is high. However, its structure and charge distribution makes a strong case that it should not be considered as a carbanion or zwitterion for the purpose of qualitatively estimating its kinetic reactivity or its coordination with CO_2 (see next section).

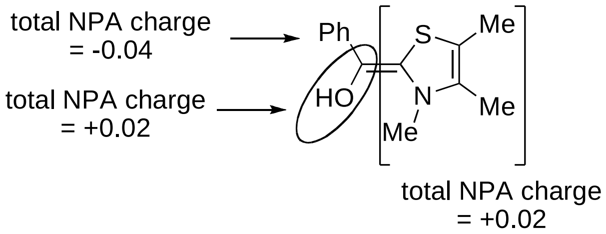


Figure 5.13. NPA charge of the thiamin ring.

If one (with some justification) mistrusts charge calculations, the absence of a significant positive charge in dihydrothiazol ring at the transition state for decarboxylation is clearly signified by the relatively strong binding of pyridinium ions in the area of the dihydrothiazol ring. This absence of charge may seem surprising if one focuses on the zwitterionic resonance structure above, but it is rationalizable at a qualitative level if one considers that there would also be a contribution from a zwitterionic enol resonance structure that reverses the polarization.

5.6.3 On the Nature of 36a / 36b and the Rate of Diffusional Separation of CO_2

The nature of the intermediate **36a** following the decarboxylation step requires some discussion. The term "complex" is not used in the Kluger papers,[133-135] and we too would avoid this term as it has a connotation of a substantial energetic attraction that, as will be discussed below, is not justified. Another way to think of **36a** is as a pair of molecules in a solvent cage, and the analysis below makes this description seem most applicable.

The description of this intermediate is somewhat confused by the depiction in the 2005 paper[134] of "rehybridization and partial separation" as a distinct kinetic step. It is assumed here that the intermediate is chemically normal so that structural and solvent relaxation is fast. We have shown in other contexts that this is not always the case,[43] but here such processes would surely be fast relative to the protonation of the enol by a pyridinium ion in the literature mechanism, making them kinetically irrelevant for the analysis of catalysis observations.

An important question is the magnitude of the energetic attraction of the two molecules in **36a**. If their attraction were sufficiently strong, as in the tight ion pairs of S_N1 reactions, then diffusional separation would proceed more slowly than what would be expected from Einsteinian diffusion theory and macroscopic diffusion constants. Carbon dioxide is not very polarizable but it has a quadrupole moment and the enol is a polar molecule, so some electrostatic attraction is certain. The same is true for the interaction of CO_2 with water. Kluger asserts that the rate constant for diffusional separation of CO_2 would be 10^8 s^{-1}.[154,155] This would require a free energy barrier for diffusional separation of approximately 6.5 kcal/mol. We calculationally examined whether there was any support for such a barrier. Proceeding forward by IRC from the two low-energy decarboxylation transition states for the calculational model leads to structures **36b-1** and **36b-2** depicted in Figure 5.9 (the full geometries are in a later section). These structures are potential energy minima on the M06-2X/6-31+G** surface. However, the enthalpy of **36b-2** relative to separate enol product and CO_2 is after counterpoise correction only -1.7 kcal/mol. The weakness of this interaction is most easily understood by consideration of the harmonic free energy estimates for the complex versus separate molecules; the free energy of the complex is uphill by 6.8

kcal/mol at standard state. Of this 6.8 kcal/mol, roughly 4.3 kcal/mol is a concentration effect [calculated from RT ln (55 M / 1 atm)] and 2.5 kcal/mol is the amount that the complex is disfavored versus free molecules by the entropic cost of restricting degrees of freedom. This means that if a mixture were made of the enol and CO_2 at a concentration of 55 M, 98% of the molecules would be uncomplexed.

Another way to look at the small enthalpy of interaction in **36b** is that if the enthalpy price of 1.7 kcal/mol had to be paid fully in order for CO_2 to diffuse away, it would only slow diffusion by about a factor of 20 at 25 °C. However, entropy is being gained as the CO_2 departs due to the decreasing energy of modes that are changing into rotation / translation. At this small level of enthalpic interaction, departure of the CO_2 may not involve any free energy barrier.

The approximations in the discussion above are crude, and the biggest approximation is the acceptance of the calculational predictions at face value. It should be understood that no current calculation of the energy of interaction of two neutral molecules in water is going to be reliable at a level that is completely convincing. The key point is not so much what the calculations predict, but rather that they provide no support for an interaction in **36b** strong enough to substantially inhibit diffusional separation of CO_2.

5.6.4 The CO_2 Diffusion Constant In Water

For a discussion of CO_2 diffusion constants, see the work of Sandall and coworkers.[153] The main text reference was to a seminal measurement.

5.6.5 Comparison of Predicted Absolute Barriers and Relative Barriers with Experiment

The predicted free-energy barrier for the uncatalyzed reaction in our calculational model for MTh, listed in a later section, is 18.1 kcal/mol. This is low by about 4 kcal/mol versus the barrier associated with the experimental rate constant of 3×10^{-4} s^{-1}. An error of this magnitude is not unusual for any calculation of absolute reaction barriers, and considering the difficulty of the problem and the simplifications of the model, we view the calculation as performing well. A particular issue in the prediction of this barrier is that the starting material is a zwitterion while the transition state has a much lower degree of charge separation, and error in the absolute solvation energy of the zwitterion could readily contribute the to error in the overall barrier.

Earlier text makes a comparison of the barrier for the uncatalyzed MTh reaction with that of a pyridinium-catalyzed process. This is a calculation of *relative* barriers for two processes, and it has the advantage of a canceling out of errors that are common to the two processes (e.g., solvation of the starting zwitterion, error due to the difference between model and experimental systems, or general error in the calculation of decarboxylation barriers). Because of this, it is not surprising that the performance of the calculations in predicting the catalysis is highly accurate, despite the lower accuracy in the absolute barriers.

5.7 Summary

The mechanism of decarboxylations in water and the catalysis of mandelylthiamin (MTh) decarboxylation by pyridinium ions is explored. It has been recently proposed that a decarboxylation step forming an intermediate molecule/CO_2 pair is reversible and that pyridinium ions catalyze the MTh decarboxylation by trapping the intermediate, preventing reversion to MTh. A calculation of the barrier for the back reaction goes against this proposal, as the diffusional separation of CO_2 would be on the order of 10,000 times faster. A comparison of predicted and experimental isotope effects for a series of decarboxylations including the MTh reaction shows in each case the absence of significant reversibility of the decarboxylation step. An alternative origin of the pyridinium catalysis of decarboxylation is proposed, based on the formal binding of the pyridinium ions to the decarboxylation transition state.

In summary, a comparison of predicted and experimental isotope effects shows that there is no significant reversibility in simple decarboxylations in water. From diffusion versus recombination rates, no reversibility is to be expected for the MTh decarboxylation. The calculations suggest that the catalysis that had been the evidence for reversibility arises from simple formal binding to the transition state.

CHAPTER VI

CONCLUSIONS

Several physical organic techniques have been applied to a series of organic reactions that are of importance to the fundamental understanding of reaction mechanisms. The role of recrossing in cycloadditions of ketenes has been examined using a combination of experimental ^{13}C KIEs and quasiclassical dynamic trajectories. From this a new statistical approach was created to predict the existence of dynamical bottlenecks arising from entropic intermediates in reactions proceeding with a significant amount of recrossing, particularly cycloadditions. Theoretical predictions of KIEs have been used to examine the role of heavy-atom tunneling in organic reactions exhibiting unusually large experimental KIEs, as well as elucidate the rate-limiting step of mechanisms that have unclear experimental information. The techniques utilized fro experimental and theoretical study will have a wide range of applications in the study of reaction mechanisms and unusual physical phenomena in chemical reactions.

The microcanonical RRKM approach to statistically predicting a dynamical bottleneck is a significant development for uncovering "concerted" processes which will truly proceed in a stepwise fashion due to the existence of entropic intermediates. While quasiclassical dynamic trajectories might be a more appropriate way of examining the surface of these reactions, the view of the free energy surface utilizes a different view to help better understand the broad scope of these reactions.

The largest known ^{13}C KIEs have been measured at a variety of temperatures for the ring-opening of cyclopropylcarbinyl radical and this occurrence highlights the significance of heavy-atom tunneling in organic reactions. In addition, the use of small curvature tunneling approximations and application of an Arrhenius diagram have been useful tools for uncovering the importance of heavy-atom tunneling in this reaction.

Moreover, theoretical techniques have been shown again to help elucidate rate-limiting steps of mechanisms and the case of decarboxylation of mandelylthiamin is no different. While the catalysis of this process from pyridinium proved to be more of a theoretical challenge. Nonetheless, theoretical binding motifs were discovered to aid in the understanding of the experimentally observed catalysis.

In conclusion, a myriad of experimental and theoretical techniques have been used to probe reaction mechanisms of importance and novel statistical methods have been developed with high applicability to a variety of mechanistic studies.

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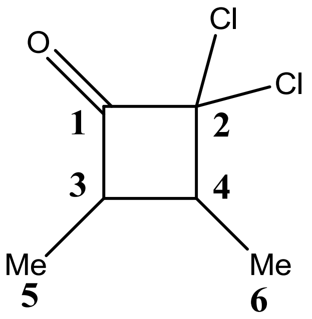
APPENDIX A

Table of Contents

Intramolecular ^{13}C NMR KIE Sample Integration Results for 2,2-Dichloro-3,4-dimethylcyclobutanone

All integrations are relative integrations of C3 versus an integration of 1000 for C4. A complication in the numerical interpretation of these integrations is that C4 is subject to three ^{1}J ^{13}C-^{13}C coupling with satellites not included in the integration range, while C3 is subject to four such satellite couplings due to a long range coupling with the C2 position. To allow for this, the integrations at C3 were adjusted by the 0.0107(8) natural abundance of ^{13}C. The 95% confidence ranges were calculated in a standard way.(See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf.)



Integrations for cycloaddition of dichloroketene and cis-2-butene C3 vs C4

992.243	992.423	992.861	991.878	992.714	991.772
996.087	997.466	998.202	996.034	997.897	995.595
998.141	998.852	1000.100	997.638	996.429	995.946
992.004	997.171	998.115	1000.530	995.739	997.890

AVE	KIE
995.989	**1.007**
Corrected	95%

1006.646	Confidence
	0.001

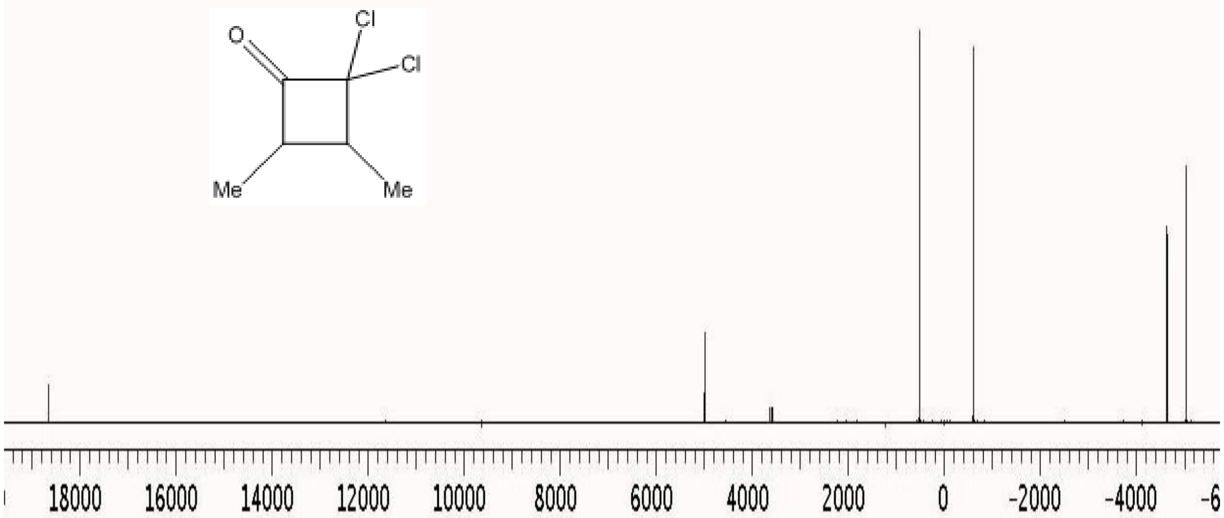
Integrations of methyl peaks C5 vs C6

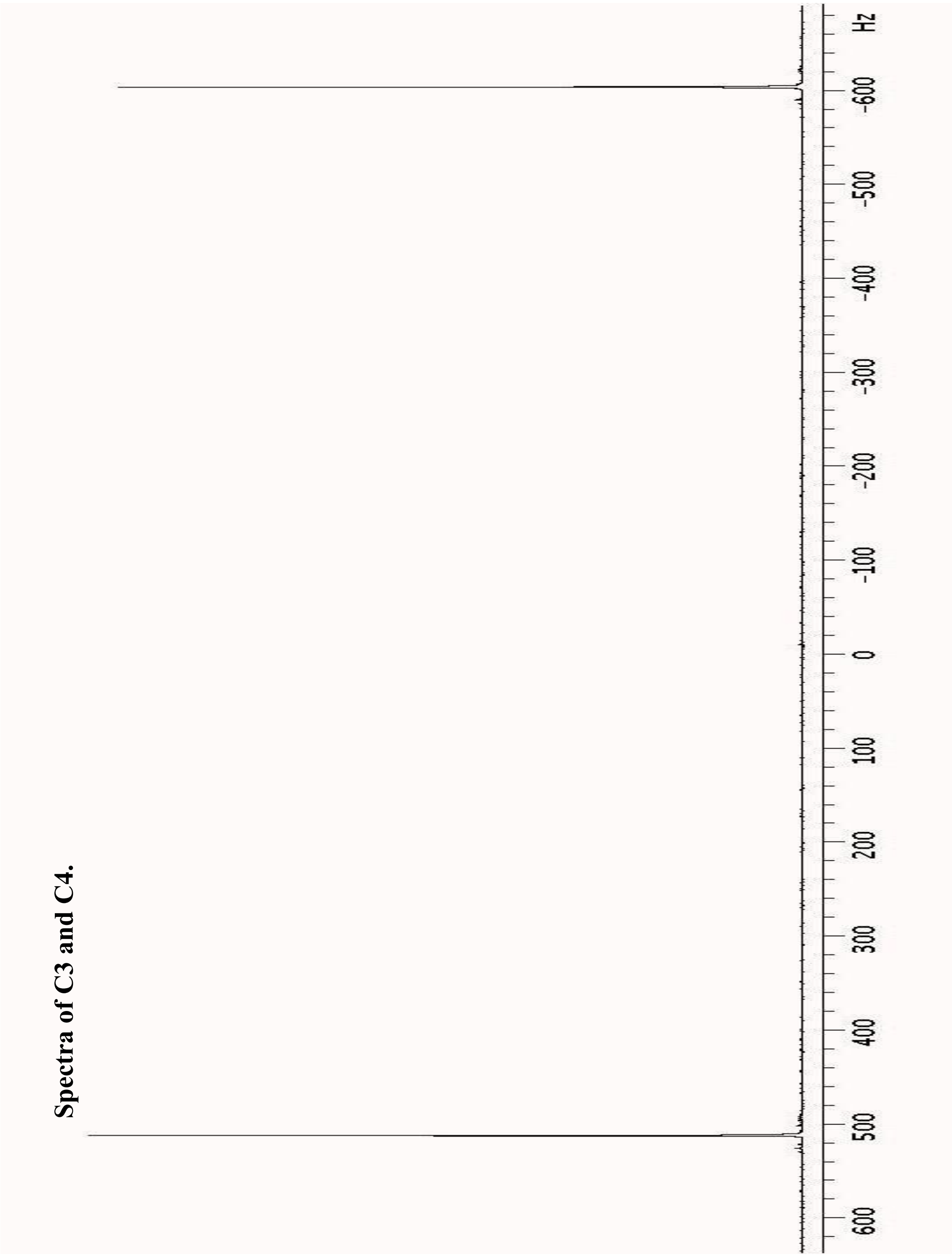
1003.790	1004.710	1003.639	1003.301	1003.597	1005.246
1001.097	1001.744	1001.313	999.253	1000.886	1000.160
1002.062	999.759	997.321	1001.030	999.275	1001.094
995.807	996.357	990.113	995.555	999.546	994.247

AVE	KIE
1000.038	**1.000**
	95% Confidence
	0.002

2,2-Dichloro-3,4-dimethylcyclobutanone - ^{13}C NMR for KIEs

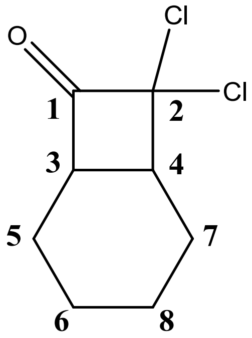
Full Spectra





Spectra of C3 and C4.

Intramolecular ^{13}C NMR KIE Sample Integration Results for 8,8-Dichloro-bicyclo[4.2.0]octan-7-one. All integrations are relative integrations of C3 versus an integration of 1000 for C4. A complication in the numerical interpretation of these integrations is that C4 is subject to three ^{1}J ^{13}C-^{13}C coupling with satellites not included in the integration range, while C3 is subject to four such satellite couplings due to a long range coupling with the C2 position. To allow for this, the integrations at C3 were adjusted by the 0.0107(8) natural abundance of ^{13}C. The 95% confidence ranges were calculated in a standard way.



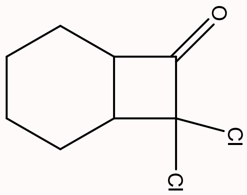
Integrations for cycloaddition of dimethylketene and cyclohexene C3 vs C4

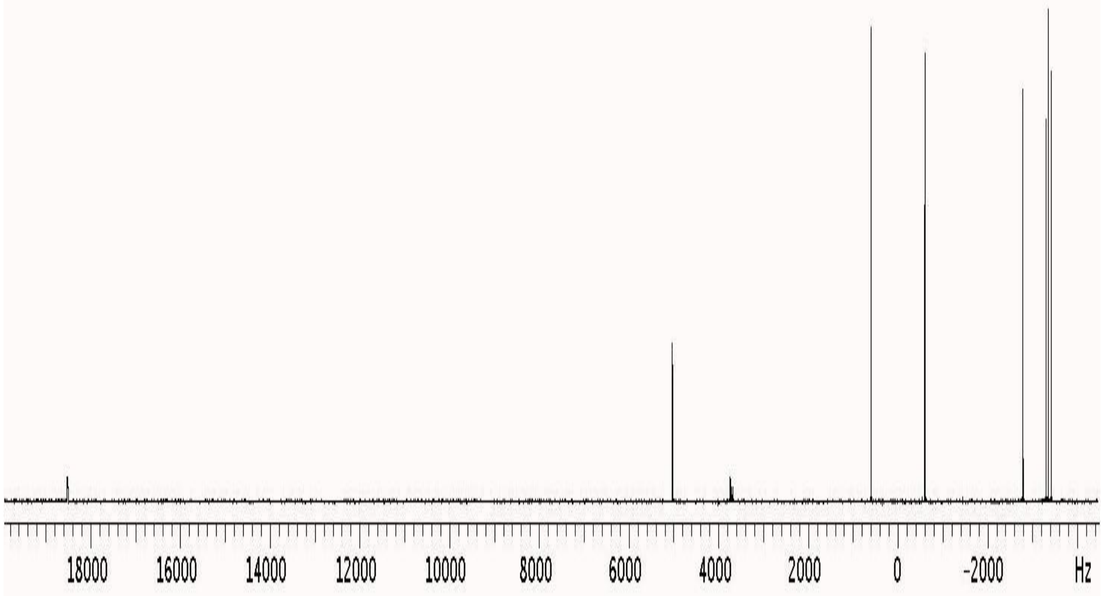
982.44	982.29	981.91	983.24	981.81	985.42
982.75	983.44	982.27	984.86	983.66	984.36
985.47	985.73	983.01	989.91	974.88	977.99

AVE	KIE
983.08	**1.006**
Corrected	95% Confidence
993.60	**0.002**

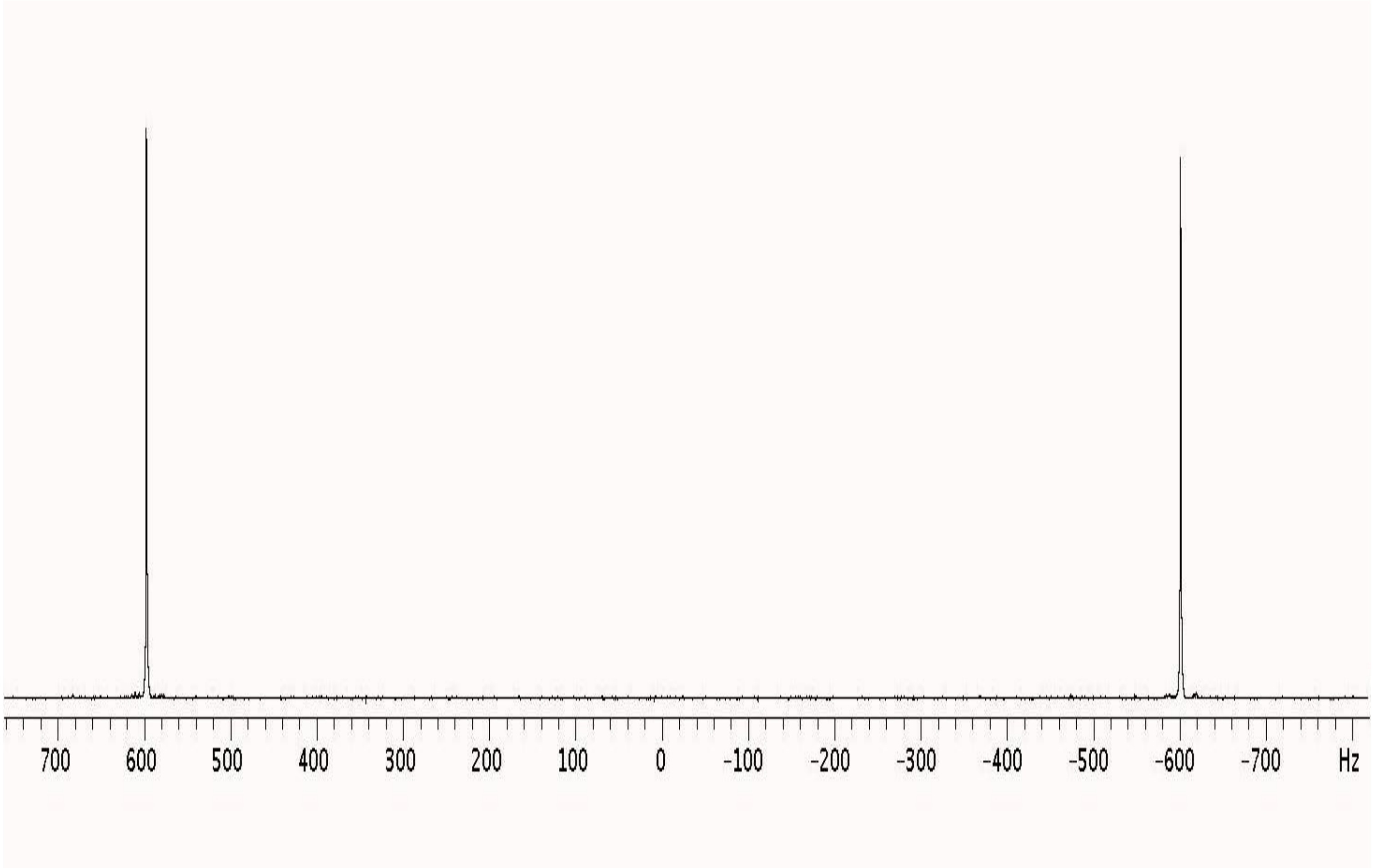
8,8-Dichloro-bicyclo[4.2.0]octan-7-one - ^{13}C NMR for KIEs

Full Spectra



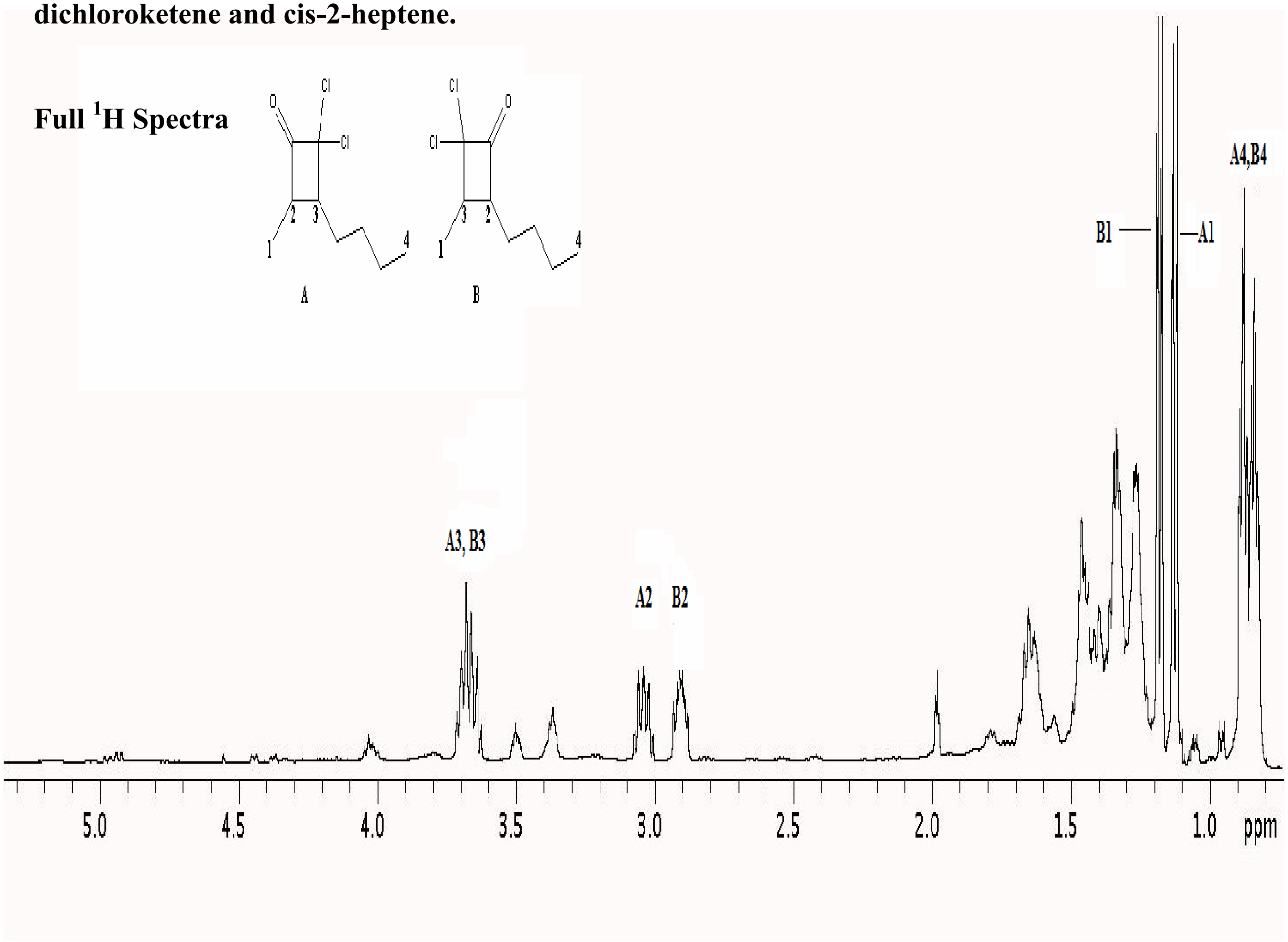


Spectra of C3 and C4.

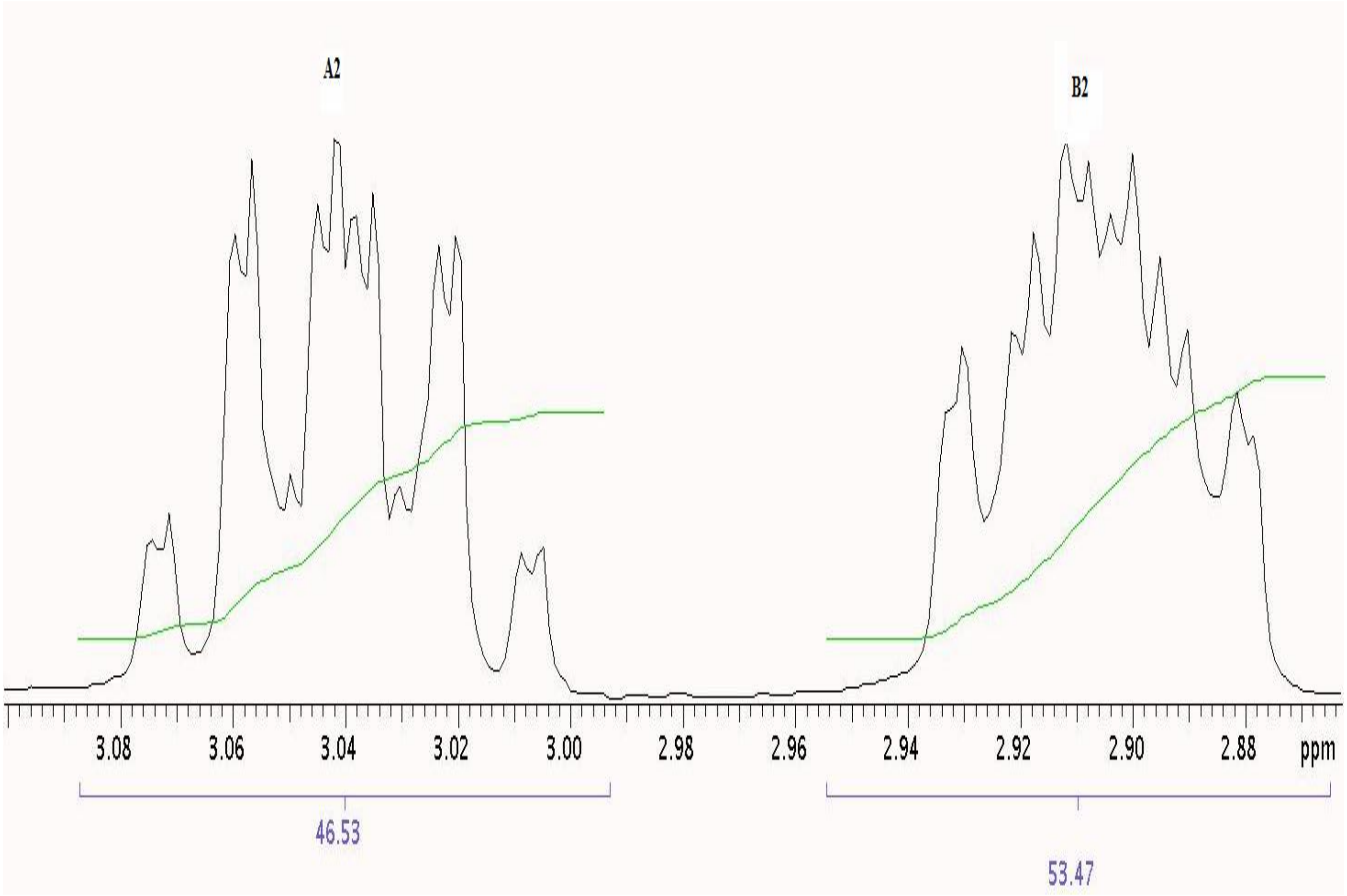


Spectra of product ratio determination for the cycloaddition of dichloroketene and cis-2-heptene.

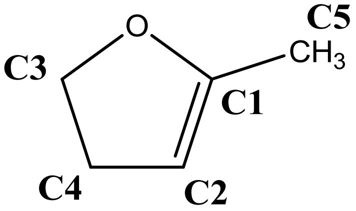
Full ^{1}H Spectra



Spectra of A2 and B2.



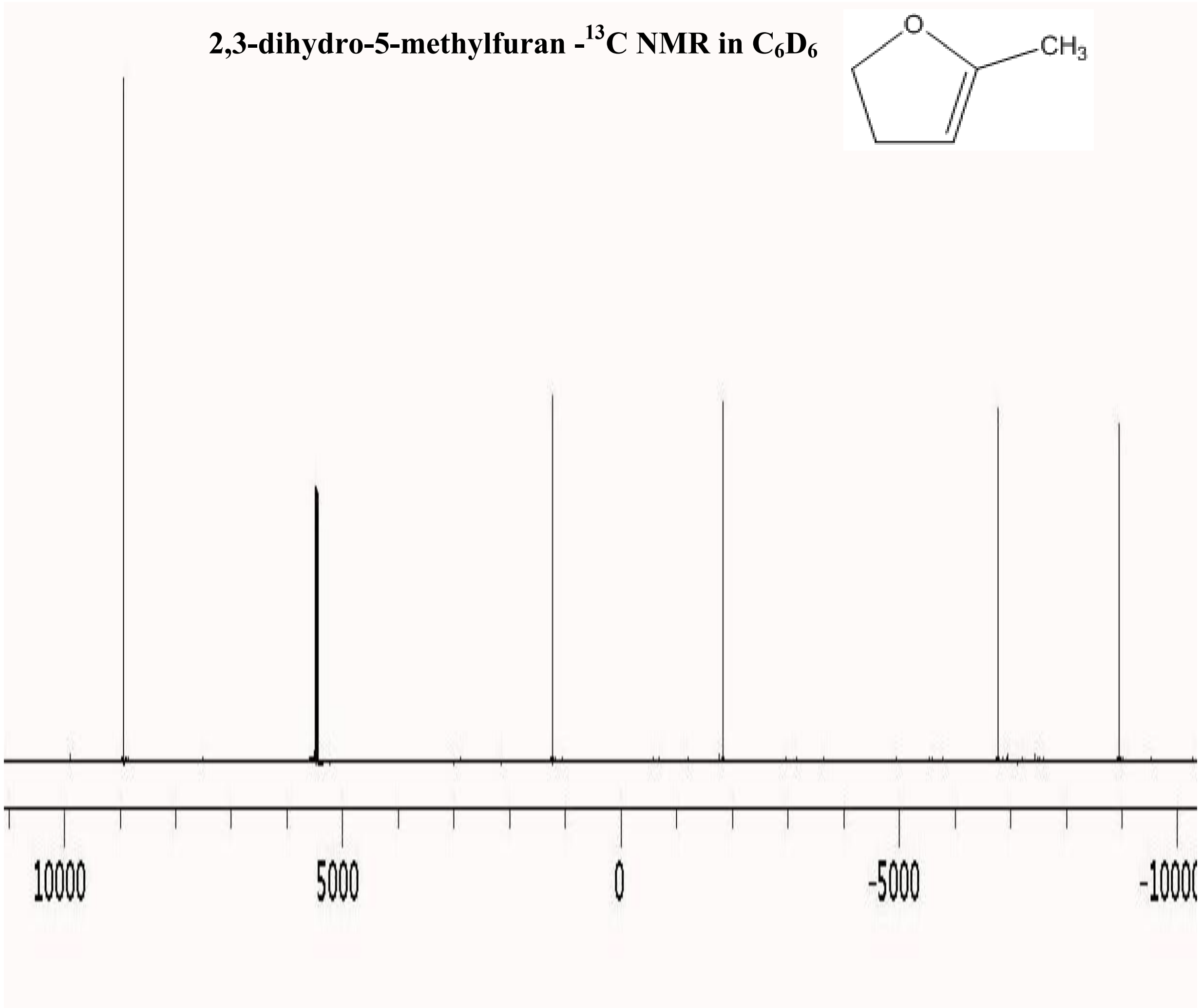
Intermolecular Starting Material ^{13}C NMR KIE Sample and Standard Integration Results for 2,3-dihydro-5-methylfuran. All integrations are relative integrations versus an integration of 1000 for C5.



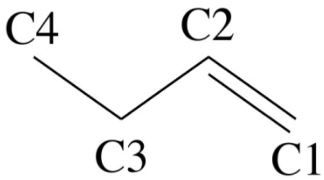
Integrations for cycloaddition of dimethylketene and 2,3-dihydro-5-methylfuran

% conversion	C1	C2	C3	C4	C5	N
Standard	988.5 ± 2	1004.6 ± 3	1037.4 ± 4	950.9 ± 3	1000.0	6
Sample **85.5%**	995.6 ± 1	998.1 ± 4	1039.5 ± 2	952.9 ± 2	1000.0	6
KIE **SD**	1.004 ± 2	0.997 ± 4	1.001 ± 4	1.001 ± 4	1.000	
Standard	1004.3 ± 2	995.6 ± 3	1036.9 ± 4	955.6 ± 3	1000.0	6
Sample **92.2%**	998.7 ± 4	994.4 ± 5	1031.0 ± 5	948.5 ± 3	1000.0	6
KIE **SD**	0.998 ± 4	0.999 ± 6	0.998 ± 6	0.997 ± 4	1.000	

2,3-dihydro-5-methylfuran -^{13}C NMR in C_6D_6



Intramolecular ^{13}C NMR KIE Sample Integration Results for 1-butene. All integrations are relative integrations of C3 versus an integration of 1000 for C4. A complication in the numerical interpretation of these integrations is that C4 is subject to one ^{1}J ^{13}C-^{13}C coupling with satellites not included in the integration range, while C3 is subject to two such satellite couplings. To allow for this, the integrations at C3 were adjusted by the 0.0107(8) natural abundance of ^{13}C. The 95% confidence ranges were calculated in a standard way.(See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf.)



Integrations for 80 °C

1047.42	1048.24	1047.53	1044.53	1051.33	1045.65
1055.43	1052.93	1055.96	1052.63	1056.07	1054.88

AVE	KIE
1051.05	**1.062**
Corrected	95%
1062.296	Confidence
	0.003

Integrations for 22 °C

1075	1067.68	1060.93	1064.25	1067.98	1065.11
1069.9	1066.61	1068.6	1069.85	1066.12	1066.99

AVE	KIE
1067.418	**1.079**
Corrected	95%
1078.84	Confidence
	0.002

Integrations for 0 °C

1075.16	1071.96	1072.3	1073.46	1064.93	1067.01
1068.85	1083.04	1073.49	1076.76	1079.98	1076.32

AVE	KIE
1073.605	**1.085**
Corrected	95%
1085.093	Confidence
	0.003

Integrations for -78 °C

1120.3	1118.94	1117.41	1119.76	1119.3	1121.94
1115.68	1121.18	1118.49	1118.42	1111.12	1111.7
1124.06	1117.04	1122.54	1119.06	1123.65	1124.63

AVE	KIE
1119.179	**1.131**
Corrected	95%
1131.154	Confidence
	0.002

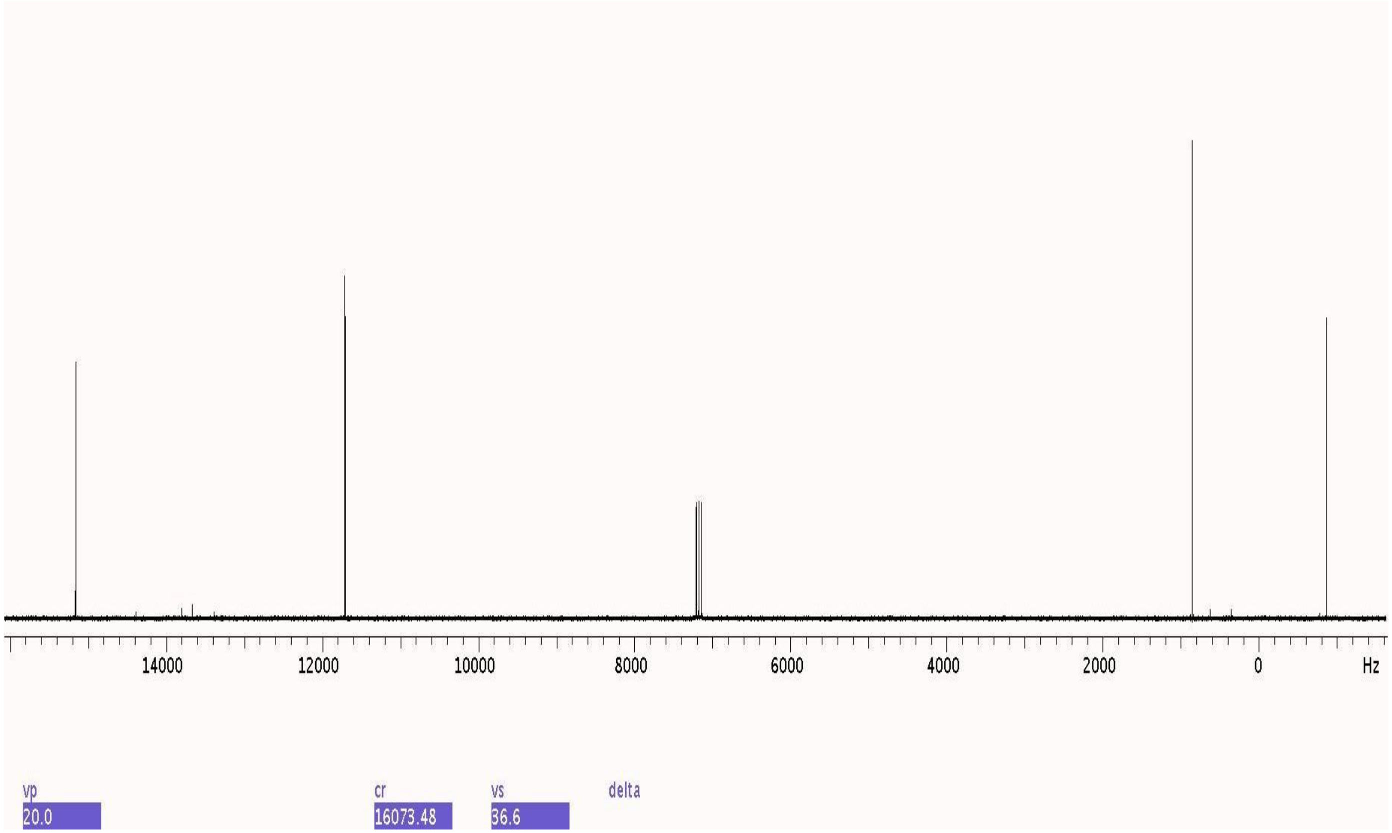
Integrations for -100 °C

1146.83	1150.08	1156.91	1152.91	1150.61	1147.89

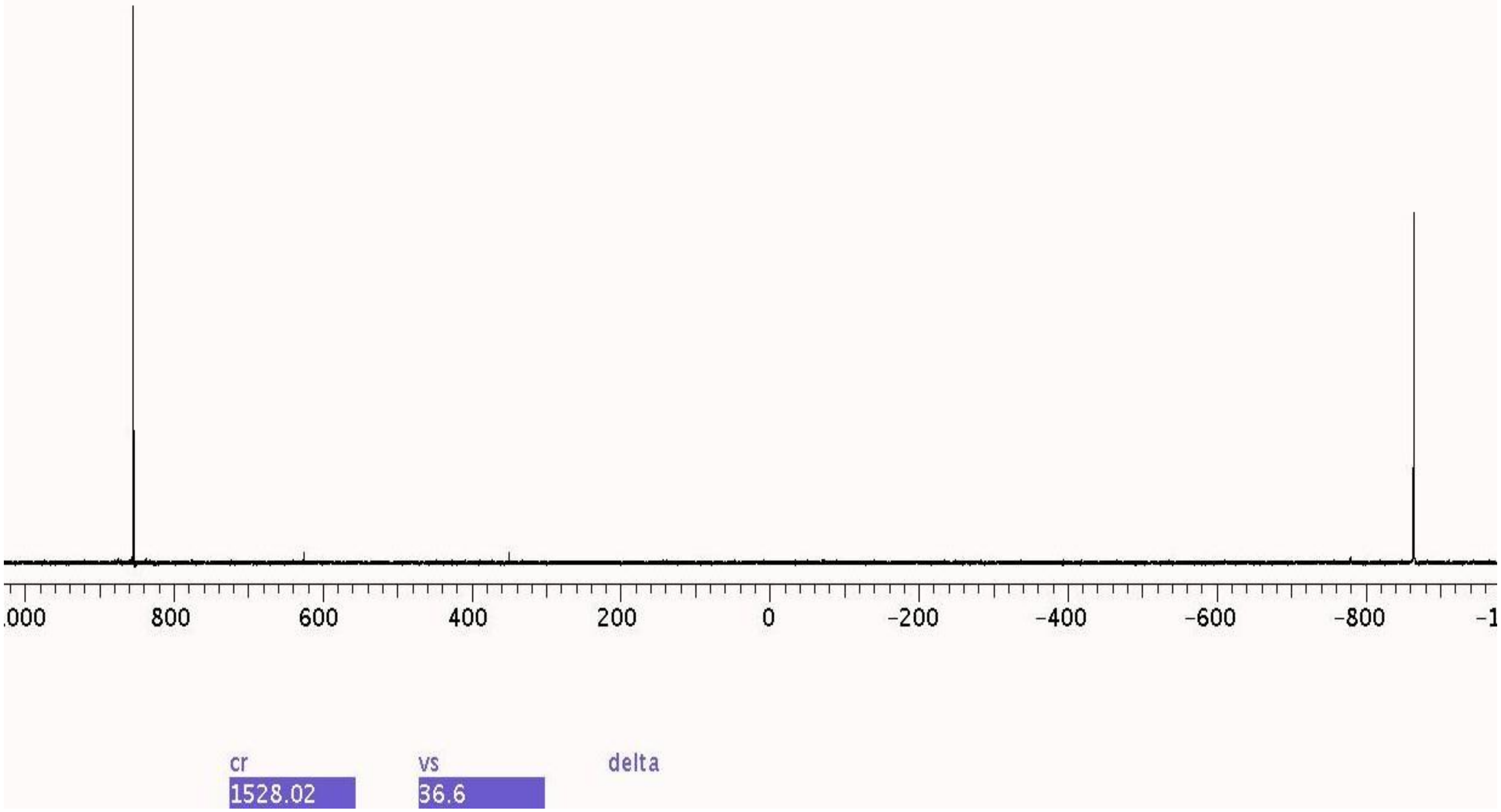
AVE	KIE
1150.872	**1.163**
Corrected	95%
1163.186	Confidence
	0.004

1-butene - ^{13}C NMR for KIEs

Full Spectra



Spectra of Aliphatic Peaks.



APPENDIX B

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Theoretical Structures for the cycloaddition of cis-2-butene and dichloroketene.

Cis-2-butene Starting Material

#HF/3-21G
E(RHF) = -155.243947631

Zero-point correction= 0.116262 (Hartree/Particle)
Thermal correction to Energy= 0.121589
Thermal correction to Enthalpy= 0.122533
Thermal correction to Gibbs Free Energy= 0.088411
Sum of electronic and ZPE= -155.127686
Sum of electronic and thermal Energies= -155.122359
Sum of electronic and thermal Enthalpies= -155.121415
Sum of electronic and thermal Free Energies= -155.155537

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	76.298	16.870	71.816

```
C,0,1.0875664781,0.7730580456,-0.3141171792
C,0,2.0777245599,1.4886901542,0.5740492324
C,0,2.2122956637,2.7887684161,0.7497780916
C,0,1.4108880312,3.8966327958,0.1080895073
H,0,2.7401734238,0.8362112266,1.1165173771
H,0,2.9774684807,3.1286940828,1.4263873123
H,0,0.9222159981,4.4968281561,0.8703022817
H,0,2.065521781,4.5573651671,-0.453061517
H,0,0.6515923822,3.5249734287,-0.5648969638
H,0,0.467581045,0.1047524708,0.2766357094
H,0,0.4371677468,1.453349216,-0.8449248391
H,0,1.6108954414,0.1652588419,-1.046722049
```

Transition State

#HF/3-21G
E(RHF) = -1219.46491561

Zero-point correction= 0.134983 (Hartree/Particle)
Thermal correction to Energy= 0.144478
Thermal correction to Enthalpy= 0.145422
Thermal correction to Gibbs Free Energy= 0.100127
Sum of electronic and ZPE= -1219.329933
Sum of electronic and thermal Energies= -1219.320438
Sum of electronic and thermal Enthalpies= -1219.319493

```
Sum of electronic and thermal Free Energies= -1219.364789

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 90.661 33.866 95.332

 C,0,1.114422697,0.8480132725,-0.4777908159
 C,0,2.1250896529,1.5987056039,0.3756541851
 H,0,2.7199206826,0.9781736657,1.0179524174
 C,0,1.7896442668,2.8725927478,0.9225796818
 C,0,3.1479786743,2.4694242106,-0.663033419
 O,0,2.7254325074,2.682020573,-1.7958196838
 C,0,4.2127977297,2.9837522363,0.0155397703
 Cl,0,5.4498355737,3.9016364238,-0.9077421381
 Cl,0,4.8267429185,2.4071637258,1.6192606426
 C,0,0.7738072676,3.7456829226,0.2804733624
 H,0,2.2976757022,3.2106030307,1.8019053746
 H,0,0.7603544521,4.7366975081,0.7070011566
 H,0,0.9961306784,3.7975300062,-0.7842653225
 H,0,-0.2097554809,3.2931596619,0.3832811699
 H,0,0.8235572111,1.4357271594,-1.3333592307
 H,0,1.5666182929,-0.0649764017,-0.8424119335
 H,0,0.2420011738,0.5846356535,0.1097807829
```

Cis-2-butene Starting Material

```
#HF/6-31+G**
E(RHF) = -156.124502727

Zero-point correction= 0.114921 (Hartree/Particle)
Thermal correction to Energy= 0.120259
Thermal correction to Enthalpy= 0.121203
Thermal correction to Gibbs Free Energy= 0.087149
Sum of electronic and ZPE= -156.009582
Sum of electronic and thermal Energies= -156.004244
Sum of electronic and thermal Enthalpies= -156.003299
Sum of electronic and thermal Free Energies= -156.037354

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 75.464 17.097 71.674

 C,0,1.0885133671,0.7610830818,-0.3138488038
 C,0,2.0689486017,1.487199913,0.566396075
 C,0,2.2042092503,2.7939509239,0.7430282559
```

```
C,0,1.4142145008,3.9076719871,0.111471735
H,0,2.740428878,0.8461010212,1.1171853342
H,0,2.9757089748,3.1191344494,1.4244284334
H,0,0.9307027937,4.5095768791,0.8767781425
H,0,2.0725792737,4.5700396141,-0.4449380727
H,0,0.6487477699,3.55266657,-0.5660809111
H,0,0.4731413808,0.0893239451,0.2792988869
H,0,0.428856539,1.4281002508,-0.85328065
H,0,1.6150394234,0.1497333512,-1.0424011395
```

Transition State

```
#HF/6-31+G**
E(RHF) = -1225.57421853

Zero-point correction= 0.134332 (Hartree/Particle)
Thermal correction to Energy= 0.143933
Thermal correction to Enthalpy= 0.144877
Thermal correction to Gibbs Free Energy= 0.099283
Sum of electronic and ZPE= -1225.439887
Sum of electronic and thermal Energies= -1225.430286
Sum of electronic and thermal Enthalpies= -1225.429342
Sum of electronic and thermal Free Energies= -1225.474935

     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 90.319 33.979 95.960

 C,0,1.1475514087,0.8155940104,-0.5042789061
 C,0,2.091167291,1.6166295812,0.3700926397
 H,0,2.6728425021,1.0164574056,1.0484148678
 C,0,1.7647163572,2.896074932,0.8643082078
 C,0,3.1489179038,2.5156056869,-0.6025643875
 O,0,2.759639288,2.7268858913,-1.7356076394
 C,0,4.2917250341,2.9270011461,0.0333679188
 Cl,0,5.5199943376,3.6956952658,-0.8966589851
 Cl,0,4.8043225338,2.4535181766,1.6219625702
 C,0,0.7330279018,3.7879580555,0.2698951548
 H,0,2.2781963641,3.237800894,1.7426438464
 H,0,0.8140555336,4.7950548734,0.6541734757
 H,0,0.8267038978,3.7940971658,-0.8102725023
 H,0,-0.2499779791,3.3923462884,0.5201738544
 H,0,0.6555873634,1.4284016529,-1.2430544765
 H,0,1.7012198794,0.046427298,-1.0271058731
 H,0,0.4025643828,0.3349936763,0.1235162346
```

Cis-2-butene Starting Material
#HF/6-31+G pcm(THF)**
E(RHF) = -156.125663690

Zero-point correction= 0.114710 (Hartree/Particle)
Thermal correction to Energy= 0.120059
Thermal correction to Enthalpy= 0.121003
Thermal correction to Gibbs Free Energy= 0.086913
Sum of electronic and ZPE= -156.010953
Sum of electronic and thermal Energies= -156.005605
Sum of electronic and thermal Enthalpies= -156.004661
Sum of electronic and thermal Free Energies= -156.038751

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	75.338	17.129	71.749

C,0,1.087960736,0.7605525109,-0.3143498148
C,0,2.0688202598,1.4866189166,0.5662606876
C,0,2.2042047682,2.794560598,0.7430530625
C,0,1.4137950386,3.9084155405,0.1111414274
H,0,2.7403121052,0.8451370273,1.117043513
H,0,2.9757934093,3.120104958,1.4245469154
H,0,0.9317216681,4.510659279,0.8770143656
H,0,2.0729165347,4.5710838978,-0.4439109019
H,0,0.6482882611,3.553560434,-0.5664395541
H,0,0.4739190913,0.0880299244,0.2792157023
H,0,0.4282297845,1.4274430802,-0.8538410565
H,0,1.6151296878,0.1484158512,-1.0416977451

Transition State
#HF/6-31+G pcm(THF)**
E(RHF) = -1225.58910344

Zero-point correction= 0.133870 (Hartree/Particle)
Thermal correction to Energy= 0.143900
Thermal correction to Enthalpy= 0.144845
Thermal correction to Gibbs Free Energy= 0.097967
Sum of electronic and ZPE= -1225.455234
Sum of electronic and thermal Energies= -1225.445203
Sum of electronic and thermal Enthalpies= -1225.444259
Sum of electronic and thermal Free Energies= -1225.491137

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 90.299 34.540 98.663

C,0,1.2101330558,0.7665712028,-0.5730874694
C,0,1.9479867551,1.5379388215,0.4630471472
H,0,2.6299457769,0.9777674174,1.0757708874
C,0,1.7996658718,2.8851774117,0.7517177817
C,0,3.1221509301,2.9423129567,-0.4888120588
O,0,2.7207859066,3.2010663243,-1.6079173083
C,0,4.3642518682,2.8570480926,0.03984831
Cl,0,5.7117620546,3.2844586958,-0.9630677592
Cl,0,4.7845243471,2.4903212526,1.6771829761
C,0,0.6598540383,3.7499293965,0.2719747352
H,0,2.2536549573,3.2129659649,1.6690803473
H,0,0.9638064224,4.788604474,0.2609663219
H,0,0.3166626422,3.4810811761,-0.7140605822
H,0,-0.1611517632,3.6443642471,0.9746473578
H,0,0.7856071045,1.3943336254,-1.3397907832
H,0,1.8495675696,0.0164415456,-1.0192721983
H,0,0.4036024625,0.2501573951,-0.0544557049

Cis-2-butene Starting Material
B3LYP/6-31+G*
E(RB3LYP) = -157.231466068

Zero-point correction= 0.108282 (Hartree/Particle)
Thermal correction to Energy= 0.113806
Thermal correction to Enthalpy= 0.114750
Thermal correction to Gibbs Free Energy= 0.080400
Sum of electronic and ZPE= -157.123185
Sum of electronic and thermal Energies= -157.117661
Sum of electronic and thermal Enthalpies= -157.116716
Sum of electronic and thermal Free Energies= -157.151066

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.414 18.155 72.295

C,0,1.0890940535,0.7605527731,-0.3133709285
C,0,2.0737490849,1.4780721301,0.5701264112
C,0,2.2106449471,2.8006186695,0.7488933937
C,0,1.4148773357,3.9079300745,0.1120555526

H,0,2.7510031198,0.8271847116,1.1254557136
H,0,2.9896441417,3.1326848672,1.4370869474
H,0,0.9199043754,4.5218162687,0.8773575856
H,0,2.0710205122,4.582768494,-0.4550518941
H,0,0.6435212146,3.5405374289,-0.5711525514
H,0,0.4600913105,0.0797924186,0.2769364984
H,0,0.4263143666,1.4419298776,-0.8548404704
H,0,1.6112263118,0.1406942742,-1.0554589955

Transition State
B3LYP/6-31+G*
E(RB3LYP) = -1228.98459450

Zero-point correction= 0.125363 (Hartree/Particle)
Thermal correction to Energy= 0.135862
Thermal correction to Enthalpy= 0.136806
Thermal correction to Gibbs Free Energy= 0.089062
Sum of electronic and ZPE= -1228.859232
Sum of electronic and thermal Energies= -1228.848733
Sum of electronic and thermal Enthalpies= -1228.847789
Sum of electronic and thermal Free Energies= -1228.895533

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.254	36.452	100.486

C,0,1.2004139497,0.7760880428,-0.5529996217
C,0,1.9748968331,1.4941274801,0.4966153352
H,0,2.7018188676,0.9343776372,1.0778839835
C,0,1.8227433054,2.8578969667,0.7819933165
C,0,3.1175811984,2.9780585752,-0.5297093121
O,0,2.6715322459,3.2181761653,-1.6422282032
C,0,4.3931801457,2.8788284465,-0.0122385829
Cl,0,5.7150582037,3.4076774439,-1.0094538112
Cl,0,4.8217613092,2.5399214759,1.6460011699
C,0,0.6418461911,3.6800358931,0.322744234
H,0,2.3103845032,3.2133435767,1.6866013254
H,0,0.880498355,4.746973622,0.3554168804
H,0,0.3396937125,3.4320770591,-0.6962334623
H,0,-0.2041440217,3.4988602045,0.9989461374
H,0,1.3026194914,1.3111249475,-1.5105701288
H,0,1.5440563963,-0.2531486707,-0.6795042035
H,0,0.1288693133,0.7661211343,-0.3094930564

Cis-2-butene Starting Material
B3LYP/6-31+G* pcm(THF)
E(RB3LYP) = -157.232498241

Zero-point correction= 0.108072 (Hartree/Particle)
Thermal correction to Energy= 0.113613
Thermal correction to Enthalpy= 0.114557
Thermal correction to Gibbs Free Energy= 0.080152
Sum of electronic and ZPE= -157.124426
Sum of electronic and thermal Energies= -157.118885
Sum of electronic and thermal Enthalpies= -157.117941
Sum of electronic and thermal Free Energies= -157.152346

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	71.293	18.200	72.412

C,0,1.0886290207,0.7597129553,-0.3138102636
C,0,2.0733785312,1.4775421377,0.5697836736
C,0,2.210398675,2.8012834038,0.7487113901
C,0,1.4146042211,3.9089316264,0.1118635468
H,0,2.750617404,0.8263029465,1.1250854837
H,0,2.9894549928,3.1336919083,1.4369707257
H,0,0.9214125554,4.523425401,0.8777302053
H,0,2.0715402855,4.5843241687,-0.4535320848
H,0,0.6430176362,3.5425428134,-0.5714992503
H,0,0.4612385967,0.0778668768,0.2768332493
H,0,0.4254202191,1.4402295275,-0.8556798172
H,0,1.6113788944,0.1387282364,-1.0544198949

Transition State
B3LYP/6-31+G* pcm(THF)
E(RB3LYP) = -1228.99274784

Zero-point correction= 0.125094 (Hartree/Particle)
Thermal correction to Energy= 0.135909
Thermal correction to Enthalpy= 0.136853
Thermal correction to Gibbs Free Energy= 0.088039
Sum of electronic and ZPE= -1228.867653
Sum of electronic and thermal Energies= -1228.856839
Sum of electronic and thermal Enthalpies= -1228.855895
Sum of electronic and thermal Free Energies= -1228.904709

	E	CV	S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 85.284 36.793 102.737

C,0,1.1854767605,0.7750667098,-0.5560158449
C,0,1.9670023991,1.5250519307,0.4727138695
H,0,2.683896841,0.96184393,1.0632671828
C,0,1.7612255975,2.8544195395,0.8172912443
C,0,3.1813177794,2.8985283566,-0.5747576173
O,0,2.7321072073,3.1492819011,-1.6824374602
C,0,4.4178317821,2.8944613148,0.007530147
Cl,0,5.7666655118,3.4514387939,-0.9597251055
Cl,0,4.8197510363,2.489993639,1.6530609262
C,0,0.6383078405,3.7126574845,0.3115500682
H,0,2.2786429185,3.2202036097,1.7000373458
H,0,0.9149014587,4.7706072563,0.3329134073
H,0,0.3304150024,3.447264524,-0.7014177354
H,0,-0.2237427966,3.5786656358,0.9794145699
H,0,1.0328755172,1.3786606832,-1.4573315406
H,0,1.6833151213,-0.1581734205,-0.8300171285
H,0,0.1928200229,0.5305681117,-0.1523043284

Dichloroketene Starting Material
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1071.72174242

Zero-point correction= 0.016271 (Hartree/Particle)
Thermal correction to Energy= 0.021228
Thermal correction to Enthalpy= 0.022173
Thermal correction to Gibbs Free Energy= -0.013388
Sum of electronic and ZPE= -1071.705471
Sum of electronic and thermal Energies= -1071.700514
Sum of electronic and thermal Enthalpies= -1071.699570
Sum of electronic and thermal Free Energies= -1071.735130

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 13.321 15.071 74.843

Cl,0,1.1394989217,1.1790502808,-0.4430569264
Cl,0,2.7524527893,1.732220456,1.9813664815
C,0,2.0273643984,0.6130482833,0.9072787553
C,0,2.1521448582,-0.6774992247,1.1185386062
O,0,2.2618600324,-1.8131217954,1.3042120834

Cis-2-butene Starting Material
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -157.198685414

Zero-point correction= 0.110986 (Hartree/Particle)
Thermal correction to Energy= 0.116456
Thermal correction to Enthalpy= 0.117400
Thermal correction to Gibbs Free Energy= 0.083138
Sum of electronic and ZPE= -157.087700
Sum of electronic and thermal Energies= -157.082229
Sum of electronic and thermal Enthalpies= -157.081285
Sum of electronic and thermal Free Energies= -157.115548

```
    E     CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.077 17.826 72.112
```

```
 C,0,1.0924978651,0.7779415164,-0.3096367879
 C,0,2.070746273,1.4842343855,0.567810653
 C,0,2.2065271902,2.796016635,0.7451247217
 C,0,1.4146078889,3.8898552359,0.1109993694
 H,0,2.7439842145,0.8388327899,1.1199191464
 H,0,2.9805777756,3.1245589336,1.4288803414
 H,0,0.9222016216,4.4982231061,0.8701666947
 H,0,2.0653103818,4.5587533265,-0.4529792886
 H,0,0.6501927309,3.5205153655,-0.5662987634
 H,0,0.4672752857,0.103495103,0.2761357595
 H,0,0.4367556843,1.4582061364,-0.8450969859
 H,0,1.6104140885,0.1639494662,-1.0469878601
```

Transition State
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.91125508

Zero-point correction= 0.128793 (Hartree/Particle)
Thermal correction to Energy= 0.139476
Thermal correction to Enthalpy= 0.140420
Thermal correction to Gibbs Free Energy= 0.091187
Sum of electronic and ZPE= -1228.782462
Sum of electronic and thermal Energies= -1228.771779
Sum of electronic and thermal Enthalpies= -1228.770835
Sum of electronic and thermal Free Energies= -1228.820068

```
    E     CV       S
```

```
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 87.522 35.977 103.621

 C,0,-2.4913065465,-0.191493205,1.5059266627
 C,0,-1.5965828733,0.6628401978,0.6817917688
 C,0,-1.5965828733,0.6628401978,-0.6817917688
 C,0,-2.4913065465,-0.191493205,-1.5059266627
 C,0,-0.0573081075,-0.6984962799,0.
 C,0,1.0971247845,-0.0072929876,0.
 Cl,0,1.3131292915,1.6942645086,0.
 O,0,-0.505957456,-1.8002023592,0.
 H,0,-0.9986390729,1.4082719702,1.1857346672
 H,0,-0.9986390729,1.4082719702,-1.1857346672
 H,0,-2.2422555148,-0.1269471884,-2.5600104499
 H,0,-2.4177047308,-1.2330694007,-1.1941619709
 H,0,-3.5288971499,0.1186567285,-1.3773523453
 H,0,-2.4177047308,-1.2330694007,1.1941619709
 H,0,-2.2422555148,-0.1269471884,2.5600104499
 H,0,-3.5288971499,0.1186567285,1.3773523453
 Cl,0,2.5476168057,-0.934706976,0.
```

Cis-2-butene Starting Material

```
#m05/6-31+G**
E(RM05) = -157.097451650

Zero-point correction= 0.108567 (Hartree/Particle)
Thermal correction to Energy= 0.114104
Thermal correction to Enthalpy= 0.115048
Thermal correction to Gibbs Free Energy= 0.080744
Sum of electronic and ZPE= -156.988885
Sum of electronic and thermal Energies= -156.983348
Sum of electronic and thermal Enthalpies= -156.982404
Sum of electronic and thermal Free Energies= -157.016707

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.601 18.300 72.198

 C,0,1.0909636245,0.7656450739,-0.3115234724
 C,0,2.069646471,1.4793178196,0.5666378508
 C,0,2.206471536,2.8011851042,0.7453137773
 C,0,1.4156325211,3.9022631634,0.1124495685
 H,0,2.7477619095,0.8327898324,1.1229100524
 H,0,2.985411162,3.128716259,1.433248477
```

H,0,0.9230022935,4.5140788175,0.8763621464
H,0,2.0708384838,4.5748581253,-0.4522507354
H,0,0.6454453348,3.5381132966,-0.5696003904
H,0,0.4647066829,0.0867351825,0.2779249953
H,0,0.4286468723,1.4434225486,-0.8527626077
H,0,1.6125638618,0.147456764,-1.0506723758

Transition State
#m05/6-31+G**
E(RM05) = -1228.78963476

Zero-point correction= 0.125769 (Hartree/Particle)
Thermal correction to Energy= 0.136676
Thermal correction to Enthalpy= 0.137620
Thermal correction to Gibbs Free Energy= 0.088470
Sum of electronic and ZPE= -1228.663866
Sum of electronic and thermal Energies= -1228.652959
Sum of electronic and thermal Enthalpies= -1228.652015
Sum of electronic and thermal Free Energies= -1228.701164

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.765	36.963	103.444

C,0,-2.5118877928,-0.1016030547,1.5139944176
C,0,-1.5747253432,0.682906591,0.6595567022
C,0,-1.5917966283,0.6977165524,-0.7116435143
C,0,-2.5180117316,-0.1082858471,-1.555159572
C,0,-0.0700494854,-0.7904141661,0.0310473127
O,0,-0.6012287449,-1.8638564353,0.0246343833
C,0,1.1340159714,-0.1620002445,0.0280248639
Cl,0,2.5275627468,-1.1886536068,0.0662714571
Cl,0,1.4532416179,1.53236218,0.0169523548
H,0,-0.9339314564,1.4033941771,1.1591810613
H,0,-0.9378549095,1.4062151533,-1.2113158601
H,0,-2.3043726835,0.0175680863,-2.6167330272
H,0,-2.4356275826,-1.1722204284,-1.3082375968
H,0,-3.5576830881,0.1851547909,-1.3740628653
H,0,-2.115470079,-0.2298019758,2.5224494929
H,0,-3.4665352135,0.4314571179,1.5946410496
H,0,-2.7144755972,-1.0890498901,1.0943703405

Cis-2-butene Starting Material
#m052x/6-31+G**

```
E(RM052X) = -157.202035129

Zero-point correction= 0.109309 (Hartree/Particle)
Thermal correction to Energy= 0.114967
Thermal correction to Enthalpy= 0.115911
Thermal correction to Gibbs Free Energy= 0.080949
Sum of electronic and ZPE= -157.092726
Sum of electronic and thermal Energies= -157.087069
Sum of electronic and thermal Enthalpies= -157.086124
Sum of electronic and thermal Free Energies= -157.121086

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.143 18.164 73.582

 C,0,1.0882040911,0.7731361927,-0.3135650187
 C,0,2.0749399772,1.4806446508,0.571272215
 C,0,2.211262241,2.7976504404,0.7492903629
 C,0,1.4114785779,3.8962855554,0.1085877458
 H,0,2.7492113439,0.8320025139,1.1241277688
 H,0,2.9869567176,3.1288478587,1.4345889143
 H,0,0.9181330463,4.5031452858,0.8723476158
 H,0,2.0666515253,4.5639598224,-0.4570597753
 H,0,0.6471959327,3.5198359518,-0.5689210242
 H,0,0.4622458867,0.0990885824,0.2770567121
 H,0,0.4340225399,1.4601398286,-0.847356084
 H,0,1.6107888735,0.159845304,-1.0523321462
```

Transition State

```
#m052x/6-31+G**
E(RM052X) = -1228.89726124

Zero-point correction= 0.126801 (Hartree/Particle)
Thermal correction to Energy= 0.137792
Thermal correction to Enthalpy= 0.138737
Thermal correction to Gibbs Free Energy= 0.088894
Sum of electronic and ZPE= -1228.770460
Sum of electronic and thermal Energies= -1228.759469
Sum of electronic and thermal Enthalpies= -1228.758525
Sum of electronic and thermal Free Energies= -1228.808368

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 86.466 36.788 104.903
```

C,0,-2.4418762643,-0.2941429554,1.5309030294
C,0,-1.6431327611,0.6749384914,0.7149818717
C,0,-1.7135302661,0.7826999908,-0.6348406962
C,0,-2.5921354497,-0.0696763257,-1.5015848254
C,0,0.0675752582,-0.7858216408,-0.0822836682
O,0,-0.4811604515,-1.8317732752,-0.1295971672
C,0,1.1799680269,-0.0410239742,-0.0683497507
Cl,0,2.6665767419,-0.9418603103,-0.1388643885
Cl,0,1.3407171723,1.6707085028,0.0093583383
H,0,-1.0356199715,1.3914154442,1.2566936129
H,0,-1.1440267849,1.5717395183,-1.1126226179
H,0,-2.3837972547,-1.1302683478,-1.3355805643
H,0,-3.6459068242,0.100079631,-1.2657801198
H,0,-2.434903515,0.1516923668,-2.5555070119
H,0,-1.8632008885,-0.6517765704,2.3831829339
H,0,-3.3332018455,0.2071344818,1.9207827352
H,0,-2.7611749221,-1.1531760273,0.9430792888

Cis-2-butene Starting Material
#m06/6-31+G**
E(RM06) = -157.098913870

Zero-point correction= 0.107354 (Hartree/Particle)
Thermal correction to Energy= 0.112906
Thermal correction to Enthalpy= 0.113851
Thermal correction to Gibbs Free Energy= 0.079455
Sum of electronic and ZPE= -156.991560
Sum of electronic and thermal Energies= -156.986007
Sum of electronic and thermal Enthalpies= -156.985063
Sum of electronic and thermal Free Energies= -157.019458

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 70.850 18.383 72.391
```

C,0,1.0929274275,0.7773973599,-0.3092890375
C,0,2.074453483,1.4800500806,0.5708244658
C,0,2.2109174793,2.7984270833,0.749028389
C,0,1.4151303988,3.8901908472,0.1114635037
H,0,2.7521071162,0.8289720932,1.1264897139
H,0,2.9903370131,3.1305042725,1.4375854236
H,0,0.9147034438,4.5055633936,0.8702932499
H,0,2.064012094,4.5664207824,-0.4600245982

H,0,0.646083578,3.513837272,-0.5701591456
H,0,0.4584588155,0.0980350814,0.2745344921
H,0,0.434171345,1.4663493412,-0.8469414012
H,0,1.6077885589,0.1588343795,-1.0557677694

Transition State
#m06/6-31+G**
E(RM06) = -1228.71870471

Zero-point correction= 0.124760 (Hartree/Particle)
Thermal correction to Energy= 0.135312
Thermal correction to Enthalpy= 0.136256
Thermal correction to Gibbs Free Energy= 0.088322
Sum of electronic and ZPE= -1228.593945
Sum of electronic and thermal Energies= -1228.583393
Sum of electronic and thermal Enthalpies= -1228.582449
Sum of electronic and thermal Free Energies= -1228.630383

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 84.909 36.785 100.886
```

C,0,-2.498318952,-0.1817629434,1.5057652643
C,0,-1.5857921754,0.6604436095,0.6866805897
C,0,-1.5857029484,0.6606227715,-0.6864575449
C,0,-2.4981863632,-0.1813065929,-1.5058891765
C,0,-0.0742203952,-0.6890759998,-0.0001042179
C,0,1.0997640638,-0.0101199649,0.0001020747
Cl,0,1.3509372601,1.7037704804,0.0003604192
O,0,-0.5159600879,-1.8065048738,-0.0002977879
H,0,-0.9723340919,1.4017941116,1.1955341759
H,0,-0.9722301146,1.4021513563,-1.1950313776
H,0,-2.3344384979,-0.0338385431,-2.5754379629
H,0,-2.3438563135,-1.2443667128,-1.2735568414
H,0,-3.5474349297,0.0492424513,-1.2792105945
H,0,-2.3438646103,-1.2447507801,1.2731644471
H,0,-2.3347380106,-0.0345652892,2.5753761515
H,0,-3.5475557423,0.0487474936,1.2789915383
Cl,0,2.5477654508,-0.9703964637,0.0000108428

Cis-2-butene Starting Material
#m062x/6-31+G**
E(RM062X) = -157.144292220

```
Zero-point correction= 0.108512 (Hartree/Particle)
Thermal correction to Energy= 0.114160
Thermal correction to Enthalpy= 0.115105
Thermal correction to Gibbs Free Energy= 0.080267
Sum of electronic and ZPE= -157.035780
Sum of electronic and thermal Energies= -157.030132
Sum of electronic and thermal Enthalpies= -157.029188
Sum of electronic and thermal Free Energies= -157.064026

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.637 18.276 73.323

 C,0,1.0893859644,0.7757319631,-0.3124252319
 C,0,2.0768369893,1.4799482854,0.5728786775
 C,0,2.2132159645,2.7975039512,0.7509715618
 C,0,1.4120824405,3.893298823,0.10897322
 H,0,2.752151716,0.8284098194,1.1265022339
 H,0,2.9904936556,3.1310226371,1.4377437365
 H,0,0.9146652309,4.5036401733,0.8706085439
 H,0,2.0644029436,4.5645200335,-0.4602093537
 H,0,0.6462308091,3.5140747263,-0.5700184901
 H,0,0.458797571,0.0997773077,0.2753439754
 H,0,0.4342674376,1.4660588894,-0.8468762111
 H,0,1.6085600307,0.1605953776,-1.055455376
```

Transition State

```
#m062x/6-31+G**
E(RM062X) = -1228.78286075

Zero-point correction= 0.126920 (Hartree/Particle)
Thermal correction to Energy= 0.136733
Thermal correction to Enthalpy= 0.137677
Thermal correction to Gibbs Free Energy= 0.091784
Sum of electronic and ZPE= -1228.655941
Sum of electronic and thermal Energies= -1228.646128
Sum of electronic and thermal Enthalpies= -1228.645184
Sum of electronic and thermal Free Energies= -1228.691077

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 85.801 35.363 96.590

 C,0,-2.3660334487,-0.2604962812,1.5418154825
```

```
C,0,-1.5153954304,0.6325166436,0.7125561586
C,0,-1.4660221164,0.5418116354,-0.7032448945
C,0,-2.5190550494,-0.1971057559,-1.4926946437
C,0,-0.2489662477,-0.5461297262,-0.248602563
C,0,0.9547690947,0.0701698243,0.0790985783
Cl,0,1.2954576034,1.7615089963,-0.0492268983
O,0,-0.5353914171,-1.7418333123,-0.2645401846
H,0,-0.9656891078,1.4332469836,1.1971352942
H,0,-1.0060203199,1.3857645841,-1.2122013671
H,0,-2.1431924909,-0.4334726785,-2.4898411677
H,0,-2.7925577515,-1.1339795771,-1.0074771713
H,0,-3.40572907,0.4367036249,-1.5928535286
H,0,-2.1653663969,-1.305109038,1.2640468499
H,0,-2.1802959016,-0.1210817958,2.6062756201
H,0,-3.4249476742,-0.0663214821,1.3303657051
Cl,0,2.3282692662,-0.9261085348,0.32938873
```

Cis-2-butene Starting Material

```
#m062x/6-31+G** pcm(THF)
E(RM062X) = -157.145432810

Zero-point correction= 0.108237 (Hartree/Particle)
Thermal correction to Energy= 0.113935
Thermal correction to Enthalpy= 0.114879
Thermal correction to Gibbs Free Energy= 0.079818
Sum of electronic and ZPE= -157.037196
Sum of electronic and thermal Energies= -157.031498
Sum of electronic and thermal Enthalpies= -157.030554
Sum of electronic and thermal Free Energies= -157.065615

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.495 18.345 73.793

C,0,1.0886767648,0.773973188,-0.313117849
C,0,2.076217434,1.479420412,0.5723209533
C,0,2.212731129,2.7982731851,0.7505884505
C,0,1.4117616413,3.8952831753,0.1087853673
H,0,2.7515512576,0.8275016044,1.1259450824
H,0,2.9901043589,3.1321470174,1.437460127
H,0,0.9165987719,4.5058344471,0.8715353507
H,0,2.0655052061,4.5666679852,-0.4583199137
H,0,0.6455868964,3.5173914447,-0.5704242854
H,0,0.4602275224,0.0970694332,0.2756093393
```

H,0,0.4329753559,1.4631650556,-0.848114939
H,0,1.6091544371,0.1578550401,-1.0542304232

1st Transition State

#m062x/6-31+G** pcm(THF)
E(RM062X) = -1228.79017767

Zero-point correction= 0.125995 (Hartree/Particle)
Thermal correction to Energy= 0.136927
Thermal correction to Enthalpy= 0.137871
Thermal correction to Gibbs Free Energy= 0.088325
Sum of electronic and ZPE= -1228.664183
Sum of electronic and thermal Energies= -1228.653251
Sum of electronic and thermal Enthalpies= -1228.652307
Sum of electronic and thermal Free Energies= -1228.701852

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.923	36.913	104.277

C,0,-2.4407243628,-0.2966633486,1.5324064606
C,0,-1.658174269,0.6862189988,0.7182506564
C,0,-1.7294803399,0.7956057806,-0.6307919893
C,0,-2.597355956,-0.0631637221,-1.5016891931
C,0,0.0945357975,-0.8037869865,-0.0869366192
O,0,-0.4676718499,-1.8405571025,-0.1317283119
C,0,1.2003388925,-0.0510673051,-0.071613917
Cl,0,2.6935147772,-0.9508779221,-0.1360626808
Cl,0,1.3491832308,1.660648038,-0.0021486359
H,0,-1.0543640573,1.407586755,1.2643462929
H,0,-1.1687811182,1.5940250483,-1.1106325325
H,0,-2.4185363284,-1.1268360247,-1.307075704
H,0,-3.6565071958,0.1284226189,-1.2974264849
H,0,-2.4110521256,0.1312062277,-2.5584437549
H,0,-1.8597290962,-0.6449711247,2.3901299958
H,0,-3.3444840295,0.1867559821,1.9217995041
H,0,-2.7495419694,-1.1616569131,0.9415879138

2nd Transition State

#m062x/6-31+G** pcm(THF)
E(RM062X) = -1228.79238063

Zero-point correction= 0.126980 (Hartree/Particle)
Thermal correction to Energy= 0.136735

```
Thermal correction to Enthalpy= 0.137680
Thermal correction to Gibbs Free Energy= 0.091810
Sum of electronic and ZPE= -1228.665401
Sum of electronic and thermal Energies= -1228.655645
Sum of electronic and thermal Enthalpies= -1228.654701
Sum of electronic and thermal Free Energies= -1228.700570

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 85.803 35.242 96.540

 C,0,-2.3697835451,-0.2652900743,1.5473744676
 C,0,-1.5165181857,0.6173162961,0.7137407515
 C,0,-1.4611802938,0.5247942163,-0.7042089706
 C,0,-2.5166780782,-0.2077694138,-1.4961892194
 C,0,-0.2443040886,-0.5303062943,-0.2501204071
 C,0,0.9580007799,0.086146729,0.0683353303
 Cl,0,1.2948473501,1.7759054352,-0.0351737274
 O,0,-0.501868249,-1.7444296271,-0.271471994
 H,0,-0.974089326,1.4237905943,1.1974655049
 H,0,-1.0136237866,1.3775916819,-1.2097304252
 H,0,-2.129973239,-0.4724550392,-2.4818986719
 H,0,-2.834766215,-1.1211013432,-0.9944622946
 H,0,-3.3795202699,0.4521058559,-1.6250522775
 H,0,-2.2370258888,-1.309280091,1.2381699737
 H,0,-2.145211177,-0.1586053523,2.6076059
 H,0,-3.4222365121,-0.006994658,1.3730324294
 Cl,0,2.3377642666,-0.911334805,0.3225836301
```

Intermediate

```
#m062x/6-31+G** pcm(THF)
E(RM062X) = -1228.79257705

Zero-point correction= 0.127140 (Hartree/Particle)
Thermal correction to Energy= 0.138035
Thermal correction to Enthalpy= 0.138979
Thermal correction to Gibbs Free Energy= 0.090250
Sum of electronic and ZPE= -1228.665437
Sum of electronic and thermal Energies= -1228.654543
Sum of electronic and thermal Enthalpies= -1228.653598
Sum of electronic and thermal Free Energies= -1228.702327

      E      CV        S
```

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 86.618 37.739 102.559

C,0,1.2309646668,0.8274518535,-0.5851982959
C,0,2.0929891493,1.5704872776,0.3881001792
C,0,1.7961627042,2.842839392,0.8754178938
C,0,0.6270539942,3.6543980838,0.4235525168
C,0,3.0765160747,2.8182588596,-0.5769688198
C,0,4.3327583924,2.9578870015,-0.0478847085
Cl,0,4.8528055333,2.497118926,1.5326563445
O,0,2.6002631586,3.0976276266,-1.67560093
Cl,0,5.5680639614,3.604890003,-1.0665802721
H,0,2.8271851359,0.9854049465,0.9350423556
H,0,2.3508473576,3.1922950849,1.7413820678
H,0,0.7052042268,4.6829655556,0.7751526679
H,0,0.5527326637,3.6477428319,-0.667045467
H,0,-0.2884331419,3.2095600522,0.83000306
H,0,1.8282118727,0.1329208644,-1.1781234012
H,0,0.4983501044,0.2491043167,-0.0115110949
H,0,0.6999091459,1.5034803243,-1.2546330961

Cis-2-butene Starting Material
MP2/6-31+G**
-0.5719268940D+00 EUMP2

Zero-point correction= 0.110422 (Hartree/Particle)
Thermal correction to Energy= 0.116055
Thermal correction to Enthalpy= 0.117000
Thermal correction to Gibbs Free Energy= 0.082184
Sum of electronic and ZPE= -156.585253
Sum of electronic and thermal Energies= -156.579619
Sum of electronic and thermal Enthalpies= -156.578675
Sum of electronic and thermal Free Energies= -156.613491

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.826 18.122 73.276

C,0,1.0888214669,0.7708160734,-0.3131367589
C,0,2.0749825167,1.4756268125,0.5710812013
C,0,2.212318815,2.8024272046,0.7504229898
C,0,1.4125396447,3.8982383105,0.109591893
H,0,2.7496741388,0.8292545261,1.1244052644
H,0,2.9879556931,3.1312750769,1.4355652716

H,0,0.9164400998,4.5048427181,0.869530819
H,0,2.0635479982,4.565579815,-0.4582410503
H,0,0.6500293853,3.5184733457,-0.5665382567
H,0,0.460327752,0.0985618292,0.2739415084
H,0,0.4369991862,1.4602292682,-0.8447686472
H,0,1.607453774,0.1592569918,-1.0538166209

Transition State
MP2/6-31+G**
-0.1311210389D+01 EUMP2

Zero-point correction= 0.127845 (Hartree/Particle)
Thermal correction to Energy= 0.138482
Thermal correction to Enthalpy= 0.139426
Thermal correction to Gibbs Free Energy= 0.090312
Sum of electronic and ZPE= -1226.757128
Sum of electronic and thermal Energies= -1226.746491
Sum of electronic and thermal Enthalpies= -1226.745547
Sum of electronic and thermal Free Energies= -1226.794661

	E	**CV**	**S**
	KCal/Mol	**Cal/Mol-K**	**Cal/Mol-K**
Total	**86.899**	**36.130**	**103.370**

C,0,-2.4764475718,-0.203927326,1.5116305209
C,0,-1.5475474464,0.6322024601,0.6928273883
C,0,-1.5469489883,0.6300239192,-0.6950339328
C,0,-2.475202851,-0.208603199,-1.5120179231
C,0,-0.148710285,-0.641073443,0.0013872797
C,0,1.0481513826,0.0310373296,0.0008645133
Cl,0,1.2914958052,1.7383151157,-0.0016693061
O,0,-0.5348141111,-1.8033448274,0.0030300217
H,0,-0.9725461314,1.3992860605,1.1960562598
H,0,-0.9715435537,1.3955495857,-1.2001706231
H,0,-2.2211157913,-0.1552111973,-2.5680625812
H,0,-2.4264057144,-1.2500584399,-1.1888833935
H,0,-3.5017975986,0.1413490724,-1.3803400026
H,0,-2.427019552,-1.2464442752,1.1920200649
H,0,-2.2234924365,-0.1469398412,2.5677579178
H,0,-3.5030037482,0.1452766428,1.3776930799
Cl,0,2.4807821338,-0.9273535266,0.002910716

Cis-2-butene Starting Material
#mpwlyp/6-31+G**

```
E(RmPW+HF-LYP) = -157.239293349

Zero-point correction= 0.107835 (Hartree/Particle)
Thermal correction to Energy= 0.113383
Thermal correction to Enthalpy= 0.114327
Thermal correction to Gibbs Free Energy= 0.079917
Sum of electronic and ZPE= -157.131458
Sum of electronic and thermal Energies= -157.125911
Sum of electronic and thermal Enthalpies= -157.124966
Sum of electronic and thermal Free Energies= -157.159376

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.149 18.256 72.422

 C,0,1.089436696,0.7643656844,-0.312900711
 C,0,2.0743446054,1.4782678522,0.5706491349
 C,0,2.2111743206,2.8001768612,0.7493301746
 C,0,1.4144326764,3.9041394907,0.1114983582
 H,0,2.7510437214,0.8282546417,1.1255390622
 H,0,2.989466192,3.1316451088,1.4368854114
 H,0,0.9191949446,4.5177302272,0.8749113423
 H,0,2.068683429,4.5785976116,-0.4556131914
 H,0,0.6446548988,3.53469244,-0.5704409577
 H,0,0.4602843721,0.0844349867,0.2756698774
 H,0,0.4285823449,1.4470305725,-0.8526509948
 H,0,1.6097925521,0.1452465099,-1.0548402201
```

Transition State

```
#mpwlyp/6-31+G**
E(RmPW+HF-LYP) = -1229.00679093

Zero-point correction= 0.124886 (Hartree/Particle)
Thermal correction to Energy= 0.135410
Thermal correction to Enthalpy= 0.136355
Thermal correction to Gibbs Free Energy= 0.088512
Sum of electronic and ZPE= -1228.881905
Sum of electronic and thermal Energies= -1228.871381
Sum of electronic and thermal Enthalpies= -1228.870436
Sum of electronic and thermal Free Energies= -1228.918279

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 84.971 36.531 100.693
```

```
C,0,-2.4642386658,-0.2284077586,1.5716288721
C,0,-1.6062265281,0.6629795695,0.7462127847
C,0,-1.5059744181,0.5703374108,-0.6479124174
C,0,-2.485156373,-0.1960591211,-1.5025223372
C,0,-0.1616547682,-0.6058953531,-0.1693776042
C,0,1.048658403,0.0331565958,-0.0011212201
Cl,0,1.3335104299,1.7539460311,-0.0601301128
O,0,-0.5100367877,-1.7775155583,-0.165655058
H,0,-1.0223652693,1.4306466435,1.2445115238
H,0,-0.9919826934,1.3885926594,-1.1450360937
H,0,-2.0607519738,-0.39235175,-2.4899378699
H,0,-2.7552443926,-1.152689278,-1.0537540088
H,0,-3.3927395408,0.4054039565,-1.6343282211
H,0,-2.2159488874,-1.2771483436,1.3456047553
H,0,-2.32882166,-0.049200264,2.6393094083
H,0,-3.5235959997,-0.093856209,1.3178463714
Cl,0,2.4864026668,-0.9418551204,0.0046612275
```

```
VRI Structure
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.91144852

Zero-point correction= 0.128809 (Hartree/Particle)
Thermal correction to Energy= 0.139440
Thermal correction to Enthalpy= 0.140385
Thermal correction to Gibbs Free Energy= 0.089352
Sum of electronic and ZPE= -1228.782639
Sum of electronic and thermal Energies= -1228.772008
Sum of electronic and thermal Enthalpies= -1228.771064
Sum of electronic and thermal Free Energies= -1228.822096

    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 87.500 35.766 107.407

6 1.495821 1.968062 1.507230
6 1.495821 0.728605 0.687076
6 1.495821 0.728605 -0.687076
6 1.495821 1.968062 -1.507230
6 -0.400428 0.528032 0.000000
6 -0.708653 -0.791996 0.000000
17 0.385391 -2.115450 0.000000
```

8 -0.978501 1.581307 0.000000
1 1.666476 -0.213384 1.187583
1 1.666476 -0.213384 -1.187583
1 1.381976 1.743830 -2.562575
1 0.682482 2.623800 -1.198599
1 2.433385 2.506476 -1.365462
1 0.682482 2.623800 1.198599
1 1.381976 1.743830 2.562575
1 2.433385 2.506476 1.365462
17 -2.370441 -1.222675 0.000000

Rearrangement Transition Structure
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.91188370

Zero-point correction= 0.129296 (Hartree/Particle)
Thermal correction to Energy= 0.139492
Thermal correction to Enthalpy= 0.140436
Thermal correction to Gibbs Free Energy= 0.093179
Sum of electronic and ZPE= -1228.782588
Sum of electronic and thermal Energies= -1228.772392
Sum of electronic and thermal Enthalpies= -1228.771448
Sum of electronic and thermal Free Energies= -1228.818705

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 87.532 35.364 99.461
```

C,0,-2.4510110458,-0.2183519891,1.5236051265
C,0,-1.5185346745,0.5904561429,0.6934656135
C,0,-1.517993897,0.5872171105,-0.6967837836
C,0,-2.4496189849,-0.2257061951,-1.5238334044
C,0,-0.228402671,-0.5664875811,0.0018486346
C,0,0.9907530229,0.0574154575,0.000873033
Cl,0,1.2767431353,1.7502383918,-0.0031893639
O,0,-0.5526843276,-1.7411036679,0.0045748902
H,0,-0.9711475082,1.3828128921,1.1827279819
H,0,-0.970087507,1.3771826217,-1.1893198761
H,0,-2.1559345667,-0.2123745985,-2.5683966213
H,0,-2.462402618,-1.2563062107,-1.1768822267
H,0,-3.4574688861,0.1820478028,-1.4408764508
H,0,-2.4636179065,-1.2506308589,1.1816853218
H,0,-2.1582805048,-0.1999585307,2.5683590773
H,0,-3.4587248672,0.189130799,1.4377402019

Cl,0,2.3922473488,-0.915497476,0.0044018459

Cyclobutanone Product
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.99719575

Zero-point correction= 0.133228 (Hartree/Particle)
Thermal correction to Energy= 0.142798
Thermal correction to Enthalpy= 0.143742
Thermal correction to Gibbs Free Energy= 0.098011
Sum of electronic and ZPE= -1228.863968
Sum of electronic and thermal Energies= -1228.854397
Sum of electronic and thermal Enthalpies= -1228.853453
Sum of electronic and thermal Free Energies= -1228.899185

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	89.607	34.113	96.251

6	-0.986648	1.917236	-0.726862
6	-0.561453	0.488427	-0.979065
1	-0.351552	0.333893	-2.033432
6	-1.488129	-0.595374	-0.345881
6	-0.483423	-0.707117	0.782053
8	-0.525977	-1.030171	1.922800
6	0.593828	-0.011158	-0.071098
17	1.618060	1.158242	0.734716
17	1.574892	-1.245093	-0.892378
6	-2.926818	-0.301691	0.005906
1	-1.421687	-1.507861	-0.940862
1	-3.348105	-1.133835	0.564548
1	-3.018867	0.589390	0.621320
1	-3.523738	-0.161671	-0.892822
1	-1.160298	2.118252	0.328464
1	-0.224523	2.610325	-1.073183
1	-1.907748	2.127391	-1.266501

Starting Material Complex Used for RRKM Calculations
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.92152325

Zero-point correction= 0.127628 (Hartree/Particle)
Thermal correction to Energy= 0.140548
Thermal correction to Enthalpy= 0.141492

Thermal correction to Gibbs Free Energy= 0.079397
Sum of electronic and ZPE= -1228.793896
Sum of electronic and thermal Energies= -1228.780975
Sum of electronic and thermal Enthalpies= -1228.780031
Sum of electronic and thermal Free Energies= -1228.842126

	E	**CV**	**S**
	KCal/Mol	**Cal/Mol-K**	**Cal/Mol-K**
Total	**88.195**	**38.827**	**130.689**

6	**-2.061176**	**1.754334**	**-0.924882**
6	**-2.075067**	**0.280315**	**-1.155289**
6	**-2.689991**	**-0.651480**	**-0.430065**
6	**-3.518573**	**-0.457274**	**0.794994**
6	**0.677639**	**-0.162809**	**1.251337**
6	**1.525954**	**-0.171891**	**0.248048**
17	**1.560046**	**-1.486605**	**-0.846536**
8	**-0.062304**	**-0.141973**	**2.138626**
1	**-1.518697**	**-0.056009**	**-2.022449**
1	**-2.589530**	**-1.678949**	**-0.760700**
1	**-3.099715**	**-1.010756**	**1.635572**
1	**-3.597645**	**0.584359**	**1.091284**
1	**-4.528200**	**-0.838058**	**0.638593**
1	**-2.593294**	**2.046946**	**-0.024580**
1	**-1.037806**	**2.122016**	**-0.844305**
1	**-2.514601**	**2.279016**	**-1.766452**
17	**2.606143**	**1.141902**	**0.037075**

Fixed Distances Between the carbonyl carbon of the ketene and Olefinic Carbons of Cis-2-butene.

M06-2x/6-31+G** energy grid

	2.3	2.2	2.1	2	1.9	1.8	1.7	1.6
2.3	-1228.785657	-1228.78556	-1228.784625	-1228.782924	-1228.780663	-1228.778173	-1228.77551	-1228.853204
2.2	-1228.78556	-1228.785448	-1228.785079	-1228.78412	-1228.782645	-1228.780945	-1228.779272	-1228.858597
2.1	-1228.784625	-1228.785079	-1228.784948	-1228.784542	-1228.7837	-1228.782649	-1228.78181	-1228.85821
2	-1228.782924	-1228.78412	-1228.784542	-1228.784331	-1228.783916	-1228.783328	-1228.782836	-1228.852674
1.9	-1228.780663	-1228.782645	-1228.7837	-1228.783916	-1228.783517	-1228.78301	-1228.782495	-1228.842507
1.8	-1228.778173	-1228.780945	-1228.782649	-1228.783328	-1228.78301	-1228.782145	-1228.781129	-1228.827754
1.7	-1228.77551	-1228.779272	-1228.78181	-1228.782836	-1228.782495	-1228.781129	-1228.779074	-1228.776188
1.6	-1228.853204	-1228.858597	-1228.85821	-1228.852674	-1228.842507	-1228.827754	-1228.776188	-1228.771517

CCSD(T)/6-31+G** energy grid based on M06-2x/6-31+G** optimized geometries.

	2.3	2.2	2.1	2	1.9	1.8	1.7	1.6
2.3	-1227.002920	-1227.002420	-1227.001280	-1226.999852	-1226.998536	-1226.997909	-1226.998898	-1227.075714
2.2	-1227.002420	-1227.001971	-1227.001390	-1227.000610	-1226.999946	-1226.999932	-1227.001626	-1227.080823
2.1	-1227.001280	-1227.001390	-1227.001050	-1227.000723	-1227.000523	-1227.000916	-1227.002904	-1227.079937
2	-1226.999852	-1227.000610	-1227.000723	-1227.000487	-1227.000499	-1227.000987	-1227.002656	-1227.073413
1.9	-1226.998536	-1226.999946	-1227.000523	-1227.000499	-1227.000297	-1227.000532	-1227.001412	-1227.061740
1.8	-1226.997909	-1226.999932	-1227.000916	-1227.000987	-1227.000532	-1227.000051	-1226.999869	-1227.045013
1.7	-1226.998898	-1227.001626	-1227.002904	-1227.002656	-1227.001412	-1226.999869	-1226.998311	-1226.996206
1.6	-1227.075714	-1227.080823	-1227.079937	-1227.073413	-1227.061740	-1227.045013	-1226.996206	-1226.992179

CCSD(T)/6-31+G** PCM(CH2Cl2) energy grid based on M06-2x/6-31+G** optimized geometries.

	2.3	2.2	2.1	2.0	1.9	1.8	1.7	1.6
2.3	-1227.006840	-1227.006760	-1227.006153	-1227.005329	-1227.004529	-1227.003989	-1227.003934	-1227.080738
2.2	-1227.006760	-1227.006769	-1227.006723	-1227.006504	-1227.006332	-1227.006480	-1227.007467	-1227.085774
2.1	-1227.006153	-1227.006723	-1227.006906	-1227.007112	-1227.007413	-1227.008024	-1227.009554	-1227.084807
2.0	-1227.005329	-1227.006504	-1227.007112	-1227.007395	-1227.007868	-1227.008679	-1227.010133	-1227.078323
1.9	-1227.004529	-1227.006332	-1227.007413	-1227.007868	-1227.008146	-1227.008745	-1227.009711	-1227.066832
1.8	-1227.003989	-1227.006480	-1227.008024	-1227.008679	-1227.008745	-1227.008856	-1227.008794	-1227.050471
1.7	-1227.003934	-1227.007467	-1227.009554	-1227.010133	-1227.009711	-1227.008794	-1227.007620	-1227.005555
1.6	-1227.080738	-1227.085774	-1227.084807	-1227.078323	-1227.066832	-1227.050471	-1227.005555	-1227.001633

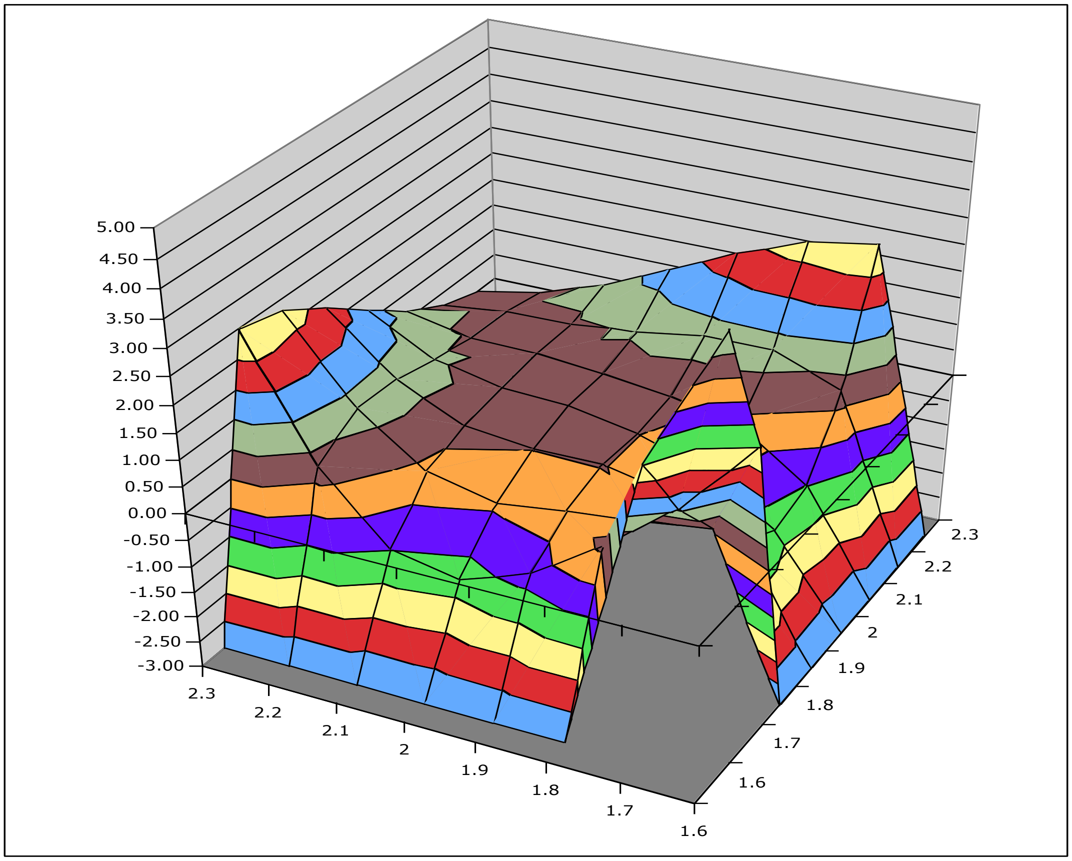
CCSD(T)/6-311+G** PCM(CH2Cl2) energy grid based on M06-2x/6-31+G** optimized geometries.

	2.3	2.2	2.1	2.0	1.9	1.8	1.7	1.6
2.3	-1227.189256	-1227.188867	-1227.188196	-1227.187307	-1227.186382	-1227.185609	-1227.185262	-1227.264464
2.2	-1227.188867	-1227.188622	-1227.188591	-1227.188374	-1227.188070	-1227.188026	-1227.188824	-1227.269317
2.1	-1227.188196	-1227.188591	-1227.188616	-1227.188792	-1227.189034	-1227.189469	-1227.190846	-1227.268318
2.0	-1227.187307	-1227.188374	-1227.188792	-1227.188871	-1227.189236	-1227.189928	-1227.191246	-1227.261752
1.9	-1227.186382	-1227.188070	-1227.189034	-1227.189236	-1227.189225	-1227.189650	-1227.190494	-1227.250039
1.8	-1227.185609	-1227.188026	-1227.189469	-1227.189928	-1227.189650	-1227.189407	-1227.189132	-1227.233294
1.7	-1227.185262	-1227.188824	-1227.190846	-1227.191246	-1227.190494	-1227.189132	-1227.187508	-1227.185256
1.6	-1227.264464	-1227.269317	-1227.268318	-1227.261752	-1227.250039	-1227.233294	-1227.185256	-1227.180864

CCSD(T)/aug-cc-pvdz PCM(CH2Cl2) energy grid based on M06-2x/6-31+G** optimized geometries.

	2.3	2.2	2.1	2.0	1.9	1.8	1.7	1.6
2.3	-1227.144894	-1227.144894	-1227.144527	-1227.143935	-1227.143329	-1227.142934	-1227.142984	-1227.221945
2.2	-1227.144894	-1227.145022	-1227.145169	-1227.145123	-1227.145055	-1227.145305	-1227.146490	-1227.225967
2.1	-1227.144527	-1227.145169	-1227.145389	-1227.145642	-1227.145986	-1227.146618	-1227.148320	-1227.224260
2.0	-1227.143935	-1227.145123	-1227.145642	-1227.145778	-1227.146121	-1227.146857	-1227.148385	-1227.217133

1.9	-1227.143329	-1227.145055	-1227.145986	-1227.146121	-1227.146029	-1227.146334	-1227.147198	-1227.204955
1.8	-1227.142934	-1227.145305	-1227.146618	-1227.146857	-1227.146334	-1227.145911	-1227.145401	-1227.187996
1.7	-1227.142984	-1227.146490	-1227.148320	-1227.148385	-1227.147198	-1227.145401	-1227.143439	-1227.140915
1.6	-1227.221945	-1227.225967	-1227.224260	-1227.217133	-1227.204955	-1227.187996	-1227.140915	-1227.136011



3D representation of the energy surface for CCSD(T)/6-311+G PCM(CH2Cl2) energy grid based on M06-2x/6-31+G** optimized geometries.**

Complete Regression Statistics

Regression Statistics	
Multiple R	0.988304
R Square	0.976745
Adjusted R Square	0.965117
Standard Error	0.000317
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	8.42E-06	8.42E-06	84.00153	0.011696
Residual	2	2.01E-07	1E-07		
Total	3	8.62E-06			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.989563	0.000795	1244.994	6.45E-07	0.986144	0.992983	0.986144	0.992983
X Variable 1	0.001298	0.000142	9.165235	0.011696	0.000689	0.001907	0.000689	0.001907

Cyclohexene Starting Material
B3LYP/6-31G*
E(RB+HF-LYP) = -234.648294956

Zero-point correction= 0.146986 (Hartree/Particle)
Thermal correction to Energy= 0.152475
Thermal correction to Enthalpy= 0.153419
Thermal correction to Gibbs Free Energy= 0.118350
Sum of electronic and ZPE= -234.501309
Sum of electronic and thermal Energies= -234.495820
Sum of electronic and thermal Enthalpies= -234.494875
Sum of electronic and thermal Free Energies= -234.529945

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.680 21.313 73.810

C,0,1.498911,0.048016,0.110756
C,0,0.665935,1.306097,0.057183
C,0,-0.666225,1.305947,-0.057218
C,0,-1.498881,0.047775,-0.110713
C,0,-0.698154,-1.192295,0.318734
C,0,0.69841,-1.192173,-0.318772
H,0,1.244917,-2.105862,-0.054456
H,0,0.593138,-1.192261,-1.412754
H,0,1.889178,-0.08997,1.13207
H,0,2.386547,0.164055,-0.526767
H,0,1.19924,2.254758,0.112664

H,0,-1.199604,2.254573,-0.11272
H,0,-1.889496,-0.090467,-1.131886
H,0,-2.386489,0.163576,0.526939
H,0,-1.244519,-2.10607,0.054373
H,0,-0.592894,-1.192542,1.412727

TS for cyclohexene and dichloroketene
B3LYP/6-31G*
E(RB+HF-LYP) = -1306.39270193

Zero-point correction= 0.163919 (Hartree/Particle)
Thermal correction to Energy= 0.174600
Thermal correction to Enthalpy= 0.175544
Thermal correction to Gibbs Free Energy= 0.127053
Sum of electronic and ZPE= -1306.228783
Sum of electronic and thermal Energies= -1306.218102
Sum of electronic and thermal Enthalpies= -1306.217158
Sum of electronic and thermal Free Energies= -1306.265649

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	109.563	39.780	102.058

C,0,0.1375821407,-1.127191428,1.242750595
C,0,0.4496848634,0.6498190911,1.1677579531
C,0,0.2197570023,0.4557320624,-0.2022912423
H,0,1.0525328957,0.2071497252,-0.8523101533
H,0,1.4851180173,0.7629094095,1.4803929672
C,0,-1.1509238687,0.5836220795,-0.7785637356
C,0,-1.9613450501,1.6898594551,-0.0725018249
C,0,-1.983284908,1.4532238655,1.4426666626
C,0,-0.5657322165,1.378052331,2.0380964848
H,0,-0.5942751014,0.9163408576,3.0304287172
H,0,-0.1624549593,2.3917844246,2.1770513744
H,0,-2.540791023,2.2537647568,1.9436181822
H,0,-2.5029421931,0.5140232244,1.6502896187
H,0,-2.9822795618,1.7041050025,-0.4706103661
H,0,-1.6671825457,-0.3789432363,-0.6240549608
H,0,-1.0882109854,0.7422169831,-1.8606208921
H,0,-1.5172813535,2.6683803863,-0.3016271304
O,0,-0.9981600081,-1.4402994644,1.5662763173
C,0,1.2759223523,-1.867808596,0.9733200654
Cl,0,1.2579150391,-3.5547913545,1.3983940948
Cl,0,2.8567474638,-1.2379205756,0.5761712726

Starting Material for cyclohexene
mpwpw91/6-31+G**
E(RmPW+HF-PW91) = -234.616113044

Zero-point correction= 0.150500 (Hartree/Particle)
Thermal correction to Energy= 0.155892
Thermal correction to Enthalpy= 0.156836
Thermal correction to Gibbs Free Energy= 0.121945
Sum of electronic and ZPE= -234.465613
Sum of electronic and thermal Energies= -234.460221
Sum of electronic and thermal Enthalpies= -234.459277
Sum of electronic and thermal Free Energies= -234.494168

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 97.824 20.768 73.435
```

```
C,0,1.4860614471,0.042281338,0.1122978203
C,0,0.6620057603,1.2915620253,0.0591952891
C,0,-0.6622808857,1.2914297282,-0.059172302
C,0,-1.4860855254,0.0419959851,-0.1122521852
C,0,-0.6893892375,-1.1804787642,0.3205114067
C,0,0.6896115421,-1.1803337842,-0.320515673
H,0,1.2320639965,-2.0914462919,-0.0692049235
H,0,0.5773713794,-1.1690011457,-1.406669647
H,0,1.8665685931,-0.0969545293,1.1284932245
H,0,2.368668576,0.1603769166,-0.5183506066
H,0,1.1880993567,2.2361059869,0.1171533972
H,0,-1.1885452436,2.2358765075,-0.1171728676
H,0,-1.8666295452,-0.0973046148,-1.1284261403
H,0,-2.368691116,0.1599045688,0.5184381953
H,0,-1.2316704325,-2.0916848851,0.0691696153
H,0,-0.5771446651,-1.1691720412,1.4066653968
```

Ts for cycloaddition of cyclohexene and dichloroketene
mpwpw91/6-31+G**
E(RmPW+HF-PW91) = -1306.32660791

Zero-point correction= 0.168498 (Hartree/Particle)
Thermal correction to Energy= 0.179061
Thermal correction to Enthalpy= 0.180005
Thermal correction to Gibbs Free Energy= 0.131574
Sum of electronic and ZPE= -1306.158109

```
Sum of electronic and thermal Energies= -1306.147547
Sum of electronic and thermal Enthalpies= -1306.146603
Sum of electronic and thermal Free Energies= -1306.195034

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.362 38.976 101.931

 C,0,0.0901560123,-1.2420248364,1.1153226419
 C,0,0.4620744602,0.7741916611,1.1236185754
 C,0,0.1944218322,0.4220521191,-0.1696684906
 H,0,1.0106859337,0.1289553476,-0.8135648662
 H,0,1.4891212589,0.7932086609,1.4588886039
 C,0,-1.1643283012,0.5881181184,-0.7603513198
 C,0,-1.9479100642,1.6874159349,-0.0542576465
 C,0,-1.9651196581,1.4487535648,1.4459533987
 C,0,-0.5548803815,1.3969585606,2.0246094908
 H,0,-0.5503224339,0.8830227039,2.9854168967
 H,0,-0.1861265635,2.4070437729,2.2255103245
 H,0,-2.5301882994,2.231807052,1.9495733228
 H,0,-2.4672651846,0.5062310038,1.6496315052
 H,0,-2.9647592816,1.7201186542,-0.4419010719
 H,0,-1.6997517228,-0.3602111397,-0.6665393141
 H,0,-1.0630892294,0.7899259724,-1.8255578862
 H,0,-1.4939272881,2.6556477105,-0.2765142288
 O,0,-1.0461718944,-1.4713378517,1.4091462473
 C,0,1.2858956696,-1.8688487585,1.0491714784
 Cl,0,1.3329957439,-3.5098388834,1.5592510438
 Cl,0,2.7888853921,-1.2171603674,0.5368952946
```

Cis-2-undecene Starting Material

mpwpw91/6-31G*

```
E(RmPW+HF-PW91) = -432.328512762

Zero-point correction= 0.318113 (Hartree/Particle)
Thermal correction to Energy= 0.332639
Thermal correction to Enthalpy= 0.333583
Thermal correction to Gibbs Free Energy= 0.274591
Sum of electronic and ZPE= -432.010400
Sum of electronic and thermal Energies= -431.995874
Sum of electronic and thermal Enthalpies= -431.994930
Sum of electronic and thermal Free Energies= -432.053922

      E      CV       S
```

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 208.734 50.537 124.160

C,0,1.4930766468,0.8918210919,-1.1276593251
C,0,1.9625860949,1.4647287263,0.197440346
C,0,1.7587696656,2.9673015665,0.3008534597
C,0,2.2251284639,3.5501145005,1.6243835673
C,0,2.0208530291,5.052506213,1.7279177523
C,0,2.483868981,5.6332682534,3.0536492667
C,0,2.2819120031,7.135711856,3.1560042088
C,0,2.7420812625,7.7105814867,4.4920420879
C,0,2.4802774238,9.1771170872,4.6024590281
C,0,3.3600075641,10.1558703451,4.7852762961
C,0,4.8391963558,10.0406191399,4.9421655426
H,0,5.3547857384,10.6244078245,4.1780435161
H,0,2.0301947571,1.342108447,-1.9626708181
H,0,0.4303534643,1.0792980393,-1.2822755927
H,0,1.6495149884,-0.1849552198,-1.1758838042
H,0,1.4331026224,0.9727709325,1.0166011157
H,0,3.0208052737,1.2344993905,0.3408390471
H,0,2.2885474689,3.460252631,-0.5190038271
H,0,0.6997181711,3.1982276503,0.1564716179
H,0,1.6951364382,3.0561702918,2.4434143066
H,0,3.2840587774,3.3185854631,1.7681151699
H,0,2.5529917766,5.5470116424,0.9108059831
H,0,0.9623819084,5.2843922374,1.5818980935
H,0,3.541776476,5.3992421813,3.2009119007
H,0,1.9498346092,5.1403527938,3.8707553537
H,0,2.8199067781,7.6359896289,2.3479139213
H,0,1.2248341475,7.3708453771,3.0067236261
H,0,2.2097702922,7.1929734662,5.2959378539
H,0,3.7989623268,7.4886632165,4.6365852315
H,0,1.4368118449,9.4585749584,4.5072132587
H,0,2.9742522069,11.1679033375,4.8315464882
H,0,5.1934630964,9.0157648318,4.8730631359
H,0,5.1577663465,10.4387296119,5.9069821919

TS for dichloroketene and cis-2-undecene
mpwpw91/6-31G*
E(RmPW+HF-PW91) = -1504.03819966

Zero-point correction= 0.336047 (Hartree/Particle)
Thermal correction to Energy= 0.355785
Thermal correction to Enthalpy= 0.356729

```
Thermal correction to Gibbs Free Energy= 0.284639
Sum of electronic and ZPE= -1503.702153
Sum of electronic and thermal Energies= -1503.682415
Sum of electronic and thermal Enthalpies= -1503.681470
Sum of electronic and thermal Free Energies= -1503.753560

      E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 223.259 68.704 151.726

 C,0,1.1833088205,0.4404957415,-0.3362689105
 Cl,0,2.0643246442,1.3199100038,0.8543830318
 C,0,0.1287283077,1.069200007,-0.8878598666
 O,0,-0.4751485634,2.0941465119,-0.8759660424
 Cl,0,1.7650818973,-1.1411435648,-0.6582755302
 C,0,-0.3209948779,0.0264034673,-2.7383797577
 C,0,-1.1136913242,-0.4385329573,-1.7314264119
 C,0,-2.4889220767,0.0501632323,-1.4346598756
 C,0,-2.9038189463,-0.1427389429,0.0155748046
 C,0,-4.3394532682,0.2822391375,0.2719331509
 C,0,-4.7644146489,0.1070695839,1.7203075343
 C,0,-6.1999888578,0.5331636361,1.9791725029
 C,0,-6.6277137593,0.360810949,3.4270748777
 C,0,-8.0634018197,0.7869782199,3.686367252
 C,0,-8.4817175438,0.6109925057,5.1350368492
 C,0,-0.7055008782,1.1206973013,-3.6692833703
 H,0,0.1058016719,1.3644021735,-4.3484188765
 H,0,0.6044438253,-0.4973261353,-2.9293401502
 H,0,-0.7821339099,-1.3167009596,-1.1934268646
 H,0,-2.5731681331,1.1009716789,-1.7093479972
 H,0,-3.174897372,-0.4974649802,-2.0901531871
 H,0,-0.9685583535,2.0174689854,-3.1063828004
 H,0,-1.5762966576,0.8348868379,-4.2600403378
 H,0,-2.7775245067,-1.1915998036,0.2958445826
 H,0,-2.2332971014,0.4340769706,0.6541276704
 H,0,-4.4611379555,1.3295152413,-0.0158613018
 H,0,-5.0101558497,-0.2909973878,-0.3743098121
 H,0,-4.6396482517,-0.9396113091,2.0105716068
 H,0,-4.0941505865,0.6815721292,2.3645592045
 H,0,-6.323941611,1.5796753286,1.6880733917
 H,0,-6.8700620521,-0.0411247882,1.3335164497
 H,0,-6.5037571905,-0.6855032065,3.7196089335
 H,0,-5.9586510885,0.9354251528,4.0732565927
 H,0,-8.1864301364,1.8325493862,3.3948949205
```

```
 H,0,-8.7314961912,0.2127419245,3.0403890592
 H,0,-9.5123327474,0.9249182548,5.2945615512
 H,0,-8.4017027158,-0.4315823164,5.4432810913
 H,0,-7.8496111918,1.1990699908,5.8005590352
```

Theoretical Structures for the cycloaddition of 2,3-dihydro-5-methylfuran and dimethylketene.

Starting Material for dimethylketene
mpwpw91/6-31+G**
E(RmPW+HF-PW91) = -231.168014719

```
Zero-point correction= 0.092081 (Hartree/Particle)
Thermal correction to Energy= 0.098113
Thermal correction to Enthalpy= 0.099057
Thermal correction to Gibbs Free Energy= 0.063049
Sum of electronic and ZPE= -231.075934
Sum of electronic and thermal Energies= -231.069902
Sum of electronic and thermal Enthalpies= -231.068958
Sum of electronic and thermal Free Energies= -231.104966

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 61.567 19.599 75.786
```

```
 O,0,1.3911250455,1.9571650453,-0.4436955835
 C,0,1.4327665436,1.6905590681,0.6891072696
 H,0,3.1536145263,1.0885357064,3.2650612027
 H,0,3.2944957883,2.5274831064,2.2623475261
 H,0,2.1962209945,2.5191650289,3.6369668196
 C,0,2.5943939377,1.9133843764,2.8223764398
 C,0,1.4795665174,1.3909949249,1.9619795489
 C,0,0.4189693825,0.521867272,2.5749536776
 H,0,-0.0944518651,1.0539060624,3.3764535592
 H,0,-0.3284161029,0.2101123454,1.850304916
 H,0,0.8629312323,-0.3767179361,3.0045056239
```

Starting Material 2,3-dihydro-5-methylfuran
mpwpw91/6-31G*
E(RmPW+HF-PW91) = -270.475457295

```
Zero-point correction= 0.125089 (Hartree/Particle)
Thermal correction to Energy= 0.130968
Thermal correction to Enthalpy= 0.131912
```

Thermal correction to Gibbs Free Energy= 0.095711
Sum of electronic and ZPE= -270.350368
Sum of electronic and thermal Energies= -270.344490
Sum of electronic and thermal Enthalpies= -270.343545
Sum of electronic and thermal Free Energies= -270.379746

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 82.183 20.641 76.191

6 0.101462 1.164368 0.044207
6 1.525099 0.705161 -0.065763
6 1.348432 -0.809567 0.087273
8 -0.044169 -1.081594 -0.087339
6 -0.701172 0.108057 -0.000584
6 -2.177272 0.001803 0.010223
1 -2.513750 -0.589270 0.861550
1 -2.633249 0.985845 0.063411
1 -2.529113 -0.499154 -0.891379
1 -0.220945 2.190050 0.090845
1 1.966490 0.975536 -1.027890
1 2.176263 1.109321 0.708412
1 1.629962 -1.144012 1.085395
1 1.898404 -1.394498 -0.643769

Transition State of dimethylketene and 2,3-dihydro-5-methylfuran
mpwpw91/6-31+G**
E(RmPW+HF-PW91) = -501.636535919

Zero-point correction= 0.218485 (Hartree/Particle)
Thermal correction to Energy= 0.230456
Thermal correction to Enthalpy= 0.231400
Thermal correction to Gibbs Free Energy= 0.180736
Sum of electronic and ZPE= -501.418051
Sum of electronic and thermal Energies= -501.406080
Sum of electronic and thermal Enthalpies= -501.405136
Sum of electronic and thermal Free Energies= -501.455800

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 144.613 43.073 106.632

C,0,2.320945296,2.9207079007,2.5315822553
C,0,1.8414526114,3.8582534334,1.4248392321

```
O,0,1.5677916814,3.009218923,0.2854445215
C,0,1.8628954928,1.7635267694,0.5715910853
C,0,2.4760914499,1.6141504163,1.7952946473
C,0,1.5278545406,0.7852182383,-0.4823309149
C,0,4.2624041174,1.7508629219,0.9775037256
C,0,4.8020610379,0.540054461,0.7493524443
C,0,6.2407099065,0.5553154595,0.3066573648
C,0,4.2223127626,-0.8209896096,0.9384134078
O,0,4.525813866,2.9275523459,0.9025743864
H,0,4.8610635096,-1.4176206974,1.5944582891
H,0,3.2271217029,-0.8343682277,1.3702705904
H,0,4.1693819316,-1.3631631041,-0.0101191577
H,0,6.8877282035,0.072316408,1.0434030994
H,0,6.3624258471,0.007493032,-0.6312356696
H,0,6.5992857333,1.5686921061,0.1546532832
H,0,2.0660619856,1.0329721334,-1.3945530472
H,0,1.7780538531,-0.2242682521,-0.1838558121
H,0,0.4627128422,0.849856738,-0.69773545
H,0,2.5007239893,0.673284421,2.3144381211
H,0,1.5891034806,2.826940716,3.3324338003
H,0,3.2628990703,3.2640738188,2.9489245403
H,0,2.603678938,4.5610487452,1.1151262948
H,0,0.9151741503,4.3786469033,1.6513149629
```

Starting Material Dimethylketene
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -231.156611964

Zero-point correction= 0.092574 (Hartree/Particle)
Thermal correction to Energy= 0.098575
Thermal correction to Enthalpy= 0.099519
Thermal correction to Gibbs Free Energy= 0.063583
Sum of electronic and ZPE= -231.064038
Sum of electronic and thermal Energies= -231.058037
Sum of electronic and thermal Enthalpies= -231.057093
Sum of electronic and thermal Free Energies= -231.093029

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 61.857 19.500 75.634
```

```
O,0,1.391122328,1.9575973564,-0.4450987674
C,0,1.4327467757,1.6902500237,0.6901718003
H,0,3.1516309543,1.0874211733,3.2654943846
```

```
H,0,3.2960974096,2.5284059031,2.2628885964
H,0,2.1944829697,2.5176383194,3.6372457559
C,0,2.5947014594,1.9137712785,2.8216514371
C,0,1.4795570036,1.3912240242,1.9607790381
C,0,0.4186089269,0.5218204111,2.5741684958
H,0,-0.0924091963,1.0547855594,3.3771821615
H,0,-0.3299958266,0.2090013404,1.8505098414
H,0,0.8646731958,-0.3754603896,3.0053682563
```

Starting Material 2,3-dihydro-5-methylfuran
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -270.475457295

```
Zero-point correction= 0.125089 (Hartree/Particle)
Thermal correction to Energy= 0.130968
Thermal correction to Enthalpy= 0.131912
Thermal correction to Gibbs Free Energy= 0.095711
Sum of electronic and ZPE= -270.350368
Sum of electronic and thermal Energies= -270.344490
Sum of electronic and thermal Enthalpies= -270.343545
Sum of electronic and thermal Free Energies= -270.379746
```

```
    E      CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 82.183 20.641 76.191
```

```
6 0.101462 1.164368 0.044207
6 1.525099 0.705161 -0.065763
6 1.348432 -0.809567 0.087273
8 -0.044169 -1.081594 -0.087339
6 -0.701172 0.108057 -0.000584
6 -2.177272 0.001803 0.010223
1 -2.513750 -0.589270 0.861550
1 -2.633249 0.985845 0.063411
1 -2.529113 -0.499154 -0.891379
1 -0.220945 2.190050 0.090845
1 1.966490 0.975536 -1.027890
1 2.176263 1.109321 0.708412
1 1.629962 -1.144012 1.085395
1 1.898404 -1.394498 -0.643769
```

Transition State 1 dimethylketene and 2,3-dihydro-5-methylfuran
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.613397279

Zero-point correction= 0.219523 (Hartree/Particle)
Thermal correction to Energy= 0.231595
Thermal correction to Enthalpy= 0.232539
Thermal correction to Gibbs Free Energy= 0.181457
Sum of electronic and ZPE= -501.393874
Sum of electronic and thermal Energies= -501.381803
Sum of electronic and thermal Enthalpies= -501.380858
Sum of electronic and thermal Free Energies= -501.431941

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 145.328 43.091 107.511
```

```
 C,0,2.3119828737,2.9239988178,2.536672496
 C,0,1.8131957333,3.8605610465,1.4354941562
 O,0,1.5973141284,3.029532443,0.2742727345
 C,0,1.8559745916,1.7715020008,0.5739448536
 C,0,2.4214606751,1.6121695793,1.8082665346
 C,0,1.5181072601,0.7967065599,-0.483845791
 C,0,4.3072170654,1.7522083766,0.9374547861
 C,0,4.8302568446,0.5353169171,0.7478197838
 C,0,6.2701221769,0.5317927484,0.2984772422
 C,0,4.2382986639,-0.8187965747,0.9469490218
 O,0,4.5339913321,2.9310611905,0.8597435214
 H,0,4.8554465573,-1.4063310544,1.6319157127
 H,0,3.2313700659,-0.8162932928,1.3485662152
 H,0,4.2100248128,-1.3758643435,0.0063677704
 H,0,6.9100517988,0.0276481406,1.0277361275
 H,0,6.3807945416,-0.0084254961,-0.645664105
 H,0,6.6525781538,1.5388068446,0.1550595055
 H,0,2.0664741416,1.0298407155,-1.3944358104
 H,0,1.7431703298,-0.2179435854,-0.180546347
 H,0,0.4558652037,0.8757441308,-0.7105065202
 H,0,2.4602113486,0.6706304123,2.3241061203
 H,0,1.6025884024,2.8523050151,3.3593008217
 H,0,3.2674164527,3.2565870751,2.9328540852
 H,0,2.5393423097,4.61263279,1.156392374
 H,0,0.862492536,4.3343855431,1.6620507114
```

Intermediate for dimethylketene and 2,3-dihydro-5-methylfuran
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.620704172

Zero-point correction= 0.221135 (Hartree/Particle)
Thermal correction to Energy= 0.232952
Thermal correction to Enthalpy= 0.233896
Thermal correction to Gibbs Free Energy= 0.183806
Sum of electronic and ZPE= -501.399569
Sum of electronic and thermal Energies= -501.387752
Sum of electronic and thermal Enthalpies= -501.386808
Sum of electronic and thermal Free Energies= -501.436898

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	146.180	43.243	105.423

O,0,0.8774816782,0.5507617014,-0.1580535272
C,0,0.7795777231,-0.182571725,0.8893040199
C,0,1.9353138739,-1.0143049738,1.0951739826
C,0,3.0229721563,-0.3327770508,0.2817495429
C,0,2.2291734618,0.5038855017,-0.7082386538
C,0,-0.4696992194,-0.0719808337,1.6585618016
C,0,1.3637357832,-2.2979159666,0.3018356377
O,0,1.6029086744,-2.272310416,-0.9293835172
C,0,0.6670270135,-3.2243842447,1.0305947726
C,0,0.4671765353,-3.2588244622,2.510915204
C,0,0.165877037,-4.4349364462,0.3067361506
H,0,0.8162617176,-4.2112639555,2.9225793227
H,0,0.9850618101,-2.475047741,3.0589495933
H,0,-0.5923598054,-3.1919242537,2.783084972
H,0,0.7159464094,-5.3406042813,0.5850726777
H,0,-0.8840401057,-4.6316392788,0.5445312844
H,0,0.2583320242,-4.3024078169,-0.7678045163
H,0,-1.3250977049,-0.0274172316,0.9895697843
H,0,-0.5821525981,-0.8876043833,2.3596435017
H,0,-0.4352423566,0.8691542322,2.2110842041
H,0,2.170871626,-1.2355818151,2.1265632438
H,0,3.6450994333,0.2906794541,0.9194247741
H,0,3.6385627267,-1.0603674886,-0.2344389639
H,0,2.1422559277,0.0444149052,-1.6811893815
H,0,2.5464471785,1.5374945702,-0.7921109102

Transition State 2 Cyclobutanone Product 28
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.619103462

Zero-point correction= 0.221865 (Hartree/Particle)

Thermal correction to Energy= 0.232395
Thermal correction to Enthalpy= 0.233339
Thermal correction to Gibbs Free Energy= 0.186763
Sum of electronic and ZPE= -501.397238
Sum of electronic and thermal Energies= -501.386709
Sum of electronic and thermal Enthalpies= -501.385764
Sum of electronic and thermal Free Energies= -501.432340

	E	**CV**	**S**
	KCal/Mol	**Cal/Mol-K**	**Cal/Mol-K**
Total	**145.830**	**40.680**	**98.027**

```
C,0,0.4696039676,0.2696104544,0.8461235476
C,0,1.5343332561,-0.6901574482,1.3390729744
C,0,2.2510958947,-1.0820562519,0.0542280388
O,0,1.8769882971,-0.0706707706,-0.9173886267
C,0,0.9977385655,0.758328286,-0.4268885938
C,0,0.9591107689,2.0781751137,-1.0870997664
C,0,-0.6558214857,-0.502962187,0.078074349
O,0,-0.5054736155,-1.7306185246,-0.0712358496
C,0,-1.5691074519,0.3025411467,-0.5991302492
C,0,-2.0213743661,1.6578474977,-0.1608971868
C,0,-2.4785112831,-0.3712381576,-1.5734013739
H,0,-3.0536498094,1.5991599692,0.1993442406
H,0,-1.4338164135,2.0902983996,0.6446184739
H,0,-2.0369971888,2.3724792633,-0.9882318276
H,0,-3.437096382,-0.6416719199,-1.1175015072
H,0,-2.7094027605,0.2895601192,-2.411397876
H,0,-2.0268610754,-1.2855048603,-1.9492741481
H,0,0.9809521945,1.9652728906,-2.1676860488
H,0,0.1068972808,2.6723362617,-0.7930750752
H,0,1.8682174043,2.6094284469,-0.7927994148
H,0,0.1326694457,1.0198405947,1.54942228
H,0,2.2069371775,-0.1968160121,2.0366933906
H,0,1.0865751211,-1.5573552996,1.8126662057
H,0,1.9267960011,-2.0352438385,-0.3366058005
H,0,3.334115457,-1.0447401734,0.119190844
```

Transition State 2 Oxetane Product 29
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.617813557

Zero-point correction= 0.220633 (Hartree/Particle)
Thermal correction to Energy= 0.231950

Thermal correction to Enthalpy= 0.232894
Thermal correction to Gibbs Free Energy= 0.183867
Sum of electronic and ZPE= -501.397180
Sum of electronic and thermal Energies= -501.385864
Sum of electronic and thermal Enthalpies= -501.384920
Sum of electronic and thermal Free Energies= -501.433947

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 145.551 41.455 103.186

C,0,0.6027350255,-0.0461580161,0.8637844978
C,0,1.7921971103,-0.9920536425,1.0531314194
C,0,2.5754557005,-0.8354754069,-0.2354990004
O,0,2.1199291617,0.4460628199,-0.782775543
C,0,1.0806602711,0.8452674441,-0.1918847225
C,0,0.454976586,2.1002670921,-0.6144394846
C,0,-0.6031474995,-0.7358307456,0.1493407903
O,0,-0.2387313289,-1.2315436893,-0.9681171983
C,0,-1.8390579767,-0.6981056763,0.7162244589
C,0,-2.2075892537,-0.1451353555,2.0569238526
C,0,-2.9743134063,-1.3307269168,-0.0301442962
H,0,-2.6302053774,-0.9216396184,2.704804781
H,0,-1.3792310335,0.2968533881,2.6069094506
H,0,-2.982462386,0.6255517573,1.9771087478
H,0,-3.3989534513,-2.1851751847,0.5092925181
H,0,-3.8015114328,-0.6288760958,-0.1831438964
H,0,-2.6399444398,-1.6803257599,-1.0035130911
H,0,0.7850539507,2.4007836037,-1.6021339155
H,0,-0.6252212059,1.9848462705,-0.5731615354
H,0,0.7292157701,2.8704275689,0.1084516941
H,0,0.3197191222,0.5079429146,1.7513926266
H,0,2.3913756841,-0.6912767271,1.9092013429
H,0,1.4690314395,-2.0178760268,1.1932282733
H,0,2.3180406095,-1.5675903991,-0.9872455643
H,0,3.6487383605,-0.7399685982,-0.1267672058

Cyclobutanone product 28
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.686153289

Zero-point correction= 0.223497 (Hartree/Particle)
Thermal correction to Energy= 0.234310
Thermal correction to Enthalpy= 0.235254

Thermal correction to Gibbs Free Energy= 0.188015
Sum of electronic and ZPE= -501.462656
Sum of electronic and thermal Energies= -501.451844
Sum of electronic and thermal Enthalpies= -501.450899
Sum of electronic and thermal Free Energies= -501.498138

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 147.032 41.470 99.422

C,0,0.8564867086,0.8103684882,-0.6608210381
C,0,0.4891317619,0.4029519317,0.7891306479
C,0,1.5455497042,-0.6007736988,1.2063889142
C,0,1.9523278616,-1.1780038872,-0.1400340214
O,0,1.8461086051,-0.1168939448,-1.0666610529
C,0,-0.7855186665,-0.205722318,0.2227559473
C,0,-0.5807307133,0.413575861,-1.1514740893
C,0,-0.6787461147,-0.5113674668,-2.3449935892
C,0,1.3738166272,2.1918357518,-0.9565744719
O,0,-1.6059784258,-0.9526227743,0.675331258
C,0,-1.5246994244,1.6025629654,-1.3044469383
H,0,-1.6905816488,-0.9041986549,-2.4323882359
H,0,-0.4456430151,0.0296779271,-3.2614910478
H,0,0.0098841983,-1.348310296,-2.2668874869
H,0,1.5515193002,2.3101000017,-2.0246303587
H,0,0.6769621539,2.9624255024,-0.6382226836
H,0,2.3182784962,2.3456599336,-0.4380852051
H,0,0.318506353,1.2088594832,1.4996051086
H,0,2.3808619523,-0.0888985486,1.6805805091
H,0,1.1671819318,-1.3565124966,1.8905666357
H,0,1.2878144009,-2.0003441999,-0.4219868734
H,0,2.9744574363,-1.5458974064,-0.1698358638
H,0,-1.2483543988,2.1952803336,-2.1753951284
H,0,-2.5435849963,1.2449121486,-1.4434571033
H,0,-1.5196270875,2.2573393639,-0.4341028326

Oxetane product 29
mpwpw91/6-31G* pcm(dichloromethane)
E(RmPW+HF-PW91) = -501.678179772

Zero-point correction= 0.223711 (Hartree/Particle)
Thermal correction to Energy= 0.234638
Thermal correction to Enthalpy= 0.235582
Thermal correction to Gibbs Free Energy= 0.187585

Sum of electronic and ZPE= -501.454468
Sum of electronic and thermal Energies= -501.443542
Sum of electronic and thermal Enthalpies= -501.442598
Sum of electronic and thermal Free Energies= -501.490595

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 147.238 41.187 101.020
```

```
 C,0,0.8399162746,0.6456842626,-0.5571257437
 C,0,0.5745844507,0.3853958901,0.9397209781
 C,0,1.7338710041,-0.509735011,1.3535374995
 C,0,2.2023993083,-1.0683274656,0.0175371892
 O,0,1.9945995551,-0.0148540195,-0.9110049437
 C,0,-0.6520834165,-0.3091885659,0.4294512563
 O,0,-0.3450492947,-0.1130648076,-0.9022878835
 C,0,0.8114204012,2.0140267756,-1.1598298576
 C,0,-1.7215318384,-0.9106786739,0.9272400911
 H,0,0.8512438701,1.9381728446,-2.2445572151
 H,0,-0.1023204726,2.5300883316,-0.8785403934
 H,0,1.6674869319,2.5903287376,-0.8179414396
 H,0,0.4178004587,1.2457592389,1.5830225637
 H,0,2.5182513457,0.0941852111,1.8067940862
 H,0,1.4487428493,-1.2890782164,2.0552315345
 H,0,1.6159759325,-1.9399482942,-0.2751951922
 H,0,3.2555550905,-1.3291984183,-0.0097653659
 C,0,-2.7789589234,-1.4866627884,0.0410277872
 C,0,-1.9117034619,-1.032563293,2.40533187
 H,0,-1.0985434378,-0.572514918,2.9633899869
 H,0,-2.8438014385,-0.5581497383,2.7195684548
 H,0,-1.9754771272,-2.0797007154,2.7089464849
 H,0,-3.7516175755,-1.0366389545,0.2505184167
 H,0,-2.5518140457,-1.3290362295,-1.0102382447
 H,0,-2.8873274406,-2.5603831825,0.2077920803
```

Starting Material Dimethylketene
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -231.132807796

Zero-point correction= 0.090179 (Hartree/Particle)
Thermal correction to Energy= 0.096268
Thermal correction to Enthalpy= 0.097212
Thermal correction to Gibbs Free Energy= 0.061103
Sum of electronic and ZPE= -231.042629

```
Sum of electronic and thermal Energies= -231.036540
Sum of electronic and thermal Enthalpies= -231.035596
Sum of electronic and thermal Free Energies= -231.071705

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 60.409 19.910 75.997

 O,0,1.3904710959,1.9623872012,-0.4648893378
 C,0,1.4322865661,1.6930289661,0.6780957741
 H,0,3.1504439649,1.0791802888,3.2692327441
 H,0,3.3051785323,2.5332524588,2.2678481836
 H,0,2.1874649074,2.5178801256,3.6431711511
 C,0,2.5993606305,1.9156807232,2.8262465775
 C,0,1.4793954445,1.3924333808,1.9551368038
 C,0,0.4142416458,0.5179512564,2.5777762487
 H,0,-0.0907329268,1.0605996585,3.384125936
 H,0,-0.3388682734,0.202332233,1.8534895899
 H,0,0.8719744128,-0.3782712926,3.0101273293
```

Starting Material 2,3-dihydro-5-methylfuran

```
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -270.438872855

Zero-point correction= 0.121821 (Hartree/Particle)
Thermal correction to Energy= 0.127716
Thermal correction to Enthalpy= 0.128660
Thermal correction to Gibbs Free Energy= 0.092613
Sum of electronic and ZPE= -270.317052
Sum of electronic and thermal Energies= -270.311157
Sum of electronic and thermal Enthalpies= -270.310213
Sum of electronic and thermal Free Energies= -270.346260

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 80.143 21.248 75.867

 C,0,0.1064094411,1.1712679446,0.0667581595
 C,0,1.5367495121,0.7051345775,-0.0858330111
 C,0,1.3588207806,-0.8121246592,0.0984285081
 O,0,-0.0393902869,-1.083810668,-0.1375010445
 C,0,-0.7056640375,0.1130238874,-0.0041024132
 C,0,-2.1894564168,-0.0014296815,0.0071301035
 H,0,-2.5177292432,-0.6293578832,0.8407422118
```

H,0,-2.6463860518,0.984640061,0.1011957124
H,0,-2.538597893,-0.4679868564,-0.9192510142
H,0,-0.2188995927,2.1996993971,0.1436764623
H,0,1.9376230256,0.9583302268,-1.0753872795
H,0,2.2181898104,1.1188857296,0.6620106222
H,0,1.5829927815,-1.1116093461,1.1285695075
H,0,1.9417811706,-1.4226127297,-0.5918445247

Starting Material Trimethylammmonium
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -174.840243649

Zero-point correction= 0.137111 (Hartree/Particle)
Thermal correction to Energy= 0.142692
Thermal correction to Enthalpy= 0.143636
Thermal correction to Gibbs Free Energy= 0.109452
Sum of electronic and ZPE= -174.703133
Sum of electronic and thermal Energies= -174.697552
Sum of electronic and thermal Enthalpies= -174.696607
Sum of electronic and thermal Free Energies= -174.730792

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 89.541 19.210 71.947

N,0,0.0084712266,-0.0304970962,0.0273403563
C,0,-0.0091314757,0.003590098,1.5209335531
C,0,1.4050230622,0.0235603884,-0.5026481275
C,0,-0.7275886772,-1.2189920619,-0.5000112603
H,0,-0.4796618535,0.8055761016,-0.3067526635
H,0,-1.0443165154,0.0046811752,1.8581352796
H,0,0.5087471982,-0.8832521457,1.8862947961
H,0,0.5014158327,0.9052694408,1.8545922002
H,0,1.365278355,0.0347729903,-1.5908241376
H,0,1.8855583172,0.9269554054,-0.1302645464
H,0,1.9339058645,-0.8622751141,-0.1514636713
H,0,-0.7262626047,-1.1768537818,-1.5880101469
H,0,-0.2133568479,-2.1154502963,-0.1543281664
H,0,-1.7476538819,-1.1963221039,-0.1196784654

Transition State 1 dimethylketene and 2,3-dihydro-5-methylfuran
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -501.559804192

Zero-point correction= 0.213657 (Hartree/Particle)
Thermal correction to Energy= 0.225837
Thermal correction to Enthalpy= 0.226781
Thermal correction to Gibbs Free Energy= 0.175493
Sum of electronic and ZPE= -501.346147
Sum of electronic and thermal Energies= -501.333967
Sum of electronic and thermal Enthalpies= -501.333023
Sum of electronic and thermal Free Energies= -501.384311

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	**141.715**	**43.973**	**107.946**

C,0,2.3066189193,2.941940195,2.5565013431
C,0,1.8243688436,3.8737008059,1.4313467056
O,0,1.6252904882,3.0154383582,0.2663066163
C,0,1.8843962059,1.7544118839,0.5849343829
C,0,2.4425026714,1.6145809697,1.8384794698
C,0,1.5698270847,0.7584087805,-0.4728244042
C,0,4.2621671262,1.7602905528,0.9635833236
C,0,4.8044773382,0.5446049867,0.7541579446
C,0,6.2456583695,0.5495850392,0.2854130565
C,0,4.2081926786,-0.8224537302,0.9219589232
O,0,4.5130339023,2.9493971495,0.8701664975
H,0,4.8764571495,-1.4490600034,1.5261428
H,0,3.2310805177,-0.8349808512,1.4030763167
H,0,4.1022832145,-1.324100556,-0.0500332779
H,0,6.8954030391,0.0427397136,1.0108208866
H,0,6.3415829583,0.0076953677,-0.6648793493
H,0,6.62036037,1.5644290438,0.1396018378
H,0,2.21891305,0.9200748325,-1.3384790412
H,0,1.6999463849,-0.2590603651,-0.109616765
H,0,0.5348297738,0.9018028402,-0.7942609825
H,0,2.4711955581,0.6736811588,2.3677490046
H,0,1.573806406,2.8671427207,3.36378605
H,0,3.2577281549,3.2816488378,2.9703808365
H,0,2.5634362483,4.6207307658,1.1498073666
H,0,0.8621915467,4.3471275039,1.6343264583

Transition State 1 Catalyzed dimethylketene and 2,3-dihydro-5-methylfuran with trimethylammonium pcm(dichloromethane)
m062x/6-31+G**
E(RM062X) = -676.415684805

```
Zero-point correction= 0.352727 (Hartree/Particle)
Thermal correction to Energy= 0.371853
Thermal correction to Enthalpy= 0.372797
Thermal correction to Gibbs Free Energy= 0.305140
Sum of electronic and ZPE= -676.062957
Sum of electronic and thermal Energies= -676.043832
Sum of electronic and thermal Enthalpies= -676.042888
Sum of electronic and thermal Free Energies= -676.110545

      E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 233.341 68.614 142.397
```

```
C,0,2.4232056832,1.4749719595,2.0386511931
C,0,2.3109437595,2.8837794642,2.569926727
C,0,1.3717229325,3.5396045077,1.5386770318
O,0,1.0953990887,2.5212030194,0.5399080267
C,0,1.6358039579,1.3557501111,0.9356023788
C,0,1.2712558266,0.1829515606,0.0956069991
C,0,4.0731492016,1.8240870108,0.4222320121
O,0,3.948171593,3.0134087143,0.2400915807
C,0,4.7152879765,0.6845564555,0.1946613668
C,0,4.4516272085,-0.703755981,0.6961272165
C,0,5.8973410926,0.8261248261,-0.7533392032
H,0,5.3776787373,-1.127890994,1.0994572423
H,0,3.6963671608,-0.7500495452,1.4771047337
H,0,4.1314940977,-1.3525241802,-0.1282345984
H,0,6.823408428,0.5247198767,-0.2508301719
H,0,5.7594053055,0.1688961871,-1.6195018432
H,0,6.0158187794,1.8493753072,-1.1165642415
H,0,1.6788272097,0.3029246012,-0.9127752662
H,0,1.6485312883,-0.7428866521,0.5267785884
H,0,0.182512103,0.1265682171,0.0162717558
H,0,2.8268397372,0.6481220725,2.6039430751
H,0,1.8814831876,2.8936949939,3.5749766397
H,0,3.2814276227,3.3877402478,2.614967053
H,0,1.8193016297,4.3874444637,1.0205088309
H,0,0.4109185772,3.8335199597,1.966758131
H,0,5.093376164,4.2262848639,0.7642146876
N,0,5.6993529775,5.0713772383,0.7783166278
C,0,7.0971351842,4.6356056937,1.049153031
C,0,5.5673122002,5.6813879113,-0.5748240029
C,0,5.1895105745,5.9794590678,1.8423733882
H,0,7.7442901183,5.5132744102,1.035015962
```

```
H,0,7.1322599074,4.1562468239,2.0267288125
H,0,7.3995572057,3.9322439563,0.2737586621
H,0,5.7833091636,6.8943647741,1.8359860307
H,0,4.1439117026,6.206335472,1.636162005
H,0,5.2821747268,5.4778444826,2.8048470859
H,0,6.1817329775,6.5815133234,-0.6155981489
H,0,5.9032344631,4.9564795916,-1.3157797646
H,0,4.5196844499,5.9276581873,-0.7444606345
```

Intermediate of Dimethylketene and 2,3-dihydro-5-methylfuran
m062x/6-31+G pcm(dichloromethane)**
E(RM062X) = -501.564355524

```
Zero-point correction= 0.214975 (Hartree/Particle)
Thermal correction to Energy= 0.227111
Thermal correction to Enthalpy= 0.228055
Thermal correction to Gibbs Free Energy= 0.176977
Sum of electronic and ZPE= -501.349380
Sum of electronic and thermal Energies= -501.337245
Sum of electronic and thermal Enthalpies= -501.336301
Sum of electronic and thermal Free Energies= -501.387379
```

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 142.514 44.457 107.503
```

```
O,0,0.8978627434,0.6022800466,-0.1463481098
C,0,0.7869300536,-0.1493679442,0.8943033172
C,0,1.9342891396,-1.003511513,1.0940192273
C,0,3.0422016982,-0.3337945083,0.2793430016
C,0,2.2626800822,0.5393145346,-0.7058396702
C,0,-0.4837484912,-0.0663587129,1.6483470988
C,0,1.3306956507,-2.2940253362,0.2921187152
O,0,1.5320574389,-2.2394579759,-0.9607171938
C,0,0.67173965,-3.2419117784,1.0311635208
C,0,0.4763520231,-3.2750028219,2.5221975029
C,0,0.1561254957,-4.4625422661,0.3146463354
H,0,0.8285857616,-4.2327557467,2.9295778398
H,0,0.9948078383,-2.4859311398,3.0710100132
H,0,-0.5896508241,-3.2079480476,2.7876727168
H,0,0.7296042369,-5.3621424485,0.5821274448
H,0,-0.8872599784,-4.6648010434,0.5936136426
H,0,0.2095744887,-4.3337798928,-0.7679892939
H,0,-1.3306023861,-0.1169967151,0.9600966432
```

H,0,-0.5521975606,-0.8568300503,2.3918216348
H,0,-0.513162287,0.9092416607,2.1465065319
H,0,2.1631470531,-1.2425622083,2.1279451795
H,0,3.6806067346,0.2698479469,0.9277560348
H,0,3.6424605536,-1.0734143237,-0.2495300296
H,0,2.1604389491,0.0907803096,-1.6898523917
H,0,2.5979529359,1.5741959748,-0.7698347116

Intermediate Catalyzed of Dimethylketene and 2,3-dihydro-5-methylfuran with trimethylammonium
m062x/6-31+G pcm(dichloromethane)**
E(RM062X) = -676.445638203

Zero-point correction= 0.352295 (Hartree/Particle)
Thermal correction to Energy= 0.371117
Thermal correction to Enthalpy= 0.372061
Thermal correction to Gibbs Free Energy= 0.305293
Sum of electronic and ZPE= -676.093343
Sum of electronic and thermal Energies= -676.074521
Sum of electronic and thermal Enthalpies= -676.073577
Sum of electronic and thermal Free Energies= -676.140346

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	**232.880**	**68.114**	**140.527**

C,0,1.662761063,1.0999091339,-0.4973014327
C,0,0.6776242667,0.6686260755,0.539043315
C,0,1.5898743778,-0.0033975209,1.5871074336
C,0,2.8594483234,-0.332912213,0.8083704666
O,0,2.8002806469,0.5697243279,-0.3683215972
C,0,-0.2542785464,-0.2970250939,-0.1823075115
C,0,-1.5732747156,-0.114587837,-0.3606712696
C,0,-2.3685516063,-1.072628989,-1.2075465557
C,0,1.4075579801,2.019596267,-1.6141667923
O,0,0.4720142421,-1.3309950442,-0.693374842
C,0,-2.3748407746,1.0164162712,0.225891512
H,0,-3.2705063332,0.6158766791,0.7135102248
H,0,-1.837401229,1.6102514015,0.9656756374
H,0,-2.7214942299,1.6891676232,-0.567335468
H,0,-3.0293713491,-1.6957491318,-0.5923203313
H,0,-3.0162918449,-0.5087842356,-1.8881989446
H,0,-1.7280052182,-1.7251083796,-1.804343259
H,0,2.1968203999,1.9692727182,-2.3618351051

H,0,0.4273886412,1.7974121137,-2.0440061379
H,0,1.3538626203,3.0318290819,-1.1940487532
H,0,0.1379586364,1.5399721702,0.9111405003
H,0,1.8032201359,0.6900790111,2.4017907759
H,0,1.1319385913,-0.9041611134,1.9958963246
H,0,2.8788255808,-1.3362578678,0.3862397773
H,0,3.795904797,-0.093460497,1.3070306559
H,0,0.0300465575,-2.2512593673,-0.5082338889
N,0,-0.3916440929,-3.696985209,-0.0464849836
C,0,0.9168091522,-4.3125549452,0.2002508262
C,0,-1.1521229468,-3.5969289489,1.202335548
C,0,-1.1346823106,-4.4697845267,-1.0458071825
H,0,-1.2808618331,-5.5085445436,-0.713858199
H,0,-2.1136805669,-4.014831849,-1.210391335
H,0,-0.5825486964,-4.4736013326,-1.988770206
H,0,-1.3294609282,-4.5895393245,1.6426849128
H,0,-0.5972627385,-2.9881837732,1.9211379712
H,0,-2.1156304109,-3.1196387004,1.008483607
H,0,0.8095664868,-5.3384847365,0.5819712727
H,0,1.4885724318,-4.3376916359,-0.7308343122
H,0,1.4656504402,-3.7187050585,0.9358753458

Transition State 2 Cyclobutanone Product 28
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -501.561050107

Zero-point correction= 0.215511 (Hartree/Particle)
Thermal correction to Energy= 0.226388
Thermal correction to Enthalpy= 0.227332
Thermal correction to Gibbs Free Energy= 0.179811
Sum of electronic and ZPE= -501.345540
Sum of electronic and thermal Energies= -501.334662
Sum of electronic and thermal Enthalpies= -501.333718
Sum of electronic and thermal Free Energies= -501.381239

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 142.060 41.905 100.016
```

C,0,0.4723953859,0.2726895695,0.8746986395
C,0,1.5462944046,-0.6910029743,1.3666759001
C,0,2.2559180174,-1.1022055948,0.0708895782
O,0,1.8466392455,-0.1069209007,-0.9249811547
C,0,0.9718412859,0.740963908,-0.4263779584

C,0,0.9374623262,2.064386685,-1.1027165216
C,0,-0.6568652378,-0.495095922,0.0835839295
O,0,-0.4991529986,-1.7334875998,-0.0927867159
C,0,-1.5722000062,0.3136918349,-0.5938498323
C,0,-2.0249744241,1.6785258466,-0.1574725702
C,0,-2.4639950744,-0.3557369348,-1.5986689562
H,0,-3.0669976087,1.6140087591,0.185936207
H,0,-1.4423249371,2.1065767463,0.6601523068
H,0,-2.0235970618,2.3907056838,-0.9930225908
H,0,-3.3628771402,-0.7731739287,-1.1214957287
H,0,-2.8039507546,0.3636225873,-2.3516514679
H,0,-1.9433703557,-1.1828100628,-2.0875950227
H,0,0.8745810374,1.938278714,-2.1856160846
H,0,0.1272388523,2.6936724018,-0.7503387782
H,0,1.8896402889,2.560018019,-0.8745136035
H,0,0.1321671583,1.033109321,1.5728175597
H,0,2.2280217286,-0.1848473872,2.0534287409
H,0,1.101261342,-1.5574958402,1.8568162692
H,0,1.9367033173,-2.0730305396,-0.2976190588
H,0,3.3440602088,-1.0385993915,0.1205279134

Transition State 2 Catalyzed Cyclobutanone Product 28 with trimethylammonium

m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -676.429356481

Zero-point correction= 0.353377 (Hartree/Particle)
Thermal correction to Energy= 0.370938
Thermal correction to Enthalpy= 0.371882
Thermal correction to Gibbs Free Energy= 0.308349
Sum of electronic and ZPE= -676.075979
Sum of electronic and thermal Energies= -676.058419
Sum of electronic and thermal Enthalpies= -676.057474
Sum of electronic and thermal Free Energies= -676.121008

```
    E     CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 232.767 65.781 133.717
```

C,0,0.9915193247,0.6475235138,-0.7760032196
C,0,1.111608765,0.8342066678,0.694202934
C,0,2.2765925964,-0.064587891,1.0918861761
C,0,2.3331033248,-1.0846366403,-0.0542729708
O,0,1.5413774478,-0.4984659528,-1.1392760063
C,0,-0.2406797476,0.0900037011,0.7494908517

C,0,-1.2800119021,0.6768889673,0.0281819568
C,0,-2.413222331,-0.2083715372,-0.3996537422
C,0,0.8054868829,1.6252610312,-1.8857635096
O,0,-0.2148705124,-1.1403393855,1.0979813614
C,0,-1.5514328357,2.1520571193,-0.0424828323
H,0,-2.4493008457,2.360439403,0.5536808781
H,0,-0.747000028,2.772989582,0.3541144664
H,0,-1.7784756845,2.4699283047,-1.0661628276
H,0,-3.1303159491,-0.3645225787,0.4195526961
H,0,-2.9664330444,0.246096971,-1.2262618541
H,0,-2.0397322212,-1.1869939785,-0.717122107
H,0,0.1887053413,1.2012832084,-2.6814070623
H,0,0.3865489427,2.566719067,-1.5461498315
H,0,1.8041518569,1.8162644314,-2.2950466945
H,0,1.1243471181,1.8574619377,1.0609963103
H,0,3.19663875,0.5195563708,1.1534213
H,0,2.0921424407,-0.5574693502,2.0470048353
H,0,1.8755078232,-2.0368163104,0.2015651598
H,0,3.3336203344,-1.2312970251,-0.4632005407
H,0,-1.2866313096,-2.1497296233,1.3485268087
N,0,-1.814795512,-3.020061514,1.7402220805
C,0,-2.6469694731,-3.6423974129,0.6827658307
C,0,-0.7371699842,-3.9402429524,2.1850156716
C,0,-2.6373943483,-2.5627017172,2.8862885855
H,0,-3.1005897957,-4.5549912113,1.0753187913
H,0,-3.4270544662,-2.942882644,0.3828760772
H,0,-2.0122341475,-3.8804474754,-0.1712374927
H,0,-3.1178793349,-3.4246490023,3.3538103312
H,0,-1.9878430694,-2.0601094577,3.603035842
H,0,-3.3947382827,-1.8669459329,2.5240084776
H,0,-1.1830810226,-4.8373520743,2.6195710341
H,0,-0.1257379188,-4.2034675451,1.3216353779
H,0,-0.1247491822,-3.4242100641,2.9241538569

Transition State 2 Oxetane Product 29
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -501.561705034

Zero-point correction= 0.214989 (Hartree/Particle)
Thermal correction to Energy= 0.226397
Thermal correction to Enthalpy= 0.227341
Thermal correction to Gibbs Free Energy= 0.178306
Sum of electronic and ZPE= -501.346716
Sum of electronic and thermal Energies= -501.335308

Sum of electronic and thermal Enthalpies= -501.334364
Sum of electronic and thermal Free Energies= -501.383399

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 142.066 42.424 103.203

C,0,0.5662548985,0.0365199742,0.8306775926
C,0,1.7193525724,-0.956055541,1.0954672269
C,0,2.5712139272,-0.8630506695,-0.1665426619
O,0,2.1945608501,0.4369147582,-0.7637778138
C,0,1.1243006632,0.8795982049,-0.252029449
C,0,0.549633966,2.1383336485,-0.7517648862
C,0,-0.6504103983,-0.6166109669,0.1133571285
O,0,-0.316184146,-0.9911945318,-1.0856643646
C,0,-1.8616019532,-0.7087747703,0.7313531938
C,0,-2.1812444097,-0.2944076855,2.1436165746
C,0,-3.0128585643,-1.3335241847,-0.0134238397
H,0,-2.5212833916,-1.1554247361,2.7374089784
H,0,-1.3392669239,0.1469916242,2.6819005081
H,0,-3.0044040334,0.4344702772,2.1669653877
H,0,-3.3711504577,-2.2440856759,0.4892262348
H,0,-3.872644058,-0.6497785673,-0.0646735468
H,0,-2.7192252194,-1.5978120448,-1.0313124552
H,0,0.9688148272,2.4126815204,-1.718169469
H,0,-0.5362721706,2.0260395963,-0.8022401419
H,0,0.7680742885,2.920007225,-0.0146430364
H,0,0.2967843806,0.6483525515,1.6925729908
H,0,2.2937868897,-0.6573700795,1.9747018698
H,0,1.3431585111,-1.9690420608,1.2415817391
H,0,2.3102441647,-1.6005242643,-0.9233188255
H,0,3.6471257868,-0.8120086017,-0.0102999351

Transition State 2 Catalyzed Oxetane Product 29 with trimethylammonium
m062x/6-31+G pcm(dichloromethane)**
E(RM062X) = -676.439029827

Zero-point correction= 0.348984 (Hartree/Particle)
Thermal correction to Energy= 0.367493
Thermal correction to Enthalpy= 0.368437
Thermal correction to Gibbs Free Energy= 0.302947
Sum of electronic and ZPE= -676.090046
Sum of electronic and thermal Energies= -676.071537
Sum of electronic and thermal Enthalpies= -676.070592

```
Sum of electronic and thermal Free Energies= -676.136083

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 230.605 67.496 137.836

 C,0,1.128883119,-1.0589606012,1.9452773375
 C,0,2.4741289871,-1.2053244584,1.2439670082
 O,0,2.785414002,0.1543772657,0.7728874921
 C,0,1.729259378,0.8632271029,0.6958206033
 C,0,0.5074470959,0.1760417902,1.2591567052
 C,0,1.847499977,2.2818360133,0.31741919
 C,0,-0.2346891667,-0.0830247041,-0.0389524303
 O,0,0.6658462216,0.1192115886,-1.0375614416
 C,0,-1.5332460496,-0.3951854565,-0.1630009414
 C,0,-2.4240645197,-0.6267736235,1.0274633395
 C,0,-2.1764353422,-0.5243977424,-1.5165648297
 N,0,1.0097857694,-1.5001924294,-2.8792294498
 C,0,0.298735776,-1.1910635076,-4.1360752312
 C,0,2.4688387563,-1.3468596621,-3.0541660433
 C,0,0.6694473102,-2.8517556336,-2.3927782387
 H,0,-2.8612464115,-1.6322077773,0.9921585632
 H,0,-1.895873982,-0.532124738,1.9794797115
 H,0,-3.2607277334,0.0822223935,1.0298181387
 H,0,-2.3832253006,-1.5712368698,-1.7766860576
 H,0,-3.1408483737,-0.0037880614,-1.52767554
 H,0,-1.5498036658,-0.086543403,-2.2978396151
 H,0,2.1015401621,2.8339021965,1.2310953225
 H,0,2.6417632413,2.4211247249,-0.4154733892
 H,0,0.8933230284,2.6472458712,-0.0593841414
 H,0,-0.0291426293,0.8251724307,1.9559682435
 H,0,1.2735805046,-0.8699434437,3.0108719046
 H,0,0.5097818916,-1.9484390821,1.8227656775
 H,0,2.4392842964,-1.8245396672,0.3464190653
 H,0,3.3060804225,-1.5032287578,1.8779741792
 H,0,0.7355321695,-0.706603542,-1.998872523
 H,0,2.8408222708,-2.0696088785,-3.7864665878
 H,0,2.6790075872,-0.3325610645,-3.3970305802
 H,0,2.961278371,-1.5093823834,-2.0938898945
 H,0,0.6604447696,-1.8427412699,-4.9379715627
 H,0,-0.7704505042,-1.3522514848,-3.9953776771
 H,0,0.4791815552,-0.1478486386,-4.4004573507
 H,0,0.9724434216,-3.6046144973,-3.1271054689
 H,0,1.1871671137,-3.0350221152,-1.4492691757
```

H,0,-0.4076425192,-2.9113358837,-2.2283823122

Cyclobutanone product 28
m062x/6-31+G** pcm(dichloromethane)
E(RM062X) = -501.622910552

Zero-point correction= 0.217460 (Hartree/Particle)
Thermal correction to Energy= 0.228364
Thermal correction to Enthalpy= 0.229308
Thermal correction to Gibbs Free Energy= 0.182081
Sum of electronic and ZPE= -501.405451
Sum of electronic and thermal Energies= -501.394547
Sum of electronic and thermal Enthalpies= -501.393602
Sum of electronic and thermal Free Energies= -501.440829

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	143.301	42.542	99.397

C,0,0.8604053,0.8236354235,-0.6576997005
C,0,0.496667174,0.4138849043,0.8045142306
C,0,1.5533194587,-0.6081925321,1.2135587257
C,0,1.9410166362,-1.1932103208,-0.1458642283
O,0,1.8646810595,-0.105300333,-1.0669169548
C,0,-0.780918629,-0.2033179243,0.2313424395
C,0,-0.5786405897,0.4117158969,-1.1509219471
C,0,-0.6651493102,-0.5244349048,-2.346265835
C,0,1.3649982612,2.2156252495,-0.9603764146
O,0,-1.5993393635,-0.9664637144,0.6844611291
C,0,-1.5316516281,1.6039572777,-1.308030623
H,0,-1.6898401757,-0.889890019,-2.4621456285
H,0,-0.3848348141,0.0122440335,-3.2585904652
H,0,0.0022146038,-1.3824012756,-2.2400903826
H,0,1.529670017,2.3325989992,-2.0363561673
H,0,0.6575072172,2.9796701771,-0.6321594361
H,0,2.3164035357,2.3757550514,-0.4455102281
H,0,0.3286230971,1.224616949,1.5182755371
H,0,2.4042989651,-0.1029225562,1.6786295285
H,0,1.1683138105,-1.3642842277,1.9021540086
H,0,1.2389011028,-1.9893828521,-0.4374266319
H,0,2.9560122304,-1.5925532466,-0.1858659432
H,0,-1.2460402153,2.1984253587,-2.181670997
H,0,-2.5520088956,1.2378174063,-1.4533906634
H,0,-1.5291858477,2.2584111797,-0.4307823525

Oxetane product 29
m062x/6-31+G pcm(dichloromethane)**
E(RM062X) = -501.613494085

Zero-point correction= 0.217531 (Hartree/Particle)
Thermal correction to Energy= 0.228644
Thermal correction to Enthalpy= 0.229588
Thermal correction to Gibbs Free Energy= 0.181257
Sum of electronic and ZPE= -501.395963
Sum of electronic and thermal Energies= -501.384850
Sum of electronic and thermal Enthalpies= -501.383906
Sum of electronic and thermal Free Energies= -501.432237

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	143.476	42.328	101.722

C,0,0.8439169363,0.666005535,-0.5656061096
C,0,0.5725864421,0.4078839192,0.9405519907
C,0,1.728204404,-0.5033596395,1.3634269286
C,0,2.1835387408,-1.0864106517,0.0225146899
O,0,2.0025275078,-0.0161850362,-0.9158278134
C,0,-0.658614609,-0.2944501903,0.4261673751
O,0,-0.3517158836,-0.0942019587,-0.919303459
C,0,0.828132399,2.0398534623,-1.171827368
C,0,-1.7227763139,-0.9157716597,0.9273882818
H,0,0.867307611,1.9594663855,-2.2614249804
H,0,-0.0875018931,2.5610025693,-0.885531568
H,0,1.6934369847,2.6080366728,-0.8232373952
H,0,0.4132847263,1.2772244234,1.5801863633
H,0,2.5274192979,0.0962188218,1.8085968072
H,0,1.4268519451,-1.27608652,2.0742412556
H,0,1.5603316083,-1.9395541885,-0.2713867296
H,0,3.2338633999,-1.3772063446,-0.0070767027
C,0,-2.7805090294,-1.5100128744,0.0392300514
C,0,-1.9028501547,-1.0437751096,2.41536516
H,0,-1.0835569574,-0.5761659621,2.9686311956
H,0,-2.8409013612,-0.5739015663,2.7344340118
H,0,-1.9558793707,-2.098313529,2.7119711956
H,0,-3.7631150377,-1.0800909963,0.2672622436
H,0,-2.5632846431,-1.3344593894,-1.0165744694
H,0,-2.8590777496,-2.5918281731,0.2004530452

Theoretical Structures for the Ring-Opening of Cyclopropylcarbinyl Radical.

Cyclopropylcarbinyl radical Starting Material.

B3LYP/6-31G*
E(UB+HF-LYP) = -156.541563220

Zero-point correction= 0.094974 (Hartree/Particle)
Thermal correction to Energy= 0.099982
Thermal correction to Enthalpy= 0.100926
Thermal correction to Gibbs Free Energy= 0.067496
Sum of electronic and ZPE= -156.446589
Sum of electronic and thermal Energies= -156.441581
Sum of electronic and thermal Enthalpies= -156.440637
Sum of electronic and thermal Free Energies= -156.474067

```
     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.740 17.495 70.359
```

```
 C,0,-0.0073407354,-0.0050877901,-0.0126901013
 C,0,-0.0043119958,-0.0029694213,1.4452634325
 C,0,1.3130211632,-0.0002137677,2.2304582284
 C,0,0.4609892051,1.2295193418,2.2304650965
 H,0,0.7594872773,0.5257224928,-0.5690994382
 H,0,-0.7704803837,-0.5328502255,-0.5727709915
 H,0,-0.812323512,-0.5627558703,1.9114179773
 H,0,-0.0878714502,1.4857949091,3.1331667119
 H,0,0.7912452773,2.0868171055,1.6498791682
 H,0,1.3601776844,-0.6040960054,3.1331749495
 H,0,2.2317102494,0.007847176,1.6498898853
```

Transition State for ring-opening of cyclopropylcarbinyl radical

B3LYP/6-31G*
E(UB+HF-LYP) = -156.550835532

Zero-point correction= 0.093444 (Hartree/Particle)
Thermal correction to Energy= 0.097962
Thermal correction to Enthalpy= 0.098906
Thermal correction to Gibbs Free Energy= 0.066480
Sum of electronic and ZPE= -156.457391
Sum of electronic and thermal Energies= -156.452874
Sum of electronic and thermal Enthalpies= -156.451930

```
Sum of electronic and thermal Free Energies= -156.484355

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 61.472 16.398 68.245

 C,0,0.0087142174,0.0011022075,-0.0027272287
 C,0,-0.0123396752,0.0036824084,1.4804710984
 C,0,1.4640223989,0.0016630195,1.2376200439
 C,0,2.2804481482,-1.1174907302,1.316878919
 H,0,-0.0336746245,-0.9325122773,-0.5486097244
 H,0,-0.0264040011,0.9270081759,-0.5645927073
 H,0,-0.3950802706,-0.9033016539,1.9507717001
 H,0,-0.4118837043,0.8991156911,1.9582014569
 H,0,1.8749021127,-2.0985716538,1.5483922288
 H,0,3.3385413749,-1.0545673569,1.0871734232
 H,0,1.9270154841,0.9742218634,1.0948921879
```

3-buten-1-yl radical Product Structure

```
B3LYP/6-31G*
E(UB+HF-LYP) = -156.547992920

Zero-point correction= 0.093695 (Hartree/Particle)
Thermal correction to Energy= 0.099328
Thermal correction to Enthalpy= 0.100272
Thermal correction to Gibbs Free Energy= 0.065184
Sum of electronic and ZPE= -156.454297
Sum of electronic and thermal Energies= -156.448665
Sum of electronic and thermal Enthalpies= -156.447721
Sum of electronic and thermal Free Energies= -156.482809

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.329 18.616 73.850

 C,0,-0.1577860567,-0.3456392917,1.538430583
 C,0,1.2220867402,-0.2712123362,0.9631144762
 C,0,1.2903828868,0.5380959766,-0.310179067
 C,0,1.6827252428,0.069383573,-1.4950036579
 H,0,-1.0163230335,-0.4736670861,0.8865115799
 H,0,-0.3166565435,-0.4125597407,2.6099882833
 H,0,1.6125503138,-1.284886943,0.7577390542
 H,0,1.9035240629,0.1611613812,1.7114542864
```

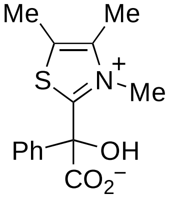
H,0,1.9986693127,-0.9641667893,-1.6247108678
H,0,1.7069826125,0.698615233,-2.3807900192
H,0,0.9740884619,1.5782600231,-0.2234926511

Theoretical Structures and Energies for the Decarboxylation of Mandelylthiamin.

Key to Structure Titles and Structure Listings

The structure titles in the following section have retained the original file names for the computational output files. This lets us use a single code name for structures, energies in tables, and our records, but a problem is that the titles are sometimes clear and sometimes relatively cryptic. I will give here some general explanation of the titles along with structural drawings where appropriate. The first line under each title is the description used by the researcher in the calculational input file. The second line is the calculational method and basis set (though the use of PCM does not show up in this). The third line is the potential energy. Other lines are self-explanatory.

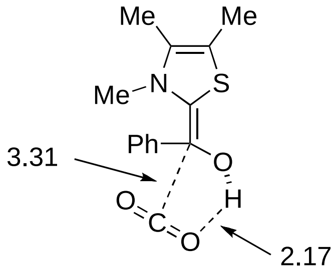
Structures "dimeSMAm062x", "dimeSMBm062x", and "dimeSMCm062x" are conformers of the MTh model **1b**.



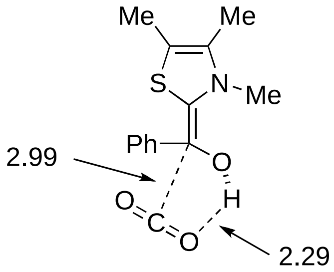
1b

Structures "dimeTSAm062x" and "dimeTSBm062x" are transition structures for the uncatalyzed decarboxylation step **1b**. Structures "dimeprod", "dimeprodB", and "dimeprodC" are conformers for the product enol **4b**.

Structures "complex" (**2b-2**) and "complexrev" (**2b-1**) are the initial potential energy minima arising from the decarboxylation transition structures.

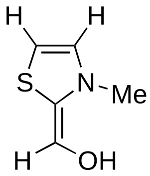


2b-1
complex from
lowest-energy TS



2b-2
complex from
second-best TS

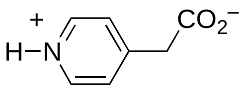
"Pyridinium", "H2O", "CO2", and "trichloroacetateSM" are self-explanatory.

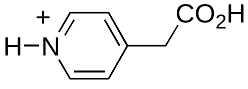


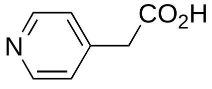
Structures "pyridiniumTSA1", "pyridiniumTSC1", "pyridiniumTSD1", "pyridiniumTSI3", "pyridiniumTSJ5", "pyridiniumTSL1", "pyridiniumTSO1", "pyridiniumTSQ1", "pyridiniumTSS1", "pyridiniumTST1", "pyridiniumTSU1", "pyridiniumTSV1", "pyridiniumTSW1", "pyridiniumTSX1", "pyridiniumTSY1", "pyridiniumTSZ1", "pyridiniumTSAA1", and "pyridiniumTSBB1" are M06-2X/6-31+G**/PCM(water) transition structures for decarboxylation of **1b** in the presence of pyridinium.

Structures "pyridiniumTSB3", "pyridiniumTSG", and "pyridiniumTSH4" are transition structures for decarboxylation of **1b** in the presence of pyridinium that were located in M05-2X/6-31+G**/PCM(water) calculations but could not be obtained in the M06-2X/6-31+G**/PCM(water) calculations, either because they unavoidably exhibited two imaginary frequencies in the latter or because they were not minima. These structures are reported because we find them interesting but they were not among the lowest-energy structures.

Structures starting with "Oleary…" are for the 4-pyridiylacetic acid system. A zwitterion complexed to an explicit water molecule ("OlearySMzwitH2O") was considered in an attempt to explain the small difference between experimental and calculated KIEs but this, while correcting the KIE in the right direction, did not make enough difference to justify the use of a more complicated calculation. "OlearyTSA" and "Olearycomplex" are sructures for the decarboxylation step and the subsequent potential energy minimum, respectively.


OlearySMzwitA
OlearySMzwitE
OlearySMzwitF


OlearySMprot


OlearySMA

Structures starting with "Kempsnitro…" are for the 5-nitro-3-carboxybenzisoxazole system and the endings SMb, TS, and complex are self-explanatory.

"MethylenethiaminMP2" is an MP2/6-311G** optimization of N-methyl-2-methylenedihydrothiazol. "Thiaminepyridinium2MP2" and "Thiaminepyridinium3MP2" are the face-face and T-shaped complexes shown in a previous section.

"TrichloroacetateTS2.47" is the approximate canonical variational transition structure for decarboxylation of trichloroacetate.

```
dimeSMAm062x
 dimeSMAm062x
M062X/6-31+G**
E(RM062X) = -1220.82827822

Zero-point correction= 0.270274 (Hartree/Particle)
Thermal correction to Energy= 0.288536
Thermal correction to Enthalpy= 0.289480
Thermal correction to Gibbs Free Energy= 0.223231
Sum of electronic and ZPE= -1220.558004
Sum of electronic and thermal Energies= -1220.539743
Sum of electronic and thermal Enthalpies= -1220.538798
Sum of electronic and thermal Free Energies= -1220.605047

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 181.059 68.590 139.433

 C,0,2.8928120345,-0.3084833744,-0.0581458426
 C,0,2.4090956325,-1.5511359251,0.211644293
 S,0,0.6822337105,-1.52877885,0.2347946923
 C,0,0.6435739202,0.1329927462,-0.1098878662
 N,0,1.87043531,0.6253668298,-0.2277281463
 C,0,4.3262829512,0.0923004668,-0.1721254056
 C,0,3.188337801,-2.807689282,0.4581842691
 C,0,-0.6267171609,0.9317361585,-0.3002334481
 C,0,2.1734314261,2.0330225866,-0.5298990009
 H,0,2.4090869234,2.1269761738,-1.5909339154
 H,0,1.3177039914,2.6569373927,-0.2908656223
 H,0,3.0252668009,2.3358772697,0.0759362189
 C,0,-1.8522075739,0.0195401598,-0.1829888715
 C,0,-0.7083876597,2.0707276148,0.8022078935
 O,0,-0.5542497216,1.5320655628,-1.570072221
 C,0,-2.2812828901,-0.4649751772,1.0584633459
 C,0,-3.3835480982,-1.3147828286,1.1349857946
 C,0,-4.0667663699,-1.686915774,-0.0230125406
 C,0,-3.6423619071,-1.2033338345,-1.2597335542
 C,0,-2.5396172547,-0.3531346119,-1.3406071188
 H,0,-1.7519214231,-0.1706456407,1.9595710131
 H,0,-3.710719544,-1.6827754771,2.1024692769
 H,0,-4.9263694151,-2.346911472,0.0387505359
 H,0,-4.1698563527,-1.4863316913,-2.1653488012
 H,0,-2.206633622,0.0277118561,-2.2995882914
 H,0,-0.8717352004,2.4440174347,-1.4075391134
```

```
 O,0,-1.1022752013,3.1661427423,0.3412551835
 O,0,-0.3804064892,1.7589774307,1.9594920235
 H,0,4.621967887,0.7509914302,0.6498234638
 H,0,4.9521104636,-0.7994152742,-0.1347373266
 H,0,4.520022462,0.6067910197,-1.1169962457
 H,0,2.5287061736,-3.6283513602,0.7431018199
 H,0,3.7303968251,-3.1046915104,-0.4436082203
 H,0,3.9104375709,-2.6570397917,1.2641497281

dimeSMBm062x
 dimeSMBm062x
E(RM062X) = -1220.82972396

Zero-point correction= 0.269418 (Hartree/Particle)
Thermal correction to Energy= 0.286909
Thermal correction to Enthalpy= 0.287854
Thermal correction to Gibbs Free Energy= 0.223514
Sum of electronic and ZPE= -1220.560306
Sum of electronic and thermal Energies= -1220.542815
Sum of electronic and thermal Enthalpies= -1220.541870
Sum of electronic and thermal Free Energies= -1220.606210

     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.038 66.729 135.413

 C,0,2.4645799809,-0.9145861076,0.5110994888
 C,0,3.0539428448,-0.1899831812,-0.4771722092
 S,0,1.9114702721,0.8968464428,-1.1916890826
 C,0,0.6807318631,0.3635225378,-0.1484209943
 N,0,1.1160603452,-0.5771156807,0.6784297215
 C,0,3.0917775575,-1.9553805451,1.3789752016
 C,0,4.4761967627,-0.2330082461,-0.9448010769
 C,0,-0.7015114378,0.9666544839,-0.2585349329
 C,0,0.2900930359,-1.2842837067,1.6724946845
 H,0,0.8508717009,-1.3309524652,2.6052135927
 H,0,-0.6239489882,-0.7255068757,1.8384091125
 H,0,0.0847923508,-2.2913162995,1.3033331047
 C,0,-1.7892871974,-0.1019887697,-0.3168399472
 C,0,-0.9063393026,1.9776494217,0.9549815423
 O,0,-0.7121508047,1.7135191385,-1.4547848371
 C,0,-3.0083502325,0.0676445053,0.3417374665
 C,0,-4.0157324935,-0.8886157801,0.2094489901
 C,0,-3.8110416557,-2.0201411177,-0.5785351713
```

```
 C,0,-2.5964216695,-2.1902354162,-1.2436460116
 C,0,-1.5924531982,-1.2330531523,-1.1142558335
 H,0,-3.1759323224,0.9399859044,0.9670945792
 H,0,-4.9597032592,-0.7487331491,0.7266703045
 H,0,-4.5935628118,-2.7660002809,-0.6754117447
 H,0,-2.4289910828,-3.0670514756,-1.8611957122
 H,0,-0.6487676345,-1.3707259716,-1.6381472048
 H,0,-0.9494182649,2.6163065799,-1.1483424702
 O,0,-1.1875369235,3.1383983239,0.5834701781
 O,0,-0.7752847837,1.5123866135,2.0984060774
 H,0,4.8887332499,-1.2353416022,-0.8191504108
 H,0,4.5474909702,0.0302180723,-2.0016932848
 H,0,5.0918473801,0.4685750091,-0.3752499473
 H,0,2.5263895553,-2.890314905,1.3528474234
 H,0,4.1042174522,-2.1576199862,1.0312429873
 H,0,3.1538707413,-1.6178363186,2.4177644164
```

```
dimeSMCm062x
 dimeSMCm062x
M062X/6-31+G**
E(RM062X) = -1220.82964494
```

```
Zero-point correction= 0.270111 (Hartree/Particle)
Thermal correction to Energy= 0.288352
Thermal correction to Enthalpy= 0.289296
Thermal correction to Gibbs Free Energy= 0.222437
Sum of electronic and ZPE= -1220.559534
Sum of electronic and thermal Energies= -1220.541293
Sum of electronic and thermal Enthalpies= -1220.540349
Sum of electronic and thermal Free Energies= -1220.607208
```

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.943 68.480 140.716
```

```
 C,0,2.4717521938,-0.9209096257,0.488635706
 C,0,3.1115291191,-0.0762111025,-0.3648928767
 S,0,2.0107729424,1.0974837332,-0.9976701238
 C,0,0.7138021667,0.4201936691,-0.134102285
 N,0,1.1157193639,-0.6082892668,0.6029777271
 C,0,3.0563584777,-2.0570207961,1.2612446587
 C,0,4.5631337131,-0.0492354041,-0.734111648
 C,0,-0.7356573399,0.8644282991,-0.2120638534
 C,0,0.2248309277,-1.3992065647,1.4680805688
```

```
H,0,0.7672501936,-1.6491878255,2.3777125866
H,0,-0.654614633,-0.8115334621,1.7145349652
H,0,-0.0741330395,-2.3054136907,0.9399941748
C,0,-1.1612179349,1.5710977431,1.0761973663
C,0,-0.925201275,1.8774289997,-1.4137919901
O,0,-1.5222840809,-0.2716949075,-0.4653844076
C,0,-0.2871140006,2.413354124,1.7694003432
C,0,-0.716459798,3.0796505284,2.9156636455
C,0,-2.022869681,2.913633408,3.3764111024
C,0,-2.8971666053,2.0769559399,2.684010132
C,0,-2.4689245566,1.406910875,1.5380689478
H,0,0.7297075263,2.5579899137,1.4146172078
H,0,-0.0285795223,3.7279148554,3.4493309463
H,0,-2.3554556215,3.4318663895,4.2702737203
H,0,-3.9148192099,1.9406478604,3.036444968
H,0,-3.1430061471,0.7468345109,1.0025213908
H,0,-2.0138124177,-0.0223564998,-1.2773640884
O,0,-1.8685996329,1.5754478933,-2.1769014587
O,0,-0.1365576457,2.8384177303,-1.4536717065
H,0,4.9712798442,-1.06147112,-0.7422680957
H,0,4.7055561855,0.378274339,-1.7281460944
H,0,5.1335424341,0.5484841416,-0.0180057013
H,0,2.5010532361,-2.9826566997,1.0892597105
H,0,4.0890192227,-2.2135903864,0.9511885996
H,0,3.0563285951,-1.8466926018,2.3348228621
```

dimeTSAm062x
dimeTSAm062x
M062X/6-31+G**
E(RM062X) = -1220.79859882

Zero-point correction= 0.267765 (Hartree/Particle)
Thermal correction to Energy= 0.286343
Thermal correction to Enthalpy= 0.287287
Thermal correction to Gibbs Free Energy= 0.220833
Sum of electronic and ZPE= -1220.530834
Sum of electronic and thermal Energies= -1220.512256
Sum of electronic and thermal Enthalpies= -1220.511312
Sum of electronic and thermal Free Energies= -1220.577766

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	179.683	69.402	139.864

```
C,0,0.0180528171,-0.0206871034,-0.4439978673
C,0,-0.4747494373,-1.2264005882,-0.0948726978
S,0,0.7419780545,-2.4733543112,-0.3019389296
C,0,1.9077125578,-1.3167686846,-0.8872623084
N,0,1.3609845638,-0.0694107284,-0.8627700683
C,0,-0.7088190949,1.2869300916,-0.4293181666
C,0,-1.827656718,-1.6097175243,0.4155042209
C,0,3.2052295433,-1.6481462063,-1.3066704833
C,0,2.1475642692,1.1481432237,-1.0787213318
H,0,1.6069328666,1.9887194564,-0.6515026109
H,0,3.1052050031,1.0534265295,-0.5650200338
H,0,2.3275380848,1.320161032,-2.1390324039
C,0,3.6667387693,-3.0513521902,-1.4295667686
O,0,3.7666263559,-0.7653948282,-2.2255196151
C,0,4.3210566343,-1.0848795056,0.6011526721
C,0,4.4186840364,-3.4283803648,-2.556862532
C,0,4.8818957771,-4.7335318533,-2.7063425808
C,0,4.6142817185,-5.6975611397,-1.7338098297
C,0,3.8871467517,-5.3322446449,-0.6011365617
C,0,3.4245451509,-4.0277507175,-0.445293967
H,0,4.6309704217,-2.6875460081,-3.3194634287
H,0,5.4523564927,-4.9987445588,-3.591799392
H,0,4.9740385487,-6.7146536377,-1.8521570106
H,0,3.6865583911,-6.0629563268,0.1766746375
H,0,2.9066274218,-3.7612074017,0.4697187541
H,0,4.6134037907,-0.4567532643,-1.8620629161
O,0,5.1878462835,-0.4601727758,0.0782389071
O,0,3.7427646158,-1.5735113296,1.5089630006
H,0,-1.7472152595,-2.1308976513,1.3740959065
H,0,-2.4476863055,-0.7253456299,0.5669518682
H,0,-2.3425874672,-2.273058307,-0.2856722845
H,0,-0.6064362356,1.8018646354,-1.388643969
H,0,-1.7697561496,1.1171887424,-0.2509585395
H,0,-0.3368622529,1.9494835709,0.3579763301
```

dimeTSBm062x
kluger ts no catalysis based on best pyr ts
M062X/6-31+G**
E(RM062X) = -1220.79896411

Zero-point correction= 0.267427 (Hartree/Particle)
Thermal correction to Energy= 0.286006
Thermal correction to Enthalpy= 0.286950
Thermal correction to Gibbs Free Energy= 0.220668

```
Sum of electronic and ZPE= -1220.531538
Sum of electronic and thermal Energies= -1220.512958
Sum of electronic and thermal Enthalpies= -1220.512014
Sum of electronic and thermal Free Energies= -1220.578297

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 179.472 69.606 139.504

 C,0,4.3153436431,-0.6566859488,-0.5279964952
 C,0,4.5130046685,0.6415081706,-0.2215388114
 S,0,2.9905859639,1.4247887417,0.1770974254
 C,0,2.1067721779,-0.0578757179,-0.0938294569
 N,0,2.9607948173,-1.0460469466,-0.4729485389
 C,0,5.3435253808,-1.6701135101,-0.9188372842
 C,0,5.7773829677,1.4403793418,-0.1894361945
 C,0,0.712530277,-0.0461029747,0.0092605787
 C,0,2.5576303161,-2.3958226904,-0.8684709002
 H,0,3.0829811716,-2.668104917,-1.7840597605
 H,0,2.7934321614,-3.116443891,-0.0800375243
 H,0,1.4922170849,-2.4110692876,-1.0697046775
 C,0,-0.1312971895,-1.1937413214,0.4245873099
 O,0,0.2025331134,1.1942643968,0.4107106604
 C,0,0.4206584114,0.1506441293,-2.2912407311
 C,0,0.3417552159,-2.1970998773,1.2830687025
 C,0,-0.4910374282,-3.2370848367,1.6937922086
 C,0,-1.8201572736,-3.2805928479,1.2743931275
 C,0,-2.312003519,-2.2703851178,0.4447225404
 C,0,-1.476222996,-1.2397494726,0.0257632843
 H,0,1.3665643196,-2.1543683175,1.6436481358
 H,0,-0.1030663761,-4.005071611,2.3561871058
 H,0,-2.4695213207,-4.0879108102,1.5978735685
 H,0,-3.3477019458,-2.2889056564,0.1192846278
 H,0,-1.867118394,-0.4569795635,-0.6201936205
 H,0,-0.1195553387,1.6629422028,-0.3773989371
 O,0,-0.1580956799,1.1867141364,-2.2687495654
 O,0,0.9056201972,-0.8118083888,-2.7725520375
 H,0,5.9447800468,1.8740696497,0.8008837565
 H,0,6.6363569169,0.8144144392,-0.4348168632
 H,0,5.7394882027,2.260676103,-0.9127212644
 H,0,5.2398424738,-1.9620398637,-1.9683897219
 H,0,6.3428545084,-1.2591327435,-0.7814907538
 H,0,5.2601604252,-2.571944999,-0.3058338935
```

complex
product complex
M062X/6-31+G**
E(RM062X) = -1220.80842603

Zero-point correction= 0.267261 (Hartree/Particle)
Thermal correction to Energy= 0.287271
Thermal correction to Enthalpy= 0.288215
Thermal correction to Gibbs Free Energy= 0.217257
Sum of electronic and ZPE= -1220.541165
Sum of electronic and thermal Energies= -1220.521155
Sum of electronic and thermal Enthalpies= -1220.520211
Sum of electronic and thermal Free Energies= -1220.591169

	E	**CV**	**S**
	KCal/Mol	**Cal/Mol-K**	**Cal/Mol-K**
Total	**180.265**	**72.067**	**149.344**

C,0,-0.0463472451,0.0027444155,-0.4598350094
C,0,-0.566499814,-1.1799722046,-0.0848571105
S,0,0.6281296015,-2.4774985152,-0.2435123835
C,0,1.8099918834,-1.35248949,-0.9387086194
N,0,1.2880153087,-0.0670368472,-0.8979092086
C,0,-0.7457644704,1.3272207761,-0.4635877477
C,0,-1.9269719696,-1.523184442,0.4314437208
C,0,2.9920950122,-1.7114517524,-1.5227521067
C,0,2.1522965894,1.1104897965,-0.9358098236
H,0,1.6510485973,1.9329920957,-0.4288737321
H,0,3.0818939619,0.8944576205,-0.4030155145
H,0,2.3975051033,1.4040793752,-1.9569619751
C,0,3.5847383897,-3.0522589329,-1.5294093636
O,0,3.5935110443,-0.7711207604,-2.3525045443
C,0,4.7427513435,-1.2239900537,0.8528112764
C,0,4.4364656798,-3.4162317932,-2.592235239
C,0,5.0208928801,-4.6776596592,-2.6444693696
C,0,4.781777088,-5.6132944046,-1.6362926563
C,0,3.9592060388,-5.2604623937,-0.5668324545
C,0,3.3750134092,-3.9970005245,-0.5063509351
H,0,4.6243845175,-2.7024929972,-3.3872595102
H,0,5.6642710009,-4.933033101,-3.4813526996
H,0,5.2378511877,-6.597152231,-1.6786016269
H,0,3.7801246089,-5.9670607597,0.2381353973
H,0,2.7844286298,-3.7376252144,0.3661832596
H,0,4.5073788708,-0.6294462421,-2.0628680265

```
 O,0,5.4341031996,-0.7924415316,0.019148559
 O,0,4.0773837156,-1.6422364305,1.7081935149
 H,0,-1.8603659434,-2.0073920494,1.411514478
 H,0,-2.5364613929,-0.625178138,0.5443142567
 H,0,-2.4505804332,-2.2088340947,-0.2425616917
 H,0,-0.5814334424,1.8488070598,-1.4110377335
 H,0,-1.8186057249,1.1856900527,-0.335914689
 H,0,-0.3946702262,1.9754383713,0.3453733081
```

complexrev
complex from best ts for uncatalyzed decarboxylation
M062X/6-31+G**
E(RM062X) = -1220.81002492

Zero-point correction= 0.267197 (Hartree/Particle)
Thermal correction to Energy= 0.287077
Thermal correction to Enthalpy= 0.288021
Thermal correction to Gibbs Free Energy= 0.218110
Sum of electronic and ZPE= -1220.542828
Sum of electronic and thermal Energies= -1220.522948
Sum of electronic and thermal Enthalpies= -1220.522004
Sum of electronic and thermal Free Energies= -1220.591915

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.143 72.150 147.141
```

```
 C,0,4.1703844543,-0.6796001811,-0.4860533107
 C,0,4.3575290943,0.6472403904,-0.3674757742
 S,0,2.8255735062,1.4866434992,-0.0698705123
 C,0,1.9540350212,-0.0574920241,-0.0668485843
 N,0,2.8286811938,-1.0946670861,-0.3546672818
 C,0,5.2155439534,-1.7239331473,-0.7311643684
 C,0,5.616347746,1.4507442181,-0.4375984716
 C,0,0.6120687208,-0.0953954305,0.163723727
 C,0,2.3661412061,-2.3110297566,-1.01929149
 H,0,3.0245735256,-2.5382116843,-1.8585621051
 H,0,2.3358151521,-3.1668280776,-0.3388056845
 H,0,1.3587418876,-2.1408757885,-1.4048187875
 C,0,-0.1941192567,-1.2528383185,0.5620858926
 O,0,-0.0424654312,1.135506321,0.2157191364
 C,0,1.3872013978,0.6148031515,-2.9713769615
 C,0,0.3609082605,-2.3262127853,1.281824635
 C,0,-0.4293412036,-3.3984002246,1.6865015659
```

```
 C,0,-1.7949818198,-3.4182644626,1.3982087596
 C,0,-2.3636044936,-2.3438317188,0.7110580533
 C,0,-1.5757264251,-1.2715825408,0.3016106434
 H,0,1.4140325222,-2.3021977356,1.5481165976
 H,0,0.0207139769,-4.2142266759,2.2445059626
 H,0,-2.4103173206,-4.2532839507,1.7178651347
 H,0,-3.4272426606,-2.3416425486,0.491298345
 H,0,-2.0247395723,-0.4365101186,-0.2273008815
 H,0,-0.1234126033,1.5013009168,-0.6778037743
 O,0,0.4657816132,1.2960933844,-2.7566311404
 O,0,2.3083190449,-0.0552078462,-3.1976039505
 H,0,5.8144605736,1.9686110649,0.5063239795
 H,0,6.4715435958,0.8113808011,-0.6622317765
 H,0,5.5488229797,2.2091175419,-1.2246214891
 H,0,5.2017708262,-2.0775978382,-1.7669002496
 H,0,6.2088996055,-1.3243032749,-0.5281310864
 H,0,5.0536129291,-2.5867370742,-0.0784697525

dimeprod
 kluger product conf 1
M062X/6-31+G**
E(RM062X) = -1032.28371727

Zero-point correction= 0.254579 (Hartree/Particle)
Thermal correction to Energy= 0.270442
Thermal correction to Enthalpy= 0.271386
Thermal correction to Gibbs Free Energy= 0.211085
Sum of electronic and ZPE= -1032.029139
Sum of electronic and thermal Energies= -1032.013275
Sum of electronic and thermal Enthalpies= -1032.012331
Sum of electronic and thermal Free Energies= -1032.072633

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.705 60.051 126.915

 C,0,-3.9822321959,-0.7095452135,0.2326372758
 C,0,-4.0306646039,0.2231743961,-0.7307271694
 S,0,-2.4471521664,0.9995688257,-0.9944252314
 C,0,-1.8121797345,0.1410088572,0.4273974988
 N,0,-2.7125475267,-0.868123459,0.8599692447
 C,0,-5.0959001539,-1.5951687478,0.6994694296
 C,0,-5.177671972,0.6729146523,-1.5778774548
 C,0,-0.7314377885,0.4626935766,1.1731638793
```

```
C,0,-2.1844040787,-2.24695288,0.8219453492
H,0,-2.8462133888,-2.9013408492,1.3914396434
H,0,-2.1095048824,-2.6121217145,-0.2105477291
H,0,-1.1961710086,-2.267382871,1.2815196817
C,0,0.2901103116,1.4658451289,0.8561657383
O,0,-0.5473247994,-0.1648373749,2.3849236534
C,0,0.9816279295,2.0962795428,1.9048450207
C,0,1.9258369993,3.0821796711,1.6377944053
C,0,2.2047662478,3.4548980661,0.32106677
C,0,1.5410296607,2.8183938537,-0.7268924099
C,0,0.5986937124,1.825671638,-0.4648121057
H,0,0.7634797226,1.8085027074,2.9275879842
H,0,2.4455067308,3.5638193936,2.4605372599
H,0,2.9411712445,4.2251503541,0.1146890943
H,0,1.7681076059,3.0824613977,-1.7551782521
H,0,0.1344187544,1.3041036914,-1.2961537338
H,0,-1.4121585708,-0.4848802271,2.6898027825
H,0,-4.9295973838,0.5768432978,-2.6401497738
H,0,-6.0664870118,0.0706580925,-1.3837668554
H,0,-5.4237309203,1.7226147955,-1.3892049353
H,0,-5.1485498964,-1.5901074153,1.7924847194
H,0,-6.0544580382,-1.2570295829,0.3061031859
H,0,-4.9465847983,-2.6301756032,0.3751230343
```

dimeprodB
dimeprod for comparison with complex
M062X/6-31+G**
E(RM062X) = -1032.28213067

Zero-point correction= 0.254421 (Hartree/Particle)
Thermal correction to Energy= 0.270406
Thermal correction to Enthalpy= 0.271350
Thermal correction to Gibbs Free Energy= 0.211238
Sum of electronic and ZPE= -1032.027710
Sum of electronic and thermal Energies= -1032.011725
Sum of electronic and thermal Enthalpies= -1032.010781
Sum of electronic and thermal Free Energies= -1032.070892

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.682 60.630 126.516
```

```
C,0,-0.0462305334,-0.0009551293,-0.4665722965
C,0,-0.5680550701,-1.1853851468,-0.0991092843
```

S,0,0.6315084117,-2.4828317995,-0.2461192285
C,0,1.816628897,-1.3515536683,-0.9342562376
N,0,1.2921473905,-0.0646298499,-0.8917140111
C,0,-0.7473329903,1.3228136037,-0.4755035109
C,0,-1.932960767,-1.5319365813,0.4023542067
C,0,2.9942782648,-1.703961924,-1.5234465713
C,0,2.1632468523,1.1089399436,-0.8877688693
H,0,1.672914877,1.9133629641,-0.3415064524
H,0,3.0958854583,0.8603145103,-0.375839923
H,0,2.3989850338,1.4448603224,-1.8985604269
C,0,3.5906752181,-3.041471182,-1.5297032253
O,0,3.5859046649,-0.7566300016,-2.3532778538
C,0,4.4035841542,-3.4276418398,-2.6141219198
C,0,4.9822478106,-4.6920860983,-2.6617420969
C,0,4.772040334,-5.6077134418,-1.6291090721
C,0,3.986006871,-5.232001289,-0.5392849473
C,0,3.4108498324,-3.9649937446,-0.4828706652
H,0,4.5653829334,-2.7307746445,-3.43000886
H,0,5.5975653907,-4.965576147,-3.5138589343
H,0,5.2222849963,-6.5944800948,-1.6682009467
H,0,3.8321087767,-5.9235295921,0.2838534937
H,0,2.8503888949,-3.6816708576,0.4024008972
H,0,4.5212138066,-0.6636875528,-2.1258313026
H,0,-1.8754141839,-2.0176424501,1.3824049425
H,0,-2.5454565476,-0.6353742693,0.5110091083
H,0,-2.4492117902,-2.2180092192,-0.2771107472
H,0,-0.5628422735,1.8497921665,-1.4162683052
H,0,-1.8226235644,1.1815182492,-0.3702173825
H,0,-0.4123991486,1.9669777635,0.3434334224

dimeprodC
dime prod new conf based on best ts
M062X/6-31+G**
E(RM062X) = -1032.28264308

Zero-point correction= 0.254363 (Hartree/Particle)
Thermal correction to Energy= 0.270344
Thermal correction to Enthalpy= 0.271288
Thermal correction to Gibbs Free Energy= 0.211469
Sum of electronic and ZPE= -1032.028280
Sum of electronic and thermal Energies= -1032.012299
Sum of electronic and thermal Enthalpies= -1032.011355
Sum of electronic and thermal Free Energies= -1032.071174

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.643 60.650 125.900
```

```
 C,0,4.1614584451,-0.681969122,-0.4969586624
 C,0,4.3549728979,0.6429682395,-0.3635902707
 S,0,2.8258700802,1.4918146156,-0.083205408
 C,0,1.9453436957,-0.0468253051,-0.0916573733
 N,0,2.81418258,-1.0859272257,-0.3912623759
 C,0,5.2054737491,-1.7306401017,-0.7298971782
 C,0,5.6200970511,1.4387656787,-0.4129259233
 C,0,0.6077010991,-0.0902198069,0.1525877244
 C,0,2.3402707651,-2.2963348285,-1.0551565845
 H,0,3.0503848107,-2.5886690583,-1.8285894091
 H,0,2.2079722605,-3.1289121741,-0.3582950843
 H,0,1.3769135909,-2.0827195026,-1.524619768
 C,0,-0.188722686,-1.2498734683,0.5603582093
 O,0,-0.056048077,1.1375902463,0.2072543967
 C,0,0.3749352833,-2.3110636581,1.2917202401
 C,0,-0.4046693302,-3.3878702189,1.7057681617
 C,0,-1.7696928883,-3.4240800952,1.4168101762
 C,0,-2.3480202344,-2.3611127209,0.719491587
 C,0,-1.5707260839,-1.2850782696,0.3004007733
 H,0,1.4274094715,-2.2732014473,1.5595710164
 H,0,0.0542037547,-4.1934448406,2.2715072403
 H,0,-2.3778077731,-4.262126271,1.7422761636
 H,0,-3.4116912907,-2.3713737643,0.4999955222
 H,0,-2.0280341219,-0.4593689774,-0.236049978
 H,0,-0.1224558664,1.5179261262,-0.6791787977
 H,0,5.8080372663,1.951743232,0.5357508907
 H,0,6.4747846282,0.7957198462,-0.628978009
 H,0,5.5671095421,2.2012475373,-1.1970666204
 H,0,5.208411221,-2.0818199731,-1.7664844395
 H,0,6.1969177661,-1.3356660459,-0.5091717749
 H,0,5.0296673934,-2.5945916465,-0.0821754449
```

pyridinium
pyridinium
M062X/6-31+G**
E(RM062X) = -248.634682320

Zero-point correction= 0.103955 (Hartree/Particle)
Thermal correction to Energy= 0.108306
Thermal correction to Enthalpy= 0.109251

```
Thermal correction to Gibbs Free Energy= 0.076471
Sum of electronic and ZPE= -248.530727
Sum of electronic and thermal Energies= -248.526376
Sum of electronic and thermal Enthalpies= -248.525432
Sum of electronic and thermal Free Energies= -248.558212

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.963 16.692 68.991

 N,0,0.070037623,0.,0.0404360757
 C,0,0.0297615956,0.,1.3843467048
 C,0,1.2142516593,0.,2.0963282746
 C,0,2.4212454862,0.,1.3979079706
 C,0,2.42259907,0.,0.0034101437
 C,0,1.2137597657,0.,-0.6664000637
 H,0,-0.9500839899,0.,1.841894416
 H,0,1.1841436087,0.,3.1781112305
 H,0,3.3602591769,0.,1.9400500274
 H,0,3.3443963321,0.,-0.5635547876
 H,0,1.1200841124,0.,-1.7437458929
 H,0,-0.8110782656,0.,-0.4682844013
```

```
pyridiniumTSA1
 kluger ts with pyridinium top left from A1
M062X/6-31+G**
E(RM062X) = -1469.44239084

Zero-point correction= 0.372541 (Hartree/Particle)
Thermal correction to Energy= 0.397438
Thermal correction to Enthalpy= 0.398383
Thermal correction to Gibbs Free Energy= 0.315401
Sum of electronic and ZPE= -1469.069850
Sum of electronic and thermal Energies= -1469.044952
Sum of electronic and thermal Enthalpies= -1469.044008
Sum of electronic and thermal Free Energies= -1469.126989

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.396 92.032 174.648

 C,0,-4.1248293868,-0.3122642039,0.1124623457
 C,0,-3.9074865453,0.73952914,-0.7025589459
 S,0,-2.2275901005,1.2443010651,-0.6258765339
```

```
C,0,-1.8527661034,0.0066215524,0.5471737695
N,0,-2.9686187874,-0.7390814369,0.7928126768
C,0,-5.4257810679,-1.0140710245,0.3452315416
C,0,-4.8462287964,1.4780525009,-1.6031447171
C,0,-0.5904291043,-0.1686770554,1.1219605028
C,0,-2.936568788,-1.991225572,1.5528229167
H,0,-3.8322304585,-2.5602605503,1.3182662803
H,0,-2.0654050879,-2.5749801413,1.2514254008
H,0,-2.8849248266,-1.8034216059,2.6243692672
C,0,0.5270436115,0.7774360179,0.9065592656
O,0,-0.5797614997,-0.8156083944,2.3543784501
C,0,0.0991231946,-1.8843547331,-0.2989675662
C,0,1.3058712431,1.1690917335,2.0110435989
C,0,2.3474094379,2.0825941873,1.8675801347
C,0,2.6530509462,2.6190875924,0.6162447281
C,0,1.915545041,2.208767942,-0.4949362236
C,0,0.8714541085,1.2966259577,-0.3566829771
H,0,1.0727780563,0.7619554719,2.9884748149
H,0,2.9205326801,2.3788599141,2.7414553265
H,0,3.4626632757,3.3341645641,0.5054701289
H,0,2.1565868655,2.5937091131,-1.4820066286
H,0,0.3411303923,0.9699260731,-1.2452148901
H,0,0.0133673047,-1.5818483143,2.2883464891
O,0,0.5327426406,-2.5808499001,0.5588553549
O,0,-0.1512728429,-1.5394954561,-1.3983830745
H,0,-4.471078824,1.4866260639,-2.6308784179
H,0,-5.8277311891,1.0027172196,-1.6096269806
H,0,-4.9707280982,2.5164984668,-1.2820606597
H,0,-5.6420575481,-1.0906856083,1.4145507763
H,0,-6.2349872204,-0.4544161983,-0.1219486844
H,0,-5.4254852175,-2.022877172,-0.0782415715
N,0,4.7961418721,0.4599739857,-0.7115587698
C,0,4.5093531372,0.1580915062,-1.9898328317
C,0,3.6704866478,-0.9059810911,-2.260764833
C,0,3.1435202938,-1.6358000871,-1.1958106103
C,0,3.4432315473,-1.2767957684,0.1182168565
C,0,4.2897734367,-0.2067179672,0.3401400508
H,0,4.9677537675,0.7774141767,-2.7496365181
H,0,3.4443432821,-1.1585210405,-3.2886605763
H,0,2.5055369155,-2.4909009915,-1.3937187485
H,0,3.0331132966,-1.818418949,0.9618324378
H,0,4.584733471,0.1376386562,1.3225972891
H,0,5.4197950272,1.2432103611,-0.5303196452
```

pyridiniumTSC1
kluger ts with pyridinium top left from C1
M062X/6-31+G**
E(RM062X) = -1469.44371711

Zero-point correction= 0.372370 (Hartree/Particle)
Thermal correction to Energy= 0.397222
Thermal correction to Enthalpy= 0.398166
Thermal correction to Gibbs Free Energy= 0.316460
Sum of electronic and ZPE= -1469.071348
Sum of electronic and thermal Energies= -1469.046495
Sum of electronic and thermal Enthalpies= -1469.045551
Sum of electronic and thermal Free Energies= -1469.127258

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.261 92.093 171.967
```

```
 C,0,-3.8827866872,-0.8154433645,0.0752685011
 C,0,-3.9410327068,0.2317570582,-0.7721248901
 S,0,-2.4222958035,1.110714068,-0.7740565288
 C,0,-1.7319772195,0.0279877239,0.4077017744
 N,0,-2.6360492917,-0.9443160665,0.716067571
 C,0,-4.9778668537,-1.7883532708,0.3800870284
 C,0,-5.0529930278,0.7038176537,-1.654489885
 C,0,-0.4406205605,0.1625013303,0.9328027931
 C,0,-2.2897578192,-2.1331167124,1.5001385502
 H,0,-3.03630283,-2.9002860267,1.3124396647
 H,0,-1.3176518421,-2.5071397922,1.1757993449
 H,0,-2.2485012544,-1.9071440831,2.5645000571
 C,0,0.4134002389,1.3403904085,0.6561181606
 O,0,-0.2429943696,-0.420494132,2.1810748231
 C,0,0.5918202048,-1.3769372663,-0.4541189424
 C,0,1.1188815388,1.931541948,1.7212579424
 C,0,1.932415122,3.0432686075,1.5157640671
 C,0,2.0772857293,3.5902361971,0.239347371
 C,0,1.4045507528,2.9985248276,-0.8305899394
 C,0,0.588385835,1.8868356939,-0.6294971516
 H,0,1.0137987949,1.5133674646,2.7159697282
 H,0,2.4552695515,3.4849418652,2.3589946627
 H,0,2.7126146341,4.4552380312,0.0785770875
 H,0,1.5241370817,3.3947074574,-1.8346850822
 H,0,0.1193340674,1.4203511585,-1.4895230709
 H,0,0.5056170309,-1.0354719144,2.1099274552
```

O,0,1.1809522041,-1.9487689466,0.4048739796
O,0,0.2589876421,-1.1240507377,-1.5576447183
H,0,-4.7280786496,0.7436902898,-2.6985168578
H,0,-5.9061403168,0.0270012198,-1.5958918559
H,0,-5.3891872987,1.7049252845,-1.3687815364
H,0,-5.1258089141,-1.8832305005,1.4595606892
H,0,-5.9131324073,-1.441175372,-0.0570177058
H,0,-4.7640943,-2.7816675052,-0.0258710608
C,0,3.5849897544,0.284496492,-0.1808434298
C,0,3.3621373661,-0.1409037218,-1.4899267278
C,0,3.5962253183,-1.470321994,-1.842299492
C,0,4.0552728688,-2.3472864943,-0.8775022963
N,0,4.2663687227,-1.8997917517,0.3723996019
C,0,4.0439284962,-0.6289746344,0.7496640286
H,0,2.9944009335,0.5622723063,-2.2305371182
H,0,3.4243042062,-1.829629917,-2.8489390888
H,0,4.2617934915,-3.3932903504,-1.0607941432
H,0,4.602543738,-2.5590775081,1.0703174606
H,0,4.2413010796,-0.3873486866,1.7859964319
H,0,3.4009057491,1.3093336632,0.1213827471

pyridiniumTSD1
kluger ts with pyridinium bottom right back D1
M062X/6-31+G**
E(RM062X) = -1469.44756142

Zero-point correction= 0.372876 (Hartree/Particle)
Thermal correction to Energy= 0.397411
Thermal correction to Enthalpy= 0.398355
Thermal correction to Gibbs Free Energy= 0.317882
Sum of electronic and ZPE= -1469.074685
Sum of electronic and thermal Energies= -1469.050150
Sum of electronic and thermal Enthalpies= -1469.049206
Sum of electronic and thermal Free Energies= -1469.129680

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.379 91.586 169.371
```

C,0,2.6535917263,-1.1201632921,0.1558110177
C,0,2.4646224901,-0.3568364452,1.2515615536
S,0,0.7639693914,0.0110721568,1.4610485406
C,0,0.3403252224,-0.8580682811,0.0094868986
N,0,1.4560506805,-1.4328721506,-0.5152848756

```
C,0,3.9586204314,-1.6104400174,-0.3867110264
C,0,3.4515942551,0.1903524168,2.2327130346
C,0,-0.9581575757,-0.920453328,-0.5330695586
C,0,1.4221028385,-2.4283984868,-1.5944802131
H,0,2.3409464593,-3.0074231207,-1.5523209334
H,0,0.5792901378,-3.1007147714,-1.4351629544
H,0,1.3250637812,-1.9516615759,-2.5691083973
C,0,-2.0574434067,-0.0505373398,-0.0539632631
O,0,-0.9895562571,-1.1815373718,-1.9008244973
C,0,-1.6247303737,-2.8697978547,0.3478628534
C,0,-2.2916255988,0.2279681789,1.3052335103
C,0,-3.309726948,1.0973894736,1.6928413066
C,0,-4.1357812908,1.6953433617,0.7418873881
C,0,-3.9439440104,1.3922565972,-0.6067800766
C,0,-2.9249485907,0.5287957592,-1.0006099924
H,0,-1.7075856078,-0.2646413322,2.0744607655
H,0,-3.4636282163,1.295187063,2.7493732138
H,0,-4.9267094704,2.3724114133,1.0476839458
H,0,-4.5885523777,1.8342971712,-1.3606944296
H,0,-2.7807925521,0.3091526862,-2.0526231454
H,0,-1.5242073534,-1.9810846716,-2.0415567317
O,0,-1.9618360928,-3.39572307,-0.6660524901
O,0,-1.4696775542,-2.7992050019,1.5185739111
H,0,3.1935255861,-0.1095683706,3.2524563901
H,0,4.4546478049,-0.179362118,2.017204363
H,0,3.4756531648,1.2847107707,2.2009702421
H,0,4.0460833928,-1.384343578,-1.4534968759
H,0,4.7809758243,-1.1168796359,0.1294931374
H,0,4.0757878231,-2.6898413843,-0.2524760067
C,0,-0.2934949735,2.6463392175,-0.8146410753
C,0,0.3136170443,1.7723038913,-1.6992754102
C,0,1.7020496435,1.6467782708,-1.6774604314
C,0,2.4568908919,2.3828785616,-0.7628691944
C,0,1.807639391,3.2451514918,0.1003191702
N,0,0.4676705061,3.3520992262,0.0391413238
H,0,-0.2991236314,1.1863045595,-2.3758346899
H,0,2.1962092331,0.968959157,-2.366718527
H,0,3.5352398443,2.2932132726,-0.71536715
H,0,2.310663162,3.8574570095,0.8373768649
H,0,0.0043295046,3.9916237938,0.6810877322
H,0,-1.3648071608,2.7992340122,-0.7566941806
```

pyridiniumTSI3
kluger ts with pyridinium bottom right front I3

```
M062X/6-31+G**
E(RM062X) = -1469.44840092

Zero-point correction= 0.372715 (Hartree/Particle)
Thermal correction to Energy= 0.397274
Thermal correction to Enthalpy= 0.398218
Thermal correction to Gibbs Free Energy= 0.317350
Sum of electronic and ZPE= -1469.075686
Sum of electronic and thermal Energies= -1469.051127
Sum of electronic and thermal Enthalpies= -1469.050183
Sum of electronic and thermal Free Energies= -1469.131051

     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.293 91.567 170.200

 C,0,2.6096890886,-1.0007149692,0.3006263953
 C,0,2.2875721285,-0.6755188553,1.5708343926
 S,0,0.5622482448,-0.435501545,1.7263529182
 C,0,0.3136000536,-0.7142964644,0.0259319793
 N,0,1.4933310598,-1.0661381106,-0.551900238
 C,0,3.9775897163,-1.2662263132,-0.2431081944
 C,0,3.1595970104,-0.4923967814,2.7720421922
 C,0,-0.9248261926,-0.5780127463,-0.6411666564
 C,0,1.5988999109,-1.6286485044,-1.9037797504
 H,0,2.5135860843,-2.2135522175,-1.9574453369
 H,0,0.7521213437,-2.2897940911,-2.0843072363
 H,0,1.6132160106,-0.8447093955,-2.6618232367
 C,0,-2.1054529323,0.0499683763,-0.0012829809
 O,0,-0.7998841408,-0.3028031403,-2.0035881076
 C,0,-1.6070778487,-2.6814201596,-0.6292530274
 C,0,-2.4711865222,-0.1742209853,1.3391062965
 C,0,-3.5720013132,0.4701835983,1.8987558129
 C,0,-4.351864949,1.3407012837,1.1379274998
 C,0,-4.0318113371,1.5345484142,-0.2051483947
 C,0,-2.932100752,0.892795221,-0.7705086794
 H,0,-1.929769604,-0.8937249235,1.9425271996
 H,0,-3.8261945248,0.2765474295,2.9364284002
 H,0,-5.2060492334,1.8429821093,1.5799698907
 H,0,-4.6417758327,2.1864555458,-0.8230982554
 H,0,-2.722383753,1.0292104561,-1.8268822169
 H,0,-1.2676647148,-0.9992400919,-2.4962652337
 O,0,-1.8224775207,-2.7982921443,-1.7963460926
 O,0,-1.5792499518,-3.0598192582,0.4923849877
```

```
H,0,2.8167073159,-1.1174862796,3.6012829311
H,0,4.1894838203,-0.7698408466,2.5455196771
H,0,3.1498220683,0.5493989451,3.1077534126
H,0,4.1511539266,-0.7034978779,-1.1651876711
H,0,4.7284223328,-0.958738679,0.4837176947
H,0,4.129829561,-2.328180902,-0.457904128
N,0,0.0597597784,2.3077006774,-1.1682228306
C,0,0.1938444497,2.6756605798,0.1165705151
C,0,1.4576856838,2.7285092663,0.6755785109
C,0,2.5587575849,2.3932467084,-0.1124705182
C,0,2.3779688402,2.0320029192,-1.4491869098
C,0,1.0964681113,1.9901584538,-1.9640394597
H,0,-0.7201931895,2.8946901243,0.6564184011
H,0,1.5686425047,3.0105015165,1.7151706593
H,0,3.5567315987,2.4168838711,0.3130421062
H,0,3.2160924173,1.7759477297,-2.0856862163
H,0,0.8539194699,1.702329317,-2.9786605367
H,0,-0.8813031942,2.2259855928,-1.551721838
```

pyridiniumTSJ5
kluger ts with pyridinium top right J1
M062X/6-31+G**
E(RM062X) = -1469.44666004

```
Zero-point correction= 0.372750 (Hartree/Particle)
Thermal correction to Energy= 0.397229
Thermal correction to Enthalpy= 0.398173
Thermal correction to Gibbs Free Energy= 0.318115
Sum of electronic and ZPE= -1469.073910
Sum of electronic and thermal Energies= -1469.049431
Sum of electronic and thermal Enthalpies= -1469.048487
Sum of electronic and thermal Free Energies= -1469.128545

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.265 91.797 168.496

6 -1.790952 0.409419 -1.620772
6 -1.618464 -0.928344 -1.573580
16 -0.020379 -1.325328 -0.962402
6 0.402091 0.366203 -0.814915
7 -0.675662 1.131513 -1.158062
6 -2.986402 1.137602 -2.149329
6 -2.533403 -2.031043 -2.010515
```

6	1.666166	0.831268	-0.440391
6	-0.715645	2.584390	-0.973126
1	-1.756183	2.900352	-0.941784
1	-0.240463	2.841197	-0.025211
1	-0.193655	3.100166	-1.778531
6	2.815857	-0.072056	-0.203759
8	1.992982	2.091424	-0.930335
6	1.279309	1.332649	1.799881
6	2.714355	-1.277168	0.515805
6	3.830998	-2.083934	0.720833
6	5.080563	-1.705357	0.230502
6	5.199504	-0.501046	-0.463499
6	4.085350	0.306176	-0.676718
1	1.768795	-1.575378	0.957222
1	3.722862	-3.007697	1.281270
1	5.949254	-2.334516	0.396073
1	6.165994	-0.186108	-0.845694
1	4.188896	1.238085	-1.220984
1	2.309211	2.635300	-0.190556
8	1.860737	2.360519	1.796328
8	0.657330	0.431497	2.253509
1	-2.468287	-2.888045	-1.333605
1	-3.571753	-1.693330	-2.018649
1	-2.273780	-2.383137	-3.013743
1	-2.692129	1.844745	-2.930517
1	-3.686866	0.424713	-2.583456
1	-3.513698	1.693110	-1.368088
7	-1.992930	-0.545253	1.764795
6	-2.538734	0.681692	1.721877
6	-3.857829	0.827229	1.334283
6	-4.588890	-0.311421	0.995681
6	-3.991631	-1.569761	1.061808
6	-2.668762	-1.663691	1.453590
1	-1.901052	1.506754	2.014872
1	-4.297914	1.816137	1.301741
1	-5.623666	-0.218663	0.684064
1	-4.537718	-2.469956	0.809227
1	-2.122289	-2.596004	1.523697
1	-1.008631	-0.610663	2.031990

pyridiniumTSL1
kluger ts with pyridinium bottom right L1
M062X/6-31+G**
E(RM062X) = -1469.44737829

```
Zero-point correction= 0.372726 (Hartree/Particle)
Thermal correction to Energy= 0.397379
Thermal correction to Enthalpy= 0.398323
Thermal correction to Gibbs Free Energy= 0.316912
Sum of electronic and ZPE= -1469.074652
Sum of electronic and thermal Energies= -1469.049999
Sum of electronic and thermal Enthalpies= -1469.049055
Sum of electronic and thermal Free Energies= -1469.130467

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.359 91.654 171.345

 C,0,-2.6834709231,1.0514467808,0.2142618189
 C,0,-2.4782783158,0.2776936308,1.3008908248
 S,0,-0.77450375,-0.0907245192,1.480182641
 C,0,-0.3719810157,0.7981290513,0.03758002
 N,0,-1.49640042,1.3722934327,-0.4689214716
 C,0,-3.9966500246,1.5442727035,-0.3057153841
 C,0,-3.4465933275,-0.2436918139,2.3150592147
 C,0,0.9223621556,0.8835949637,-0.5161252446
 C,0,-1.4772242767,2.3821206658,-1.5347648717
 H,0,-2.3997189296,2.953889595,-1.4790582783
 H,0,-0.6384256253,3.0588671605,-1.3721888053
 H,0,-1.3826565758,1.9211820258,-2.5171779494
 C,0,2.054556774,0.0558073525,-0.035542312
 O,0,0.9351967703,1.1381482837,-1.8857722718
 C,0,1.5469577594,2.8405024612,0.3434870537
 C,0,2.2957596011,-0.2141026578,1.3238689824
 C,0,3.355939852,-1.0296642876,1.7153460159
 C,0,4.2172372862,-1.581367974,0.7676276336
 C,0,4.0165718384,-1.2851299872,-0.58106452
 C,0,2.9563408277,-0.4748073419,-0.9781820854
 H,0,1.6836428101,0.2454073529,2.0915177403
 H,0,3.5140507928,-1.2218053929,2.7723035199
 H,0,5.0405794493,-2.2178221703,1.0752417051
 H,0,4.6875181339,-1.6900000993,-1.3329110057
 H,0,2.8126348696,-0.2547386405,-2.0302449929
 H,0,1.4491770106,1.9501376311,-2.0349387094
 O,0,1.8879509148,3.3650065618,-0.6710743441
 O,0,1.3839951893,2.7874614433,1.5149467268
 H,0,-3.2186073883,0.1557572442,3.3078456639
```

```
H,0,-4.465465658,0.0500733927,2.0606803872
H,0,-3.4114691864,-1.335321669,2.3780603087
H,0,-4.0973749342,1.3262881779,-1.3731526144
H,0,-4.8109926648,1.0446218058,0.2172299629
H,0,-4.1144814439,2.6221082792,-0.1604025411
C,0,-0.0925202714,-1.8266833392,-1.7504187992
C,0,-1.4555296838,-1.5466747564,-1.8572357544
C,0,-2.3417313092,-2.2051884466,-1.0262653535
N,0,-1.8705695307,-3.1077633723,-0.1460318376
C,0,-0.5643319454,-3.4007520157,-0.0132191608
C,0,0.359127574,-2.760214565,-0.8170514616
H,0,-1.8311548728,-0.822847435,-2.5702711098
H,0,-3.4128873922,-2.048801428,-1.0359788801
H,0,-2.5363948819,-3.5901907454,0.4530118956
H,0,-0.3068761609,-4.1379724709,0.7361745263
H,0,1.4144290142,-2.9802199673,-0.7023592681
H,0,0.6159704102,-1.3014981787,-2.3837567251
```

pyridiniumTSO1
kluger ts with pyridinium in front
M062X/6-31+G**
E(RM062X) = -1469.44125158

```
Zero-point correction= 0.371781 (Hartree/Particle)
Thermal correction to Energy= 0.396788
Thermal correction to Enthalpy= 0.397733
Thermal correction to Gibbs Free Energy= 0.315537
Sum of electronic and ZPE= -1469.069471
Sum of electronic and thermal Energies= -1469.044463
Sum of electronic and thermal Enthalpies= -1469.043519
Sum of electronic and thermal Free Energies= -1469.125715

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 248.988 92.260 172.996
```

```
C,0,3.5083244091,-1.7877566624,-0.4328769851
C,0,4.1077871229,-0.5908885749,-0.2630269182
S,0,2.9089814595,0.6814004578,-0.0791924263
C,0,1.605841795,-0.463794429,-0.2074836688
N,0,2.1007818469,-1.7139274383,-0.3970884925
C,0,4.1731626163,-3.1079717336,-0.6599713587
C,0,5.5596387842,-0.2313895245,-0.2355783408
C,0,0.284451497,-0.0736884153,0.0045429143
```

C,0,1.2424739985,-2.8982346565,-0.3600206721
H,0,1.8662163957,-3.7810627882,-0.2494017141
H,0,0.5657249107,-2.8291983871,0.4948103803
H,0,0.6498716555,-2.9833633513,-1.2707929825
C,0,-0.0416117614,1.3916606562,0.0101767453
O,0,-0.7607960128,-0.8908928036,-0.4783946392
C,0,0.2157687133,-0.8384432406,2.2082025765
C,0,-0.2547381995,2.1165785347,1.1887297979
C,0,-0.6509702414,3.453662863,1.1447657485
C,0,-0.8329721857,4.089833245,-0.0826455559
C,0,-0.6059029394,3.3872481774,-1.266718875
C,0,-0.2122160891,2.0515900649,-1.217344329
H,0,-0.1200524751,1.6379603979,2.1549390054
H,0,-0.8227456118,3.9938535733,2.070680067
H,0,-1.148385589,5.1278869061,-0.1160574059
H,0,-0.7360454831,3.8777582066,-2.226352473
H,0,-0.0347540656,1.5102329528,-2.1445430946
H,0,-0.8161579827,-0.822628124,-1.4433222589
O,0,-0.9180324107,-1.1889814566,2.2121040771
O,0,1.2950566611,-0.655208,2.6493697625
H,0,5.8243045043,0.2451862443,0.7128825727
H,0,6.1806411283,-1.1205564679,-0.3494060945
H,0,5.809156352,0.4639724054,-1.0425529697
H,0,3.7835828069,-3.5919605146,-1.5602399619
H,0,5.2448083797,-2.9649850461,-0.7912179825
H,0,4.0256679543,-3.7855341384,0.1862269524
H,0,-2.9502057049,-0.0217300311,2.9196472299
C,0,-3.3047221359,0.651379931,2.1497888047
N,0,-2.9572205526,0.3486882026,0.888664972
C,0,-3.3040505415,1.0998193514,-0.1689739873
C,0,-4.0527253531,2.2459701762,0.0224020651
C,0,-4.4285494454,2.5934670136,1.3195057934
C,0,-4.0578710435,1.785514612,2.3938279839
H,0,-2.3319250658,-0.4497820262,0.7160755437
H,0,-2.9567232798,0.7609964496,-1.1366454002
H,0,-4.3246126777,2.855255413,-0.8300831333
H,0,-5.008037585,3.4939168201,1.4921768471
H,0,-4.3371095587,2.0323821557,3.4100658801

pyridiniumTSQ1
kluger ts with pyridinium in front better stack
M062X/6-31+G**
E(RM062X) = -1469.44434496

```
Zero-point correction= 0.371619 (Hartree/Particle)
Thermal correction to Energy= 0.396839
Thermal correction to Enthalpy= 0.397783
Thermal correction to Gibbs Free Energy= 0.312200
Sum of electronic and ZPE= -1469.072726
Sum of electronic and thermal Energies= -1469.047506
Sum of electronic and thermal Enthalpies= -1469.046562
Sum of electronic and thermal Free Energies= -1469.132145

     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.020 92.030 180.125

 C,0,4.0029339796,-0.670200184,-0.3951858303
 C,0,4.2315812919,0.6505663528,-0.2372631672
 S,0,2.7188531027,1.5280562509,-0.1211038921
 C,0,1.7962256779,0.0661724848,-0.292110293
 N,0,2.6331138719,-0.9946610383,-0.3987630512
 C,0,5.0197152737,-1.754435928,-0.5603925953
 C,0,5.5216570096,1.4021770748,-0.1452966335
 C,0,0.3908616533,0.0205901162,-0.2602634331
 C,0,2.1631797125,-2.3818222157,-0.3550996846
 H,0,2.9827106548,-3.0146159078,-0.0241952253
 H,0,1.3422327196,-2.4592800259,0.3583757618
 H,0,1.8135818769,-2.7134216284,-1.3331722138
 C,0,-0.431761893,1.2544791583,-0.2157015288
 O,0,-0.2160009644,-1.0624418414,-0.9250557207
 C,0,0.120726628,-0.7051163482,1.8594626113
 C,0,-0.2373275314,2.2485293085,0.7610480573
 C,0,-1.0546885642,3.3744700231,0.8096071732
 C,0,-2.0953713888,3.5359240076,-0.1067675922
 C,0,-2.3050543637,2.5560609118,-1.0751316399
 C,0,-1.4840922269,1.4309505947,-1.1300848616
 H,0,0.5405102009,2.1259612052,1.5088543097
 H,0,-0.8871151297,4.1211964419,1.5797357421
 H,0,-2.7368139505,4.409909114,-0.0607640307
 H,0,-3.1107238396,2.6633959564,-1.7950818546
 H,0,-1.6738753618,0.6814049126,-1.8923512717
 H,0,-0.1144298391,-0.9693096669,-1.8843556007
 O,0,-0.8688468513,-1.3427911077,1.6951819702
 O,0,1.0059202259,-0.2423444973,2.4943821826
 H,0,5.6191605513,1.8876876249,0.830171507
 H,0,6.3686465684,0.7270032248,-0.2717205505
 H,0,5.5841450542,2.1758156135,-0.9155648647
```

```
H,0,4.786791936,-2.3771358571,-1.4286734982
H,0,6.0053069615,-1.3171176926,-0.7139440977
H,0,5.0713353992,-2.39920193,0.3219335534
H,0,-1.9521455264,-1.3775940333,-0.2908552183
N,0,-2.9849243066,-1.373738513,-0.2353778972
C,0,-3.6757038299,-2.2126200159,-1.023317332
C,0,-3.5726675853,-0.5018119692,0.6003992567
C,0,-4.9525159079,-0.4506749423,0.6732061182
C,0,-5.7016639976,-1.3123823622,-0.1275677698
C,0,-5.058523604,-2.2035608668,-0.9855752582
H,0,-3.0939614649,-2.8666670506,-1.660464458
H,0,-2.909847944,0.1271754625,1.1824605423
H,0,-5.425737794,0.2522423497,1.3468242265
H,0,-6.785017876,-1.2882917971,-0.0836475368
H,0,-5.6146971506,-2.8816505426,-1.6199492599
```

pyridiniumTSS1
kluger ts with pyridinium in front better stack
M062X/6-31+G**
E(RM062X) = -1469.44439581

Zero-point correction= 0.371719 (Hartree/Particle)
Thermal correction to Energy= 0.396726
Thermal correction to Enthalpy= 0.397670
Thermal correction to Gibbs Free Energy= 0.313975
Sum of electronic and ZPE= -1469.072677
Sum of electronic and thermal Energies= -1469.047670
Sum of electronic and thermal Enthalpies= -1469.046726
Sum of electronic and thermal Free Energies= -1469.130421

```
   E     CV      S
 KCal/Mol Cal/Mol-K Cal/Mol-K
Total 248.949 92.310 176.152
```

```
6 3.997348 -0.585592 -0.408011
6 4.084344 0.754631 -0.280413
16 2.485969 1.470893 -0.185909
6 1.722710 -0.086132 -0.327905
7 2.669210 -1.055090 -0.412181
6 5.126145 -1.557997 -0.539991
6 5.286088 1.643464 -0.217039
6 0.333091 -0.267821 -0.277883
6 2.347315 -2.481484 -0.334493
1 3.234371 -3.020053 -0.011223
```

1	**1.553841**	**-2.633031**	**0.398143**
1	**2.014344**	**-2.868177**	**-1.298116**
6	**-0.591379**	**0.896344**	**-0.255630**
8	**-0.194364**	**-1.429418**	**-0.868275**
6	**0.263105**	**-0.967761**	**1.907915**
6	**-0.522195**	**1.875991**	**0.748996**
6	**-1.421851**	**2.939147**	**0.778067**
6	**-2.421110**	**3.045638**	**-0.189238**
6	**-2.504390**	**2.079333**	**-1.192368**
6	**-1.598635**	**1.021483**	**-1.227502**
1	**0.229578**	**1.795491**	**1.529192**
1	**-1.348289**	**3.678527**	**1.569629**
1	**-3.128225**	**3.868359**	**-0.159761**
1	**-3.276285**	**2.148153**	**-1.953574**
1	**-1.685471**	**0.278890**	**-2.015614**
1	**-0.104871**	**-1.387259**	**-1.831705**
8	**-0.678377**	**-1.688927**	**1.819129**
8	**1.148810**	**-0.423518**	**2.468933**
1	**5.274903**	**2.246225**	**0.695618**
1	**6.202554**	**1.052488**	**-0.217531**
1	**5.317695**	**2.326131**	**-1.071150**
1	**4.973989**	**-2.219322**	**-1.397652**
1	**6.061720**	**-1.021102**	**-0.690434**
1	**5.233471**	**-2.176556**	**0.356222**
1	**-2.829478**	**-0.516306**	**1.939673**
6	**-3.438185**	**-0.668561**	**1.057156**
7	**-2.923484**	**-1.467988**	**0.109944**
6	**-3.547095**	**-1.733163**	**-1.048560**
6	**-4.787882**	**-1.176052**	**-1.296791**
6	**-5.355576**	**-0.341670**	**-0.333777**
6	**-4.676639**	**-0.085820**	**0.856441**
1	**-1.970421**	**-1.824659**	**0.246212**
1	**-3.021315**	**-2.376329**	**-1.743252**
1	**-5.292284**	**-1.388852**	**-2.230602**
1	**-6.324242**	**0.112096**	**-0.512967**
1	**-5.090971**	**0.563575**	**1.616962**

pyridiniumTST1
kluger ts with pyridinium in from charges collected
M062X/6-31+G**
E(RM062X) = -1469.43906863

Zero-point correction= 0.372452 (Hartree/Particle)
Thermal correction to Energy= 0.397241

```
Thermal correction to Enthalpy= 0.398185
Thermal correction to Gibbs Free Energy= 0.316868
Sum of electronic and ZPE= -1469.066617
Sum of electronic and thermal Energies= -1469.041827
Sum of electronic and thermal Enthalpies= -1469.040883
Sum of electronic and thermal Free Energies= -1469.122201

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.273 92.216 171.147

 C,0,0.5977425016,2.795121148,0.2055873779
 C,0,1.6197748718,2.3293686709,-0.5431765404
 S,0,1.2636127532,0.7173486838,-1.135882409
 C,0,-0.2766908815,0.7085638171,-0.3290260861
 N,0,-0.4606002521,1.8735061743,0.3345981397
 C,0,0.4888742689,4.1238714443,0.8826618627
 C,0,2.9229361573,2.9702026146,-0.9013099357
 C,0,-1.0505688511,-0.4644368597,-0.3152961468
 C,0,-1.5952769553,2.1559411178,1.2134228155
 H,0,-1.2222240946,2.5866142389,2.1424638257
 H,0,-2.2919917119,2.8495148367,0.7351700104
 H,0,-2.1097648033,1.2289719622,1.4467105401
 C,0,-2.5307650677,-0.5045557251,-0.3879661675
 O,0,-0.4192613273,-1.5327592349,-0.9765296714
 C,0,-0.4811492448,-1.0860665457,1.7952492879
 C,0,-3.1970759251,-1.7072185601,-0.0989079042
 C,0,-4.5811285818,-1.7986332713,-0.2158623487
 C,0,-5.329442072,-0.6945599397,-0.6288049713
 C,0,-4.6761287164,0.4963352578,-0.945160846
 C,0,-3.289565873,0.5867430683,-0.8403531243
 H,0,-2.6159197932,-2.5657513091,0.2229351465
 H,0,-5.0784504257,-2.7351208816,0.018007818
 H,0,-6.4088518808,-0.7665652649,-0.7169401244
 H,0,-5.2436738297,1.3539266115,-1.2936127116
 H,0,-2.7892161736,1.5060683732,-1.1326349504
 H,0,-0.8647328021,-1.6904753524,-1.8223229698
 O,0,-0.5941454651,-2.2626330859,1.680776485
 O,0,-0.2188769591,-0.0960992918,2.3957518762
 H,0,3.0162642835,3.0972711758,-1.9839043742
 H,0,3.0129956472,3.9515177089,-0.4339744927
 H,0,3.7629079994,2.3561867906,-0.5617623624
 H,0,0.530344976,4.024872739,1.9715086884
 H,0,1.3092362032,4.7691331149,0.5711554685
```

```
 H,0,-0.4503555845,4.6198592785,0.6216955568
 H,0,1.1600882577,-3.0130106769,0.2670331709
 C,0,2.0935943247,-2.4712010524,0.1907456524
 C,0,2.7179183687,-1.8485710429,1.2569562286
 C,0,3.8982347191,-1.1416913239,1.03058448
 C,0,4.4375423595,-1.075103992,-0.2545163895
 C,0,3.7840622451,-1.7192336213,-1.2878967571
 N,0,2.6459585001,-2.3870381346,-1.0311664295
 H,0,2.2819298482,-1.9228280347,2.2458153263
 H,0,4.3980380514,-0.642600183,1.8535561265
 H,0,5.3514456804,-0.532298489,-0.4591341975
 H,0,4.1273833696,-1.7198155327,-2.3140752922
 H,0,2.1631758637,-2.8376183197,-1.8048944672

pyridiniumTSU1
 kluger ts with pyridinium upper left variation of C
M062X/6-31+G**
E(RM062X) = -1469.44447343

Zero-point correction= 0.371737 (Hartree/Particle)
Thermal correction to Energy= 0.396987
Thermal correction to Enthalpy= 0.397931
Thermal correction to Gibbs Free Energy= 0.313656
Sum of electronic and ZPE= -1469.072737
Sum of electronic and thermal Energies= -1469.047486
Sum of electronic and thermal Enthalpies= -1469.046542
Sum of electronic and thermal Free Energies= -1469.130817

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.113 92.349 177.372

 C,0,-4.3266052133,-0.1528405188,0.0749237402
 C,0,-4.1372598477,1.1591098988,-0.172480361
 S,0,-2.4420475783,1.5831872218,-0.0013258063
 C,0,-2.0203073201,-0.0565907376,0.4202381986
 N,0,-3.1359975475,-0.8375506407,0.3857463769
 C,0,-5.6260709841,-0.8935672065,0.0545371029
 C,0,-5.1153109504,2.2249567474,-0.5529191664
 C,0,-0.7216222712,-0.479164543,0.7072259196
 C,0,-3.0758798879,-2.2960291475,0.4813124523
 H,0,-4.0137669981,-2.7079865245,0.1188024311
 H,0,-2.2657982972,-2.6653748409,-0.1525640699
 H,0,-2.8962717951,-2.6191105832,1.5054347288
```

```
C,0,0.4275657016,0.4516020161,0.7731685947
O,0,-0.6179136465,-1.5970871197,1.5349349245

C,0,-0.2444089898,-1.4269431712,-1.3726921508
C,0,1.3385340663,0.3401415169,1.8373974776
C,0,2.4572898463,1.1686620851,1.9131733723
C,0,2.7023155125,2.1202830669,0.923903007
C,0,1.8114366987,2.2333772302,-0.1460709092
C,0,0.6939007601,1.407042849,-0.2265904738
H,0,1.1604531756,-0.4023157121,2.607971733
H,0,3.1439290038,1.0634495738,2.7484031686
H,0,3.5786626812,2.7585132812,0.97802275
H,0,1.9993450955,2.9539160656,-0.9366175947
H,0,0.0436666842,1.4845385793,-1.0936325129
H,0,0.0289083498,-2.2061745477,1.1444640891
O,0,0.6105306065,-2.1465418411,-0.9586784365
O,0,-0.9478139433,-0.9219568212,-2.1682786814
H,0,-4.8373262202,2.6837287305,-1.5065369111
H,0,-6.1174663815,1.8086108325,-0.6605174215
H,0,-5.1529677028,3.0157111266,0.2020958652
H,0,-5.7747463709,-1.4475888696,0.985714001
H,0,-6.4500182084,-0.189489719,-0.0528473093
H,0,-5.6774097424,-1.6006881297,-0.7788061428
C,0,5.4091417436,-0.6116663586,0.5173413309
C,0,5.7727250082,0.2411873849,-0.5249578555
C,0,4.8905992161,0.4693894702,-1.5795941615
C,0,3.6610114684,-0.1628416407,-1.5709028492
N,0,3.3444874135,-0.981086696,-0.5530181237
C,0,4.1681487536,-1.2186256634,0.4823820947
H,0,6.7419498102,0.7279001677,-0.514266204
H,0,5.1445771636,1.1271634297,-2.4007596971
H,0,2.9177765423,-0.0421611259,-2.3491133642
H,0,2.4273540324,-1.4362289847,-0.5650139009
H,0,3.8008226501,-1.8887085658,1.2492150419
H,0,6.0734149126,-0.8049025653,1.3499177028
```

pyridiniumTSV1
kluger ts with pyridinium trying bottom left again
M062X/6-31+G**
E(RM062X) = -1469.44417865

Zero-point correction= 0.372357 (Hartree/Particle)
Thermal correction to Energy= 0.397203
Thermal correction to Enthalpy= 0.398147

```
Thermal correction to Gibbs Free Energy= 0.315051
Sum of electronic and ZPE= -1469.071822
Sum of electronic and thermal Energies= -1469.046976
Sum of electronic and thermal Enthalpies= -1469.046032
Sum of electronic and thermal Free Energies= -1469.129128

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.248 91.354 174.890

 C,0,4.1230975728,-0.7183236203,-0.2046041105
 C,0,4.4149987299,0.5892344247,-0.0489284291
 S,0,2.965056801,1.5637418993,-0.1851255733
 C,0,1.96793097,0.1491519824,-0.3896432032
 N,0,2.7549051274,-0.9572379341,-0.4436779953
 C,0,5.0823215395,-1.865682882,-0.1551040954
 C,0,5.7270946905,1.2685244764,0.1858643413
 C,0,0.5599466342,0.1996014789,-0.3192250559
 C,0,2.2695191619,-2.2951811999,-0.8087013502
 H,0,3.118749982,-2.885347892,-1.1424575631
 H,0,1.7987096335,-2.786613711,0.0444656074
 H,0,1.5549736225,-2.2141267808,-1.6230950202
 C,0,-0.2558410266,1.3754291476,-0.7243691206
 O,0,-0.1257417429,-1.0168228469,-0.451475605
 C,0,0.4426858592,0.4236362066,1.9080418479
 C,0,0.210216116,2.4077152074,-1.5493599376
 C,0,-0.632492297,3.4510202162,-1.9362493202
 C,0,-1.961300645,3.47881548,-1.5210884565
 C,0,-2.4432912854,2.4485659036,-0.7094518506
 C,0,-1.6013584418,1.4157226136,-0.3145869359
 H,0,1.223840484,2.3894108371,-1.93548599
 H,0,-0.2467137202,4.2331424779,-2.5829094736
 H,0,-2.61648264,4.2871061217,-1.8293850281
 H,0,-3.4782473581,2.4502475381,-0.3814988154
 H,0,-1.9946720433,0.6161307376,0.3090277323
 H,0,-0.3732541222,-1.3266407233,0.4395421099
 O,0,-0.1250717852,-0.5985784025,2.1494093522
 O,0,0.9256644291,1.4653370815,2.1859457038
 H,0,5.7391527667,1.7816408576,1.1516082984
 H,0,6.5426729654,0.5449476505,0.1733616938
 H,0,5.9241335674,2.0109549111,-0.5931420878
 H,0,5.2237446132,-2.3189535244,-1.1409054299
 H,0,6.0530296671,-1.5179505058,0.1958185029
 H,0,4.7332001818,-2.6405192244,0.5329045469
```

H,0,-1.2298557248,-1.0152614319,-1.8400492502
N,0,-1.7053162408,-0.7247582887,-2.7147332753
C,0,-0.9519527097,-0.1581464857,-3.671101522
C,0,-3.0360978809,-0.8670653314,-2.8185481191
C,0,-3.6822165214,-0.4280452838,-3.9597177651
C,0,-2.929493886,0.1613360204,-4.9750935961
C,0,-1.5491711559,0.2991173757,-4.83140608
H,0,0.1110859671,-0.088512978,-3.4714813923
H,0,-3.5407108432,-1.3250543693,-1.9772782379
H,0,-4.7552728256,-0.5427853808,-4.0438936858
H,0,-3.4188217071,0.5157357463,-5.8758481612
H,0,-0.9410694793,0.7554274046,-5.6019132044

pyridiniumTSW1
kluger ts with pyridinium trying bottom left again rotated thiamin
M062X/6-31+G**
E(RM062X) = -1469.45059602

Zero-point correction= 0.372368 (Hartree/Particle)
Thermal correction to Energy= 0.397048
Thermal correction to Enthalpy= 0.397992
Thermal correction to Gibbs Free Energy= 0.315947
Sum of electronic and ZPE= -1469.078228
Sum of electronic and thermal Energies= -1469.053548
Sum of electronic and thermal Enthalpies= -1469.052604
Sum of electronic and thermal Free Energies= -1469.134649

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.151 91.445 172.679
```

C,0,4.316151467,-0.6628683039,-0.5253459019
C,0,4.511720408,0.6298671543,-0.193732491
S,0,2.9854558174,1.4115372348,0.1837270801
C,0,2.1057903888,-0.0596081913,-0.1281703578
N,0,2.9577615973,-1.042992014,-0.5064887506
C,0,5.3470258972,-1.6780013668,-0.9030641999
C,0,5.778080294,1.4223808491,-0.1174784698
C,0,0.7053434719,-0.0646405195,-0.0614835779
C,0,2.5506680045,-2.3825049373,-0.9351436695
H,0,3.0995951704,-2.6446629879,-1.8394193609
H,0,2.7560259176,-3.1173655175,-0.1517809168
H,0,1.4912685038,-2.3813997548,-1.1682717281
C,0,-0.1250631265,-1.2075054093,0.3881365893

```
O,0,0.1796613949,1.1807185539,0.3442351412
C,0,0.3909986415,0.1613787245,-2.3521754616
C,0,0.3716755277,-2.1951068228,1.2537804038
C,0,-0.4551417791,-3.2174072198,1.7192893175
C,0,-1.8001139792,-3.2565938055,1.3501850586
C,0,-2.3119969851,-2.2665622547,0.5081463575
C,0,-1.4827740112,-1.2557069858,0.0298510652
H,0,1.4058998418,-2.1489720811,1.584865294
H,0,-0.0512577718,-3.9703041505,2.3888820571
H,0,-2.4453723846,-4.0457408301,1.7221565227
H,0,-3.3586316156,-2.2833238343,0.2209756364
H,0,-1.8903464828,-0.4864337599,-0.6222511714
H,0,-0.1475890479,1.6523553637,-0.4431791443
O,0,-0.2284401561,1.1727751182,-2.303447898
O,0,0.9172327295,-0.7693879244,-2.8489831189
H,0,5.9420484795,1.806164512,0.8935778188
H,0,6.6358588469,0.8069583126,-0.3909241211
H,0,5.7442001082,2.2765724007,-0.8000947847
H,0,5.2710305429,-1.9535982283,-1.9592758839
H,0,6.3449486526,-1.2772276757,-0.7307850105
H,0,5.2393222591,-2.5874731642,-0.3052872241
H,0,-0.9050512503,1.1095653163,1.7231043141
N,0,-1.5784142983,1.1100430807,2.5168502279
C,0,-1.8109822155,-0.0381590975,3.1750035741
C,0,-2.1875728344,2.2658872311,2.8288340611
C,0,-3.0989086692,2.3024083964,3.8683083113
C,0,-3.3652401313,1.1273526829,4.5709597703
C,0,-2.7143048542,-0.0549037812,4.2223552918
H,0,-1.2585893142,-0.9101170104,2.8422138681
H,0,-1.9229347288,3.1291840078,2.2313581399
H,0,-3.5883162083,3.2350965456,4.1178334177
H,0,-4.0776338043,1.1336431284,5.3886789482
H,0,-2.9001683139,-0.9810939846,4.7510029758
```

pyridiniumTSX1
kluger ts reversed thiamin rotated pyr toward phenyl
M062X/6-31+G**
E(RM062X) = -1469.44543584

Zero-point correction= 0.372449 (Hartree/Particle)
Thermal correction to Energy= 0.397308
Thermal correction to Enthalpy= 0.398252
Thermal correction to Gibbs Free Energy= 0.314966
Sum of electronic and ZPE= -1469.072986

```
Sum of electronic and thermal Energies= -1469.048128
Sum of electronic and thermal Enthalpies= -1469.047183
Sum of electronic and thermal Free Energies= -1469.130470

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.315 91.657 175.292

 C,0,4.3541311886,-0.7417861691,-0.5033798696
 C,0,4.5968404257,0.573685141,-0.3307609963
 S,0,3.0969235923,1.4567993825,-0.1017551416
 C,0,2.1623200897,-0.0057042834,-0.2520423599
 N,0,2.9806070069,-1.0626332911,-0.4786527204
 C,0,5.3498258256,-1.8368574482,-0.717246873
 C,0,5.8951321364,1.3170052811,-0.3153465938
 C,0,0.7609104867,0.066185161,-0.2226675057
 C,0,2.5310590107,-2.4275475308,-0.7600231025
 H,0,3.084559704,-2.8103995429,-1.6175387943
 H,0,2.6987011118,-3.0754604631,0.1048149217
 H,0,1.476300322,-2.4170531897,-1.0126505039
 C,0,-0.1289466729,-0.9816944853,0.3300004112
 O,0,0.2853957103,1.3654092832,0.0078971034
 C,0,0.5205635335,-0.0027102687,-2.5242018322
 C,0,0.3062651717,-1.90744897,1.2951445884
 C,0,-0.5751363799,-2.847864568,1.8349085034
 C,0,-1.91437151,-2.8627918881,1.4426816063
 C,0,-2.3663124113,-1.9271763286,0.5078490588
 C,0,-1.4853842439,-0.9999679034,-0.0409152017
 H,0,1.3356776384,-1.8798257356,1.6418838838
 H,0,-0.2154872519,-3.5534194544,2.57732115
 H,0,-2.6003765229,-3.5873207154,1.8688429887
 H,0,-3.408728183,-1.9204007302,0.2056493499
 H,0,-1.8483390316,-0.271441117,-0.7617639864
 H,0,0.0081607798,1.7465363753,-0.8428639093
 O,0,-0.0627361192,1.0257494686,-2.6338714764
 O,0,1.0244854854,-1.0065610194,-2.8870520785
 H,0,6.0452536917,1.8273674483,0.6405134336
 H,0,6.7323398467,0.6357338208,-0.4722404678
 H,0,5.9211444492,2.0717279889,-1.1068624063
 H,0,5.2952056305,-2.2372800733,-1.7340428257
 H,0,6.3586078152,-1.4587183958,-0.5573686259
 H,0,5.1825441199,-2.6605534535,-0.0175889181
 H,0,-1.0923618959,1.5184722244,1.6994078065
 C,0,-1.7483772631,1.3225784061,2.5441175696
```

```
N,0,-1.6669611587,0.0963667501,3.0889330067
C,0,-2.6442398285,2.233625815,3.0749872101
C,0,-3.4353502031,1.8529361752,4.1580807331
C,0,-3.3193357584,0.5700356573,4.6939649021
C,0,-2.411196496,-0.3073037388,4.1323668642
H,0,-1.004077781,-0.5671624853,2.6791219644
H,0,-2.7155837453,3.2235697633,2.6431184151
H,0,-4.1424970838,2.5548427376,4.586300296
H,0,-3.9226186024,0.2497394462,5.5335669379
H,0,-2.2526056298,-1.321060077,4.4786234844
```

pyridiniumTSY1
kluger ts reversed thiamin bottom right
M062X/6-31+G**
E(RM062X) = -1469.44408514

```
Zero-point correction= 0.371649 (Hartree/Particle)
Thermal correction to Energy= 0.396708
Thermal correction to Enthalpy= 0.397653
Thermal correction to Gibbs Free Energy= 0.313997
Sum of electronic and ZPE= -1469.072436
Sum of electronic and thermal Energies= -1469.047377
Sum of electronic and thermal Enthalpies= -1469.046433
Sum of electronic and thermal Free Energies= -1469.130088

     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 248.938 92.106 176.068
```

```
C,0,4.3214625304,-0.7254559774,-0.8533539812
C,0,4.5098781789,0.5930093289,-0.6350222742
S,0,2.9862638075,1.3877394831,-0.2816641435
C,0,2.1135839547,-0.1179209505,-0.4381307949
N,0,2.9685818537,-1.1184549339,-0.7728506698
C,0,5.3578796193,-1.7631967877,-1.1432317421
C,0,5.7685378674,1.4000602533,-0.6575483242
C,0,0.7183947849,-0.1020014025,-0.2813672257
C,0,2.5764745169,-2.4704100004,-1.1839426693
H,0,3.0182272962,-2.6838575365,-2.1581190756
H,0,2.9214591711,-3.20721484,-0.4536415228
H,0,1.4984949682,-2.5232111877,-1.2808377232
C,0,-0.1158986913,-1.2178523895,0.2308399046
O,0,0.2432288073,1.1588533563,0.0968037167
C,0,0.2826963165,-0.0327154587,-2.5050231947
```

```
C,0,0.4019943403,-2.281629409,0.9838648288
C,0,-0.4306373844,-3.2791026864,1.489604108
C,0,-1.8047164789,-3.2251436271,1.2660444806
C,0,-2.3385725108,-2.1593738246,0.5376035401
C,0,-1.5051086102,-1.1693203894,0.0276996833
H,0,1.4680745154,-2.3341199246,1.1863473557
H,0,-0.0015406164,-4.0911036171,2.0684161767
H,0,-2.4546384151,-3.9995796758,1.660366241
H,0,-3.4087676936,-2.1018332472,0.3637898244
H,0,-1.9313478055,-0.3419538442,-0.5338484327
H,0,-0.1205687479,1.5972849171,-0.691359441
O,0,-0.2802993757,1.0150361474,-2.5282816234
O,0,0.7119374036,-1.0299272009,-2.9749722406
H,0,5.9287401803,1.9116615848,0.2970601406
H,0,6.6337611881,0.7644469001,-0.8498473152
H,0,5.7266629847,2.163824118,-1.4397227465
H,0,5.2465635205,-2.1769291386,-2.1495834209
H,0,6.3528935331,-1.3273986935,-1.0655267253
H,0,5.2920250378,-2.5878838331,-0.4267458052
H,0,1.5830894081,1.6928078783,3.4532356441
N,0,2.4509233549,1.2161386908,3.2174634725
C,0,3.5961151287,1.9190531167,3.2540798292
C,0,2.3914435966,-0.0824017499,2.872672613
C,0,3.557248192,-0.7487122355,2.5435380227
C,0,4.7662335883,-0.0532922558,2.5704804803
C,0,4.7864715965,1.2935357627,2.9331507535
H,0,3.5190443613,2.9589497179,3.544087227
H,0,1.40937502,-0.5411565686,2.876657848
H,0,3.5204122786,-1.7983567897,2.2765905281
H,0,5.6895211869,-0.5620007953,2.312159214
H,0,5.7095152409,1.8580217154,2.9717904593
```

pyridiniumTSZ1
kluger ts reversed thiamin with pyr right front OH twisted
M062X/6-31+G**
E(RM062X) = -1469.44638219

Zero-point correction= 0.371824 (Hartree/Particle)
Thermal correction to Energy= 0.396856
Thermal correction to Enthalpy= 0.397800
Thermal correction to Gibbs Free Energy= 0.313925
Sum of electronic and ZPE= -1469.074558
Sum of electronic and thermal Energies= -1469.049526
Sum of electronic and thermal Enthalpies= -1469.048582

Sum of electronic and thermal Free Energies= -1469.132457

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.031 92.150 176.531

C,0,4.5248285866,-1.0623202562,-0.6345593804
C,0,4.9620538782,0.0517467879,-0.0126136696
S,0,3.6235871806,0.9046968309,0.7419112802
C,0,2.4861636068,-0.289853118,0.1768289301
N,0,3.1293867599,-1.2441210286,-0.5409083979
C,0,5.3367763,-2.068465776,-1.3858262673
C,0,6.3443408043,0.6113397153,0.10284088
C,0,1.1159504017,-0.1010053239,0.3922111103
C,0,2.4733957685,-2.3689193999,-1.2093674763
H,0,2.903661128,-2.4871179437,-2.203721798
H,0,2.6081669818,-3.2905262942,-0.6360133247
H,0,1.4150694049,-2.1572808223,-1.3192579998
C,0,0.1166623413,-1.1764329245,0.6043035448
O,0,0.8378756438,1.0814170195,1.107656457
C,0,0.6993182563,0.7282886536,-1.7148056588
C,0,0.4729952718,-2.4072313166,1.1750223354
C,0,-0.490016397,-3.3866912014,1.4123326068
C,0,-1.8288637942,-3.1412696918,1.1094513277
C,0,-2.199711661,-1.9070847689,0.5715974957
C,0,-1.236671074,-0.9334830579,0.321936083
H,0,1.5095654095,-2.5929612803,1.4450703511
H,0,-0.1944895175,-4.3350898033,1.8501503629
H,0,-2.5796645446,-3.9016785996,1.2989781079
H,0,-3.240921854,-1.7052174758,0.3398325977
H,0,-1.5272555008,0.0256389333,-0.0989887433
H,0,0.5765731698,0.8588173127,2.0140854317
O,0,0.1237059583,1.7173607829,-1.3991211786
O,0,1.1558958803,-0.0588970799,-2.4678594061
H,0,6.650848591,0.6911991237,1.1499038676
H,0,7.0624265316,-0.0266144179,-0.4136826883
H,0,6.3994500881,1.6100462665,-0.3404689704
H,0,5.1185907927,-2.0393080417,-2.457654311
H,0,6.3985617299,-1.8658645641,-1.2522580651
H,0,5.1369437214,-3.0815730936,-1.0256634342
H,0,0.6387679253,2.7793856476,0.3242612134
N,0,0.8463948526,3.7861770587,0.41262842
C,0,1.5791754726,4.176338305,1.4672701206
C,0,0.383798055,4.6368622145,-0.5167312382

```
 C,0,0.659873931,5.9872812464,-0.400109519
 C,0,1.4177429111,6.4288705246,0.6839414099
 C,0,1.8843573572,5.5155065017,1.6291374233
 H,0,1.8950262788,3.3928834115,2.1455993879
 H,0,-0.1906152636,4.1990771527,-1.3229754837
 H,0,0.2867727514,6.6745710975,-1.1484084372
 H,0,1.6452772693,7.4837312265,0.792031462
 H,0,2.4748776151,5.8312394671,2.479612241
```

pyridiniumTSAA1
kluger ts reversed thiamin with pyr upper right
M062X/6-31+G**
E(RM062X) = -1469.44168340

Zero-point correction= 0.372248 (Hartree/Particle)
Thermal correction to Energy= 0.397188
Thermal correction to Enthalpy= 0.398133
Thermal correction to Gibbs Free Energy= 0.315320
Sum of electronic and ZPE= -1469.069435
Sum of electronic and thermal Energies= -1469.044495
Sum of electronic and thermal Enthalpies= -1469.043551
Sum of electronic and thermal Free Energies= -1469.126364

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.239 92.195 174.294
```

```
 C,0,4.2750199193,-1.1066798578,-0.5807734575
 C,0,4.522015117,0.2119108876,-0.4419800887
 S,0,3.0205910142,1.1168349377,-0.3162374343
 C,0,2.0761657443,-0.3567898008,-0.3994078004
 N,0,2.9020738734,-1.423537825,-0.5975941486
 C,0,5.2760800854,-2.208989203,-0.7162139856
 C,0,5.8289326114,0.9343261342,-0.3439877563
 C,0,0.6883250351,-0.2892071781,-0.2938325485
 C,0,2.4599604927,-2.8015356524,-0.8161119129
 H,0,2.9944634718,-3.2149478905,-1.6723243851
 H,0,2.6540796896,-3.4139215297,0.0691690526
 H,0,1.3984067503,-2.812093353,-1.0375791513
 C,0,-0.1743966495,-1.3327426314,0.3129143275
 O,0,0.2155398008,1.0154655321,-0.1116159693
 C,0,0.2683321663,-0.5157758879,-2.6136163053
 C,0,0.3038916859,-2.2085246432,1.2993798036
 C,0,-0.5395338699,-3.1463512284,1.8926538238
```

C,0,-1.8840696625,-3.2113861764,1.5288952254
C,0,-2.3801700313,-2.3243869326,0.5711359738
C,0,-1.5346234575,-1.3956388369,-0.0286768546
H,0,1.3405222444,-2.1407714802,1.6193208351
H,0,-0.1477566836,-3.8144645797,2.6536552415
H,0,-2.5420126674,-3.9383125748,1.9944846898
H,0,-3.4277765326,-2.359836545,0.2882126656
H,0,-1.9305381822,-0.7073030729,-0.771470203
H,0,-0.1436492769,1.3383510132,-0.9534634587
O,0,-0.3475424431,0.4899353443,-2.720066786
O,0,0.7912612243,-1.5200470513,-2.9398470894
H,0,6.0634260933,1.1833245123,0.6956961043
H,0,6.6427547453,0.3257113045,-0.7437555847
H,0,5.8020586311,1.8708120548,-0.9092411492
H,0,5.2041510445,-2.7009591236,-1.6918404886
H,0,6.2847683501,-1.8110420723,-0.6099691613
H,0,5.1290170024,-2.9716571425,0.0541203287
H,0,2.8580911686,3.089445943,-4.1327107925
N,0,3.4252155649,2.2551355553,-4.0038310876
C,0,2.8102566812,1.0580041785,-4.0138900768
C,0,4.7499815139,2.4033077943,-3.8330121144
C,0,5.5390421217,1.2815161387,-3.6605518334
C,0,4.9352762481,0.0247032234,-3.6529840784
C,0,3.5562935798,-0.0912388605,-3.8343950911
H,0,1.7401154248,1.0737757126,-4.1795794536
H,0,5.1333135942,3.4152945089,-3.8451586776
H,0,6.6074070355,1.3972989861,-3.5291497633
H,0,5.5413247447,-0.8648546861,-3.5162965516
H,0,3.0620989862,-1.0552919453,-3.8395678321

pyridiniumTSBB1
kluger ts reversed thiamin with pyr rotated toward thiamin
M062X/6-31+G**
E(RM062X) = -1469.45112468

Zero-point correction= 0.372039 (Hartree/Particle)
Thermal correction to Energy= 0.396889
Thermal correction to Enthalpy= 0.397833
Thermal correction to Gibbs Free Energy= 0.314784
Sum of electronic and ZPE= -1469.079085
Sum of electronic and thermal Energies= -1469.054236
Sum of electronic and thermal Enthalpies= -1469.053291
Sum of electronic and thermal Free Energies= -1469.136341

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 249.052 91.704 174.793

 C,0,4.6197887398,-1.0121195793,-0.9647719473
 C,0,5.1080167649,0.2267630684,-1.179549967
 S,0,3.852008727,1.4344333867,-0.961053708
 C,0,2.6762068463,0.2051521627,-0.5824970863
 N,0,3.2458464369,-1.0223923802,-0.6456751978
 C,0,5.3555172603,-2.311756638,-1.040269342
 C,0,6.4856941867,0.6653811572,-1.5634011493
 C,0,1.3378616352,0.5650490809,-0.3621765139
 C,0,2.5277324668,-2.287009586,-0.4730566894
 H,0,2.8406267301,-2.9778426473,-1.255846633
 H,0,2.7404737018,-2.7200500741,0.5082644892
 H,0,1.4616949733,-2.1137743664,-0.5748933147
 C,0,0.4142571324,-0.1194887007,0.5784129887
 O,0,1.1468038222,1.9618475667,-0.4035739612
 C,0,0.6353834163,0.0517560523,-2.4983408572
 C,0,0.8819846348,-0.8133540406,1.7061045214
 C,0,-0.0085973118,-1.3526956077,2.6316898976
 C,0,-1.3845690268,-1.1986117697,2.4558111225
 C,0,-1.8615892191,-0.4988685881,1.3464550589
 C,0,-0.9707141187,0.0349041532,0.4175650188
 H,0,1.9524274627,-0.9016611352,1.8785193414
 H,0,0.3748405171,-1.8738348207,3.5037239374
 H,0,-2.0778134677,-1.6112967802,3.1815955001
 H,0,-2.9296969308,-0.3677985035,1.2032141759
 H,0,-1.3511460461,0.5867504442,-0.4387223795
 H,0,0.741614967,2.1993232272,-1.2559898803
 O,0,0.2204003117,1.1298239254,-2.7745357977
 O,0,0.8830762084,-1.0899252169,-2.6640478752
 H,0,6.9199786164,1.3153421987,-0.7982213773
 H,0,7.1426178013,-0.1954423925,-1.6920798012
 H,0,6.4683031959,1.2206064765,-2.5058808845
 H,0,5.020051806,-2.913662722,-1.8900602455
 H,0,6.4228018624,-2.1287314305,-1.156762252
 H,0,5.2099691874,-2.8980987358,-0.1286808072
 H,0,0.7070995573,2.5810161616,1.2880699355
 N,0,0.8491150023,2.3754374718,2.2877124425
 C,0,2.1164371387,2.1962599007,2.6936078684
 C,0,-0.2145668458,2.1742011306,3.080013265
 C,0,-0.0185670745,1.7796643424,4.391307288
 C,0,1.2840874701,1.5922778654,4.8511013248
```

```
 C,0,2.3656824335,1.8037734111,3.9956061505
 H,0,2.8865092829,2.3636570732,1.9484268293
 H,0,-1.1893757468,2.324365906,2.6332739479
 H,0,-0.8750675295,1.6134088578,5.0322419699
 H,0,1.4563018349,1.2755383919,5.8740393308
 H,0,3.3863451868,1.6587163031,4.3258092628
```

pyridiniumTSB3
kluger ts with pyridinium ion
M052X/6-31+G**
E(RM052X+HF-M052X) = -1469.80668809

```
Zero-point correction= 0.370189 (Hartree/Particle)
Thermal correction to Energy= 0.395713
Thermal correction to Enthalpy= 0.396657
Thermal correction to Gibbs Free Energy= 0.310363
Sum of electronic and ZPE= -1469.436499
Sum of electronic and thermal Energies= -1469.410975
Sum of electronic and thermal Enthalpies= -1469.410031
Sum of electronic and thermal Free Energies= -1469.496325

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 248.314 92.372 181.621

6 -4.170351 -0.089929 -0.223730
6 -3.855447 1.055263 -0.859602
16 -2.163344 1.456849 -0.612142
6 -1.924195 0.048805 0.394964
7 -3.085231 -0.670043 0.455163
6 -5.512916 -0.750290 -0.174372
6 -4.698671 1.965306 -1.696073
6 -0.730415 -0.257346 1.041252
6 -3.146457 -2.031031 0.991215
1 -4.015235 -2.526969 0.570591
1 -2.253046 -2.574529 0.689655
1 -3.206187 -2.028433 2.076772
6 0.447807 0.634463 1.028834
8 -0.867366 -1.053537 2.173114
6 0.037534 -1.808594 -0.567420
6 1.167408 0.823172 2.221904
6 2.265665 1.678733 2.268381
6 2.682290 2.360280 1.125958
6 1.998836 2.154787 -0.072315
```

6	**0.902732**	**1.297487**	**-0.126852**
1	**0.847641**	**0.310344**	**3.121813**
1	**2.795370**	**1.814650**	**3.207487**
1	**3.539864**	**3.025761**	**1.162679**
1	**2.328299**	**2.652781**	**-0.980481**
1	**0.422699**	**1.127636**	**-1.083213**
1	**-0.188712**	**-1.756370**	**2.176523**
8	**0.446406**	**-2.584052**	**0.228168**
8	**-0.185862**	**-1.340793**	**-1.626519**
1	**-4.266913**	**2.082247**	**-2.692744**
1	**-5.703095**	**1.561340**	**-1.810971**
1	**-4.777535**	**2.956327**	**-1.243630**
1	**-5.792032**	**-0.984019**	**0.855121**
1	**-6.266682**	**-0.082173**	**-0.583961**
1	**-5.531853**	**-1.675371**	**-0.755281**
6	**5.089673**	**0.410620**	**-0.428234**
6	**4.776483**	**0.229824**	**-1.760892**
7	**3.916265**	**-0.740766**	**-2.110739**
6	**3.330142**	**-1.560295**	**-1.223613**
6	**3.601101**	**-1.410398**	**0.123744**
6	**4.491460**	**-0.414755**	**0.523184**
1	**5.187409**	**0.828228**	**-2.568946**
1	**3.700164**	**-0.869315**	**-3.116140**
1	**2.678460**	**-2.325688**	**-1.634731**
1	**3.129190**	**-2.069966**	**0.843398**
1	**4.722003**	**-0.284016**	**1.576977**
1	**5.784958**	**1.194048**	**-0.143721**

pyridiniumTSG
kluger ts with pyridinium ion
M052X/6-31+G**
E(RM052X+HF-M052X) = -1469.80985019

Zero-point correction= 0.371050 (Hartree/Particle)
Thermal correction to Energy= 0.395934
Thermal correction to Enthalpy= 0.396878
Thermal correction to Gibbs Free Energy= 0.313491
Sum of electronic and ZPE= -1469.438801
Sum of electronic and thermal Energies= -1469.413916
Sum of electronic and thermal Enthalpies= -1469.412972
Sum of electronic and thermal Free Energies= -1469.496359

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 248.452 91.624 175.502

6	**2.608471**	**-1.046885**	**0.188256**
6	**2.278694**	**-0.928486**	**1.489970**
16	**0.558543**	**-0.650909**	**1.669436**
6	**0.322416**	**-0.662698**	**-0.056559**
7	**1.508466**	**-0.929590**	**-0.677643**
6	**3.980098**	**-1.247220**	**-0.375461**
6	**3.136454**	**-0.980375**	**2.714840**
6	**-0.904915**	**-0.436358**	**-0.691718**
6	**1.602493**	**-1.299419**	**-2.093331**
1	**2.541188**	**-1.820879**	**-2.248121**
1	**0.782910**	**-1.970596**	**-2.343370**
1	**1.549169**	**-0.425704**	**-2.738344**
6	**-2.123144**	**0.007405**	**0.024317**
8	**-0.789592**	**0.016076**	**-2.002050**
6	**-1.506054**	**-2.608833**	**-0.954020**
6	**-2.501044**	**-0.479615**	**1.288710**
6	**-3.656637**	**-0.018973**	**1.915815**
6	**-4.477231**	**0.921568**	**1.294380**
6	**-4.132670**	**1.384826**	**0.024636**
6	**-2.975977**	**0.932457**	**-0.604797**
1	**-1.924864**	**-1.255402**	**1.777540**
1	**-3.922097**	**-0.413917**	**2.892723**
1	**-5.378309**	**1.276930**	**1.785682**
1	**-4.767292**	**2.105909**	**-0.483752**
1	**-2.726616**	**1.300943**	**-1.593424**
1	**-1.397911**	**-0.481588**	**-2.586098**
8	**-1.867791**	**-2.523962**	**-2.083707**
8	**-1.312974**	**-3.166569**	**0.072185**
1	**2.747306**	**-1.712233**	**3.425956**
1	**4.154454**	**-1.269391**	**2.459599**
1	**3.168987**	**-0.008539**	**3.213818**
1	**4.186835**	**-0.519650**	**-1.164289**
1	**4.721675**	**-1.111041**	**0.408121**
1	**4.107980**	**-2.249342**	**-0.791105**
6	**1.544222**	**2.634965**	**0.990181**
6	**0.256714**	**2.892800**	**0.519805**
6	**0.011352**	**2.801678**	**-0.836940**
7	**1.011422**	**2.466558**	**-1.666998**
6	**2.262178**	**2.214147**	**-1.250401**
6	**2.560879**	**2.294775**	**0.097124**
1	**-0.549941**	**3.162235**	**1.194707**
1	**-0.951353**	**2.995786**	**-1.295653**

1	0.806228	2.407730	-2.680993
1	2.989208	1.970009	-2.021756
1	3.575201	2.106986	0.435861
1	1.756401	2.708593	2.054154

pyridiniumTSH4
kluger ts with pyridinium ion
M052X/6-31+G**
E(RM052X+HF-M052X) = -1469.80987524

Zero-point correction= 0.370117 (Hartree/Particle)
Thermal correction to Energy= 0.395463
Thermal correction to Enthalpy= 0.396407
Thermal correction to Gibbs Free Energy= 0.310917
Sum of electronic and ZPE= -1469.439758
Sum of electronic and thermal Energies= -1469.414413
Sum of electronic and thermal Enthalpies= -1469.413469
Sum of electronic and thermal Free Energies= -1469.498958

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	248.156	92.138	179.928

6	2.637278	-1.049129	0.133075
6	2.291328	-1.058887	1.435612
16	0.563781	-0.829630	1.617671
6	0.347064	-0.679977	-0.105861
7	1.545043	-0.870551	-0.732710
6	4.017935	-1.185841	-0.427739
6	3.136118	-1.209992	2.661496
6	-0.877160	-0.405839	-0.725673
6	1.673400	-1.071386	-2.179587
1	2.606633	-1.591092	-2.370042
1	0.850609	-1.688334	-2.532157
1	1.657069	-0.124944	-2.715556
6	-2.099647	-0.027858	0.019774
8	-0.765806	0.149689	-1.996047
6	-1.472197	-2.565473	-1.155319
6	-2.485798	-0.622445	1.234531
6	-3.645838	-0.218255	1.892280
6	-4.462374	0.773317	1.350769
6	-4.108874	1.346114	0.128975
6	-2.948240	0.950460	-0.530105
1	-1.914971	-1.439624	1.657142

```
1 -3.916984 -0.697396 2.829029
1 -5.366533 1.084727 1.865441
1 -4.739598 2.110192 -0.317591
1 -2.691938 1.403925 -1.480532
1 -1.332244 -0.337243 -2.627591
8 -1.820993 -2.392018 -2.278380
8 -1.286203 -3.192641 -0.169878
1 2.730898 -1.986305 3.314009
1 4.152988 -1.493655 2.395596
1 3.175315 -0.277283 3.229998
1 4.229814 -0.387507 -1.143041
1 4.747393 -1.118055 0.375890
1 4.158760 -2.144704 -0.932066
6 1.306368 2.494434 1.186301
6 0.065574 2.796375 0.626813
6 -0.031315 2.938071 -0.744484
7 1.063741 2.777929 -1.503550
6 2.274553 2.487387 -0.999500
6 2.424803 2.339273 0.365901
1 -0.819436 2.922078 1.242325
1 -0.950863 3.182268 -1.266090
1 0.970185 2.895395 -2.529208
1 3.087839 2.396450 -1.715320
1 3.405518 2.121502 0.777543
1 1.403709 2.389726 2.264197
```

methylenethiaminMP2

```
EUMP2=      -0.64641548802050D+03
```

```
 Zero-point correction=                           0.110441 (Hartree/Particle)
 Thermal correction to Energy=                    0.117875
 Thermal correction to Enthalpy=                  0.118819
 Thermal correction to Gibbs Free Energy=         0.078303
 Sum of electronic and zero-point Energies=          -646.305048
 Sum of electronic and thermal Energies=             -646.297613
 Sum of electronic and thermal Enthalpies=           -646.296669
 Sum of electronic and thermal Free Energies=        -646.337185

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total             73.967            27.096            85.273
```

```
 C,0,1.2652359541,-2.3749219099,1.029768325
 C,0,0.7155128736,-1.4824461441,1.8807819446
```

```
S,0,-0.2994608301,-0.3347355792,1.0313845725
C,0,0.0152196043,-1.1404226491,-0.5141872147
N,0,0.9137652204,-2.1793537339,-0.2964422195
H,0,1.9397173039,-3.1835983054,1.2803183389
H,0,0.8598573237,-1.419967467,2.94825983
C,0,-0.532613874,-0.8004836132,-1.7080412227
C,0,1.2793457582,-3.0637552546,-1.3792826446
H,0,1.9709547908,-3.8179237699,-1.001925174
H,0,0.3903109796,-3.5567846991,-1.7912041479
H,0,1.7667920159,-2.4987224667,-2.1810445385
H,0,-1.2274703033,0.0256455134,-1.770364083
H,0,-0.2769939667,-1.3340357803,-2.6133453334
```

pyridiniumMP2

```
 Zero-point correction=                           0.103011 (Hartree/Particle)
 Thermal correction to Energy=                    0.107460
 Thermal correction to Enthalpy=                  0.108405
 Thermal correction to Gibbs Free Energy=         0.075465
 Sum of electronic and zero-point Energies=          -247.865304
 Sum of electronic and thermal Energies=             -247.860855
 Sum of electronic and thermal Enthalpies=           -247.859910
 Sum of electronic and thermal Free Energies=        -247.892851

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  67.432             17.159            69.328
```

```
N,0,0.061286532,0.,0.0353837421
C,0,0.0159517795,0.,1.3850477017
C,0,1.2100427945,0.,2.0955274442
C,0,2.4230462438,0.,1.3989463371
C,0,2.4198014394,0.,0.0001639904
C,0,1.2074624419,0.,-0.6787092969
H,0,-0.966133187,0.,1.8430230886
H,0,1.1794595828,0.,3.1790341155
H,0,3.3630400085,0.,1.9416519733
H,0,3.3428541456,0.,-0.5680751592
H,0,1.1130382485,0.,-1.7582075057
H,0,-0.8206220305,0.,-0.4737864294
```

thiaminepyridinium2MP2
pyridinium methylenethiamine try for stacked again
MP2/6-311G**
EUMP2= -0.89441429327966D+03

```
Zero-point correction= 0.215052 (Hartree/Particle)
Thermal correction to Energy= 0.228094
Thermal correction to Enthalpy= 0.229038
Thermal correction to Gibbs Free Energy= 0.175183
Sum of electronic and ZPE= -894.199241
Sum of electronic and thermal Energies= -894.186199
Sum of electronic and thermal Enthalpies= -894.185255
Sum of electronic and thermal Free Energies= -894.239110

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 143.131 49.526 113.348

6 -1.810673 -0.121576 -1.193038
6 -1.671760 -1.422504 -0.823878
16 -1.050233 -1.557298 0.791756
6 -0.931174 0.187861 0.932328
7 -1.355860 0.778455 -0.248830
1 -2.233229 0.248929 -2.118949
1 -2.004061 -2.292128 -1.372654
6 -0.361373 0.844567 1.990438
6 -1.678054 2.202744 -0.286365
1 -2.038616 2.452410 -1.284614
1 -2.451450 2.431696 0.453457
1 -0.788968 2.797826 -0.068363
1 -0.136634 0.294771 2.896821
1 -0.399676 1.925395 2.053325
7 1.414583 -0.603885 -1.459554
6 1.799663 -1.329595 -0.379269
6 2.151508 -0.677054 0.788375
6 2.032961 0.720980 0.869731
6 1.722193 1.437164 -0.304507
6 1.375985 0.756357 -1.452718
1 1.850657 -2.404032 -0.505717
1 2.474608 -1.266008 1.639537
1 2.361721 1.246234 1.759296
1 1.723711 2.521403 -0.316339
1 1.106487 1.239456 -2.384596
1 1.152473 -1.094836 -2.307185
```

thiaminepyridinium3MP2
thiamine pyridinium complex 3
MP2/6-311G**

EUMP2= -0.89441631593045D+03

Zero-point correction= 0.214570 (Hartree/Particle)
Thermal correction to Energy= 0.227780
Thermal correction to Enthalpy= 0.228724
Thermal correction to Gibbs Free Energy= 0.172059
Sum of electronic and ZPE= -894.201746
Sum of electronic and thermal Energies= -894.188536
Sum of electronic and thermal Enthalpies= -894.187592
Sum of electronic and thermal Free Energies= -894.244257

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	142.934	48.777	119.261

6	-1.785712	1.447057	-0.603936
6	-1.900663	0.682292	-1.703962
16	-1.770926	-1.028706	-1.345980
6	-1.748706	-0.674617	0.389087
7	-1.495860	0.715812	0.581767
1	-1.834479	2.527414	-0.547474
1	-2.060588	1.024247	-2.716975
6	-1.888160	-1.587435	1.374288
6	-1.927819	1.287177	1.866135
1	-1.765853	2.365605	1.839139
1	-2.985625	1.071297	2.048664
1	-1.329287	0.862447	2.674117
1	-2.097801	-2.619807	1.124065
1	-1.859025	-1.307335	2.419331
6	3.011965	-1.286656	0.266678
6	1.673014	-0.973260	0.474526
7	1.252098	0.290982	0.266577
6	2.068189	1.281591	-0.142155
6	3.413960	1.011658	-0.363936
6	3.892478	-0.285813	-0.155789
1	0.916697	-1.680211	0.796119
1	0.229264	0.508296	0.422360
1	1.615157	2.256024	-0.283784
1	4.069790	1.808895	-0.694448
1	4.939978	-0.514872	-0.324126
1	3.351647	-2.302225	0.434664

OlearySMA
pyridineacetic acid neutral form

```
M062X/6-31+G**
E(RM062X) = -476.012177981

Zero-point correction= 0.133335 (Hartree/Particle)
Thermal correction to Energy= 0.141802
Thermal correction to Enthalpy= 0.142746
Thermal correction to Gibbs Free Energy= 0.097531
Sum of electronic and ZPE= -475.878843
Sum of electronic and thermal Energies= -475.870376
Sum of electronic and thermal Enthalpies= -475.869432
Sum of electronic and thermal Free Energies= -475.914647

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 88.982 30.855 95.163

 C,0,-0.0501300146,-0.1538875477,-0.200540087
 H,0,-0.3279878135,-0.4329738223,0.8164891335
 C,0,1.4562155947,-0.0081154324,-0.2324901062
 H,0,-0.3176674628,-0.9719171007,-0.8767812142
 C,0,-0.7450811435,1.1196144257,-0.6244895193
 C,0,-1.182280918,1.3137186728,-1.9342884896
 C,0,-1.7968686272,2.5179168589,-2.2688873146
 N,0,-1.9961961595,3.5156282832,-1.4004314118
 C,0,-1.5748756469,3.3223899372,-0.1455868004
 C,0,-0.9514326425,2.1547966795,0.2880305064
 H,0,-1.0508146686,0.5422266332,-2.6866508239
 H,0,-2.1477672527,2.6851376696,-3.2840301159
 H,0,-1.745300791,4.1391356077,0.5513007781
 H,0,-0.6373761687,2.0579766644,1.3231569454
 O,0,1.9032136482,0.3519534582,-1.4422641378
 O,0,2.1904851032,-0.1980294501,0.7107293175
 H,0,2.8711759637,0.4254164628,-1.4083046601

OlearySMprot
 pyridineacetic acid protonated
M062X/6-31+G**
E(RM062X) = -476.454062150

Zero-point correction= 0.147549 (Hartree/Particle)
Thermal correction to Energy= 0.156059
Thermal correction to Enthalpy= 0.157003
Thermal correction to Gibbs Free Energy= 0.112281
Sum of electronic and ZPE= -476.306513
```

```
Sum of electronic and thermal Energies= -476.298003
Sum of electronic and thermal Enthalpies= -476.297059
Sum of electronic and thermal Free Energies= -476.341781

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 97.928 31.585 94.125

 C,0,-0.052663658,-0.120701782,-0.1433640754
 H,0,-0.2487616592,-0.3250559738,0.9109358589
 C,0,1.4562424318,-0.1075602734,-0.3229513928
 H,0,-0.4214400984,-0.9766538083,-0.7183402119
 C,0,-0.7384533235,1.1408739323,-0.5888222441
 C,0,-1.1645053115,1.2936820261,-1.9125751058
 C,0,-1.782364478,2.4644465641,-2.3005272578
 N,0,-1.966382209,3.4442435609,-1.3979139878
 C,0,-1.5737678442,3.3434119297,-0.116580092
 C,0,-0.9522771551,2.1881956778,0.3130897328
 H,0,-1.0188655498,0.506631907,-2.6430614198
 H,0,-2.1405421251,2.653067523,-3.3037315215
 H,0,-1.7751259117,4.1922198681,0.5235762689
 H,0,-0.640453481,2.1106622364,1.3481633654
 O,0,1.8733637824,0.8234282674,-1.1845394733
 O,0,2.1950104473,-0.8821392511,0.2360463596
 H,0,2.8384596269,0.7558249582,-1.2799081214
 H,0,-2.4276494841,4.2998866378,-1.6975356819

OlearySMzwitA
 pyridineacetic acid zwitterionic form A
M062X/6-31+G**
E(RM062X) = -476.000336126

Zero-point correction= 0.134095 (Hartree/Particle)
Thermal correction to Energy= 0.142381
Thermal correction to Enthalpy= 0.143325
Thermal correction to Gibbs Free Energy= 0.099387
Sum of electronic and ZPE= -475.866241
Sum of electronic and thermal Energies= -475.857955
Sum of electronic and thermal Enthalpies= -475.857011
Sum of electronic and thermal Free Energies= -475.900949

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 89.345 30.456 92.476
```

C,0,0.1827987045,0.1353308683,0.0864417628
H,0,-0.0234197288,0.3056787995,1.1445996165
C,0,1.6416673953,-0.4255345671,-0.0525040308
H,0,-0.4822727841,-0.6623168197,-0.2619988683
C,0,-0.0447210741,1.3717945547,-0.7119114218
C,0,-0.1820829787,1.30766265,-2.1079673648
C,0,-0.3496828278,2.4618845299,-2.8378548611
N,0,-0.3780830592,3.6511694881,-2.204010449
C,0,-0.2524768649,3.7670600346,-0.87016275
C,0,-0.0851205677,2.6333176882,-0.1028542953
H,0,-0.1541781314,0.3545286645,-2.6221706702
H,0,-0.4625383583,2.4840569352,-3.913886445
H,0,-0.2927467304,4.7695038627,-0.4645988484
H,0,0.0156311903,2.7344299293,0.9713409201
O,0,2.3199257868,-0.0265590245,-1.0251732285
O,0,1.9647462434,-1.2512099723,0.8311242583
H,0,-0.5017062147,4.4943023787,-2.7573233245

OlearySMzwitE
pyridineacetic acid zwitterionic form E
M062X/6-31+G**
E(RM062X) = -476.000336158

Zero-point correction= 0.134095 (Hartree/Particle)
Thermal correction to Energy= 0.142381
Thermal correction to Enthalpy= 0.143325
Thermal correction to Gibbs Free Energy= 0.099385
Sum of electronic and ZPE= -475.866242
Sum of electronic and thermal Energies= -475.857955
Sum of electronic and thermal Enthalpies= -475.857011
Sum of electronic and thermal Free Energies= -475.900952

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 89.345 30.457 92.481

C,0,0.1592486291,0.060533701,-0.0272853253
H,0,-0.2985498153,0.1469254915,0.9641296552
C,0,1.6768803516,-0.2507328832,0.2219979396
H,0,-0.2916636773,-0.7960401501,-0.5314584806
C,0,-0.0593304535,1.3153718983,-0.7990259376
C,0,-0.4038080652,1.2830665243,-2.1570864491
C,0,-0.5568824504,2.4596058437,-2.8602546111

```
N,0,-0.3749982668,3.6347106293,-2.2322046483
C,0,-0.0467777104,3.7204057105,-0.9276554914
C,0,0.1174317927,2.5693054854,-0.192088241
H,0,-0.5516841518,0.3399245077,-2.6698037977
H,0,-0.8216156782,2.5059793661,-3.9084732013
H,0,0.0727990363,4.7169338083,-0.5230632285
H,0,0.3867142328,2.6428952312,0.8546686187
O,0,2.4870091364,0.6921399435,0.0807142264
O,0,1.912763123,-1.4298823738,0.569713173
H,0,-0.4917760331,4.4939552663,-2.7617232011
```

OlearySMzwitF

pyridineacetic acid zwitterionic form F
M062X/6-31+G**
E(RM062X) = -476.000336113

```
Zero-point correction= 0.134095 (Hartree/Particle)
Thermal correction to Energy= 0.142381
Thermal correction to Enthalpy= 0.143325
Thermal correction to Gibbs Free Energy= 0.099385
Sum of electronic and ZPE= -475.866241
Sum of electronic and thermal Energies= -475.857955
Sum of electronic and thermal Enthalpies= -475.857011
Sum of electronic and thermal Free Energies= -475.900951
```

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 89.345 30.456 92.479
```

```
C,0,0.2261408337,-0.0981113151,-0.3760263831
H,0,-0.6679157974,-0.4904247737,0.1118086144
C,0,1.4011459757,-0.0972928598,0.6639659306
H,0,0.5180999463,-0.80360675,-1.1615293149
C,0,-0.0291521591,1.2444188343,-0.9679802098
C,0,0.8444847288,1.7821639867,-1.9268963422
C,0,0.6201750899,3.0410957034,-2.4346941902
N,0,-0.4402039499,3.7528073196,-2.003410927
C,0,-1.30689537,3.2836368218,-1.0884810545
C,0,-1.1180667356,2.0250666893,-0.5570002327
H,0,1.7011778309,1.2160922301,-2.2722704204
H,0,1.2518303802,3.5141532797,-3.1751669334
H,0,-2.1252652884,3.9370723305,-0.8159207199
H,0,-1.8203797685,1.653683129,0.1799524008
```

```
O,0,2.1927383993,0.8711248705,0.6350351907
O,0,1.4340450953,-1.1033748309,1.4080577156
H,0,-0.5915222111,4.6811803344,-2.3875181238
```

OlearySMzwitH2O
pyridineacetic acid zwitterion with water conf B
M062X/6-31+G**
E(RM062X) = -552.415427995

```
Zero-point correction= 0.157599 (Hartree/Particle)
Thermal correction to Energy= 0.169578
Thermal correction to Enthalpy= 0.170522
Thermal correction to Gibbs Free Energy= 0.116573
Sum of electronic and ZPE= -552.257829
Sum of electronic and thermal Energies= -552.245850
Sum of electronic and thermal Enthalpies= -552.244906
Sum of electronic and thermal Free Energies= -552.298855
```

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 106.412 41.084 113.546
```

```
C,0,0.1510805078,0.1663674284,0.141239137
H,0,0.0077426759,0.4055276111,1.196478969
C,0,1.5435443545,-0.5323105592,-0.0288245326
H,0,-0.5975672918,-0.583819854,-0.1371872245
C,0,-0.0080653949,1.379392388,-0.7105471084
C,0,-0.2006252807,1.2619750081,-2.0956945445
C,0,-0.3141746631,2.3941317258,-2.8722460574
N,0,-0.2356900524,3.6111432949,-2.302680317
C,0,-0.0495723564,3.7724765951,-0.983078073
C,0,0.0659806356,2.666875709,-0.1637383316
H,0,-0.2581185309,0.2865374179,-2.563550566
H,0,-0.4676333388,2.3741704672,-3.9438687537
H,0,-0.0024306781,4.7925364994,-0.6230494998
H,0,0.2129689945,2.8101406577,0.9005730339
O,0,2.1953528187,-0.2698929292,-1.0644189595
O,0,1.8464532491,-1.319970419,0.8967726698
H,0,-0.3232387469,4.4491125323,-2.9104842038
O,0,-0.4796927063,5.7301772994,-4.0542084639
H,0,-1.197019747,6.3648526092,-3.935994954
H,0,0.306876551,6.249800518,-4.26112122
```

H2O

```
 water
M062X/6-31+G**
E(RM062X) = -76.4033949319

Zero-point correction= 0.021512 (Hartree/Particle)
Thermal correction to Energy= 0.024348
Thermal correction to Enthalpy= 0.025292
Thermal correction to Gibbs Free Energy= 0.003865
Sum of electronic and ZPE= -76.381882
Sum of electronic and thermal Energies= -76.379047
Sum of electronic and thermal Enthalpies= -76.378103
Sum of electronic and thermal Free Energies= -76.399530

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 15.279 6.014 45.098

 H,0,0.0085417484,0.,0.0254377192
 O,0,0.0139470365,0.,0.9892010506
 H,0,0.9456588555,0.,1.2357412343
```

OlearyTSA

```
 pyridineacetic acid decarboxylation TS try at new rotation
M062X/6-31+G**
E(RM062X) = -475.973627449

Zero-point correction= 0.129853 (Hartree/Particle)
Thermal correction to Energy= 0.138703
Thermal correction to Enthalpy= 0.139647
Thermal correction to Gibbs Free Energy= 0.094533
Sum of electronic and ZPE= -475.843775
Sum of electronic and thermal Energies= -475.834925
Sum of electronic and thermal Enthalpies= -475.833980
Sum of electronic and thermal Free Energies= -475.879095

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 87.037 32.257 94.951

 C,0,-0.1201186769,-0.2398577303,-0.174363646
 H,0,-0.0054305786,-0.4615470066,0.8811995133
 C,0,1.9384337586,0.5300432334,-0.5331772618
```

```
 H,0,-0.0819380647,-1.0725406978,-0.8684057659
 C,0,-0.7120400464,0.9480837701,-0.5633336962
 C,0,-1.0616215273,1.2285072747,-1.9376775859
 C,0,-1.5645320499,2.4364847231,-2.3031102451
 N,0,-1.7634017961,3.4240240184,-1.3820107673
 C,0,-1.4666468947,3.2178539174,-0.0657150431
 C,0,-0.9610601597,2.0312710986,0.3609834035
 H,0,-0.9208461396,0.4648986256,-2.6944480975
 H,0,-1.836660042,2.6780796782,-3.323085068
 H,0,-1.6650101586,4.0482978851,0.6004575583
 H,0,-0.7410662782,1.8998915554,1.4145295996
 O,0,2.1385002212,0.2341031541,-1.6648793042
 O,0,2.2338670905,0.9961507835,0.517450305
 H,0,-2.1489526575,4.310379717,-1.6746878988
```

```
Olearycomplex
 Oleary complex
M062X/6-31+G**
E(RM062X) = -475.983302543

Zero-point correction= 0.129724 (Hartree/Particle)
Thermal correction to Energy= 0.139820
Thermal correction to Enthalpy= 0.140765
Thermal correction to Gibbs Free Energy= 0.091756
Sum of electronic and ZPE= -475.853579
Sum of electronic and thermal Energies= -475.843482
Sum of electronic and thermal Enthalpies= -475.842538
Sum of electronic and thermal Free Energies= -475.891546

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 87.739 34.902 103.147
```

```
 C,0,-0.4144591891,-0.4048404486,-0.1038144092
 H,0,-0.2178073994,-0.6065991562,0.9443658796

 C,0,2.2744777323,0.9828606986,-0.7061601439
 H,0,-0.2945305888,-1.2195755635,-0.8108388341
 C,0,-0.812032272,0.8255942398,-0.5161449811
 C,0,-1.0871084069,1.1511885182,-1.9155704014
 C,0,-1.4746929896,2.3899994742,-2.2945828487
 N,0,-1.6284207486,3.4055565808,-1.3814629371
 C,0,-1.3765959757,3.173723385,-0.0504434684
 C,0,-0.9861571853,1.9577083041,0.3938388285
```

```
 H,0,-0.975877799,0.3816377207,-2.6721888167
 H,0,-1.6827115632,2.6487016213,-3.3259343026
 H,0,-1.5107105363,4.0228934152,0.6089559687

 H,0,-0.7955457598,1.8223818138,1.4532753963
 O,0,2.2475243165,0.6081424078,-1.8073005551
 O,0,2.343566345,1.3745584851,0.3872058995
 H,0,-1.9163299801,4.3215865036,-1.6887832744

trichloroacetateSM
 trichloroacetate
M062X/6-31+G**
E(RM062X) = -1607.23633537

Zero-point correction= 0.021253 (Hartree/Particle)
Thermal correction to Energy= 0.028400
Thermal correction to Enthalpy= 0.029344
Thermal correction to Gibbs Free Energy= -0.012424
Sum of electronic and ZPE= -1607.215082
Sum of electronic and thermal Energies= -1607.207935
Sum of electronic and thermal Enthalpies= -1607.206991
Sum of electronic and thermal Free Energies= -1607.248759

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 17.821 22.927 87.909

 C,0,1.4211826596,0.130029885,-0.2045834911
 O,0,1.8682087645,1.2015021113,0.2330646904
 O,0,1.9822906922,-0.8386029933,-0.7330144518
 C,0,-0.1667841593,-0.0113757644,-0.0117555864
 Cl,0,-0.9896592814,1.4311667382,-0.6725768345
 Cl,0,-0.8380724893,-1.4574898238,-0.8040900203
 Cl,0,-0.5034581863,-0.118754153,1.7458156937

trichloroacetateTS2.47
 trichloroacetate decarboxylation
M062X/6-31+G**
E(RM062X) = -1607.19648445

Zero-point correction= 0.017582 (Hartree/Particle)
Thermal correction to Energy= 0.025777
Thermal correction to Enthalpy= 0.026721
Thermal correction to Gibbs Free Energy= -0.019127
```

```
Sum of electronic and ZPE= -1607.178903
Sum of electronic and thermal Energies= -1607.170708
Sum of electronic and thermal Enthalpies= -1607.169763
Sum of electronic and thermal Free Energies= -1607.215611

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 16.175 24.453 96.495

 C,0,0.4791721672,0.0143360548,0.1592630542
 O,0,-0.1230629795,0.1268149857,1.159565021
 O,0,1.3304204986,-0.1055187489,-0.6392390494
 C,0,-1.4312049898,0.0081773234,-1.4064062075
 Cl,0,-3.02140767,0.6831411148,-0.7510091297
 Cl,0,-1.132925163,0.9238832536,-2.9867793427
 Cl,0,-1.8304018635,-1.7266039833,-1.936134346

CO2
 CO2
M062X/6-31+G**
E(RM062X) = -188.518998107

Zero-point correction= 0.011808 (Hartree/Particle)
Thermal correction to Energy= 0.014426
Thermal correction to Enthalpy= 0.015371
Thermal correction to Gibbs Free Energy= -0.008888
Sum of electronic and ZPE= -188.507190
Sum of electronic and thermal Energies= -188.504572
Sum of electronic and thermal Enthalpies= -188.503628
Sum of electronic and thermal Free Energies= -188.527886

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 9.053 6.846 51.056

 O,0,0.,0.,0.0372036008
 C,0,0.,0.,1.2
 O,0,0.,0.,2.3627963992

KempsnitroSMb
 Kemps starting material
M062X/6-31+G**
E(RM062X) = -792.046560478
```

```
Zero-point correction= 0.110959 (Hartree/Particle)
Thermal correction to Energy= 0.122086
Thermal correction to Enthalpy= 0.123030
Thermal correction to Gibbs Free Energy= 0.071818
Sum of electronic and ZPE= -791.935601
Sum of electronic and thermal Energies= -791.924474
Sum of electronic and thermal Enthalpies= -791.923530
Sum of electronic and thermal Free Energies= -791.974743

    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 76.610 41.036 107.786

 C,0,3.0493001018,-0.4957631872,0.0122901126
 C,0,2.5256029522,0.7832866792,0.029909051
 C,0,1.1312878996,0.8720766524,0.0363083294
 C,0,0.283026381,-0.2341140026,0.0260307236
 C,0,0.808589797,-1.5265352714,0.0082422022
 C,0,2.1906557794,-1.6125570595,0.0019229061
 O,0,0.3985477189,1.9998618367,0.0528757982
 C,0,-1.0355999138,0.3540126478,0.0382391675
 N,0,-0.9540965167,1.650938251,0.0537692348
 C,0,-2.3787845692,-0.3851467911,0.0343297979
 O,0,-3.4120555903,0.3134326857,0.0467836144
 O,0,-2.2627637705,-1.6318460819,0.0186766718
 H,0,4.1204888054,-0.6536920999,0.0062780286
 H,0,3.1584042645,1.6620587602,0.0382306502
 H,0,0.169124889,-2.3995645179,0.0000167214
 N,0,2.7994011718,-2.9453014949,-0.0166762544
 O,0,2.0596075218,-3.9165789903,-0.0257054035
 O,0,4.0184730781,-3.0212430162,-0.0222653519

KempsnitroTS
 Kemps nitro TS
M062X/6-31+G**
E(RM062X) = -792.004822490

Zero-point correction= 0.106258 (Hartree/Particle)
Thermal correction to Energy= 0.118238
Thermal correction to Enthalpy= 0.119183
Thermal correction to Gibbs Free Energy= 0.065677
Sum of electronic and ZPE= -791.898564
Sum of electronic and thermal Energies= -791.886584
Sum of electronic and thermal Enthalpies= -791.885640
```

Sum of electronic and thermal Free Energies= -791.939145

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 74.196 42.807 112.611

6	2.060805	1.331350	-0.004228
6	1.048886	2.264564	0.004690
6	-0.310176	1.835990	0.006805
6	-0.549951	0.415189	-0.003370
6	0.462810	-0.523641	-0.009829
6	1.770149	-0.046733	-0.010510
8	-1.333431	2.593488	0.018388
6	-1.985093	0.254609	0.004388
7	-2.737128	1.214789	0.021466
6	-2.750499	-1.426362	0.007627
8	-2.732279	-1.815552	1.147024
8	-3.025517	-1.711071	-1.128814
1	3.097241	1.648244	-0.005714
1	1.270245	3.325253	0.010524
1	0.259744	-1.588644	-0.012369
7	2.857070	-0.995107	-0.016170
8	2.590540	-2.192827	-0.018950
8	4.007134	-0.568091	-0.018018

Kempsnitrocomplex
kemps complex
M062X/6-31+G**
E(RM062X) = -792.092331807

Zero-point correction= 0.106890 (Hartree/Particle)
Thermal correction to Energy= 0.120557
Thermal correction to Enthalpy= 0.121502

Thermal correction to Gibbs Free Energy= 0.062592
Sum of electronic and ZPE= -791.985442
Sum of electronic and thermal Energies= -791.971774
Sum of electronic and thermal Enthalpies= -791.970830
Sum of electronic and thermal Free Energies= -792.029740

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 75.651 46.040 123.985

```
C,0,2.1914399896,1.3961299296,-0.1115201995
C,0,1.2856180786,2.4067251881,-0.2712890386
C,0,-0.1419896456,2.2004631269,-0.1226610359
C,0,-0.5279821291,0.8341242835,0.2138099624
C,0,0.3955664908,-0.1871201664,0.3736660425
C,0,1.7513124216,0.0895492307,0.212634118
O,0,-0.9813096131,3.1165947948,-0.2700507227
C,0,-1.9214695675,0.5658420908,0.3766869674
N,0,-3.0563076085,0.3553270443,0.5068848145
C,0,-3.005959314,-2.3935872518,-0.679283744
O,0,-1.8461182642,-2.3462425495,-0.7597433435
O,0,-4.1640704847,-2.4583009675,-0.6061601936
H,0,3.253909368,1.5772581242,-0.2299480907
H,0,1.6153058367,3.4101279138,-0.5207598569
```

Gaussrate Input File (.dat)

```
*General

  TITLE
 methylcyclopropyl ring opening
 calculation of the CVT and SCT
 Information about stationary points included in the fu5 input file
 END

  ATOMS
    1       C
    2       C
    3       C
    4       C
    5       H
    6       H
    7       H
    8       H
    9       H
   10       H
   11       H
  END

  NOSUPERMOL


 INPUNIT AU
```

```
*OPTIMIZATION

 OPTMIN  OHOOK
 OPTTS   OHOOK

*SECOND

 HESSCAL HHOOK

*REACT1

 STATUS    2

# Geometry in a.u.
 GEOM
   1        2.98068545      0.00030090     -0.31999608
   2        0.51335696     -0.00013717      0.90396442
   3       -1.73107474     -1.41326461     -0.26397892
   4       -1.73108002      1.41319687     -0.26323248
   5        3.13468301      0.00180321     -2.36639373
   6        4.71080531     -0.00228637      0.77591847
   7        0.55410135     -0.00079480      2.95937608
   8       -2.99673029     -2.40331464      1.01569070
   9       -1.39258524     -2.38818004     -2.03943899
  10       -2.99676175      2.40227971      1.01719114
  11       -1.39319307      2.38934998     -2.03813886
 END

ELEC
   2   0.0
 END

 SPECIES   NONLINRP

*PROD1

 STATUS    2

# Geometry in a.u.
 GEOM
   1        3.38485810     -0.08325268     -0.50964307
   2        1.23486247     -0.35460982      0.77536320
   3       -1.18799482      1.05232388      0.23154238
   4       -3.34055839     -0.65902742     -0.43031897
```

```
   5       3.54365484     1.23059104    -2.08440191
   6       5.07134811    -1.15619095    -0.03795250
   7       1.14922776    -1.70200656     2.33259882
   8      -5.27242608    -0.17187123     0.05658396
   9      -3.03245808    -2.28899271    -1.63726142
  10      -1.71105599     2.20229613     1.88369163
  11      -0.83380500     2.41681447    -1.31034403
  END

 ELEC
   2   0.0
  END

  SPECIES   NONLINRP

 *START

  STATUS    2

# Geometry in a.u.
  GEOM
   1       3.05242727    -0.08674629    -0.20729437
   2       0.72976208     0.06206769     0.98778592
   3      -1.55063561     1.36837263    -0.05359849
   4      -2.19557927    -1.28867257    -0.66394324
   5       3.35785936     0.74399342    -2.06060182
   6       4.60205034    -1.14990654     0.61280673
   7       0.56175666    -0.64528634     2.90904986
   8      -3.30968004    -2.43071196     0.62000218
   9      -1.71198495    -2.07648107    -2.48868394
  10      -2.75514567     2.31226156     1.32974745
  11      -1.17319733     2.59099997    -1.67185311
  END

  ELEC
   2   0.0
  END

  SPECIES   NONLINTS

# end of start section

*PATH
```

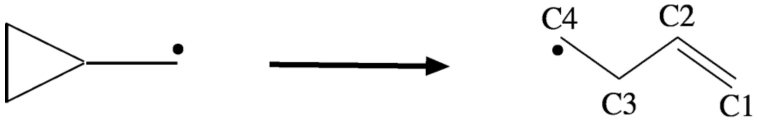
```
  SCALEMASS  1.00

  RODS
  INTMU   3
  SSTEP   0.001
  INH     10

  SRANGE
   SLP   1.25
   SLM  -1.25
  END

  RPM      pagem

  SIGN    REACTANT

  IDIRECT   1

COORD  curv3

INTDEF
  2-4 1-2-4 2-4-3 1-2-4-3 4-2-3
  2-1  3-2  4-3  5-1  6-1  7-2  8-4
  9-4  10-3  11-3  3-2-1  4-3-2  5-1-2  6-1-2
  7-2-3  8-4-3  9-4-3  10-3-2  11-3-2  4-3-2-1  5-1-2-3
  6-1-2-3  7-2-3-4  8-4-3-2  9-4-3-2  10-3-2-1  11-3-2-1
  END

  PRPATH
   COORD 2 4
   INTERVAL 1
   XMOL
  END

  EXFIRST
   EXPROD
   EXNSTEP 200
   EXSTEP 0.005
  END

  EXSECOND
   EXREACT
   EXNSTEP 200
   EXSTEP 0.005
```

```
  END

  SPECSTOP
   CURVE vag
   POINT savegrid
   PERCENTDOWN 95.
  END

*TUNNEL

 QUAD
   NQE   30
   NQTH  30
 END

   SCT

*RATE


  FORWARDK

  SIGMAF       1
  CVT

  TEMP
    100.
    102.
    104.
    110.
    120.
    123.
    125.
    127.
    130.
    140.
    148.
    150.
    152.
    160.
    170.
    173.
    175.
    177.
```

```
   180.
   190.
   200.
   202.
   210.
   220.
   223.
   225.
   227.
   230.
   240.
   248.
   250.
   252.
   260.
   270.
   280.
   290.
   296.
   298.
   300.
END
```

Gaussrate Calculated Rates.

Calculated rates for the ring-opening of cyclopropylcarbinyl radical **1** to the 3-butenyl radical **2**. Rates of a ^{13}C at position C3 and C4 are shown for CVT and CVT+SCT at temperatures ranging from 100 to 353 K.



1 **2**

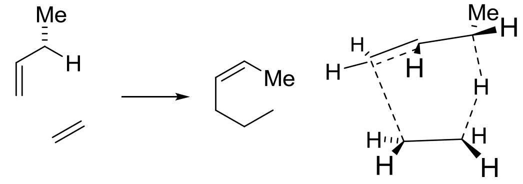
	CVT		CVT+SCT	
Temp (K)	**^{13}C at C3**	**^{13}C at C4**	**^{13}C at C3**	**^{13}C at C4**

100	3.9876E-05	3.3235E-05	1.4196E-01	2.3170E-01
102	8.5898E-05	7.1861E-05	1.7097E-01	2.7719E-01
104	1.7968E-04	1.5086E-04	2.0867E-01	3.3552E-01
110	1.4008E-03	1.1879E-03	4.0959E-01	6.3709E-01
120	2.7257E-02	2.3450E-02	1.5511E+00	2.2473E+00
123	6.0465E-02	5.2221E-02	2.3917E+00	3.3913E+00
125	1.0069E-01	8.7180E-02	3.2077E+00	4.4857E+00
127	1.6503E-01	1.4322E-01	4.3131E+00	5.9516E+00
130	3.3656E-01	2.9310E-01	6.7423E+00	9.1302E+00
140	2.9066E+00	2.5579E+00	2.9575E+01	3.8016E+01
148	1.3236E+01	1.1734E+01	9.2117E+01	1.1478E+02
150	1.8856E+01	1.6745E+01	1.2124E+02	1.5007E+02
152	2.6613E+01	2.3674E+01	1.5893E+02	1.9550E+02
170	4.1155E+02	3.7098E+02	1.4991E+03	1.7676E+03
173	7.9733E+02	7.2103E+02	2.6315E+03	3.0761E+03
180	1.4894E+03	1.3509E+03	4.5055E+03	5.2263E+03
195	8.0210E+03	7.3347E+03	1.9696E+04	2.2419E+04
200	1.3298E+04	1.2190E+04	3.0876E+04	3.4960E+04
202	1.6166E+04	1.4833E+04	3.6759E+04	4.1539E+04
210	3.4028E+04	3.1333E+04	7.1709E+04	8.0446E+04
220	8.0011E+04	7.3977E+04	1.5553E+05	1.7310E+05
223	1.0189E+05	9.4311E+04	1.9382E+05	2.1525E+05
225	1.1928E+05	1.1049E+05	2.2378E+05	2.4818E+05
227	1.3925E+05	1.2909E+05	2.5779E+05	2.8550E+05
230	1.7479E+05	1.6221E+05	3.1739E+05	3.5083E+05
240	3.5802E+05	3.3339E+05	6.1345E+05	6.7398E+05
248	6.0977E+05	5.6926E+05	1.0033E+06	1.0975E+06
250	6.9294E+05	6.4730E+05	1.1295E+06	1.2343E+06
252	7.8588E+05	7.3455E+05	1.2693E+06	1.3857E+06
260	1.2756E+06	1.1950E+06	1.9909E+06	2.1656E+06
273	2.6399E+06	2.4816E+06	3.9261E+06	4.2468E+06
280	3.7993E+06	3.5774E+06	5.5226E+06	5.9576E+06
290	6.2020E+06	5.8532E+06	8.7535E+06	9.4093E+06
296	8.1928E+06	7.7420E+06	1.1379E+07	1.2207E+07
298	8.9674E+06	8.4775E+06	1.2391E+07	1.3285E+07
300	9.8036E+06	9.2718E+06	1.3479E+07	1.4442E+07
353	7.2446E+07	6.9137E+07	9.0104E+07	9.5231E+07

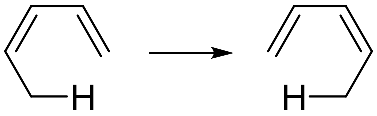
Reactions studied for A_{12}/A_{13} calculations

A slew of different reactions were examined for these calculations in order to get a broad range of the chemical reaction spectra. A list of the reactions studied is given below.

ene M1



1,5-sigmatropic parent



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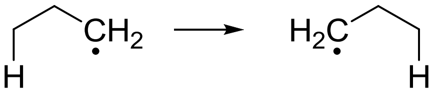

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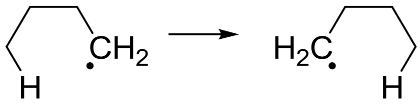
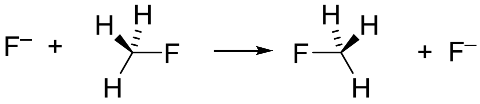
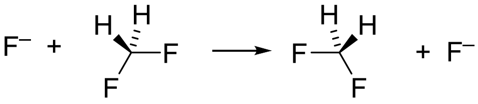


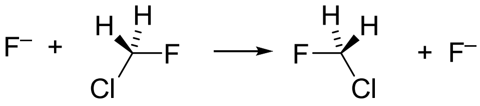
S_N2 parent



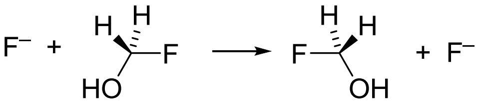
S_N2 F



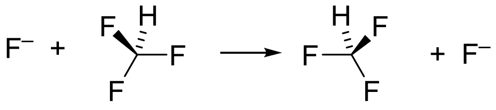
S_N2 Cl



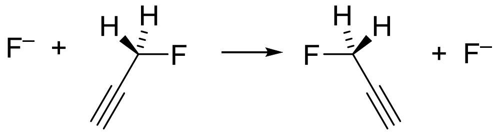
S_N2 OH



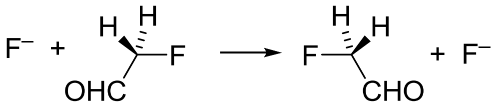
S_N2 F2



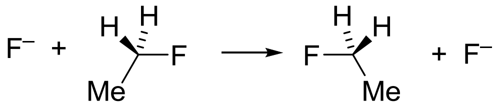
S_N2 CCH



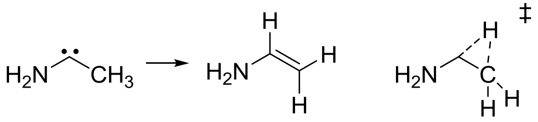
S_N2 CHO



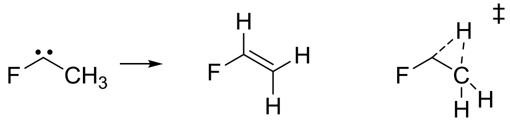
S_N2 Me



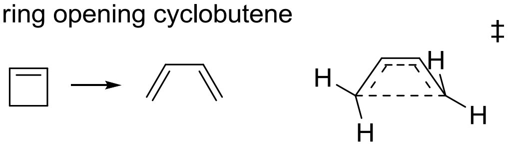
carbene rearrangement NH_2



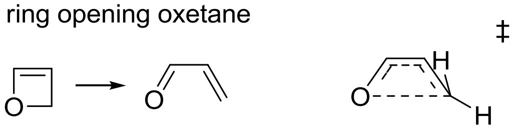
carbene rearrangement F



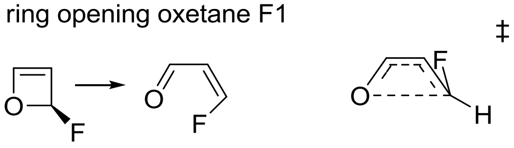
ring opening cyclobutene



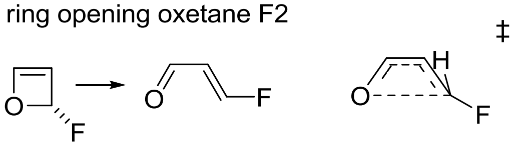
ring opening oxetane



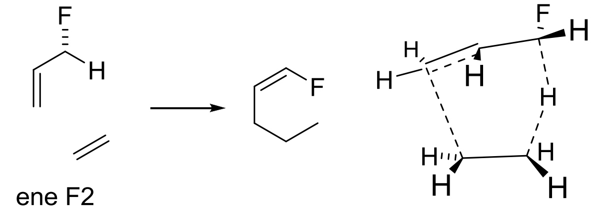
ring opening oxetane F1



ring opening oxetane F2



ene F1



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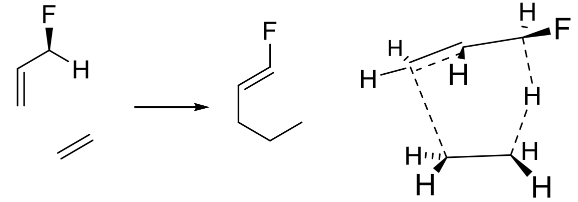

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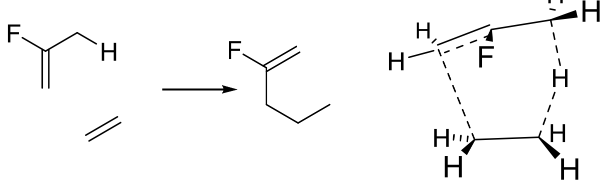

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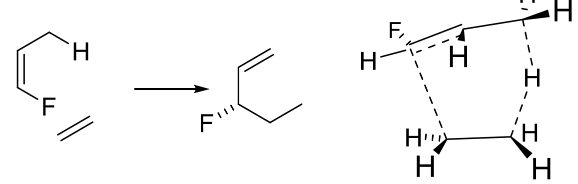
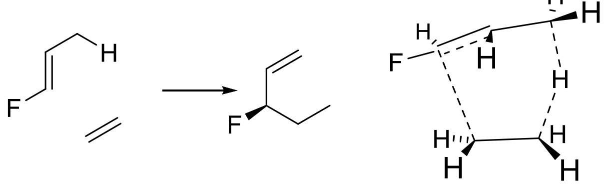
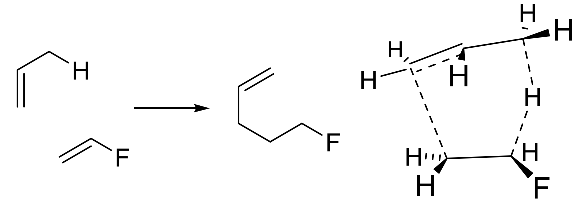


ene F5



ene F6



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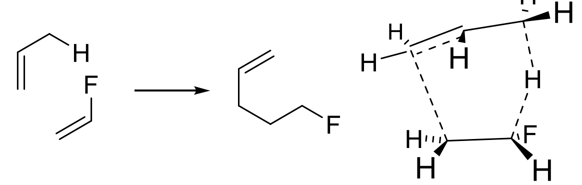
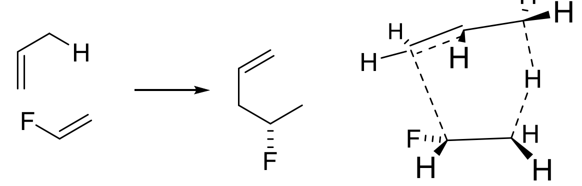
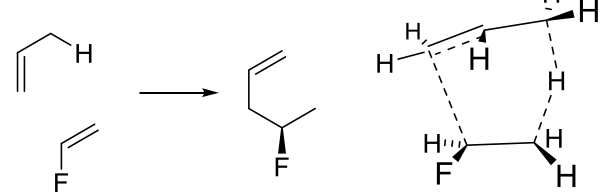


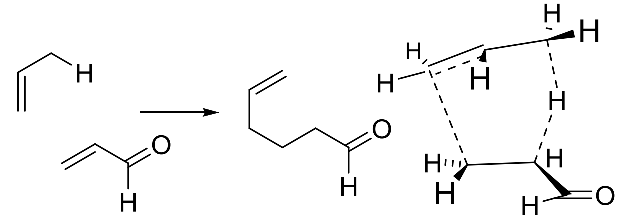
ene F8



ene F9



ene Ac



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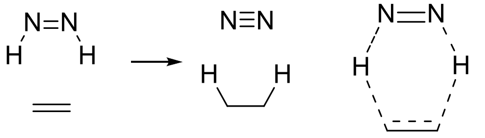

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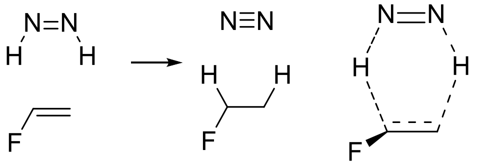
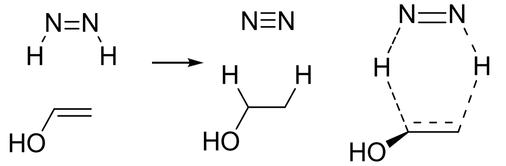


diimide 3



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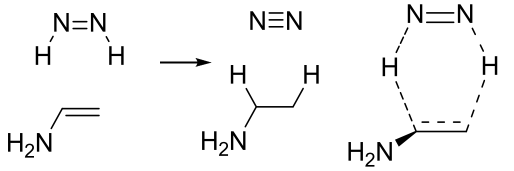

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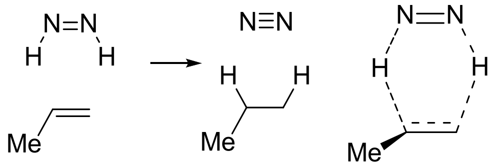

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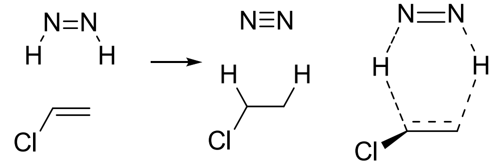

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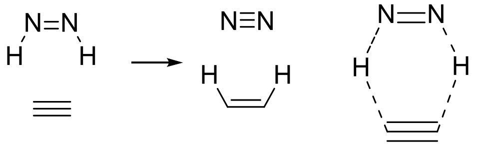

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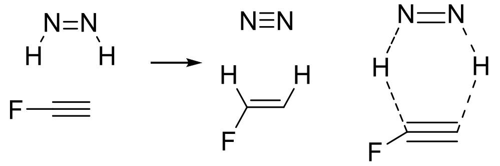

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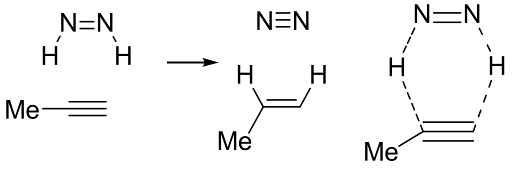

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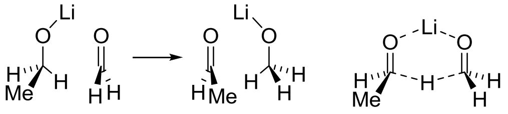

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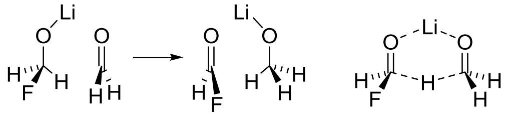

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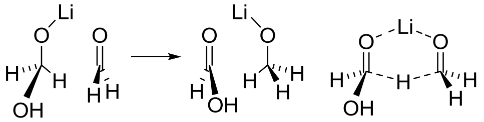

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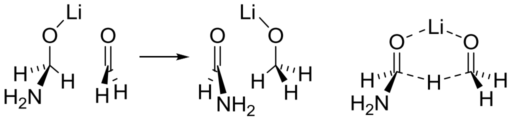

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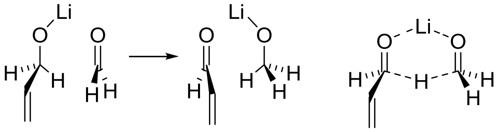

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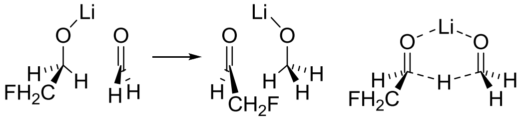

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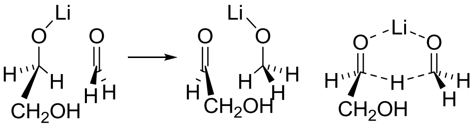
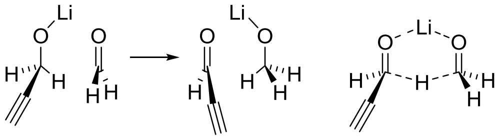


hydride transfer CCH



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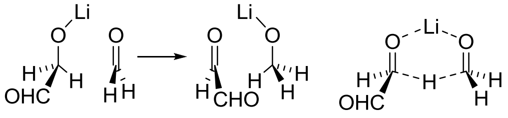

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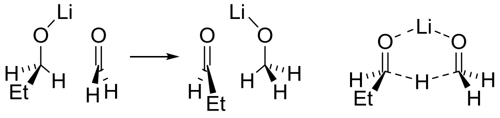

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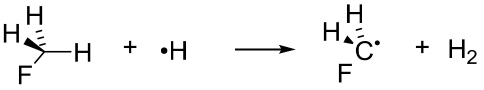

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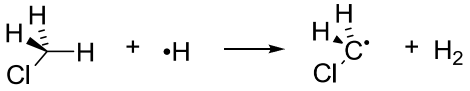

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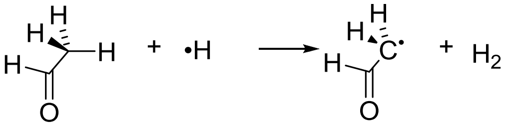

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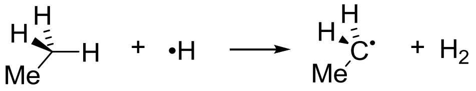

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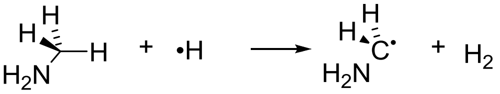
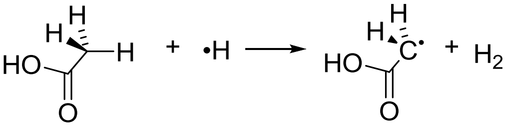
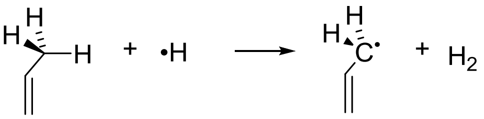


H to H transfer COOH



H to H transfer vinyl



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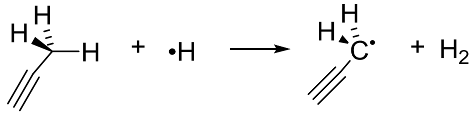
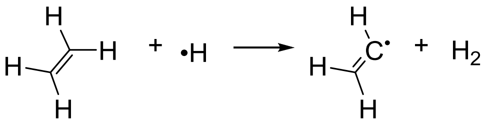
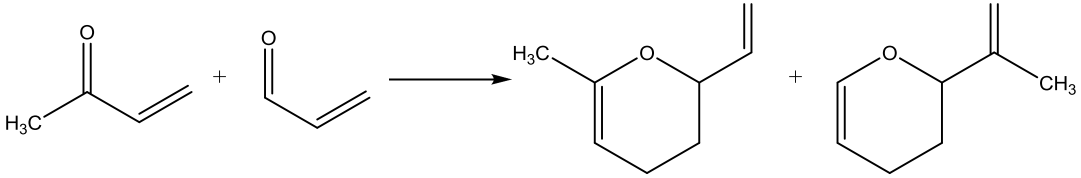


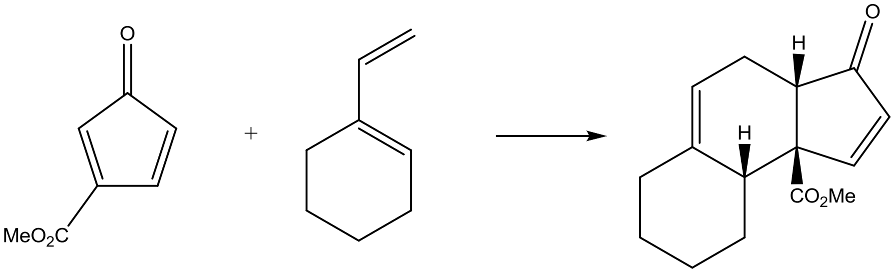
H to H transfer ethylene



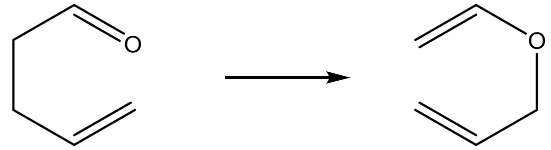
Diels Alder of methyl vinyl ketone and acrolein



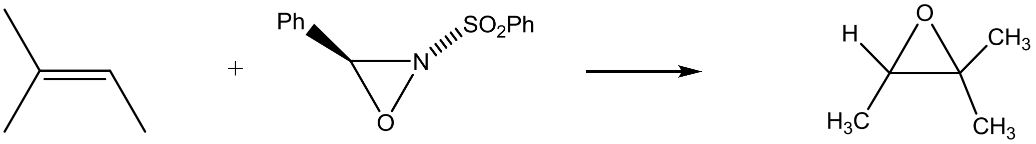
Diels Alder of 1-vinylcyclohexene and cyclopentadienone



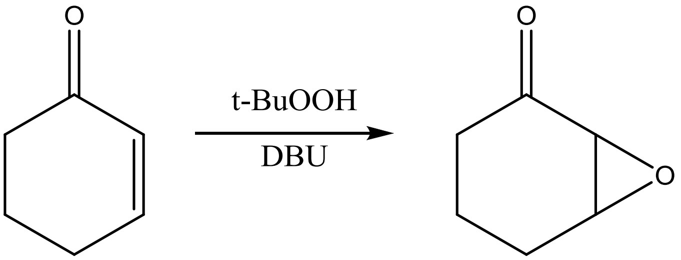
Claisen Rearrangement



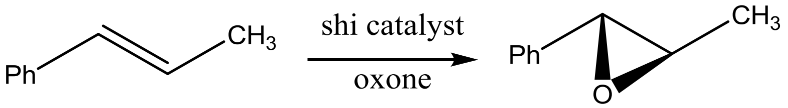
Epoxidation of 2-methyl-2-butene with oxaziridine



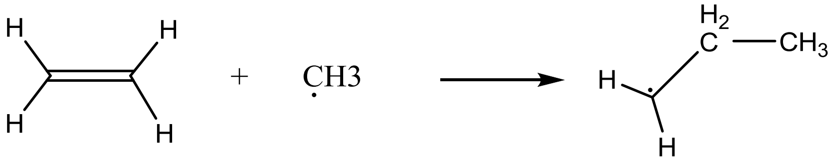
Epoxidation of Cyclohexenone with t-butyl hydroperoxide



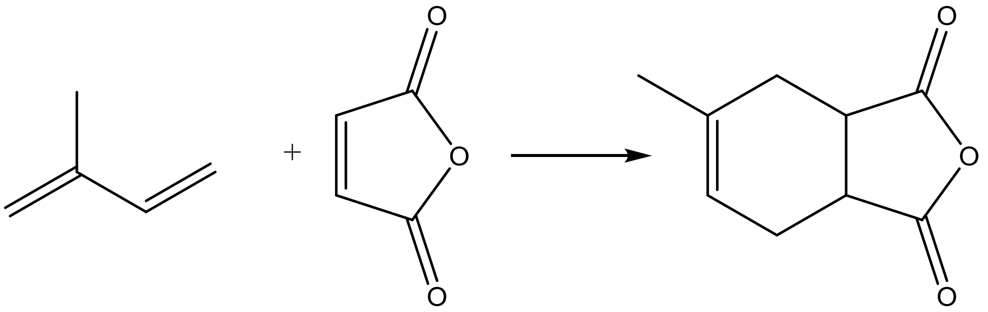
Shi Epoxidation of β-methylstyrene



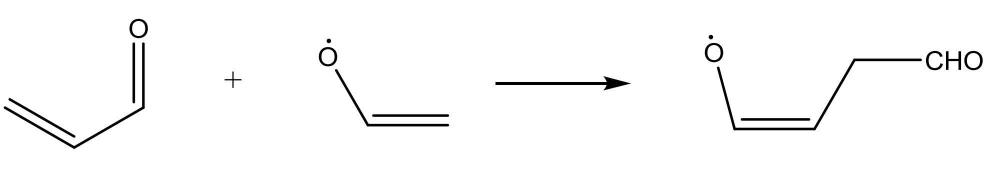
Methyl Radical Addition to ethene



Diels Alder of isoprene and maleic anhydride



Enol radical addition to acrolein



M06-2X/6-31+G**/PCM Enthalpies

All barriers are calculated versus separate reactants.

Species	M06 Enthalpies	Enthalpy Barrier
dimeSMAm062x	-1220.538798	
dimeSMBm062x	-1220.541870	
dimeSMCm062x	-1220.540349	
pyridinium	-248.525432	
dimeTSAm062x	-1220.511312	19.2
dimeTSBm062x	-1220.512014	18.7
pyridiniumTSA1	-1469.044008	14.6
pyridiniumTSC1	-1469.045551	13.6
pyridiniumTSD1	-1469.049206	11.4
pyridiniumTSI3	-1469.050183	10.7
pyridiniumTSJ5	-1469.048487	11.8
pyridiniumTSL1	-1469.049055	11.5
pyridiniumTSO1	-1469.043519	14.9
pyridiniumTSQ1	-1469.046562	13.0
pyridiniumTSS1	-1469.046726	12.9
pyridiniumTST1	-1469.040883	16.6
pyridiniumTSU1	-1469.046542	13.0
pyridiniumTSV1	-1469.046032	13.3
pyridiniumTSW1	-1469.052604	9.2
pyridiniumTSX1	-1469.047183	12.6
pyridiniumTSY1	-1469.046433	13.1
pyridiniumTSZ1	-1469.048582	11.7
pyridiniumTSAA1	-1469.043551	14.9
pyridiniumTSBB1	-1469.053291	8.8
complex	-1220.520211	
complexrev	-1220.522004	

M06-2X/6-31+G**/PCM Free Energies

The free energies below have a standard state of 1 Atm. To convert to a 1 M standard state, the entropies of each species have to be reduced by 6.35 e.u. (This is R ln(1 M / 1 Atm) = R ln (1 M / (1 /(R*298.15)) at 298.15, or in hartrees the numbers must be reduced by 0.003017. To compare the barriers at a 1 M standard state, the barriers for the pyridinium-containing TSs must be reduced by 1.893 kcal/mol.

Species	M06 Free	Free Energy

	Energies	Barrier
dimeSMAm062x	-1220.605047	
dimeSMBm062x	-1220.606210	
dimeSMCm062x	-1220.607208	
pyridinium	-248.558212	
dimeTSAm062x	-1220.577766	18.5
dimeTSBm062x	-1220.578297	18.1
pyridiniumTSA1	-1469.126989	24.1
pyridiniumTSC1	-1469.127258	23.9
pyridiniumTSD1	-1469.129680	22.4
pyridiniumTSI3	-1469.131051	21.6
pyridiniumTSJ5	-1469.128545	23.1
pyridiniumTSL1	-1469.130467	21.9
pyridiniumTSO1	-1469.125715	24.9
pyridiniumTSQ1	-1469.132145	20.9
pyridiniumTSS1	-1469.130421	22.0
pyridiniumTST1	-1469.122201	27.1
pyridiniumTSU1	-1469.130817	21.7
pyridiniumTSV1	-1469.129128	22.8
pyridiniumTSW1	-1469.134649	19.3
pyridiniumTSX1	-1469.130470	21.9
pyridiniumTSY1	-1469.130088	22.2
pyridiniumTSZ1	-1469.132457	20.7
pyridiniumTSAA1	-1469.126364	24.5
pyridiniumTSBB1	-1469.136341	18.2
complex	-1220.591169	
complexrev	-1220.591915	

MP2/6-311+G**/PCM Single Point Energies

Species	MP2 Energies
dimeSMAm062x	-1218.5407880
dimeSMBm062x	-1218.5718121
dimeSMCm062x	-1218.5712564
pyridinium	-248.0567330
dimeTSAm062x	-1218.5407880
dimeTSBm062x	-1218.5412844
pyridiniumTSA1	-1466.6141667
pyridiniumTSC1	-1466.6151121

pyridiniumTSD1	-1466.6244974
pyridiniumTSI3	-1466.6248257
pyridiniumTSJ5	-1466.6192409
pyridiniumTSL1	-1466.6240466
pyridiniumTSO1	-1466.6131189
pyridiniumTSQ1	-1466.6147568
pyridiniumTSS1	-1466.6156721
pyridiniumTST1	-1466.6097852
pyridiniumTSU1	-1466.6162134
pyridiniumTSV1	-1466.6176041
pyridiniumTSW1	-1466.6227037
pyridiniumTSX1	-1466.6168227
pyridiniumTSY1	-1466.6184247
pyridiniumTSZ1	-1466.6145844
pyridiniumTSAA1	-1466.6152994
pyridiniumTSBB1	-1466.6260015
complexrev	-1218.5521723

Listing of Dynamics Programs for Program Suite PROGDYN

Program progdynstarterHP

```
#!/bin/bash
# This is the master control program for dynamics, in the form of a Unix Shell Script.
#
# Necessary input files:
# freqinHP         - This is the standard output from a Gaussian 98 or 03 frequency
calculation using freq=hpmodes.
# progdyn.conf – This is a file giving a variety of configuration options, called on by
many of the subprograms.
#
# Optional input:
# isomernumber     - A number in file isomernumber provides a start for numbering runs.
# detour – A signal file that, by existing, signals the program to do a side calculations
# nogo – A signal file that, by existing, signals the program to stop between points
#
# Programs called:
#  proggenHP     - An awk program that starts a trajectory, giving each mode its zero
point energy (if a quasiclassical calculation) plus random additional excitations
depending on the temperature.
#  prog1stpoint – Awk program that creates the first Gaussian input file for each run
#  prog2ndpoint – Awk program that creates the second Gaussian input file for each run
```

```
#  progdynb – Creates subsequent Gaussian input files until run is completed, used the
awk
# proganal – A program to analyze the latest point and see if a run is done.  This
program must be redone for each new system.  Elaborate changes are often programmed
into proganal, such as the automatic changing of configuration variables.
# randgen – A program that generates random numbers between 0 and 1.  These are
generated all at once and stored in a file for use by proggenHP.
#
# Output files
# isomernumber – A running tab of the run number
# geoRecord – A record of all the starting positions and velocities.
# geoPlusVel – Created by proggen, this gives starting position and velocities for current
run.
# g03.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest
input
#       file for Gaussian03 for current run and latest point.
# olddynrun and olderdynrun – files containing the last two outputs from Gaussian, for
creation
# of the next point
# dyn  - A record of all of the Gaussian outputs.
# dynfollowfile – A short record of the runs and their results.
# skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the
middle of a run.
# diagnostics – optional output that follows which subprograms are running and
configuration variables, decided by variable in progdyn.conf
# vellist – optional output that list the velocities of each atom, decided by variable in
progdyn.conf
# A number of files starting with 'temp' are created then later erased.


#progdynstarterHP, made to use high-precision modes from Gaussian output with
freq=hpmodes
#updated to create a random number file temp811 that is used by proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn putting it under
control of progdynb
#version Feb 2008 moves variables like the scratch directory and location of randgen to
the beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run twice in checking for
complete runs
#version May 2009 Echeck catches bad energies after only one point, other lines written
simpler, triple while loop, revised comments
```

```
#version Aug 2010 isomernumber adds words to ease parsing, increased elements up to
bromine, runpointnumber checked for more appropriate restarts
#
#LIMITATIONS - standard version only handles elements up to bromine, must change
program to do higher atomic numbers
#   only handles up to 4000th excited state for modes - this could start to affect the
initialization of classical modes or transition vectors at
#    extremely high temperatures
#   The routine that checks whether the actual energy approximately equals the desired
energy checks for lines containing "SCF Done" or "EUMP2 =" or " Energy="
#   This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculatons
but the routine in prog2ndpoint would have to be changed for other calcs.
#
#                              OUTLINE
# A. initilize to perform Gaussian jobs and know where we are
#    start loop
# B. if no file named "skipstart" then generate a new isomer.  Instructions: Get rid of
skipstart to start new isomer.
#    the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and
second points, and sets up for continuous loop
# C. loop over propagation steps
#
#  AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system
and assigned here or by program calling this one
export LC_ALL=C
echo $1
scratchdir=$1
export g09root=/apps/lms/g09_A02_XEON
. $g09root/g09/bsd/g09.profile
origdir=`pwd`
cd $origdir
logfile=docslog
randdir=~/bin
cp /scratch/d-singleton/binall700/* /tmp/$PBS_JOBID
proggramdir=/tmp/$PBS_JOBID
freqfile=/scratch/d-singleton/binall700/freqinHP
echo ORIGDIR:
echo $origdir
echo SCRATCHDIR:
echo $scratchdir
echo PROGGRAMDIR:
echo $proggramdir
```

```
rm -f nogo    # assume that if someone is starting a job, they want it to go.
rm -f diagnostics # contains extra info from start of progFS

#### Triple 'while' loop - will have to break multiple times to get out, but advantage is
ability to control starting over
while (true)
do

# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f goingwell
while (true)
do
#  BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  if (test -f skipstart) then
    echo "skipping start and continuing from previous runs"
  else
#
B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1
generate geoPlusVel and first input file
    if [ `cat runpointnumber` = "1" ]; then
      echo "XXXX did not complete first point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "2" ]; then
      echo "XXXX did not complete second point so new isomer started" >>
dynfollowfile
    fi
    if [ `cat runpointnumber` = "3" ]; then
      echo "XXXX did not complete third point so new isomer started" >> dynfollowfile
    fi
    cd $origdir
    $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
    awk '/        1         2         3         4/,/Harmonic frequencies/ {print}' $freqfile >
temp401
    awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 >
tempfreqs
    awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempredmass
    awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempfrc
    awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
    awk '/has atomic number/ {print}' $freqfile > tempmasses
    awk '/Standard orientation:/,/tional const/ {if ($3==0) print}' $freqfile >
tempstangeos
```

```
    awk -f $proggramdir/proggenHP $freqfile > geoPlusVel
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533
> isomernumber
      rm temp533
    else
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm g09.com
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
#
B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B
2B2  if first part successfule then clean up and run the first input file, otherwise die
    if (test -s g09.com) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses
temp401 temp811
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cat $scratchdir/g09.log >> dyn
        cp $scratchdir/g09.log olderdynrun
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
#
B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B
3B3 if B2 worked then you are here.  create 2nd point, run it, and set up for propagation
loop
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
# before we decide to run this, check the energy
```

```
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    tail -1 dynfollowfile | awk '/XXXX/ {print}' > tempdone
    if (test  -s tempdone) then
      rm -f dyn
      rm -f traj
      echo 0 > runpointnumber
      break
    fi
    if (test -s g09.com) then
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olddynrun
        cat $scratchdir/g09.log >> dyn
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   /
{print}' > old
        awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   /
{print}' > older
        echo 3 > runpointnumber
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a start, so lets skipstart until instructed otherwise
    echo "forward" > skipstart
  fi
# Reverse trajectories starter routine
  if [ `cat skipstart` = "reverserestart" ]; then
    cd $origdir
    rm g09.com
    echo 1 > runpointnumber
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
    if (test -s g09.com) then
```

```
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olderdynrun
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    if (test -s g09.com) then
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olddynrun
        cat $scratchdir/g09.log >> dyn
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   /
{print}' > old
        awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   /
{print}' > older
        echo 3 > runpointnumber
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
```

```
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
    echo "reverse" > skipstart
  fi

#
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B_
__END_of_B___END_of_B___

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCC  propagation loop
  while (true)
  do
#increment runpointnumber
    cp runpointnumber temp533
    awk 'BEGIN {getline;i=$1+1;print i}' temp533 > runpointnumber
    rm temp533
    rm -f goingwell
    cd $scratchdir
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
    cd $origdir
    grep 'Normal termination' $scratchdir/g09.log > goingwell
    if (test -s goingwell) then
      mv olddynrun olderdynrun
      cp $scratchdir/g09.log olddynrun
      awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   / {print}'
> old
      awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   /
{print}' > older
      awk -f $proggramdir/progdynb olddynrun > g09.com
      rm -f old older
    else
      cp $scratchdir/g09.log $origdir/g09.log
      break
    fi

# here is a cool link that lets you interupt the dynamics with a short job, then
# it automatically goes back to the dynamics  just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test  -f detour) then
      rm detour
      date >> $logfile
```

```
      cat run.com >> $logfile
      cp run.log temp.log
      cd $scratchdir
      $g09root/g09/g09 $origdir/run.com > $origdir/run.log
      cd $origdir
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > tempdone
    if (test  -s tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ];
then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olderdynrun
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
          mv dyn dyn$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olderdynrun
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
        mv dyn dyn$a
      fi
      break
    fi
  done
```

```
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop__
__END_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done

  if (test  -f nogo) then
    break
  fi
  if (test  -s goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0
```

Program proggenHP

```
BEGIN {
# Aut 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification
of displacement on particular modes
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file
cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without
changes needed
# updated June 2008 to incorportate new method for choosing displacements with
initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
```

```
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorportates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
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  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a
point that is not a freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting proggen *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
```

```
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it
from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
```

```
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets
you isotopic substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
  if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"diagnostics"
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes
unless classical=2
```

```
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside
random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
  getline < "temp811"; randArrC[i]=$1
}
# for a QM distribution for a harmonic oscillator in its ground state, we want to generate
a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more
common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
```

```
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction
for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]       #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when
classical but the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
  if (temp<10) vibN[i]=0        # avoids working with very small temperatures - if the
temp is too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#     get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
```

```
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Ansgroms for
compatability with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]    #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]          #no zpe when classical
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but
hopefully that bug is killed and you can use disMode 0
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatability
  if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat
these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]
>> "diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
```

```
    }
  }

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g
angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5        # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a
saddle point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction,
the rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
  }

# if controlphase is being used, set the velocity on particular modes as positive or
negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based
on 1/2RT in degree of freedom
```

```
if (classical==2) {
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
  kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
      if (DRP==1) velArr[i,j]=0
      }
    }
  }

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*canno
nArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 + cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
```

```
      }
    }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use
this for other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140,
keeping momenta the same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
    printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
    }

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
    KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
    printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
    }

#anything else I add to the file will not affect the trajectories but will keep a record and
be good for analysis
for (i=1;i<=numFreq;i++) {
    if (initialDis==0) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==1) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==2) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
    }
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"   KE initial total=",KEinittotal
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-
KEinitmodes
```

```
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"   maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol  E + zpe=",zpePlusE,"
potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}
```

Program prog1stpoint

```
BEGIN {
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
#     removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
```

```
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag==1) print "***************** starting prog1stpoint *****************" >>
"diagnostics"
if (diag==1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag==1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag==1) print "processors,checkpoint,title" >> "diagnostics"
if (diag==1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
```

```
getline < "isomernumber"
isomernum = $1
#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities not needed for 1st point
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
# make the title four words exactly, leaving out spaces if necessary
print title1,title2,title3,title4
print "runpoint 1"
print "runisomer ", isomernum
print ""
print charge,multiplicity
}

END {
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
```

```
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
print ""
}
```

Program prog2ndpoint

```
BEGIN {
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that
DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
etolerance=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

blankLineTester=10
while (blankLineTester>1) {
```

```
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="DRP") DRP=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="etolerance") etolerance=$2
  if ($1=="reversetraj") reversetraj=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting prog2ndpoint *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

#get the isomer number from file
getline < "isomernumber"
isomernum = $1
```

```
#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes
faster, sometimes not
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print title1,title2,title3,title4
print "runpoint 2"
print "runisomer ", isomernum
print ""
print charge,multiplicity

# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
# so we need to set up arrays for position, velocity, and force

#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }
```

```
#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    arr[i,j]=velArr[i,j]+geoArr[i,j]
    if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
    }
  if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
  if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
  }

#pull out other information useful for testing whether total energy is right or bad
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
    }
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
  }
#get initial geometry into file traj
print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
  }
#added by Samae on 102910
scfcount=0
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if (($1=="SCF") && (scfcount==0)) newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
newPotentialEK=(newPotentialE-potentialE)*627.509
if ($1=="SCF") {
```

```
  if (scfcount==0) {
    pddga=$5
    }
  if (scfcount==1) {
    qm=$5
    }
  if (scfcount==2) {
    pddgb=$5
    pddgc=(pddga-pddgb)
    newPotentialE=(qm+pddgc)
    newPotentialEK=(newPotentialE-potentialE)*627.509
    }
  scfcount++
  }
}

# now we go ahead and translate the forces and add them
(/     1    / || /     2    / || /     3    / || /     4    / || /     5    / || /     6    / || /     7    / || /
8    / || /     9    /
|| /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /     15    / || /     16
/ || /     17    / || /     18
/ || /     19    / || /     20    / || /     21    / || /     22    / || /     23    / || /     24    / || /     25
/ || /     26    / || /     27
 / || /     28    / || /     29    / || /     30    / || /     31    / || /     32    / || /     33    / || /
34    / || /     35    /) && length($3
) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#put out Echeck but only if not a DRP
if (DRP==0) {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK,"   point 1 kinetic E=",KEinittotal,"
Total=",newPotentialEK+KEinittotal >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinittotal)>(desiredModeEnK+etolerance)) print "XXXX bad
total Energy" >> "Echeck"
```

```
  if ((newPotentialEK+KEinittotal)<(desiredModeEnK-etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  }
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if
we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
    if (DRP==1) forceArr[i,j]=0
    arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
    if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
    }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
print ""
#get second geometry into file traj
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint 2 ","runisomer ",isomernum >>
"traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
  }
```

```
}
```

Program progdynb

```
BEGIN { #this is the main routine for generating new .com files by the Verlet algorithym
# Aug 2010 increased elements handled automatically but only up to bromine!
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
damping=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
OFS="     "

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
```

```
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="keepevery") keepevery=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="damping") damping=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "**************** starting progdynb ****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

# get number of atoms and weights from geoPlusVel, and previous geometries from old
and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
```

```
  weight[i]=$5; atSym[i]=$1
  }

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
  }

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
  }

#for DRPs read in oldAdjForces and maxAtomMove
if (DRP==1) {
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

# record atom velocities for IVR analysis.  This is actually the velocity in the previous
run, which is the easiest to calculate.
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1
if (diag==3) print "runpoint ",runpointnum-1,"runisomer ",isomernum >> "vellist"
for (at=1;at<=numAtoms;at++) {
  atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2
+(oldarr[at,3]-olderarr[at,3])^2)^.5
  KEatomstotal=KEatomstotal+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
  if (diag==3) print atomVel >> "vellist"
  }
apparentTemp=KEatomstotal*2/(3*RgasK*numAtoms)
if (diag==4) print "KEatomstotal",KEatomstotal,"apparent Temperature",apparentTemp
>> "vellist"
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
```

```
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
}

#must adjust next line for weird atoms
(/     1   / || /     2   / || /     3   / || /     4   / || /     5   / || /     6   / || /     7   / || /
8   / || /     9   /
|| /     10   / || /     11   / || /     12   / || /     13   / || /     14   / || /     15   / || /     16
/ || /     17   / || /     18
/ || /     19   / || /     20   / || /     21   / || /     22   / || /     23   / || /     24   / || /     25
/ || /     26   / || /     27
 / || /     28   / || /     29   / || /     30   / || /     31   / || /     32   / || /     33   / || /
34   / || /     35   /) && length($3
) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
############routine for DRPs#############
if (DRP==1) {
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
      oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
      if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
      if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
```

```
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3])  >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3])  >>
"oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }
########

############normal routine for Verlet ##############
if (DRP==0) {
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
      if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
>> "diagnostics"
      if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
      newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
      if (boxon==1) {
        if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
```

```
        if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        }
      }
    }
  }
########

if ((runpointnum % keepevery)==0) system("cat g09.log >> dyn")
print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(maxcycle=200) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes
faster, sometimes not
print "pop=none "
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print  title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ",isomernum
if (DRP==1) print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
print ""
print charge,multiplicity
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
  print "" >> "traj"
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
  print ""
  if (length(meth5)>2) print meth5
  if (length(meth6)>2) print meth6
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
```

```
        print $0
        }
      }
  print ""
}
```

Program randgen

```
#include <stdio.h>
#include <stdlib.h>

int a,b,c;
double d;

int product(int x, int y);

int main(void)
{
  int count=1;
  srand48(time (0));
  while (count<=10000)
  {
    d = drand48();
    printf ("%.20f\n", d);
    count++;
  }
  return 0;
}

/* Function returns the product of the two values provided
int product(int x, int y)
{
    return (x * y);
}
*/
```

Program proganal

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ dichloro/ {
```

```
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<30)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }

END {
  C2C5=Distance(2,5)
  C3C5=Distance(3,5)
  C2C7=Distance(2,7)
  C3C7=Distance(3,7)
    printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f
","C2C5",C2C5,"C2C7",C2C7,"C3C5",C3C5,"C3C7",C3C7)
  if (runpoint>500) {
    print "Too many points.  XXXX"
    }
  if ((C2C5>2.2) && (C3C5>2.2)) {
    print "Recrossed to Starting Material  XXXX"
    }
  if ((C2C5<1.7) && (C3C7<1.7)) {
    print "Formed Light Product XXXX"
    }
  if ((C3C5<1.7) && (C2C7<1.7)) {
    print " Formed Heavy Product XXXX"
    }
  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
```

```
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

progdyn.conf

```
#This is the configuration file for PROGDYN.  This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running
jobs
#***The keywords are case sensitive.  The following keywords should always be
defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method mpwpw91/6-31+G**
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the
default
#If the method is U..., put unrestricted here and the .com files will have in them
guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes
things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword
checkpoint.
#method2
charge 0
multiplicity 1
processors 2
#*** memory --The following "word" is copied exactly to the gaussian input file after
%mem=.
memory 200mw
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file
name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option
with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to
bother, use killcheck 1
killcheck 1
#checkpoint dyn20.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
```

```
title dichloroketene cis-2-butene mpw1k 298dis2
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that
# those at the end by 1/e
initialdis 2
#*** timestep -- this is the time between points in the trajectory.  Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 218.15
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if needed
method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,Solvent=water)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
method3 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
#method4 IOp(3/76=1000001970)IOp(3/77=0800008000)IOp(3/78=0700010000)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
```

```
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir negative
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 1000
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 9
linkatoms 1
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
```

```
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is,
initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the
edge
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.
This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve
energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra
room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box
that is 15 x 15 x 15 angstroms
boxon 0
boxsize 7.5
#*** displacements -- This keyword lets you set the initialdis of particular modes by
using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You
should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at
large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same
thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0
#displacements 11 0
#displacements 12 0
#displacements 13 0
#*** etolerance --This sets the allowable difference between the desired energy in a
trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial
velocities.
```

```
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 3 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
#reversetraj true


#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj
```

VITA

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