KINETIC ISOTOPE EFFECTS, DYNAMIC EFFECTS, AND MECHANISTIC STUDIES OF ORGANIC REACTIONS

A Dissertation

by

ZHIHONG WANG

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 2005

Major Subject: Chemistry

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Approved by:

Chair of Committee,	Daniel A. Singleton
Committee Members,	David E. Bergbreiter
	Kevin Burgess
	Jerry Tsai
Head of Department,	Michael P. Rosynek

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ABSTRACT

Kinetic Isotope Effects, Dynamic Effects, and Mechanistic Studies of

Organic Reactions. (December 2005)

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Chair of Advisory Committee: Dr. Daniel A. Singleton

Several organic reactions that could potentially involve coarctate transition states were investigated by a combination of experimental and theoretical studies.

In the thermal fragmentation of Δ-1,3,4-oxadiazolines, the mechanism supported by kinetic isotope effects and theoretical calculations is a three-step process that does not demonstrate any special stabilization in coarctate transition states. Rather than undergoing a direct coarctate conversion to product, the mechanism avoids coarctate steps. The last step is a concerted coarctate reaction, but being concerted may be viewed as being enforced by the necessity to avoid high-energy intermediates.

In the deoxygenation of epoxides with dichlorocarbene, the stabilization from the transition state aromaticity is not great enough to compete with the preference for asynchronous bonding changes. KIEs and calculations suggested that the reaction occurs in a concerted manner but with a highly asynchronous early transition state with much more C_α-O bond breaking than C_β-O bond breaking.

In the Shi epoxidation, a large β-olefinic ^{13}C isotope effect and small α-carbon isotope effect indicated an asynchronous transition state with more advanced formation of the C–O bond to the β-olefinic carbon. The calculated lowest-energy transition structures are generally those in which the differential formation of the incipient C–O bonds, the "asynchronicity," resembles that of an unhindered model, and the imposition of greater or less asynchronicity leads to higher barriers. In reactions of *cis*-disubstituted and terminal alkenes using Shi's oxazolidinone catalyst, the asynchronicity of the epoxidation transition state leads to increased steric interaction with the oxazolidinone when a π-conjugating substituent is distal to the oxazolidinone but decreased steric interaction when the π-conjugating substituent is proximal to the oxazolidinone.

Dynamic effects were studied in Diels-Alder reaction between acrolein and methyl vinyl ketone. This reaction yields two products in a ratio of 3.0 ± 0.5. Theoretical studies shows that only one transition structure is involved in the formation of both. Quasiclassical trajectory calculations on an MP2 surface give a prediction of a product ratio of 45:14 (3.2:1), which is in good agreement with the experimental observation.

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CHAPTER I

INTRODUCTION

A central focus of physical organic chemistry is the mechanistic investigation of organic reactions. The detailed understanding of reaction mechanisms not only enriches fundamental knowledge, but also allows the rational improvement of reactions and inspires new reactions as well.

In the process of studying mechanisms, chemists seek to obtain the structures and properties of intermediates and transition states. Various types of modern techniques have been developed and employed in the detection of intermediates with short lifetimes, providing information on their physical and chemical properties.[1] However, the more elusive chemical species, the transition states, are still beyond direct observations. Thus, subtle probes are used in the investigation of these species.

Kinetic isotope effects (KIEs) have been established as an effective tool for the mechanistic studies of organic reactions.[2] When measured at high precision, KIEs coupled with appropriate theoretical models provide a sensitive probe to characterize transition state structures.[3-5] This dissertation focuses on mechanistic studies using this methodology.

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

Kinetic Isotope Effects – Fundamental Theory

The term isotope effect refers to the difference in chemical or physical properties between chemical species that differ only in their isotopic composition. Those species can be stable atoms, molecules, ions, reactive intermediates, or species with no significant lifetime, such as transition states. Among the chemical and physical properties, equilibrium constants and rate constants are of special interest to physical organic chemists. Ratios of equilibrium constants provide equilibrium isotope effects (EIEs), while kinetic isotope effects are obtained from ratios of rate constants.

Isotope effects for various kinds of atoms have been investigated; however, the most common isotopic substitution is deuretium(D) for hydrogen(H). If we have two isotopomers XH and XD involved in the same equilibrium, as in equation 1 and 2, the EIE is conventionally defined as the equilibrium constant for the lighter isotopomer divided by the equilibrium constant for the heavier isotopomer, as shown in equation 3.

$$XH + Y \underset{}{\overset{K_H}{\rightleftharpoons}} X + YH \qquad (1)$$

$$XD + Y \underset{}{\overset{K_D}{\rightleftharpoons}} X + YD \qquad (2)$$

$$EIE = \frac{K_H}{K_D} \qquad (3)$$

Similarly, when we have two isotopomers undergoing the same kind of reaction, as in equation 4 and 5, the KIE is conventionally presented as the rate constant for the lighter isotopomer divided by the rate constant for the heavier isotopomer, as shown in equation 6.

$$XH + Y \xrightarrow{k_H} X + YH \quad (4)$$

$$XD + Y \xrightarrow{k_D} X + YD \quad (5)$$

$$KIE = \frac{k_H}{k_D} \quad (6)$$

Isotopic substitution in reactants is the simplest possible change that can be made in a chemical reaction. The resulting isotope effect can reflect the difference in the nature of the bonding to the labeled atom and the chemical environment around it. However, isotopic substitution does not, to a very close approximation, affect the potential energy surface that the reaction path traverses. This fact greatly simplifies the prediction of isotopic rate ratios by avoiding the difficulty of calculating electronic energies to a high level of accuracy.

Since isotopomers react along approximately identical paths on the same potential energy surface, the difference in measured equilibrium constants or rate constants are attributed to the change in mass, which consequently changes the frequencies of vibrational modes, thereby affecting their zero-point energy (ZPE), as shown in equation 7 and 8.

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad (7)$$

υ = frequency
k = force constant
μ = reduced mass of system

$$ZPE = \frac{1}{2} h\upsilon \quad (8)$$

In the most common way, isotope effects are categorized as primary isotope effects or secondary isotope effects. A primary deuterium isotope effect occurs when the C-H or C-D bond breaks in the rate-determining step of a chemical reaction. Similarly, a primary carbon isotope effect occurs when the ^{12}C-R or ^{13}C-R bond breaks in the rate-determining step. In the simplified model, when a C-H (C-D) bond is broken, the stretching vibration of the reactants is converted to translational motion over the barrier, and the zero-point energy disappears for that particular degree of freedom. Consequently, the difference in rates primarily arises from the difference in the zero-point energy of the reactants. The C-H bond breaking starts out at a higher zero-point energy, which thus requires a lower activation energy to react and leads to a ratio of k_H/k_D greater than 1. This is then further categorized as a 'normal isotope' effect. Figure 1 illustrates this.

An alternative way to understand isotope effects is that the heavy isotope will concentrate at the site where it is bound more strongly and has larger force constant. For a kinetic effect this means that deuterium will prefer the reactant, where the force constant is higher, and hydrogen will prefer the transition state, where the force constant is lower. Thus the hydrogen compound will react faster, which, consistent with the ZPE explanation, gives rise to a normal primary isotope effect. The typical range for primary deuterium isotope effects is 2-7 while primary ^{13}C isotope effects fall between 1.01 and 1.05. The magnitude of the primary KIE is frequently used as a measure of the degree of bond forming or breaking in the transition state.

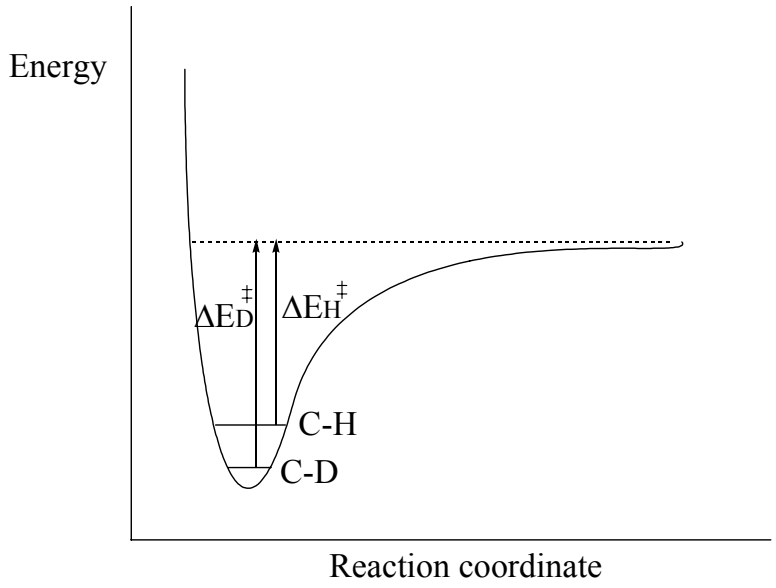

Figure 1. The origin of primary isotope effects, using C-H / C-D as example.

Secondary isotope effects are observed in reactions in which the isotopic substitution is at a bond not being broken. In general, the farther the isotopic substitution is from the reacting center, the lower the magnitude of the isotope effects. Secondary isotope effects arise from differences in the changes of force constants from the reactants to the transition state, which thus leads to the difference in zero-point energy. In a reaction in which an H/D is bound to an sp^3-hybridized carbon in the reactant and this carbon rehybridizes toward sp^2 at transition state, the C-H/D bending force constants decrease on going from reactant to transition state. The zero-point energy difference in the transition state is smaller than that in the reactant, thus the activation energy for the H-compound is lower than the activation energy for the D-compound. Consequently k_H/k_D is greater than 1. The magnitude of this type of KIE is smaller than the magnitude for primary isotope effects, and these KIEs are called normal secondary isotope effects.

Alternatively, in a reaction in which an H/D is bound to an sp^2-hybridized carbon in the reactant and this carbon rehybridizes toward sp^3 at transition state, the C-H/D bending force constants increase on going from reactant to transition state. The zero-point energy difference in the transition state is larger than that in the reactant, thus the activation energy for the H-compound is higher than the activation energy for the D-compound, and consequently k_H/k_D is less than 1. This is termed an 'inverse' secondary isotope effect. Figures 2 and 3 illustrate the normal and inverse secondary isotope effects respectively. Typical inverse secondary deuterium isotope effects fall between 0.8 and 1.0 while normal secondary isotope effects have a typical range of 1 and 1.25.

Normal secondary KIEs are often associated with a less sterically restricted transition state while inverse secondary KIEs suggest a more sterically restricted transition state.

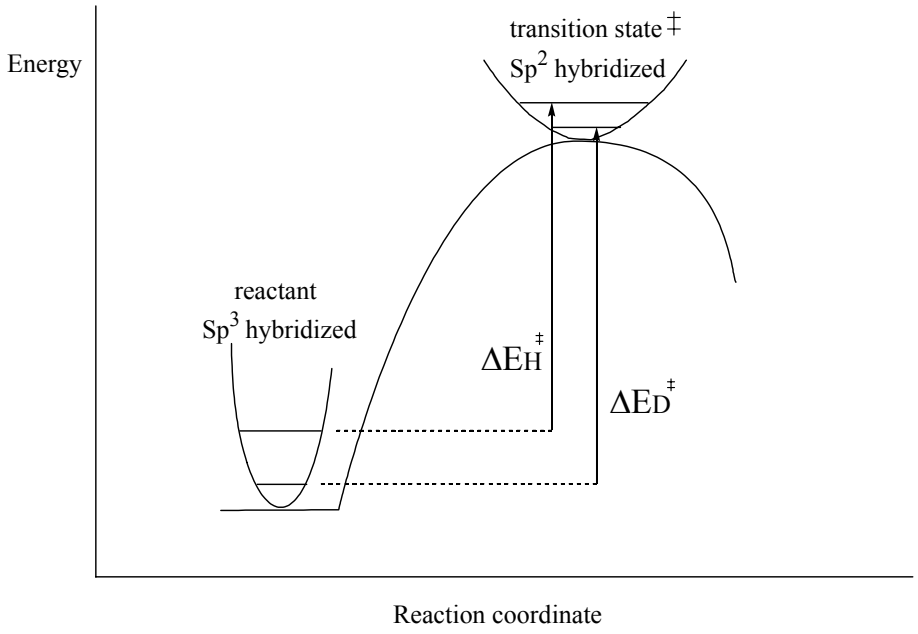

Figure 2 The origin of normal secondary isotope effects.

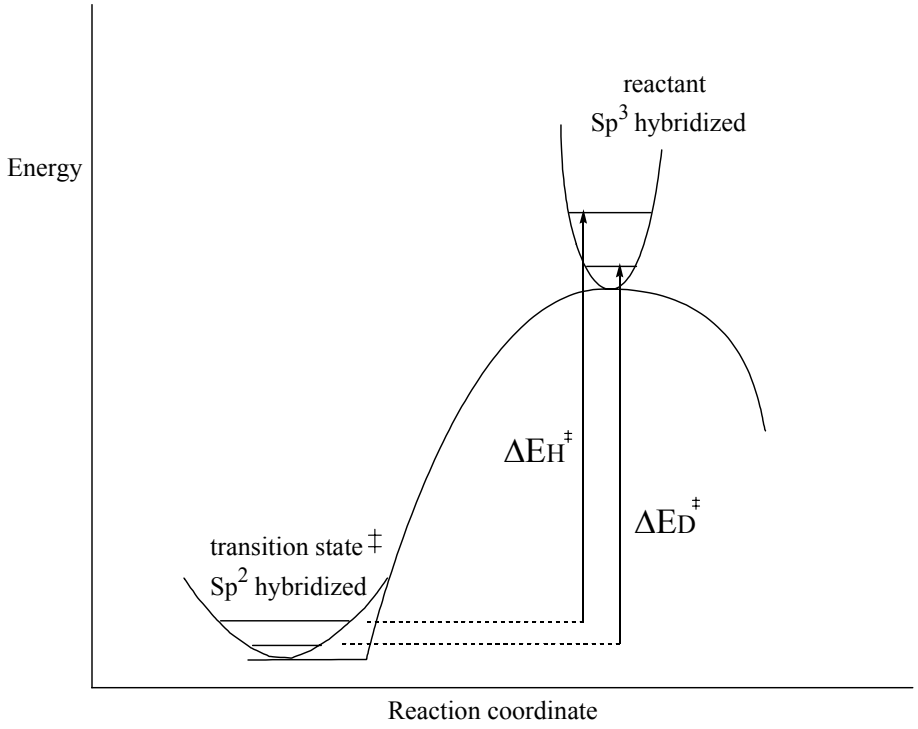

Figure 3 The origin of inverse secondary isotope effects.

Statistical Thermodynamic Expressions for Isotope Effects

Statistical thermodynamics describe the equilibrium constant K and the rate constant k in terms of partition functions Q and energy difference. The equilibrium constant K is related to the energy difference between reactants and products, while the rate constant k is related to the energy difference between reactants and transition state.

Although in principle transition-state theory permits one to predict absolute rates from the properties of the reactants and the transition state, in practice it is much easier and safer to predict relative rates. Thus the ratios of partition function are usually used to describe EIEs and KIEs. In the case in which the reactant R is substituted by its isotopic isomer R*, the equilibrium isotope effect and the kinetic isotope effect are given in the following equation 9 and 10.[6]

$$EIE = K/K^* = (Q_P/Q_P^*) / (Q_R/Q_R^*) \quad (9)$$

$$KIE = k/k^* = (Q_{TS}/Q_{TS}^*) / (Q_R/Q_R^*) \quad (10)$$

where Q's are the molecular partition functions for reactants, products, and transition states, and K* and k* represent the equilibrium constant and rate constant for the isotopic isomer R*.

The partition functions are divided into several items and evaluated within the rigid rotor, harmonic oscillator approximations. The separate items are represented in the following expressions, equation 11, 12, and 13.[7]

$$(Q/Q^*)_{trans} \bullet (Q/Q^*)_{rot} = (M/M^*)^{3/2} \bullet \prod_{i=1}^{n_{rot}} (I_i/I_i^*)^{1/2} = MMI \quad (11)$$

$$(Q/Q^*)_{vib} = \{ \exp (-\sum_{i=1}^{n_{vib}} \Delta u_i/2) \} \bullet \{ \prod_{i=1}^{n_{vib}} (1-e^{-ui}*) / (1-e^{-ui}) \} = ZPE \bullet EXP \qquad (12)$$

$$(Q/Q^*)_{elect} = 1 \qquad (13)$$

where MMI: the mass-moment of inertia term

ZPE: the zero-point energy contribution

EXC: the vibration excitation term

M = molecular mass

I_i = i^{th} moment of inertia

$u_i = h\upsilon_i/kT$

υ_i = frequency of the i^{th} vibrational mode

$\Delta ui = u_i - u_i^*$

n_{rot} = number of rotational degrees of freedom

n_{vib} = number of vibrational degrees of freedom

k: Boltzmann constant

h: Planck's constant

T: temperature in Kelvin

Here the number of rotational degrees of freedom is 2 for linear and 3 for non-linear species. The number of vibrational degrees of freedom is 3N-5 for linear and 3N-6 for non-linear N-atom molecules, 3N-6 for linear and 3N-7 for non-linear N-atom transition states since the reaction coordinate frequency has been removed.

Substitution of equation 11-13 into equation 9-10 gives the primary expression of isotope effects in equation 14:

$$IE = MMI \bullet ZPE \bullet EXC \quad (14)$$

MMI represents the mass and structural difference of the isotopic isomer, whereas ZPE and EXC represent vibrational contribution, which depend on mass and structural difference and force constant change between reactants and products or transition state. Stern and Wolfsberg have proposed that mass and structural differences alone do not lead to measurable isotope effects, but the isotope effects are sensitive probes of bonding and force constant changes during the chemical reactions.

Alternative equations 15 and 16 are also commonly employed:

$$EIE = VP \bullet ZPE \bullet EXC \quad (15)$$

$$KIE = (u_L/u_L^*) \bullet (VP \bullet ZPE \bullet EXC) = RXC \bullet VP \bullet ZPE \bullet EXC \quad (16)$$

where vibrational frequency product ratio is expressed in equation 17:

$$VP = \prod_{i=1}^{n_{vib}} (u_i/u_i^*) \quad (17)$$

RXC: reaction coordinate contribution

u_L and u_L^*: frequencies along the reaction coordinate

Kinetic Isotope Effects Prediction from Calculational Information

The calculational prediction of KIEs is based on the statistical explanation of isotope effects. *Ab initio* or DFT calculations provide information on the structures and

frequencies of the reactants and transition state, which allows accurate KIEs prediction provided that the calculational model is accurate.

Since Bigeleisen's seminal work,[6] theoretical studies on the evaluation of the isotope effects have been reported[7, 8] and several programs have been developed for predicting isotope effects.[9] In 1989, Saunders and co-workers developed the program Quiver, which calculates reduced partition function ratios and KIE values from force constants and geometry.[10] The expression of the partition function ratio is given in equation 30, 31 and 32. Frequencies are usually scaled to cancel off the deviation from the harmonic oscillator assumption, and a tunneling correction is usually applied. [11]

$$(S_2/S_1)\, f_{GS} = \prod_{i}^{3N-6} \left\{ \frac{u_{i\,(2)}}{u_{i\,(1)}} \; X \; \frac{EXP[(1/2)\, u_{i\,(1)}]}{EXP[(1/2)\, u_{i\,(2)}]} \; X \; \frac{1- EXP(-u_{i\,(1)})}{1- EXP(-u_{i\,(2)})} \right\} \qquad (18)$$

$$(S_2/S_1)\, f_{TS} = \prod_{i}^{3N^{\ddagger}-6} \left\{ \frac{u_{i}^{\ddagger}{}_{(2)}}{u_{i(1)}} \; X \; \frac{EXP[(1/2)\, u_{i}^{\ddagger}{}_{(1)}]}{EXP[(1/2)\, u_{i(2)}]} \; X \; \frac{1- EXP(-u_{i}^{\ddagger}{}_{(1)})}{1- EXP(-u_{i(2)})} \right\} \qquad (19)$$

$$KIE_{TST} = \frac{\nu^{\ddagger}_{L\,(1)}}{\nu^{\ddagger}_{L\,(2)}} \; X \; \frac{(S_2/S_1)\, f_{GS}}{(S_2/S_1)\, f_{TS}} \qquad (20)$$

Measurement of Kinetic Isotope Effects

Measurement of KIE can be obtained in two ways – non-competitively or competitively. Non-competitive measurement involves determining the rate constants of isotopic substrates separately, then using equation 6 to get the KIE value. It is more

likely to introduce errors when this method is used since it is extremely hard to make sure that the two reactions are under exactly the same conditions, and this method requires highly enriched heavier isotopomers. Thus the method is usually used only in the deuterium isotope effect measurement because such KIEs are relatively large.

In a competitive technique, both the isotopic substrates are subjected to the same reaction conditions in the same reaction flask. In this way, the labeled reactant and the ordinary reactant will react in qualitatively identical ways, but quantitatively at different rates. As the reaction goes on, the isotopomer that reacts faster is enriched in the product while the isotopomer that reacts slower is enriched in the reactant. Then the KIE can be calculated from the change of isotopic composition and the conversion. This method is often preferred in KIE studies since it secures exactly the same reaction conditions for the reactions, and partially cancels experimental errors. Another advantage of the competitive technique is that it reveals rate differences when the nonisotopic reagent is formed gradually as it is consumed and provides a way to investigate some 'hidden' reaction steps, which cannot be detected by non-competitive method.

Competitive techniques require an accurate and precise measurement if the ratio of labeled and unlabeled materials. Three techniques are commonly used in this measurement.

Scintillation counting has been used as an easy and reliable tool in the measurement of the isotopic ratio of radioactive isotopes such as tritium and ^{14}C, in which cases the radioactivity is related to the concentration of the radioactive isotope.[12, 13] However, this method requires the arduous synthesis of specifically labeled substrates and requires

extremely high purification, since the scintillation counting is highly sensitive to impurities. These disadvantages limited the application of the scintillation counting method.

The second method of measuring isotopmer ratios is mass spectroscopy. It is usually necessary to convert the substance of interest into small molecules such as CO_2 and N_2 to get information on small KIEs, since fragmentation might cause isotopic fractionation.[14] If the reactant or product has only one carbon or nitrogen, the isotope ratio can be measured in high precision at natural abundance with mass spectrometer in the form of CO_2 and N_2.[15] However, organic compounds with only one carbon atom are very rare and selective degradation of most organic compounds is not practical. As a result, the mass spectroscopy technique in the determination of isotopic ratio is also limited.

A disadvantage of both scintillation counting and mass spectroscopy is that only one site of isotopic substitution can be measured at a time. Again, these techniques require highly labor-intensive synthesis or degradation at a specific site in the molecule. On the other hand, NMR provides a technique that can determine the isotopic ratio at different sites all at the same time. It has been realized for almost two decades that natural abundance deuterium NMR spectroscopy is a powerful and convenient tool for the estimation of deuterium kinetic isotope effects in organic reactions.[16] It was also pointed out that this technique has the further advantage that primary and secondary KIEs of different types can be measured simultaneously.[17]

The NMR methodology employed in this dissertation was developed by Singleton and co-workers.[4, 5] This method uses ^{2}H or ^{13}C at natural abundance, thus saving the chemists from the arduous synthetic work on labeled starting materials. Typically, a reaction of interest is taken to a high conversion, usually 85 to 95%, and the unreacted starting material is recovered from the system and carefully purified. High precision NMR spectra are obtained and compared to spectra of a standard sample, which contains starting material that has not been subjected to the reaction conditions. An alternative is to run the reaction to a low conversion and compare NMR spectra of the separated product with those of product from a complete conversion reaction. An atom or group which is distant from the reaction site is usually selected as an internal standard, assuming that the isotopic composition on that atom or group does not change in the reaction, which gives KIE =1. The changes in the isotopic composition on other atoms are obtained from comparing the integration change to that of the internal standard. The isotopic ratio change R/R_0 is then used along with the conversion to derive the KIEs.

To get reliable results, both the recovered and the standard sample need to be prepared identically. Also the NMR spectra of both samples are taken consecutively with the same acquisition parameters. The NMR data processing also requires consistency to minimize both random and systematic errors. Another requirement for this method is considerably high concentration of the sample solution to provide signal-to-noise ratio high enough for acceptable precision. The high-concentration requirement sometimes can be the major limitation of this technique. The low solubility of the compounds and the difficulty to recover highly purified starting material will probably cause a lot of

extra work or even the failure of the project. The difficulty in obtaining a large amount of starting material for the reaction may also be a problem due to the requirement of high conversion.

The NMR methodology for the isotopic ratio determination can find its application in various isotopic atoms, such as ^{2}H, ^{13}C, ^{17}O, and ^{15}N. When applied with more strict NMR acquisition and data processing conditions, this technique can also be used in the measurement of intramolecular KIEs.[5d] Coupled with appropriate calculations, intermolecular as well as intramolecular KIEs provide a great amount of information on the mechanistic details of the reaction, especially of the transition state in the rate limiting step.[5]

Kinetic Isotope Effects from Experimental Data

In most typical cases, studies on intermolecular competitive KIEs are standard.[18] When two isotopic molecules **A** and **B** with concentration a and b undergo analogous irreversible reactions as follows, then the reaction rates are expressed as equation 21 and 22 and the rate constant ratio can be obtained as in equation 23.

$$A_{(1)} + B \xrightarrow{k_1} P_{(1)}$$

$$A_{(2)} + B \xrightarrow{k_1} P_{(2)}$$

$$-\frac{da_1}{dt} = k_1 a_1 b \tag{21}$$

$$-\frac{da_2}{dt} = k_2 a_2 b \tag{22}$$

$$\frac{k_1}{k_2} = \frac{\log\left(\frac{a_1}{a_1^{\,0}}\right)}{\log\left(\frac{a_2}{a_2^{\,0}}\right)} \tag{23}$$

In the expression of KIEs, the fraction of reaction, F, is introduced and defined as $a_1/a_1^{\,0} = 1\text{-}F_1$. Thus equation 20 becomes equation 24 and equation 25 is derived.

$$\frac{k_1}{k_2} = \frac{\log(1\text{-}F_1)}{\log(1\text{-}F_2)} \tag{24}$$

$$F_2 = 1 - (1\text{-}F_1)^{k_2/k_1} \tag{25}$$

When the isotopic reactions are experimentally analyzed by NMR or other techniques, the direct ratio of the isotopic molecules is given as $a_2^{\,0}/a_1^{\,0} = R_0$ and $a_2/a_1 = R$, and equation 20 and 21 are solved as equation 26, or alternatively, 27.

$$\frac{k_1}{k_2} = \frac{\log(1\text{-}F_1)}{\log[(1\text{-}F_1)R/R_0]} \tag{26}$$

$$R/R_0 = (1\text{-}F)^{(1/KIE-1)} \tag{27}$$

In the cases of most competitive KIE measurements, the isotopic ratio is very small, and F_1 can be replaced by the overall reaction conversion F with negligible change in the KIE results. Error analysis on equation 23 gives the partial derivatives, in equation 28 and 29,[19] which indicates that for the relatively low precision of NMR integrations, the uncertainty in the KIE decreases greatly as F increases.[4] Figure 4 shows the relationship between the fraction of reaction, F, and the isotopic ratio R/R_0.

$$\frac{\partial(k_1/k_2)}{\partial(R/R_0)} = -\frac{1}{R/R_0} X \frac{\ln(1-F_1)}{\ln^2[(1-F_1)R/R_0]} \tag{28}$$

$$\frac{\partial(k_1/k_2)}{\partial F_1} = -\frac{1}{1-F_1} X \frac{\ln(R/R_0)}{\ln^2[(1-F_1)R/R_0]} \tag{29}$$

When the isotopic ratio of the product is used instead of that of the recovered starting material, equations 26, 28, and 29 are replaced by equations 30, 31, and 32.

$$\frac{k_1}{k_2} = \frac{\log(1-F_1)}{\log[1-(F_1R_p/R_0)]} \tag{30}$$

$$\frac{\partial(k_1/k_2)}{\partial(R_p/R_0)} = \frac{F_1}{1-(F_1R_p/R_0)} X \frac{\ln(1-F_1)}{\ln^{2[}1-(F_1R_p/R_0)]} \tag{31}$$

$$\frac{\partial(k_1/k_2)}{\partial F_1} = \frac{(Rp/R0)/[1-(F_1R_p/R_0)] X \ln(1-F_1) - 1/(1-F_1) X \ln[1-(F_1R_p/R_0)]}{\ln^{2[}1-(F_1R_p/R_0)]} \tag{32}$$

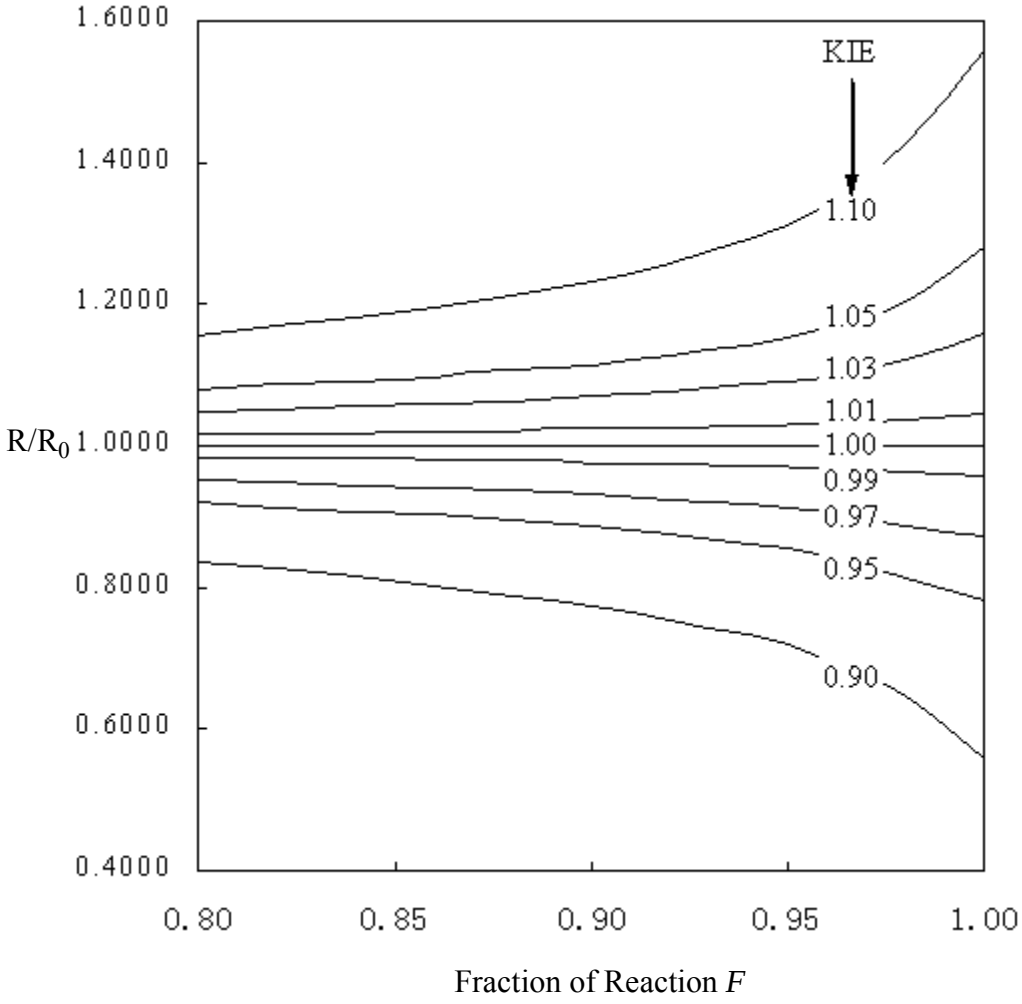

Figure 4. The relationship between fraction of reaction F, ratio of isotopic ratios R/R_0, and KIEs.

Coarctate Transition State Theory

The tremendous amount and the intrinsic complexity of organic reactions have inspired chemists to create many systems of classification of organic reactions, categorizing reactions by different view angles.

Conventionally, organic reactions are classified into two categories in a topological way: linear reactions and cyclic reactions. Described in the simplified valence bond (VB) notation, the bond breaking and forming in a single-step reaction is represented by a sequence of arrows that indicate the electron shift. Most organic reactions can be described by a linear sequence of electron-pushing arrows, and thus fall into the linear reaction category. When the electron-pushing arrows form a cycle, the reaction is classified as cyclic reaction; and it is called a pericyclic reaction if the electron shifts are concerted.

Complementary to the conventional definition of linear and cyclic reactions, the concept of 'Complex reactions' was introduced in 1994.[20] Based on the computational studies on the classification of more than 80,000 organic reactions from reaction databases, Herges proposed that there are three major topologies of electron redistribution in single-step reactions, as shown in Figure 5. He named the third class as complex reactions with 'coarctate' transition states, from the Latin 'coarctare', meaning to compress or contract. The major feature of this type of reactions is that at one or more atoms, two bonds are made and two bonds are broken at the same time.

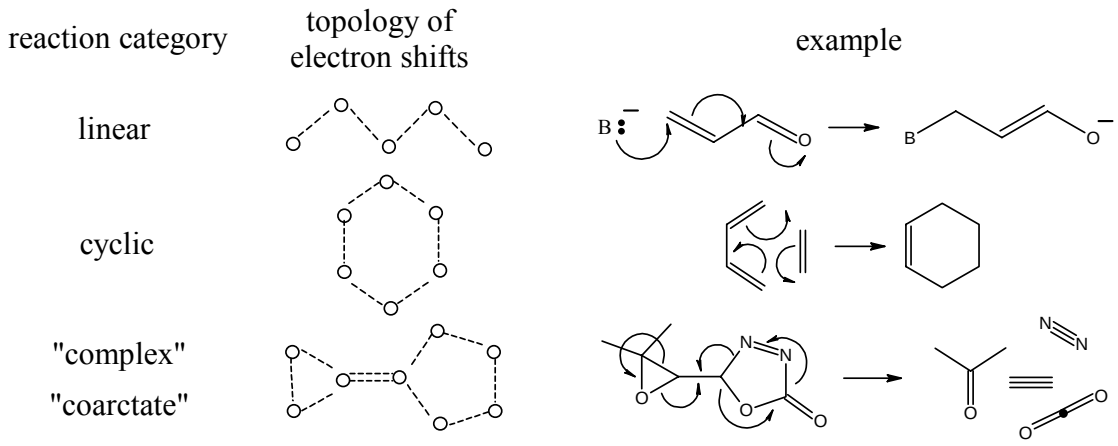

Figure 5 Topologies of the electron shifts in organic reactions.[20]

Two assumptions are made to describe reactions with coarctate transition states. First, the reactions are concerted; and second, the transition states are stabilized by conjugation, similar to pericyclic reactions.

As illustrated in Figure 6, reactions with coarctate transition states are formally described as a linear subsystem bounded at both ends by 'terminators'. Thus the linear succession of bond making and breaking is also finished by those 'terminators'. The atoms where two bonds are broken and made correspond to 'coarctations'. The terminators can be atoms with a lone pair that is formed or removed in the course of reactions, or a cyclic shift of electrons over several atoms. The length of the linear subsystem is also variable, however, the length n cannot be zero. According to this definition, complex reactions with n=0 are pericyclic reactions. In principle, any combination of different terminators and length of linear subsystem is possible. In most

cases, the length n=1, or n=2, and terminators contain lone pairs or three- and five-membered rings. Some topologically typical examples are shown in Figure 7.

Figure 6 Formal description of complex reactions with coarctate transition states.

The coarctate transition states are formally treated with the Dewar-Zimmerman topological method on the aromaticity of transition state. Similar to the transition states in pericyclic reactions, coarctate transition states follow the same rules of aromaticity. Hückel systems with an even number (including zero) of negative overlaps (nodes) are aromatic with 4n+2 electrons and antiaromatic with 4n electrons. An odd number of negative overlaps indicate a system with Möbius topology that is aromatic with 4n electrons and antiaromatic with 4n+2 electrons.

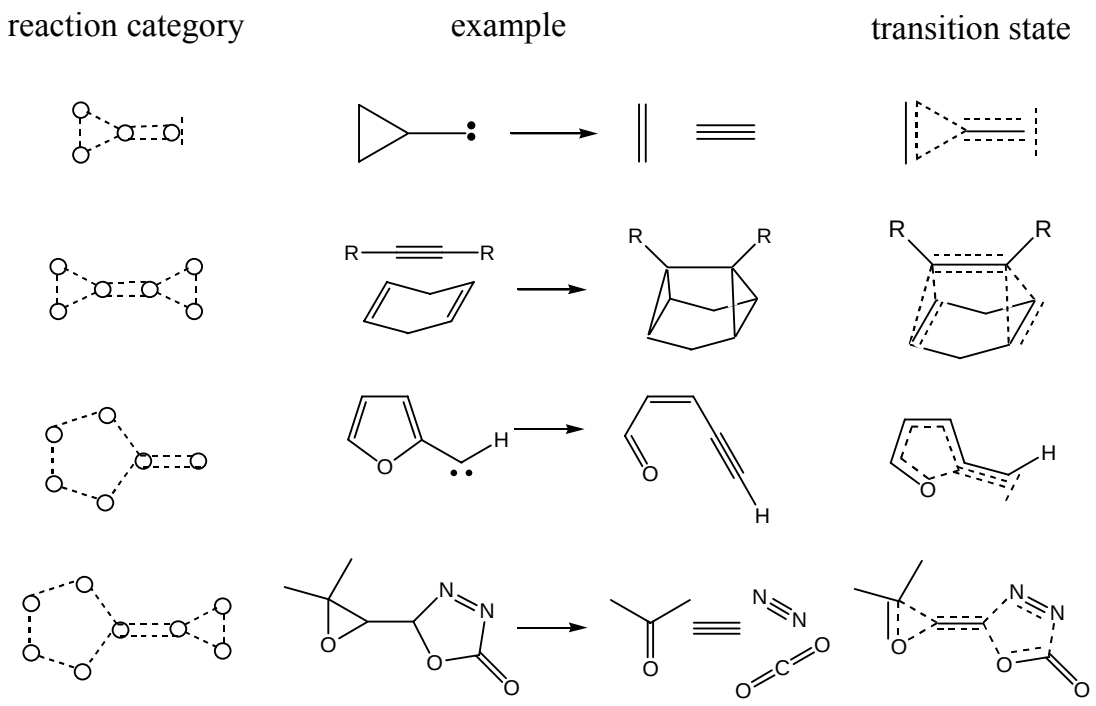

Figure 7 Examples of complex reactions with coarctate transition states.

In a simplified way, a coarctate transition state can be viewed as a topological transformation of a system in a pericyclic reaction, by compressing two particular orbitals together to give a set of two p orbitals at the center, at which two bonds are broken and made simultaneously. The two p orbitals are orthogonal to each other but not to the remaining orbitals. The transition states of complex reactions are formally derived from pericyclic reactions by constriction, which is the origin of these types of transition states being termed 'coarctate'. Since the orbital overlap is still cyclic, coarctate transition states take advantage of the same kind of stabilization as pericyclic transition states. An example is shown in Figure 8, illustrating the transformation. When the center 3 and 5 of the cyclopentadienyl anion are brought together with their basic orbitals orthogonal to

each other, the orbital basis is transformed into the transition state of the cyclopropylcarbene fragmentation.

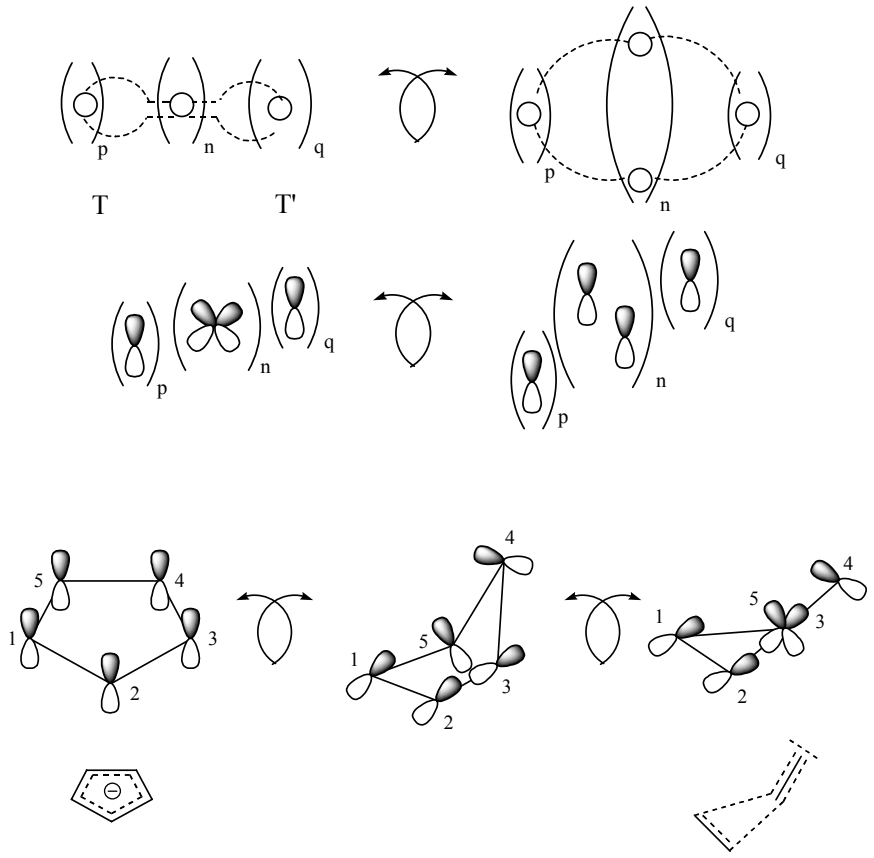

Figure 8 Topological transformation of cyclopentadienyl anion into the transition state of the cyclopropylcarbene fragmentation.

Two notations are formally used to categorize complex reactions. The first notation counts atoms, which is expressed in the general form *t-q-t'*, where t and t' indicate the number of atoms in both terminators and q gives the number of atoms in the coarctation. The second notation is electron-counting and has the general form [n+$p\chi$+n'], where n

and n' give the number of mobile electrons in each terminator and p indicates the number of mobile electrons in the coarctations. The Greek symbol χ is employed to depict that there are two orthogonal basis orbitals located at these atoms. The latter gives information about the electronic structure of the transition state.

Mathematically, there are thousands of possibilities, even from the combination of just less than ten electrons. However, most of those mathematical possibilities are not chemically feasible. In the investigation of known reactions, comparing with his conceivable models, Herges derived the following rules of complex reactions.[20]

1. Complex reactions are less probable as more bonds (and atoms) are involved in the transition state.

2. Breaking and making single bonds, especially C-C bonds, are less favorable than shifting double or triple bonds.

3. Hydrogen is by far the easiest group to be transferred. Oxygen in epoxidation reactions is the only exception.

4. Atoms with sp^3-hybridization do not react with each other.

5. All known reactions are thermodynamically highly favorable. They either start from extremely unstable educts, such as carbenes or nitrenes, or form small and stable products, such as nitrogen, carbon dioxide, or compounds with C≡N triple bonds.

6. No examples of a complex reaction with a 4-ring terminator were found, even though such reactions are conceivable.

As is well-known, along with pericyclic reactions, some reactions can be considered as pseudopericyclic, which means the cyclic delocalization of electrons in the transition state is disconnected because the orbitals involved in the delocalized system are orthogonal at some specific atomic center.[21] In analogy, some reactions can be considered as pseudocoarctate, when the disconnections occur in coarctate transition states.[22]

Theoretical tools are employed to gain further insight into the electronic structure of the coarctate/pseudocoarctate transition states and comparison to pericyclic/ pseudopericyclic transition states, among which the anisotropy of induced current density (ACID) method has been proven to be powerful for distinguishing between pericyclic/pseudopericyclic and coarctate/pseudocoarctate topologies.[23] The ACID scalar field can be interpreted as the density of delocalized electrons, and thus the ACID boundary surface can provide a continuous picture for the electron delocalization, which is cyclic for pericyclic transition states and not cyclic for coarctate transition states. Disconnection in the continuous systems of the ACID boundary surface is characteristic for pseudopericyclic and pseudocoarctate systems. Another method that has been used in the theoretical studies is the electron localization function (ELF), which provides a measure of the local pairing for the mobile electron flow and comparison between coarctate transition states and pseudocoarctate transition states.[24]

Since the concept of coarctate transition states was proposed, it has been employed in the descriptions and explanations of reaction mechanisms[25] and prediction of new reactions.[26] However, there are also calculational results suggesting some of the

reactions classified as coarctate actually do not involve the bond forming and breaking needed for the electron flow to form coarctate transition states.[27]

Most of the above-mentioned works are pure theoretical studies. Calculational results suggest the coarctate transition states as the lowest-energy pathway in those reactions. However, coarctate transition states usually need a highly organized system to fulfill the geometric requirements to line up the orbitals, which might make the pathway entropically disfavored and lead the reaction to go through other pathways in which intermediates with moderate energy are involved. Few experimental results have been provided to support that those reactions truly occur *via* coarctate transition states, or to rule out the other possible pathways. Since the concept of coarctate transition states has been more and more widely accepted, it is necessary to investigate this type of reactions experimentally to provide evidence for or against the theory before it eventually gets published in textbooks. Experimental KIE investigation coupled with theoretical studies provides a reliable method to do the work.

CHAPTER II

ISOTOPE EFFECTS AND THE MECHANISM OF FRAGMENTATION OF EPOXY IMINO-1,3,4-OXADIAZOLINES*

Introduction

To experimentally study complex reactions with coarctate transition states, we started with the prototype reaction that Herges has continually used as an example, the thermal fragmentation of epoxy imino-1,3,4-oxadiazolines.

Thermolysis of Δ^3-1,3,4-oxidiazolin-2-one **1a** and 2-phenylimino-Δ^3-1,3,4-oxidiazoline **1b** yields an alkyne, a ketone and carbon dioxide, or an alkynone and phenyl isocyanate, and nitrogen. This reaction was originally introduced by MacAlpine and Warkentin as an alternative method for the conversion of α,β-epoxyketones to alkynones and alkynals.[28] The method found applications in some synthesis and degradations of natural products.[29] Warkentin later suggested that the ketone formation occurs via a concerted mechanism.[30]

In his 1994 paper introducing the novel ideal of coarctate transition state, Herges explained the mechanism of the thermal fragmentation of epoxy imino-1,3,4-

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oxadiazolines from a new aspect, the oxirane fragmentation via an coarctate transition state, as shown in Figure 9.[20]

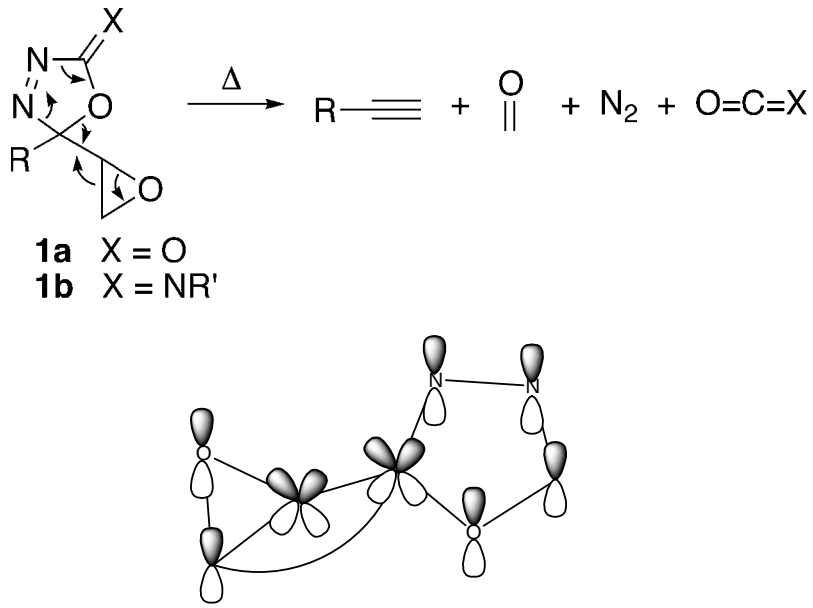


Figure 9 Oxirane fragmentation of phenylimino oxadiazoline and the proposed coarctate transition state.

Scrutinizing the known reactions that are classified as coarctate reactions, it was found that all known coarctate reactions are thermodynamically favorable. They either start from extremely unstable adducts, such as carbenes or nitrenes, or form small and stable products such as nitrogen, carbon dioxide, or compounds with nitrile functionality.

Most of the fragmentation reactions with three-membered ring terminators occur by elimination of a ketone from an epoxide. When N≡N or C≡N moieties exist in the molecule, the fragmentation should be highly thermodynamically favorable. Thus

oxirane fragmentations are often presented as typical examples for coarctate reactions. In a topological way, these reactions are categorized as 4-2-2 or [4+4χ+2] systems, which comprise ten electrons and are thermochemically allowed due to Hückel aromaticity in the transition states.

Another fact that inspired Herges was that MacAlpine and Warkentin found that the fragmentation of oxirane-substituted oxadiazolone is observed only when the oxadiazole ring and the oxirane ring are placed in a coplanar conformation by a spiro bridge. Provided a concerted mechanism is assumed, the stereochemistry can be explained by a topological analysis of the transition states. With ten mobile electrons, the reactions are thermochemically allowed by Hückel aromaticity in transition states. Oxirane and oxadiazole rings are fixed in a coplanar geometry to suit the overlap of the orbital basis and an optimal stabilization of the transition states is obtained.

However, the coarctate transition state does not look convincingly feasible in one way. As pointed out as the first rule of the complex reactions, complex reactions are less probable as more bonds and atoms are involved in the transition state. In this intriguing reaction, a total of five σ-bonds in the reactant are broken to afford five new π-bonds in the products. Thus arises the important question whether the transition state aromaticity of the coarctate reaction is sufficient to overcome this disfavor. To get detailed information on the mechanism of this reaction, we carried out a combined experimental and theoretical study.

Results and Discussions

Experimental ^{13}C kinetic isotope effects. The 2-phenylimino-Δ^3-1,3,4-oxadiazoline **2** derived from isophorone oxide, as shown in Figure 10, was chosen for study because it was previously found to afford relatively high yields of fragmentation products.[28] A significant complication with this molecule, however, is that its synthesis by oxidation of the semicarbazone of isophorone oxide affords an approximately 2:1 mixture of diastereomers. The minor isomer was found to interfere with the determination of KIEs below, so that **2** had to be purified by a tedious chromatography. This limited the scale at which **2** could be studied, negatively affecting the precision of the KIEs obtained. The stereochemistry of the major isomer **2** was predicted by calculation and verified by x-ray crystallography, as shown in Figure 11.

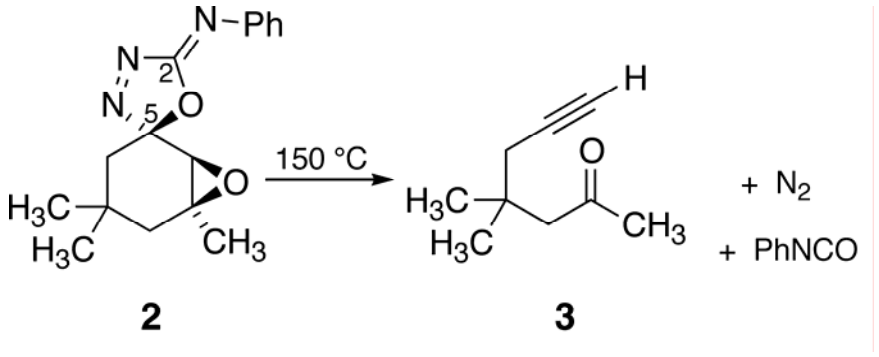


Figure 10. Thermolysis of 2-phenylimino-Δ^3-1,3,4-oxadiazoline (**2**)**.**

The ^{13}C KIEs for fragmentation of **2** were determined combinatorially by NMR methodology at natural abundance.[4] Three reactions of **2** in diphenyl ether at 145 – 150 °C were taken to 65%, 70%, and 84% conversion, and the starting **2** was recovered by

flash chromatography followed by recrystallization in CH_2Cl_2/hexanes. The samples of recovered **2** were analyzed by ^{13}C NMR, along with standard samples that had not been subjected to the reaction conditions. The change in isotopic composition in each position was determined relative to the carbon of the methyl substituent on the epoxide ring,[31] with the assumption that isotopic fractionation of this carbon was negligible. From the percentage conversions and the changes in isotopic composition, the KIEs were calculated as previously described.[4]

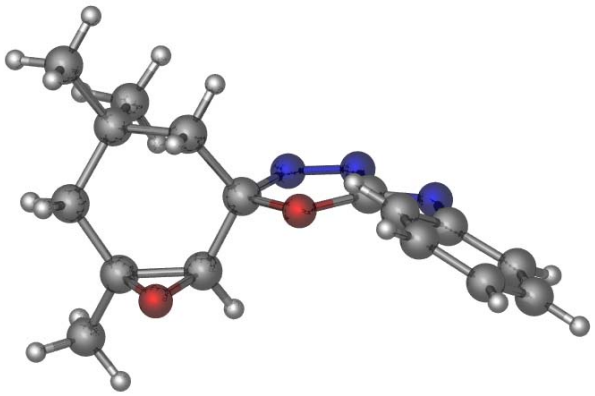


Figure 11. X-ray structure of the major diastereomer of **2**.

Figure 12 shows the average KIEs from the three independent determinations. The uncertainties in the KIEs are larger than normal, due to the limited scale and limited solubility of **2** in NMR determinations. Nonetheless, the KIEs end up acceptably reliable in their basic observations. Significant ^{13}C KIEs were observed in the C-2 and

C-5 ring carbons of the 1,3,4-oxadiazoline, and their magnitude is consistent with a primary carbon KIE. This suggests that these carbons are undergoing a σ-bonding change in the transition state for the rate-limiting step. In contrast, the remaining KIEs are smaller, mainly within experimental error of unity. The absence of a significant ^{13}C KIE at the quaternary epoxide carbon in particular suggests that the epoxide ring is not undergoing fragmentation in the rate-limiting step. Overall, these KIEs qualitatively support a transition state in which the 1,3,4-oxadiazoline is fragmenting but not the remainder of the molecule.

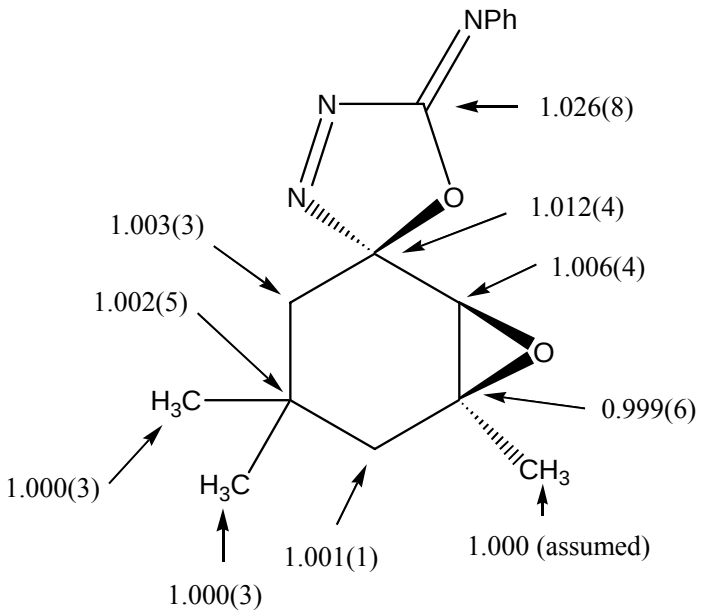


Figure 12. Experimental ^{13}C KIEs (k_{12C}/k_{13C}) for the fragmentation of **2** at 145-150 °C. Standard deviations from three independent determinations are shown in parentheses.

Calculational Studies

Theoretical calculations were used to interpret these results in greater detail and to explore the complete reaction mechanism. The fragmentation of the calculational model **4** was explored in both B3LYP and mPW1K[32] calculations, employing a 6-31G* basis set to survey the potential energy surface and reoptimizing important stationary points with a 6-31+G(d,p) basis set. The energies with ZPE of mechanism-related species **4** to **10** are listed in Table 1.

Table 1. Calculational results of energies of species **4** to **10**.

Species	Relative energy B3LYP/6-31+G(d,p) (kcal/mol)	Relative energy MPW1K/6-31+G(d,p) (kcal/mol)
4	0.0	0.0
5	32.4	44.4
6	1.6	15.4
7	29.6	46.1
8	21.9	38.9
9	22.0	44.5
10	-31.5	-6.8

Extensive efforts failed to locate a transition structure that directly affords the ultimate product **3**. Instead, two fragmentation processes were identified, and because of two distinct conformations in the 6-membered ring, a total of four fragmentation

transition structures were located, and the transition state with lowest energy is considered in the energetic profile of the reaction, which is shown in Figure 13.

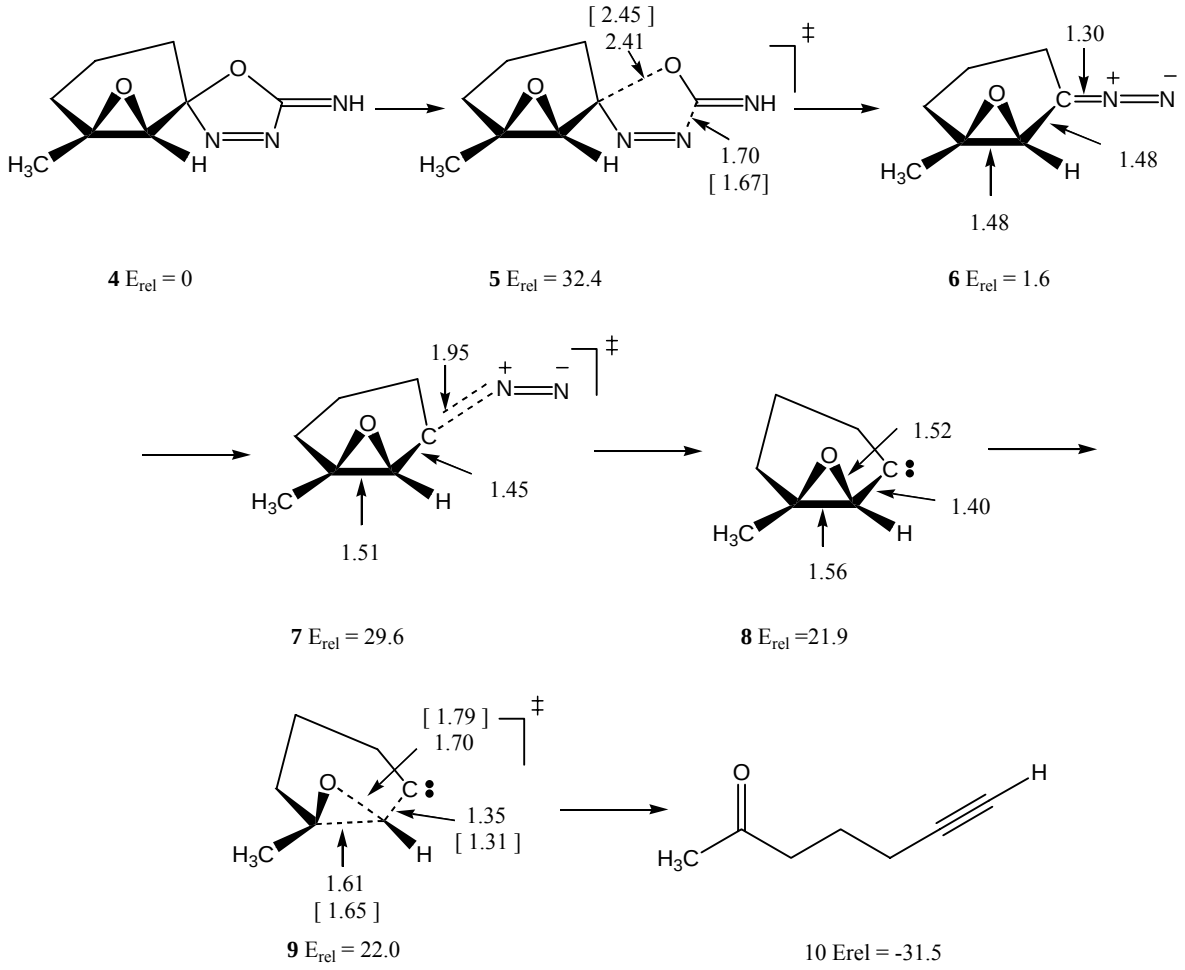


Figure 13. Predicted mechanism for the fragmentation of computational model **4**. Relative energies (B3LYP/6-31+G(d,p) + zpe) are shown in kcal/mol and select distances are shown in Å. Distance in brackets refer to structures located in mPW1K/6-31+G(d,p) calculations.

The calculationally favored fragmentation affords the diazo epoxide **6** and isocyanic acid via transition structure **5**. The predicted barrier is 32.4 kcal/mol (B3LYP/6-31+G(d,p) + zpe), which is consistent with a unimolecular reaction that occurs over the course of about an hour at 150 °C. The mPW1K-predicted barrier for fragmentation via **5** is 44.4 kcal/mol. This is too high; since this fragmentation may be viewed as a pericyclic process (a retro 1,3-dipolar cycloaddition) and since RHF calculations greatly overpredict the barrier for pericyclic reactions, it may be that the hybrid mPW1K calculation[32] mixes in too much RHF character for an accurate barrier prediction in this reaction.

The alternative fragmentation process located affords an epoxy ketone (**12**), N_2, and hydrogen isocyanide via transition structure **11,** as shown in Figure 14. The barrier in this case is predicted to be 3.6 kcal/mol higher than the barrier for formation of the diazo epoxide **6**.

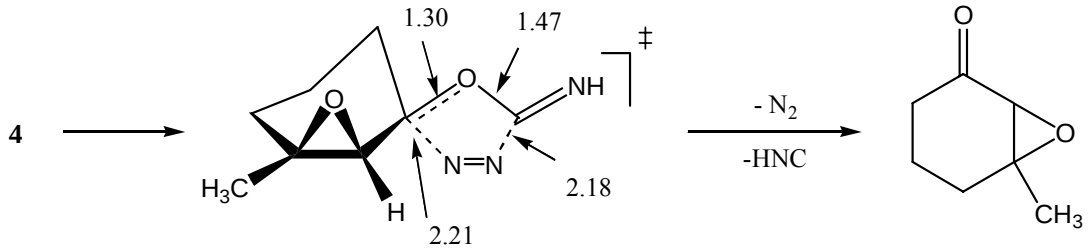
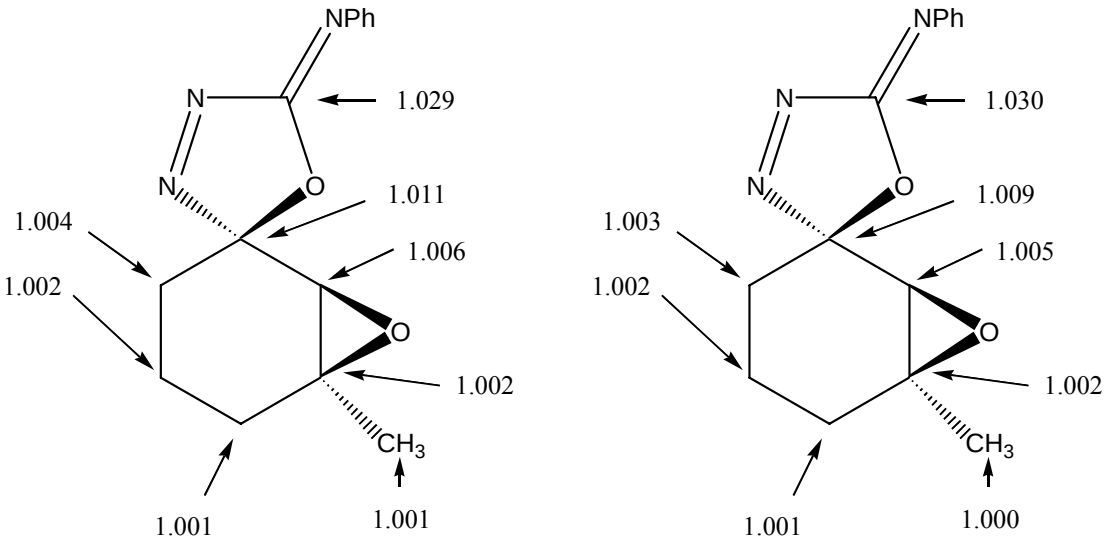


Figure 14. Transition state in the formation of epoxy ketone **12** from **4**.

The experimental relevance of transition structure **5** was gauged by comparison of predicted isotope effects based on **5** with the experimental KIEs. The KIEs for **5** were predicted from the scaled theoretical vibrational frequencies[18] using conventional transition state theory by the method of Bigeleisen and Mayer.[15] Tunneling corrections were applied using the one-dimensional infinite parabolic barrier model.[19] Such KIE predictions including a one-dimensional tunneling correction have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry.[3]



16 a 16 b

Figure 15. (a) Predicted ^{13}C KIEs based on the mPW1K/6-31+G(d,p) version of transition structure **5**. (b) Predicted ^{13}C KIEs based on the B3LYP/6-31+G(d,p) version transition structure **5**.

The results for the mPW1K and B3LYP versions of **5** are shown in Figures 15a and 15b respectively and are compared with experimental results, listed in Table 2. It is apparent that the predicted KIEs are quite similar in pattern to those observed experimentally. Considering the limited precision of the experimental KIEs, the agreement between predicted and experimental KIEs is in fact excellent. This supports the qualitative interpretation of the isotope effects above and the approximate accuracy of **5**. Little difference is seen between the mPW1K and B3LYP predictions, and one cannot tell which transition structure geometry is more accurate.

Table 2. Comparison of experimental and predicted KIEs.

	Experimental KIEs	B3LYP predicted KIEs	MPW1K predicted KIEs
C-2	1.026(8)	1.029	1.020
C-5	1.012(4)	1.011	1.009
C-6	1.006(4)	1.006	1.005
C-7	0.999(6)	1.002	1.002
C-8	1.001(1)	1.001	1.001
C-9	1.002(5)	1.002	1.002
C-10	1.003(3)	1.004	1.003

The remainder of the reaction mechanism for the calculational model involves the conversion of diazo epoxide **6** into heptynone **10**. This conversion itself could

potentially occur by a concerted coarctate process in which loss of the N_2 is accompanied by fragmentation of the epoxide. Instead, the calculations predict a two-step mechanism in which **6** first loses N_2 via transition structure **7** to afford carbene **8,** which fragments via transition structure **9** to afford **10**. Although no concerted transition structure for conversion of **6** to **10** could be located, it should be noted that the barrier for the second step on the B3LYP surface is predicted to be very low – only about 0.15 kcal/mol. Under these circumstances, a very small error in the potential energy surface can make the difference between stepwise and concerted mechanisms. The mPW1K mechanism more strongly favors the stepwise process, as the barrier for fragmentation of **8** goes up to 5.5 kcal/mol. High-level single-point energies (CCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)) predict an even larger barrier of 14.0 kcal/mol for fragmentation of **8**.[33] This large spread in the theoretical predictions is disconcerting but none of the calculations support a concerted coarctate conversion of **6** to **10**. Unfortunately the experimental KIEs can have no bearing on this issue.

In the conversion of **8** to **10**, the α-epoxide carbon is transformed into the terminal acetylenic carbon, breaking two σ-bonds and forming two new π-bonds. Thus, this is a concerted coarctate reaction in itself. Alternative two-step mechanisms may be considered for this conversion, as in the fragmentation of **13** via **14** – **17** in Figure 16, but in each case the intermediate would be expected to be very high in energy. Because of this, such a very simple coarctate reaction has no choice but to proceed by a concerted mechanism. This does not tell us anything about the degree to which transition state aromaticity stabilizes the coarctate transition state.

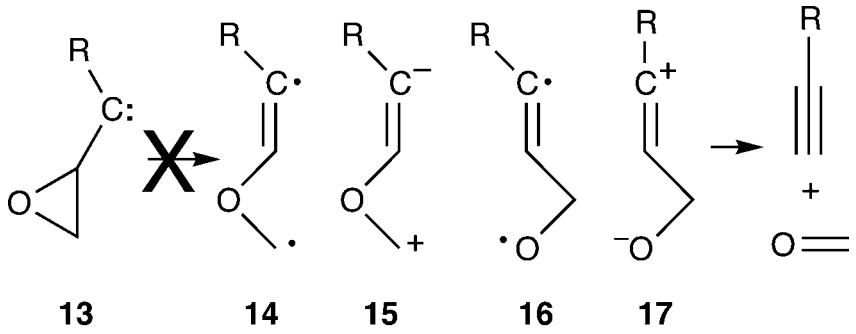


Figure 16. Alternative intermediates in the fragmentation of **8**.

Conclusion

In summary, the theoretically predicted and KIE-supported mechanism for these reactions must face a choice between a concerted coarctate reaction and multi-step process three times. At the stage of **4**, where the concerted reaction would be very complicated, the stepwise process is favored. At the stage of the diazo epoxide **6**, the stepwise process again appears to be favored. The preference for a stepwise mechanism going on from **6** is less pronounced and less certain, but there is still no sign of a transition state aromaticity effect favoring a concerted coarctate process. The last step in the mechanism, going on from **8**, is a concerted coarctate reaction, but this may be viewed as being enforced by the necessity to avoid high-energy intermediates. Overall, the example here does not appear to demonstrate any special stabilization in coarctate transition states.

CHAPTER III

ISOTOPE EFFECTS AND THE MECHANISM OF DEOXYGENATION OF EPOXIDES WITH DICHLOROCARBENE*

Introduction

As discussed before, complex reactions with coarctate transition states usually either start from extremely unstable adducts, such as carbenes or nitrenes, or form small and stable products such as nitrogen, carbon dioxide, or compounds with nitrile functionality to become thermodynamically favored. In the last chapter, the thermal fragmentation of Δ-1,3,4-oxadiazolines was discussed in which small and stable products are formed. Though it is suggested that in that particular case, aromatic stabilization in the transition state is not enough to overcome the energy barrier to reorganize the orbitals of so many atoms involved in the transition state and thus the reaction occurs in a stepwise way. In this chapter, an example will be examined in which an unstable adduct, a carbene, is involved.

Complex reactions involving singlet carbenes are the most thoroughly investigated among the coarctate reactions. The original example, the carbene additions to bicyclobutanes to afford 1,4-pentadiene supported the calculation by Jones, Jr. et al., [34]

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* Reproduced in part with permission from " Isotope effects and the mechanism of deoxygenation of epoxides with dichlorocarbene" by Singleton, D. A. Wang, Z. *Tetrahedron Lett*., **2005**, 46, 2033-2036.

suggesting that carbenes attack from above the three-membered ring without steric hinderance, and that the transition states involve either a lone pair or empty p orbital at the carbene centers to form the aromatic system (a Hückel system with the lone pair and a Möbius system with the empty p orbital).

Similarly, there are no steric problems to be expected during the attack of the carbenes from above the ring in the cases of oxiranes and aziridines. The deoxygenation of epoxides with carbenes has been suggested to be a possible concerted reaction via coarctate transition states, as shown in Figure 17.[20]

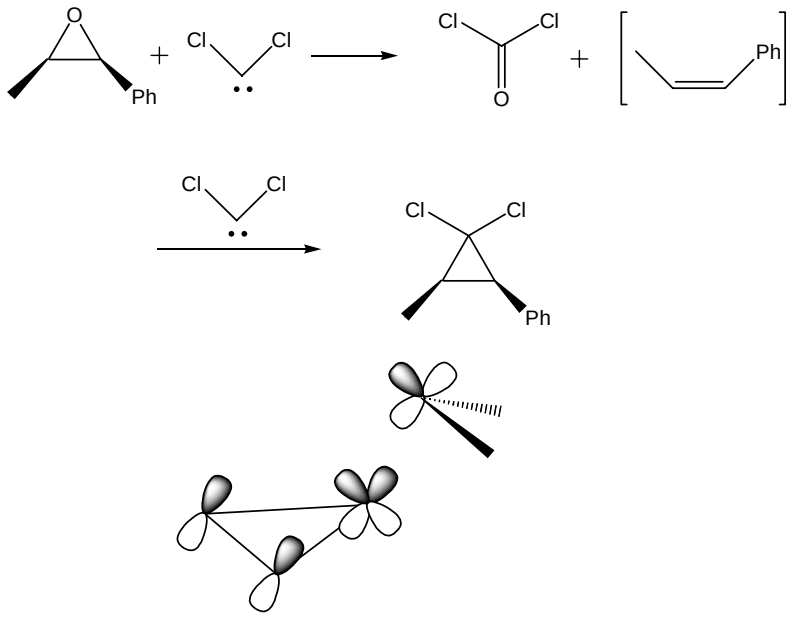


Figure 17. Addition of dichlorocarbene to oxirane and the proposed coarctate transition state.

Deoxygenation of epoxides to olefins is often required in structural and synthetic work and can be used to deprotect the epoxides in the protection of double bonds.

Various methods for this transformation have been developed. Most deoxygenation methods involve metal such as lithium in THF [35] or organometallic compounds[36] such as metallocenes.[37] Mechanisms for these reactions have been proposed to involve metallaoxetanes[38] or radicals.[39] Reagents without metal moiety have also been exploited such as methyltriphenoxyphosphonium iodide[40] and triphenyl phosphine.[41]

A very attractive reaction, which has been chosen for study here is the deoxygenation of epoxides by singlet carbene, since simple reagents are used, and an interesting mechanistic aspect, the presence of a coarctate transition state, could be involved. A possible mechanism other than a complex reaction with coarctate transition state was proposed for this deoxygenation and similar reactions,[42-44] suggesting the concerted decomposition of an oxygen ylide as a plausible pathway to interpret the stereospecific deoxygenation, as shown in Figure 18.[42] However, an attempt to observe such an ylide has not been successful[44] and later computational studies have suggested that a concerted process that does not involve ylide intermediates should play a dominant role in such oxygen abstraction reactions.[45]

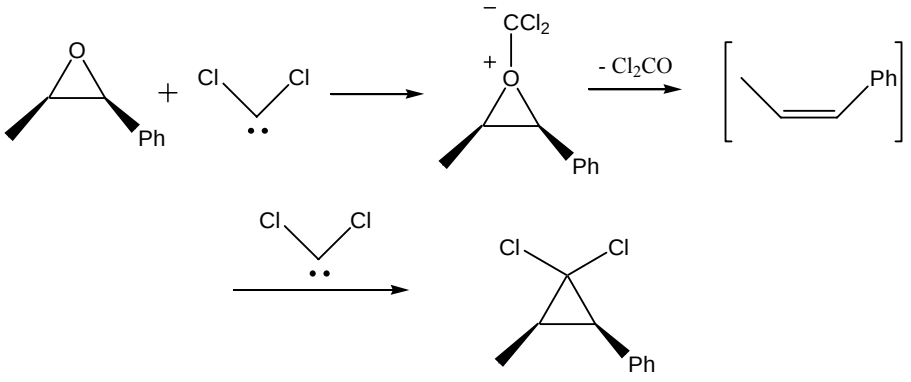


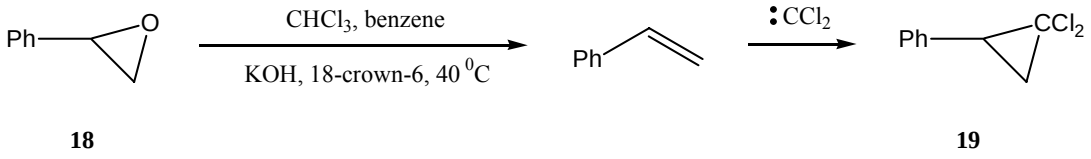
Figure 18. The ylide pathway of addition of dichlorocarbene to oxirane.

The proposed mechanism via coarctate transition states is still challenged since the coarctate transition state theory is only substantially meaningful if the reactions are both concerted and involve nearly synchronous transition states. Recent theoretical studies have suggested that oxirane undergoes a concerted deoxygenation by reaction with a CH_2 carbene via an asynchronous four-center transition state.[46] Additionally, a similar reaction, the fragmentation of aziridines, was found to proceed via a ylide intermediate and does not follow a complex mechanism.[47]

To obtain detailed mechanistic information on this reaction, KIEs studies were employed to distinguish rate-limiting formation of an ylide versus a rate-limiting deoxygenation process, and to act as a gauge of the asynchronicity of the breaking of the two C–O bonds.

Results and Discussions

Experimental ^{13}C kinetic isotope effects. To use KIEs as a gauge of the asynchronicity of the breaking of the two C–O bonds, an unsymmetrically substituted epoxide is required, as a symmetrical epoxide will lead to symmetrical isotope effects due to averaging. Therefore, the deoxygenation of styrene oxide **18** with dichlorocarbene was chosen for study, as shown in Figure 19.



18 **19**

Figure 19. Deoxygenation of styrene oxide.

Previous deoxygenation of **18** using phase-transfer / emulsifying conditions had been plagued by the side reaction of basic hydrolysis of the epoxide.[42] The use of solid KOH, with no discrete aqueous phase, and 18-crown-6 as the phase transfer catalyst appears to alleviate this problem. Under these conditions, no phenylethylene glycol could be observed, and the formation of **19** was nearly quantitative based on NMR analysis versus an internal standard.

The ^{13}C KIEs for deoxygenation of **18** were studied by NMR methodology at natural abundance.[4] A total of four reactions of **18** at 40 °C were taken to 72 – 82% conversion, and the starting **18** was recovered by an aqueous workup followed by flash chromatography and microdistillation. The ^{13}C NMR of the samples of recovered **18** was analyzed along with standard samples that had not been subjected to the reaction conditions. The change in isotopic composition in each position was determined relative to the *para* aromatic carbon, with the assumption that isotopic fractionation of this carbon was negligible. From the percentage conversions and the changes in isotopic composition, the KIEs were calculated as previously described.[4]

Figure 20a shows the average KIEs from the four independent determinations. A substantial normal (>1) ^{13}C KIE was observed at the epoxide carbon adjacent to the aromatic ring (C_α). In contrast, the KIE at the distal carbon (C_β) is surprisingly inverse (<1). The KIEs for the aromatic ring carbons are within experimental error of unity.

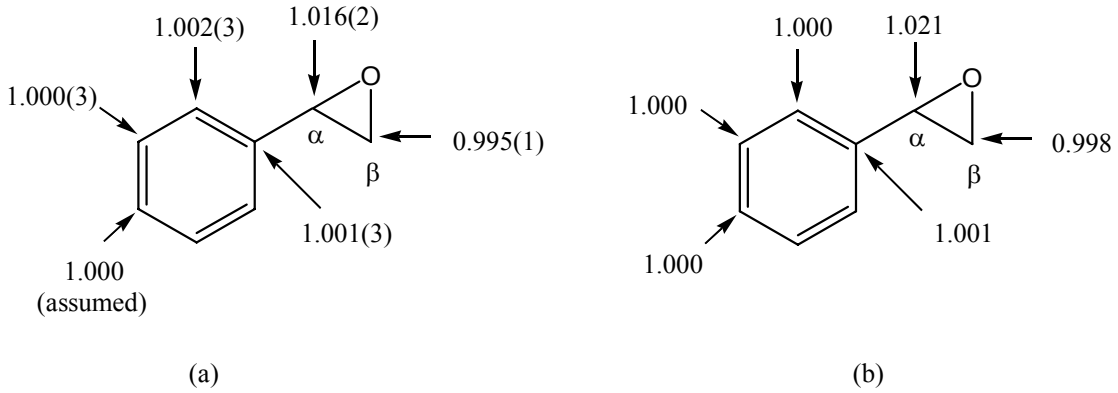


Figure 20. (a) Experimental ^{13}C KIEs (k_{12C}/k_{13C}) for the deoxygenation of styrene oxide at 40 °C. Standard deviations in the last digit from four determinations are shown in parentheses. (b) Predicted ^{13}C KIEs based on transition structure **20**.

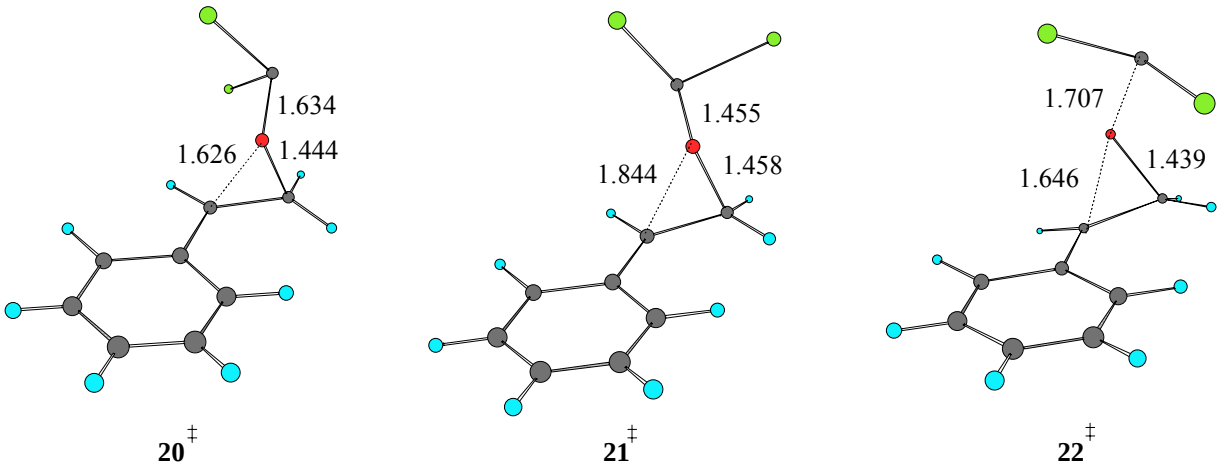
If the deoxygenation involved rate-limiting formation of an epoxide-carbene ylide complex, the C_α and C_β ^{13}C KIEs would be near unity. The observation of a substantial C_α KIE rules this out – an ylide may still be involved but it is not kinetically important. The standard qualitative interpretation of the C_α KIE is that the C_α–O bond is being broken in the rate-limiting step. However, the inverse C_βKIE suggests that the C_β–O bond has got stronger at the transition state than it was in the starting material. Together, these results are indicative of a transition state that would be best described as a ring-opening process rather than a synchronous deoxygenation. This does not rule out a formally concerted deoxygenation, but the two C–O bonds are clearly breaking in different stages of the process.

Calculation Studies

Theoretical calculations were used to interpret these results in greater detail. The deoxygenation of **18** with dichlorocarbene was studied in B3LYP calculations employing a 6-311++G(2d,p) basis set. Three transition structures **20**-**22** were located, two with the carbene attacking the epoxide oxygen anti to the phenyl group and one syn to the phenyl group. The best of these structures **20** in Figure 21 is 5.5 kcal/mol (including zpe) above separate starting materials. Structure **20** notably places the lone pair of the carbene moiety anti to the breaking C_α–O bond. This is favored by 4.3 kcal/mol over the second best structure in which the carbene lone pair is syn to the breaking C_α–O bond. Similar results were obtained in B3LYP, mPW1PW91 and MP2 calculations employing smaller basis sets, as listed in Table 3.

Table 3. Calculational results of energies in the deoxygenation of styrene oxide.

	B3LYP/ 6-31G*	B3LYP/ 6-311++G(2d,p)	mPW1PW91/ 6-31G*	MP2/ 6-31G*
Starting materials	0.0	0.0	0.0	0.0
TS **20**	1.9	5.5	3.6	-2.0
TS **21**	7.2	9.8	9.7	14.4
TS **22**	7.1	10.8		
Styrene	-83.2	-81.2		
Product **19**	-140.8	-129.4		



20‡ Erel = 5.5 kcal/mol

21‡ Erel = 9.8 kcal/mol

22‡ Erel = 10.8 kcal/mol

Figure 21. Structure of transition state **20-22** in deoxygenation of styrene oxide with dichlorocarbene. Distances are measured in Å.

As expected from the isotope effects, transition structure **20** is undergoing cleavage of the C_α–O bond but not the C_β–O bond. To test the consistency of this transition structure with the experimental isotope effects, the KIEs for **20** were predicted from the scaled theoretical vibrational frequencies[18] using conventional transition state theory by the method of Bigeleisen and Mayer.[15] Tunneling corrections were applied using the one-dimensional infinite parabolic barrier model.[19] Such KIE predictions including a one-dimensional tunneling correction have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry.[3]

The predicted KIEs are shown in Figure 20b. It is apparent that the predicted KIEs are quite similar in pattern to those observed experimentally. This supports the qualitative interpretation of the isotope effects and the approximate accuracy of **20**. Since some degree of charge buildup at the transition state would be stabilized in solution, the gas phase structure **20** cannot be expected to be perfectly accurate. Considering this limitation of the calculations, the agreement between predicted and experimental KIEs is in fact very good.

No stationary point corresponding to an ylide geometry could be located in these calculations. A very loose epoxide – CCl_2 complex with an O—C distance of 2.60 Å was found on the potential energy surface, but the energy of this complex is only 1.6 kcal/mol below separate reactants and its free energy is 7.2 kcal/mol above reactants at standard state. Such a complex is unlikely to be a minimum on the free-energy surface and is mechanistically irrelevant.

When the steepest-descent reaction path in mass-weight coordinates is followed onward from **20**, the C_α–O bond distance increases rapidly to > 2 Å while the C_β–O distance at first stays below 1.5 Å. However, there is ultimately no barrier to dissociation of the products, phosgene and styrene, which are downhill from **20** by 86.8 kcal/mol, so the C_β–O bond breaks without there being an intermediate. The deoxygenation is thus overall a formally concerted process, with very asynchronous transition state.

A More O'Ferrall-Jencks diagram, Figure 22, provides a clear way to understand reactions with such a process.[48] The transition state is early and breakage of the two C–O

bonds is highly asynchronous. The reaction path starts out in a direction that would lead to the intermediate at the adjacent corner of the diagram. However, some time after the transition state, the reaction path avoids the high-energy intermediate (either a diradical or a zwitterion) by curving toward the extremely stable products. We note that if a synchronous coarctate transition state were substantially stabilized by transition-state aromaticity, the reaction path would be expected to pass in some degree toward the middle of the More O'Ferrall-Jencks diagram. However, based on the isotope effects and the calculational predictions, this is not the case.

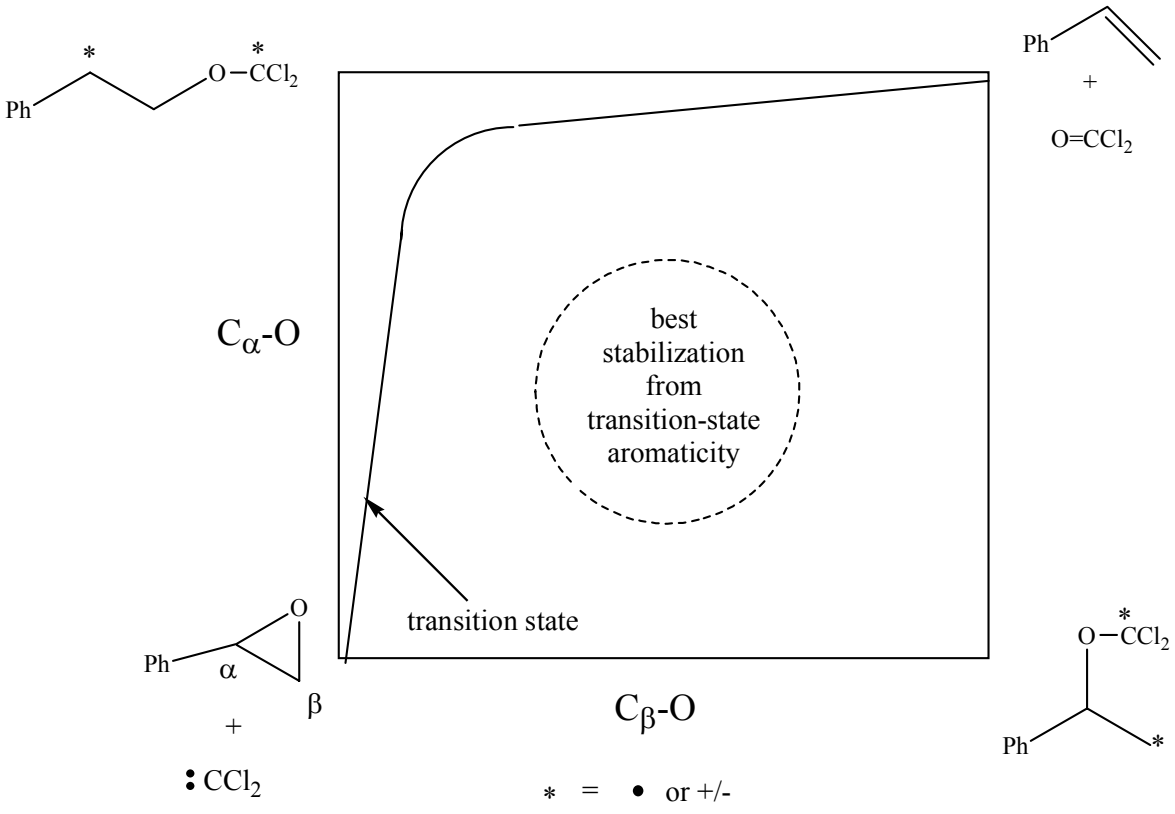
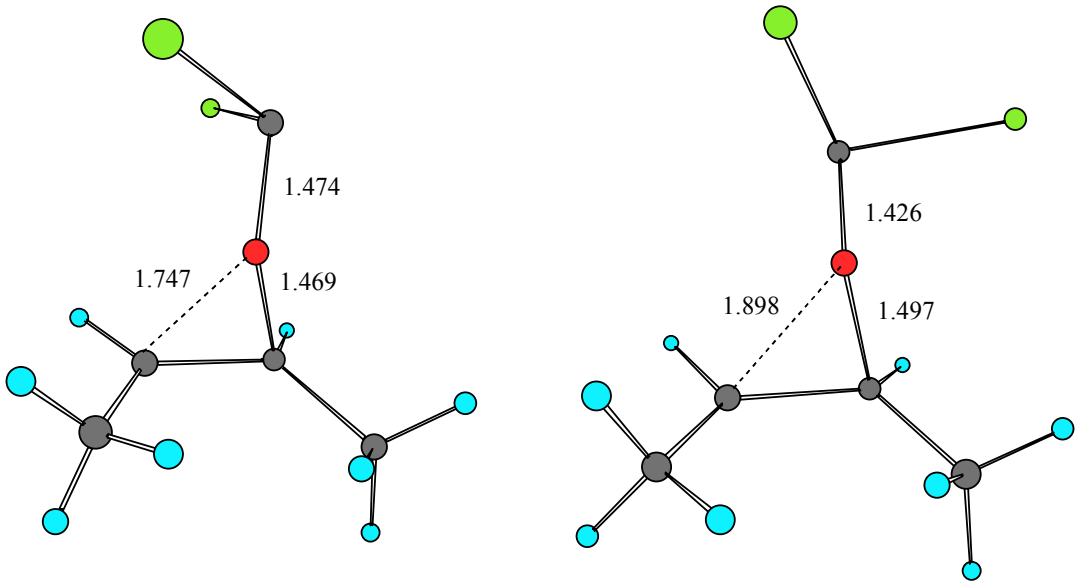


Figure 22. More O'Ferrall-Jencks diagram for the deoxygenation of styrene oxide with dichlorocarbene.

It is shown clearly here that deoxygenation of unsymmetrical olefins occurs via highly asynchronous transition states, which arise the question whether the deoxygenation of symmetrical olefins have similar transition state. As described above, this question cannot be addressed well experimentally with isotope effects. However, calculations suggest that the preference for an asynchronous pathway is general. Transition structure **23** shown in Figure 23 was located for the deoxygenation of *cis*-2,3-dimethyloxirane in B3LYP/6-311++G(2d,p) calculations. The barrier in this reaction is predicted to be 6.2 kcal/mol, 0.7 kcal/mol higher than with **18**. The transition structure is somewhat later, but it is still very early. As was true in **20, 23** places the lone pair of the carbene moiety anti to the breaking C–O bond. This arrangement is reminiscent of the anomeric effect and may be viewed as maximizing overlap between the lone pair and the σ* orbital of the breaking C–O bond, stabilizing the transition state. An alternative transition structure in which the lone pair is syn to the breaking bond **24** was 9.5 kcal/mol higher in energy. The stabilizing effect of the anti lone pair appears to enforce asynchronicity in the reaction, as the lone pair can only aid in breaking one of the two C–O bonds.



23 **24**

Figure 23. Structure transition state **23** and **24** in deoxygenation of *cis*-2,3-dimethyloxirane with dichlorocarbene.

Conclusion

In the deoxygenation of epoxides with dichlorocarbene, the stabilization from the transition state aromaticity in coarctate transition state is not great enough to compete with the preference for asynchronous bonding changes. The theoretically predicted and KIE-supported mechanism suggests that the reaction occurs in a concerted manner but with a highly asynchronous early transition state with much more C_α-O bond breaking than C_β-O bond breaking. The reaction pathway is not influenced by transition state aromaticity.

CHAPTER IV

ISOTOPE EFFECTS AND THE NATURE OF ENANTIOSELECTIVITY IN THE SHI EPOXIDATION. THE IMPORTANCE OF ASYNCHRONICITY*

Introduction

Another highly plausible example under 2-1-2 category is epoxidations with dioxiranes. These reactions, as one of several widely accepted methods of asymmetric epoxidations of prochiral alkenes, provide substantial applications in the synthesis of functionalized optically active organic substances.[49] A detailed mapping of the transition structures of these reactions is needed to understand the source of chiral discrimination and to design even more effective catalysts. A great deal of effort has been made on the mechanistic study on this type of reactions.

Computational studies by Houk[50] provided synchronous transition state with spiro geometry, which is very similar to that in epoxidations by performic acid. The transition structure is located in a relatively shallow flat minima with a distortion energy of only 2.4 kcal/mol. This synchronous transition structure was proposed to involve a dominant S_N2 character in the oxygen transfer from dioxirane to ethylene. Unsymmetric

substitution on the reactants, either on alkenes or on the dioxiranes, lead to asynchronous transition states, with the substituted groups on the carbon with the longer C-O bonds. Calculation at higher levels by Bach also supported the symmetrical transition states in the case of ethylene.[51]

Although a molecule-induced homolysis has once been suggested as a possible process in the dimethyldioxirane epoxidation of alkenes, [52] experimental results that no dioxolanes were observed rendered a homolysis pathway to be extremely unlikely.[53]

To gain more experimental information on the mechanism of the epoxidation of alkenes, we chose the Shi epoxidation as a model.

The rational control of enantioselectivity in a reaction can require a comprehensive knowledge of the reaction mechanism and a detailed geometry of the selectivity-determining transition state. This presents new challenges in efforts to understand chemical reactions. Classical mechanistic tools provide a qualitative picture but usually supply too little detail. The contrasting great detail provided by theoretical calculations has made them an integral tool in studying mechanisms. However, a purely calculational approach faces diverse limitations, particularly for enantioselective reactions. Added to the usual uncertainty as to whether a given theoretical approach is sufficient to represent the basic experimental reaction in solution, most enantioselective reactions involve large chemical systems. This limits the level of applicable theoretical methodology and can greatly increase the conformational complexity of the reaction. For a calculational study leading to a series of transition state conformers, the reliability of the relative energies will be uncertain and it may be unclear whether the best

conformer has been found. Under such circumstances, it is very difficult to confidently analyze the nature of the enantioselectivity in a reaction.

Enantioselective oxidations of alkenes provide diverse versatile entries into optically active products. Recent advances in the epoxidation of unfunctionalized alkenes have been particularly impressive.[54, 55] Shi and coworkers have developed one of the most promising of these methodologies.[55-58] In the Shi enantioselective epoxidation shown in Figure 24, a chiral ketone derived from fructose, such as **25**, catalyzes the oxidation of alkenes with Oxone™ (potassium peroxymonosulfate) as the most common stoichiometric oxidant. An example is the epoxidation of *trans*-β-methylstyrene **27** to afford the (+)-(R,R) epoxide **28**. The original catalyst **25** is most effective with *trans*-disubstituted alkenes and trisubstituted alkenes, while the oxazolidinone **26a** has been found to be effective with *cis* and terminal alkenes.[57, 58] The active oxidants are thought to be dioxiranes such as **29**, as shown in Figure 25.

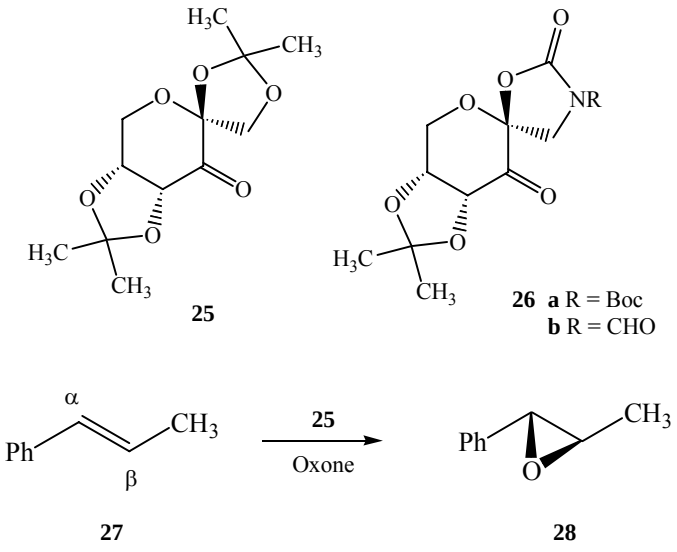
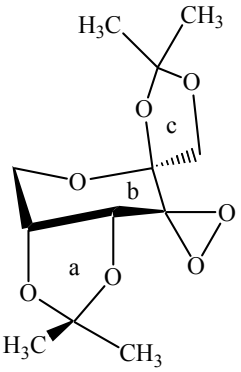
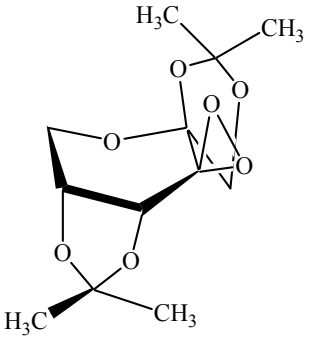


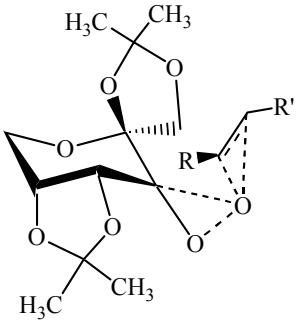
Figure 24. Asymmetric epoxidation catalyzed by Shi's catalyst.



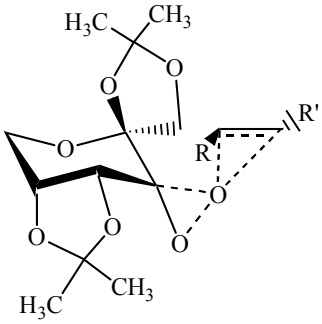
29-chair



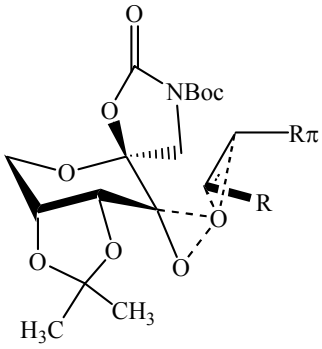
29-boat



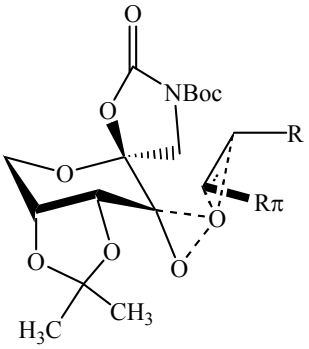
30‡(spiro)



31‡(planar)



32‡



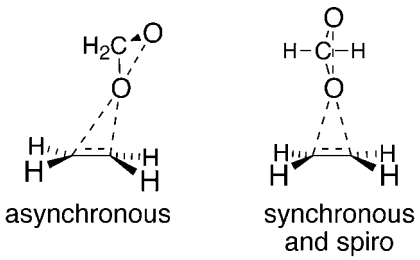
33‡

Figure 25. Proposed transition states in Shi epoxidation.

Shi has developed explanations of the enantioselectivity in these reactions based on diverse observations. Shi's model for understanding these reactions starts with a chair conformation of **29** and has the alkene approach the least-hindered equatorial oxygen of the dioxirane. The observed major products can then result from the spiro transition state **30** in which the substituents on a *trans*-disubstituted or trisubstituted alkene are positioned to avoid a steric interaction with the dioxolane c ring. The spiro transition state leading to the minor enantiomer is thought to be sterically unfeasible; instead, the planar transition state **31** is thought to be the main source of the minor enantiomer. For the reactions of *cis*-disubstituted and terminal alkenes catalyzed by **26**, Shi has proposed that the enantioselectivity results from a preference for a π-conjugating substituent (R_π) to be oriented proximal to the oxazolidinone c ring, as in **32**, as opposed to having the π-conjugating substituent away from the oxazolidinone, as in **33**.[57, 58] The origin of this preference has been unclear, though some observations have suggested an attractive interaction between π-conjugating substituents and substituents on the oxazolidinone. [55]

Theoretical studies of epoxidations mediated by dioxiranes have focused on simple model reactions.[59-62] These studies have consistently supported a preference for a *spiro* transition state, as had been deduced from experimental observations.[52] MP2 and CASSCF calculations favor a transition state for oxidation of ethylene in which there is differential formation of the incipient C–O bonds, describable as highly "asynchronous," but B3LYP and several high-level *ab initio* calculations favor essentially synchronous formation of the two new C–O bonds.[59, 60] In an in-depth study of the reaction of the

parent dioxirane with ethylene, Bach ultimately concluded that the potential energy surface is very soft and that an unsymmetrical transition structure is slightly favored.[60]



For such a large system as the Shi epoxidation, the theoretical approach is effectively limited to DFT methods with a moderate basis set, and here the geometry optimizations are carried out using B3LYP calculations with a 6-31G* basis set. Considering the diverging predictions of high-level *ab initio* calculations, the accuracy of the calculational approach cannot be asserted on theoretical grounds alone. In addition, the use of a single-reference method such as B3LYP for epoxidation calculations has recently been criticized.[63] The reasonable application of these calculations will require validation, and we accomplish this here using kinetic isotope effects (KIEs).

Results and Discussion

Experimental Isotope Effects. The prototypical enantioselective epoxidation of **27** catalyzed by **25** was chosen for study. Shi and coworkers have reported that epoxidations of **27** mediated by 30% **25** afforded the (+)-(R,R) epoxide **28** in up to 95.7% ee at –10 °C.[56b] The epoxidations here using 20% of **25** at 0 °C afforded at least

92% of the (+)-(R,R) enantiomer with an approximately quantitative formation of product.

The ^{13}C KIEs for epoxidation of **27** were determined combinatorially by NMR methodology at natural abundance.[4] Two reactions of **27** were taken to 83% and 93% conversion, and the unreacted **27** was recovered by an extractive workup followed by flash chromatography. The samples of recovered **27** were analyzed by ^{13}C NMR, along with standard samples that had not been subjected to the reaction conditions. The change in isotopic composition in each position was determined relative to the *meta* carbons of the phenyl ring,[64] with the assumption that isotopic fractionation of this position was negligible. From the percentage conversions and the changes in isotopic composition, the KIEs were calculated as previously described.[4]

The results are shown in Figure 26. The independent sets of ^{13}C KIEs agree within the standard deviation of the measurements, with the exception of the *para*-carbon's KIEs. Such a minor disagreement could simply be the result of random error. Only the C_β and C_α KIEs differ significantly from unity, with a relatively large C_β isotope effect and a much smaller KIE at C_α. These KIEs qualitatively indicate a significantly asynchronous transition state for the epoxidation, with more advanced formation of the incipient C_β-O bond than the C_α-O bond. A more quantitative interpretation of these KIEs will be possible with the aid of theoretical calculations

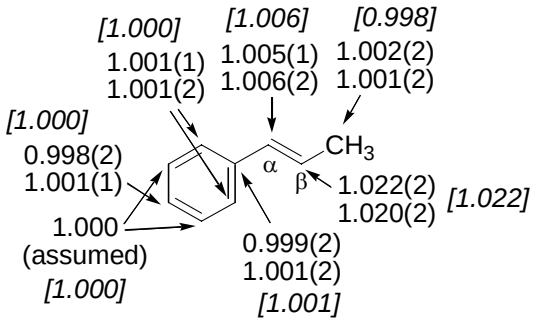


Figure 26. Experimental and predicted ^{13}C KIEs (k_{12C}/k_{13C}) for the epoxidation of **27** catalyzed by **25** at 0 °C. The two sets of experimental KIEs refer to two independent experiments, and standard deviations in the last digit from six determinations are shown in parentheses. The predicted ^{13}C KIEs are shown in italics and brackets, and are based on transition structure **34**.

Theoretical Calculations. The theoretical study of this reaction is complicated by the size of the system, the possible involvement of several conformations of **29**, and the many possible orientations for approach of the alkene. The conformations of **29** were first studied by carrying out a molecular dynamics search for conformers using an MM2 force field. Candidate structures were then optimized using B3LYP calculations with a 6-31G* basis set, and single-point energies using a 6-311+G** basis set were obtained for each optimized structure. A total of 6 conformers of **29** were identified for further study, arising from the combination of a chair and two boat conformations for the pyran b ring with two conformers each in the spiro dioxolane ring (ring c). The calculated structures of conformers **29 a-f** are shown in Figure 27 and the energies are listed in

Table 4. Interestingly, **29**-boat is predicted to be only 2.3 kcal/mol above **29**-chair (B3LYP/6-311+G**//B3LYP/6-31G* + zpe), so its reactive importance cannot be readily dismissed.

Table 4. Relative energies in kcal/mol of conformers of dioxirane **29**.

	B3LYP/ 6-31G*	B3LYP/ 6-311+G**	B3LYP/ 6-311+G** + zpe from 6-31G*
29-a-chair	0.0	0.0	0.0
29-b	0.2	0.0	0.1
29-c-boat	1.7	2.5	2.3
29-d	2.2	3.1	2.7
29-e	4.1	4.2	3.8
29-f	4.7	5.1	4.6

A variety of combinations of the six conformers of **29** with intuitively rational possibilities for approach of the alkene were then explored in B3LYP/6-31G* calculations in a search for transition structures and shown in Figure 27. In this way, a total of 18 epoxidation transition structures were located. The eight structures, **34-41,** that were predicted to be lowest in energy are shown in Figure 28; the energies of all the 18 transition structures, **34-51,** are listed in Table 5. It should be noted that a great many possibilities were left unexplored – we estimate that a total of 66 transition structures might have been located. The 18 structures located all lie within about 8 kcal/mol range,

and it would be difficult to argue convincingly from theory alone that the best transition structure had been found.

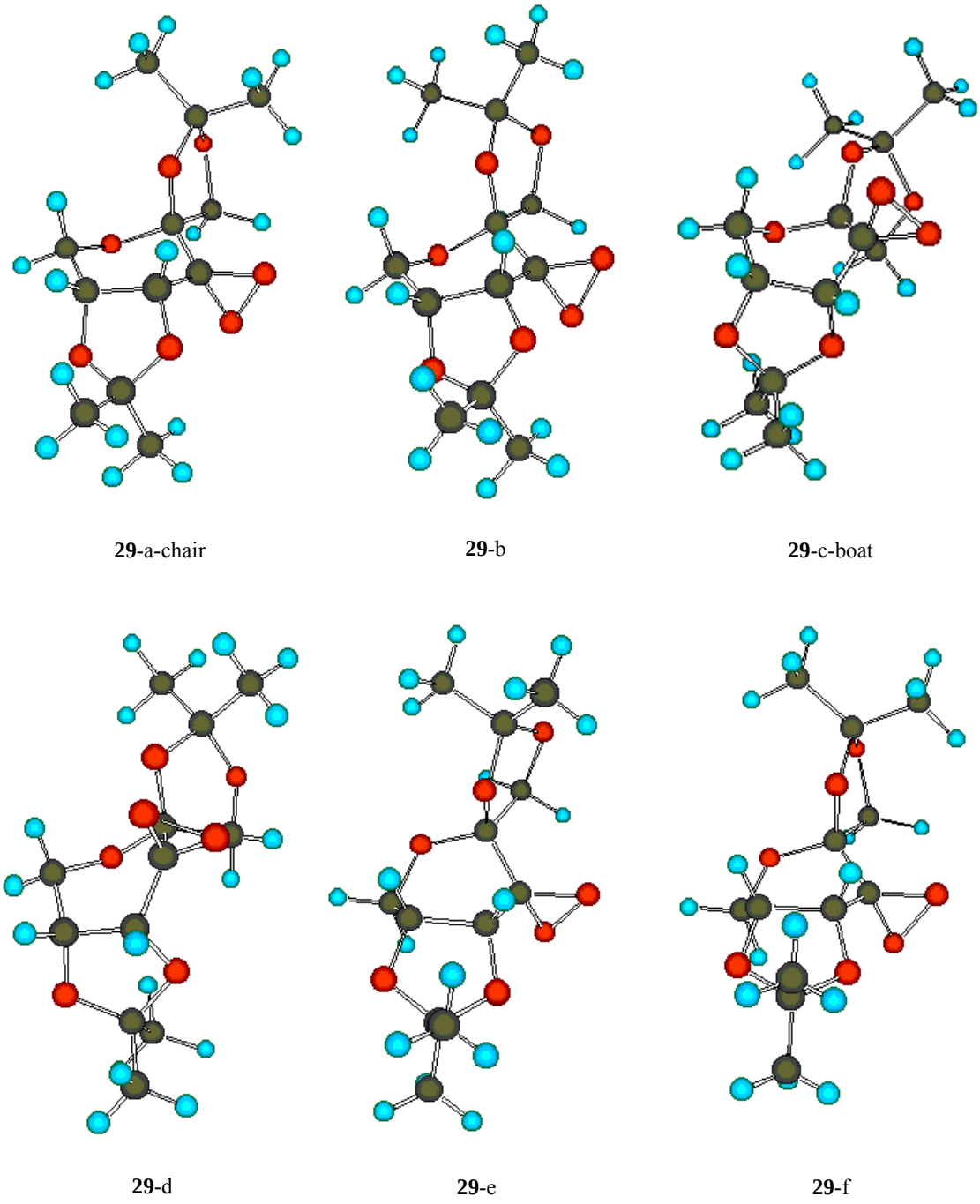
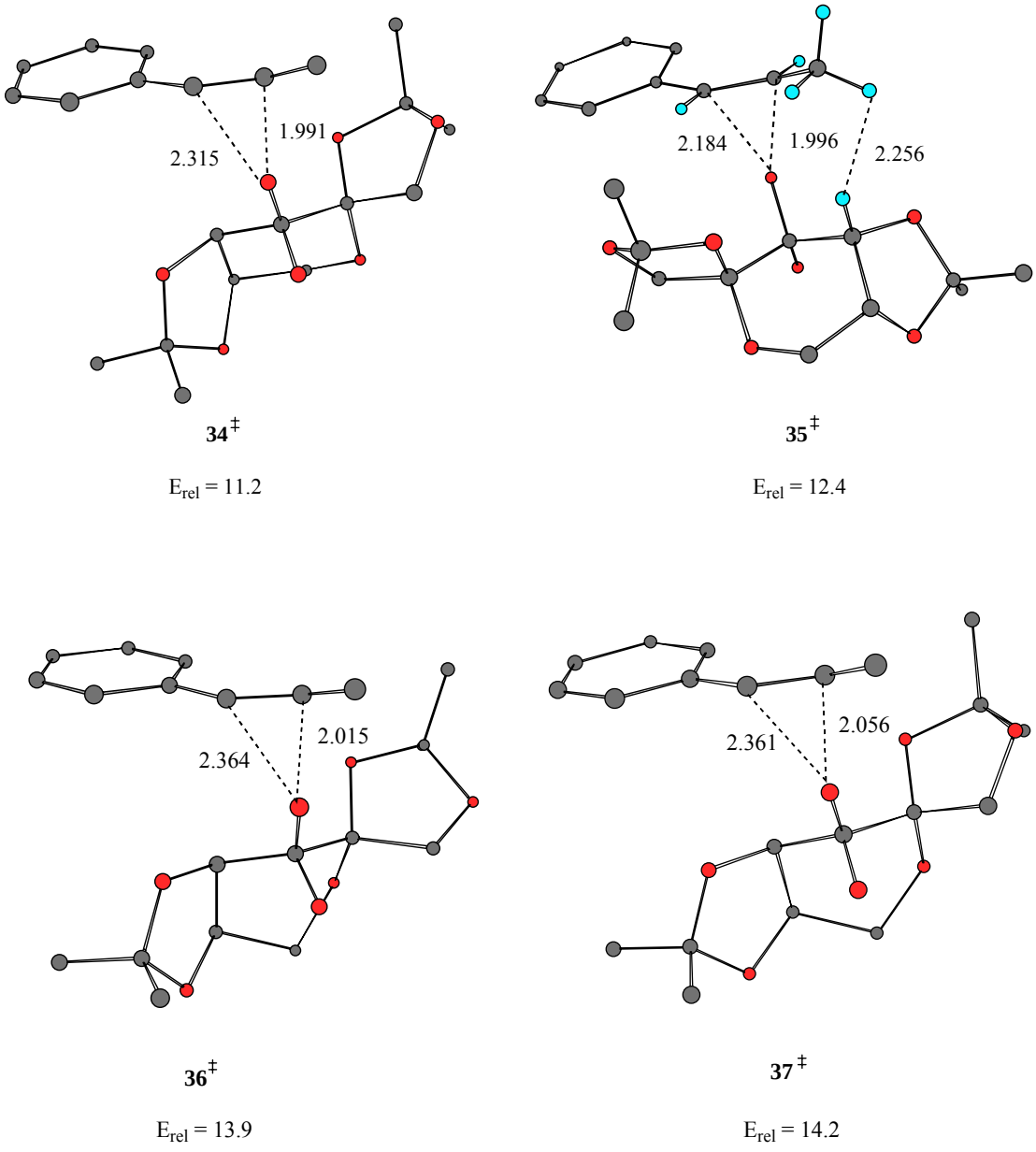


Figure 27. Calculated structures of conformers of dioxirane **29**.

Table 5. Relative energies in kcal/mol of transition structures **34-51**.

	B3LYP/ 6-31G*	B3LYP/ 6-311+G**	B3LYP/ 6-311+G** + zpe from 6-31G*
Starting materials	0.0	0.0	0.0
Transition structure **34**	10.6	10.7	11.2
Transition structure **35**	11.8	11.8	12.4
Transition structure **36**	13.0	13.9	13.9
Transition structure **37**	13.2	14.1	14.2
Transition structure **38**	13.4	14.4	14.6
Transition structure **39**	13.5	13.4	14.0
Transition structure **40**	13.6	13.7	14.2
Transition structure **41**	14.3	15.2	15.4
Transition structure **42**	14.8		
Transition structure **43**	14.9		
Transition structure **44**	15.1		
Transition structure **45**	15.2		
Transition structure **46**	15.9		
Transition structure **47**	16.0		
Transition structure **48**	17.3		
Transition structure **49**	17.3		
Transition structure **50**	18.1		
Transition structure **51**	18.7		



34‡

E_{rel} = 11.2

35‡

E_{rel} = 12.4

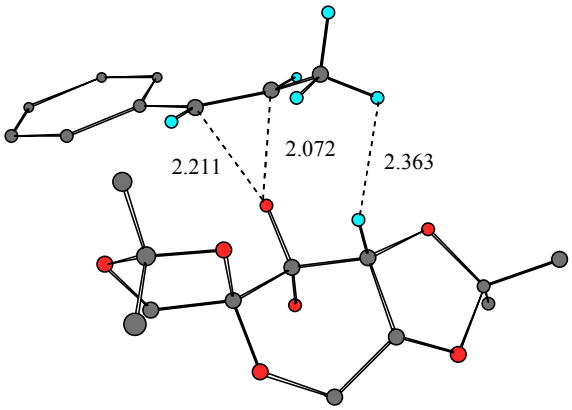
36‡

E_{rel} = 13.9

37‡

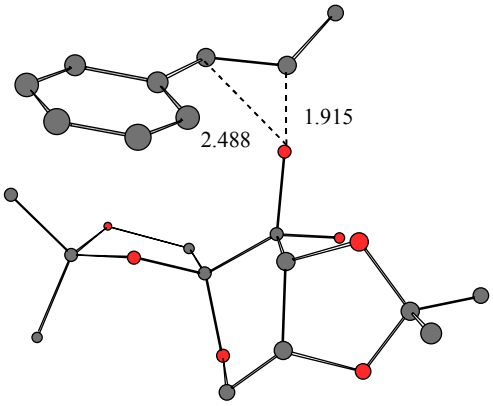
E_{rel} = 14.2

Figure 28. Calculated transition structures **34-41** for the epoxidation of **27** by **29**. Most hydrogens have been removed for clarity. Energies are B3LYP/6-311+G**//B3LYP/6-31G* + zpe reaction barriers in kcal/mol.



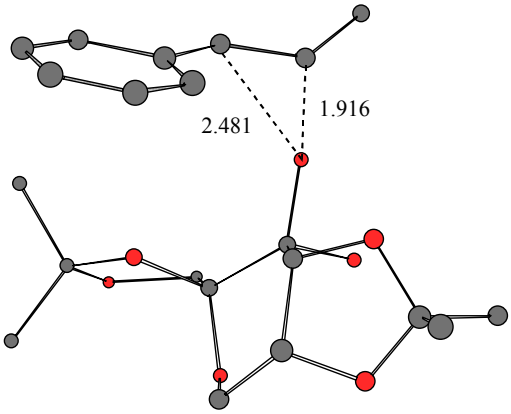
38‡

E_{rel} = 14.6



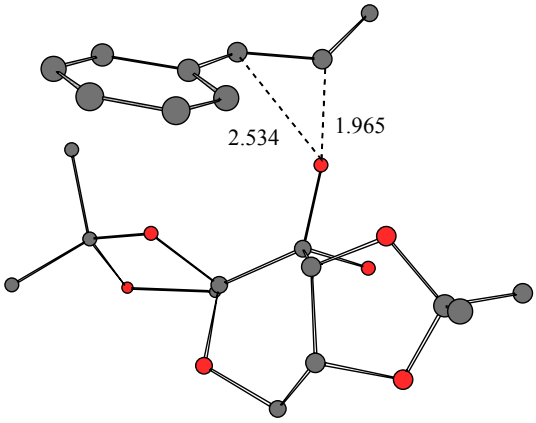
39‡

E_{rel} = 14.0



40‡

Erel = 14.2



41‡

Erel =15.4

Figure 28. Contimued

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To evaluate the experimental relevance of these structures and interpret the observed isotope effects, ^{13}C KIEs were predicted for each of the transition structures. These predictions used the scaled theoretical vibrational frequencies[18] in conventional transition state theory by the method of Bigeleisen and Mayer.[15] Tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[19] Such KIE predictions including a one-dimensional tunneling correction have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry.[3] The KIEs based on the lowest-energy transition structure **34** are shown in Figure 26, and the predicted KIEs for the remaining transition structures are shown in Table 6.

Table 6. Experimental and predicted ^{13}C kinetic isotope effects (k_{12}/k_{13}, 273 °C) for the epoxidation of **27**.

	C_β	C_α	$\underline{C}H_3$	C_{ipso}	C_{ortho}	C_{para}
			Experimental			
Exp. 1	1.022(2)	1.005(1)	1.002(2)	0.999(2)	1.001(1)	0.998(2)
Exp. 2	1.020(2)	1.006(2)	1.001(2)	1.001(2)	1.001(2)	1.001(1)
			Predicted			
34	1.022	1.006	0.998	1.001	1.000	1.000
35	1.020	1.009	0.999	1.000	1.000	1.000

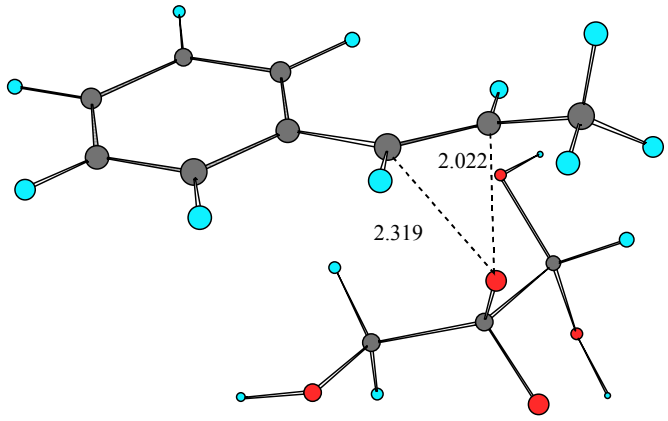
Table 6. Continued.

36	1.022	1.005	0.998	1.001	1.000	1.000
37	1.020	1.005	0.998	1.001	1.000	1.000
38	1.018	1.008	0.999	1.000	1.000	1.000
39	1.029	1.006	0.997	1.002	1.000	1.000
40	1.029	1.006	0.997	1.002	1.000	1.000
41	1.027	1.005	0.997	1.001	1.000	1.000
42	1.025	1.007	0.997	1.001	1.000	1.000
43	1.036	1.005	0.997	1.002	1.000	1.000
44	1.026	1.007	0.997	1.001	1.000	1.000
45	1.028	1.003	0.998	1.001	1.000	1.000
46	1.031	1.004	0.999	1.001	1.000	1.000
47	1.014	1.017	0.999	0.999	1.000	1.000
48	1.026	1.006	0.997	1.001	1.000	1.000
49	1.027	1.007	0.997	1.001	1.000	1.000
50	1.021	1.009	0.998	1.001	1.000	1.000
51	1.023	1.009	0.998	1.001	1.000	1.000

The agreement between the experimental and predicted KIEs is striking. With the exception of the β-methyl group, all of the predicted isotope effects are within the uncertainty of the experimental measurement. The agreement of experiment and theory for C_β and C_α in particular supports the accuracy of the calculations with regard to the asynchronicity of the oxygen transfer. Notably, the comparison of experimental and predicted KIEs also excludes most of the calculated transition structures, as 15 of the 18 transition structures lead to KIE predictions for C_β and/or C_α that are outside of experimental error. For example, structure **35** has a relatively short C_α-O distance of 2.18 Å and its predicted C_α KIE of 1.009 is too large. Only structures **34**, **36**, and **37** lead to accurate KIE predictions. The C_β and C_α KIEs appear to be very sensitive functions of the asynchronicity – there is a consistent structural trend in the predicted isotope effects in which shorter C_β--O or C_α--O distances in the transition structures are associated with larger predicted ^{13}C KIEs. The asynchronicity varies greatly among the diverse structures, and only **34**, **36**, and **37** appear to approximate the actual asynchronicity well.

The two lowest-energy transition structures **34** and **35** were re-optimized using a 6-31+G** basis set. This led to a very slight (0.01 to 0.03 Å) lengthening of the C_β--O and C_α--O distances but otherwise the geometries are changed little. The predicted barriers with these fully-optimized structures are 11.4 and 12.7 kcal/mol, very close to the single-point barriers in Figure 28. The predicted KIEs for **34** changed in each case by less than 0.0004.

Given the experimental support for the approximate accuracy of the calculational methodology, the nature of structural effects impacting the enantioselectivity can now be considered. It should be noted for further consideration that the asynchronicity in **34**, **36**, and **37** closely resembles that found in transition structure **52** (shown in Figure 29) for reaction of **27** with a trihydroxy analog of dimethyldioxirane. Considering **52** as a model for an unhindered epoxidation, the asynchronicity in **52** may be considered as the "natural" asynchronicity. In this case, the unsymmetrical alkene **27** favors having a longer partial C--O bond adjacent to the phenyl group. With a simple symmetrically substituted alkene such as *trans*-2-butene, the natural asynchronicity is very low - the predicted transition structure has nearly equal C--O distances for the olefinic carbons. When compared to **52**, the alkenyl moieties of **34**, **36**, and **37** are slightly pushed away from the dioxolane c ring, but otherwise the chiral environment of **29** allows the natural asynchronicity in these structures. In the other transition structures, **29** imposes "unnatural" asynchronicity. Any transition state is inherently flexible, and epoxidations with dioxiranes are thought to involve a particularly soft potential energy surface,[60] but departure from the natural transition state geometry necessarily imparts an energy cost. This idea provides a simple intuitive framework for understanding effects on the selectivity in these reactions.



52 ‡

E_{rel} = 11.2

Figure 29. Calculated transition structure **52** of epoxidation of **27** with trihydroxy DMDO.

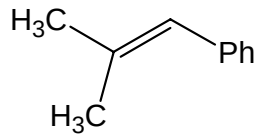
Structures **34-38** would afford the major enantiomeric product while **39-41** would afford the minor enantiomer. All of the structures giving the major enantiomer are spiro and place a hydrogen toward the most hindered quadrant containing the dioxolane c ring. This supports Shi's previous analysis.[55] A surprising result, however, is the substantial preference for structure **34** over **35**. This results from the asynchronicity of the transition structures. In **34**, the phenyl group of **27** is positioned toward the α hydrogen on the pyran ring, but since the phenyl group is adjacent to the relatively long incipient C_α--O bond, there is little steric interaction. In **35**, the methyl group of **27** is positioned toward the α hydrogen on the pyran ring. Since the methyl group is adjacent to the relatively

short C_β--O bond, an unfavorable methyl/H steric interaction results. To minimize this interaction, **35** is less asynchronous than "natural," and this is disfavored.

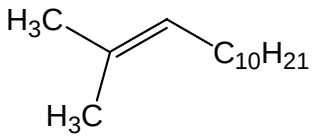
The transition structures **39**-**41** leading to the opposite enantiomer are neither spiro nor planar; rather, the plane of the incipient epoxide ring is twisted at roughly 45° from the plane of the dioxirane, and the asynchronicity of the transition structures is increased. The combination of the twisting and greater asynchronicity has the effect of minimizing a steric interaction of the phenyl group with the methyls of the dioxolane c ring. An alternative transition structure in which the methyl and phenyl groups of **39** are exchanged in position is 2.5 kcal/mol higher in energy; this structure has the same problem as **34** in that the natural asynchronicity, with a short C_β--O bond, would greatly increase steric interaction with the dioxolane. Structure **40** differs from **39** only by the conformation of the dioxolane c ring, while **41** has a boat conformation in the pyran ring. The boat transition structures **36** and **37** are sterically similar to **34** and are higher in energy by amounts that mainly reflect the ground-state boat/chair energy difference in **29**.

The asynchronicity effect that disfavors transition structure **35** in the epoxidation of **27** has no outward consequence since the major enantiomer can be formed via **34**. In other cases, however, this effect appears to have an impact. One interesting observation is that the ee for **53** is relatively low while a higher ee is obtained with **54** and a very high ee is observed with **55**.[56b] This trend may be understood by considering the facility of formation of the major enantiomer.[65] In the case of **53**, the asynchronicity would be such that a relatively short C_β--O bond would be favored at the transition state, but this

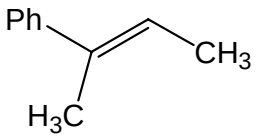
would force the *trans* methyl group into a sterically bad position (identical to that in **35**). In **54**, the asynchronicity of the transition state should be decreased, decreasing the steric interaction with the *trans* methyl group. In **55**, a phenyl group is forced toward the



53 (76% ee)



54 (87% ee)



55 (97% ee)

pyran ring but, as in **34**, the adjacent incipient C--O bond would be long at the transition state and there would little steric interaction between the phenyl group and the pyran.

***Cis*-Alkenes and Terminal Alkenes**. The major enantiomeric product in the reaction of *trans*-disubstituted or trisubstituted alkenes catalyzed by **25** arises from a spiro transition state transferring the equatorial oxygen, as Shi has proposed.[55] However, when this model is applied to epoxidations of *cis*-disubstituted and terminal alkenes using **26b**, the two transition states **32** and **33** affording opposite enantiomers would seem equally good. Why would the predominant product arise from **32** in which the π-conjugating substituent is oriented proximal to the oxazolidinone ring?

We first sought to find out if this preference could be reproduced in a calculational model. This was not obvious – if the preference arises from an attractive interaction due to a dispersion force, such interactions are not well reproduced by DFT calculations. To examine this issue, transition structures were located for the epoxidation of styrene and *cis*-β-methylstyrene with the dioxirane derived from **26b** (R = CHO). Our studies with these alkenes were limited to the chair conformation of the dioxirane and reaction of the

equatorial oxygen, as in the Shi conception. This is an incomplete examination, but based on the results with **25**, it should be sufficient to identify the major effects on the stereochemistry.

The four lowest-energy transition structures **56-59** located for the epoxidation of styrene catalyzed by **26b** are shown in Figure 30. The relative energies are listed in Table 7. The lowest-energy transition structure **56** corresponds to **32** and would afford the observed major product. The predicted preference for the major enantiomer, at 1.4 kcal/mol, fits well with the experimental product ratio of approximately 9:1.5. Transition structure **57**, corresponding to **33**, would afford the minor enantiomeric product, as would the alternative transition structure **59**. Interestingly, **59**, which places the phenyl group in what would be expected to be the most sterically hindered position toward the oxazolidinone ring, is similar in energy to **57** and **58**. (A transition structure analogous to **59** for the reaction of **27** with **29** was prohibitively high in energy.) Another surprise is that **58**, corresponding to the best transition structure **34** when **25** was the catalyst, is predicted to be significantly higher in energy than **56**.

The calculations correctly predict the major enantiomeric product, but the qualitative understanding of the enantioselectivity is a more difficult and subtle issue. One apparent contributing factor to the preference for **56** over **57** and **58** is that the asynchronicity of the transition structures in **57** and **58** forces an olefinic hydrogen into a steric interaction with the oxazolidinone ring. Model calculations using ethylene and oxazolidinone suggest that the minimum-energy distance for interaction of an olefinic hydrogen with the ring oxygen of oxazolidinone is about 2.8 Å. This is approximately

what is found in **56**, but in **57** and **58** the H--O distance is too short (Figure 30). As is normal for steric interactions, the effect is distributed into other distortions in the transition structures. For example, the approach of the alkene in **57** and **58** is "pushed" away from the oxazolidinone, so that the C_β--O--O angle in each is 166°. For comparison, the C_β--O--O angle is only 160° in both **56** and in an unstrained model (analogous to **52**, only using styrene instead of **27**). The "reversed" asynchronicity in **59** compared to **57** and **58**, as well as a twist of the transition state away from spiro by about 45°, minimizes the steric interaction of the phenyl group with the oxazolidinone. As a result, the phenyl/oxazolidinone steric interaction in **59** seems to have no more direct effect than the hydrogen/oxazolidinone interaction in **57** and **58**.

Table 7. Relative energies in kcal/mol of transition structures **56-59**.

	B3LYP/ 6-31G*	B3LYP/ 6-311+G**	B3LYP/ 6-311+G** + zpe from 6-31G*
Starting materials	0.0	0.0	0.0
Transition structure **56**	4.7	5.1	5.9
Transition structure **57**	7.5	7.0	7.4
Transition structure **58**	6.8	6.5	7.1
Transition structure **59**	7.2	6.6	7.3

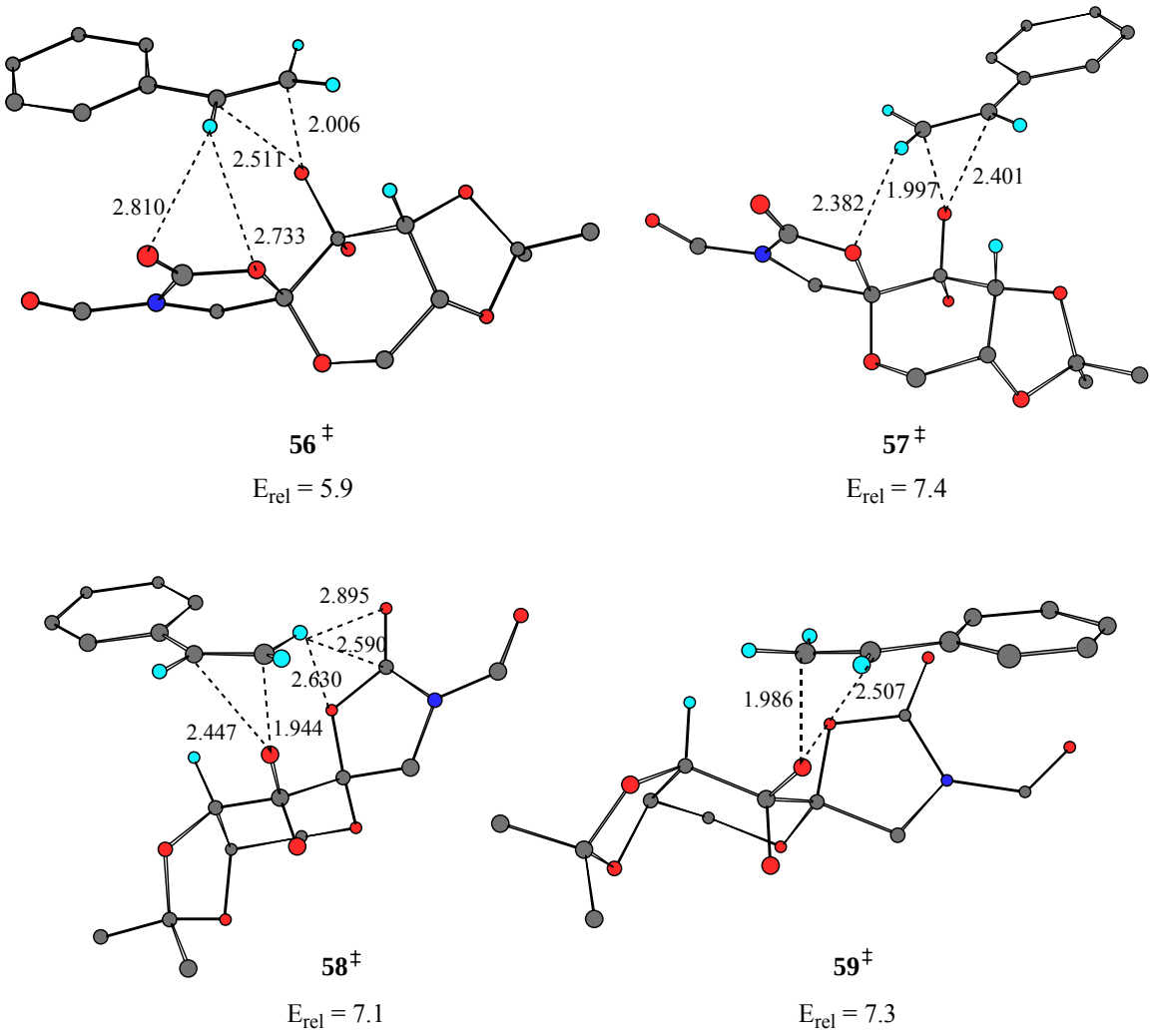
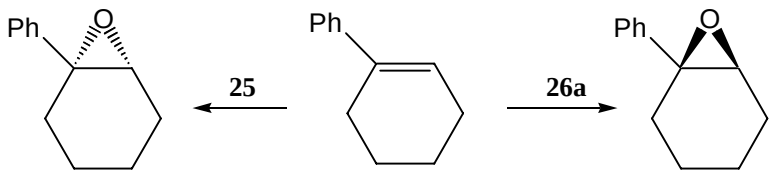


Figure 30. Calculated transition structures for the epoxidation of styrene by the dioxirane derived from **26b**. Most hydrogens have been removed for clarity. Energies are B3LYP/6-311+G**//B3LYP/6-31G* + zpe reaction barriers in kcal/mol.

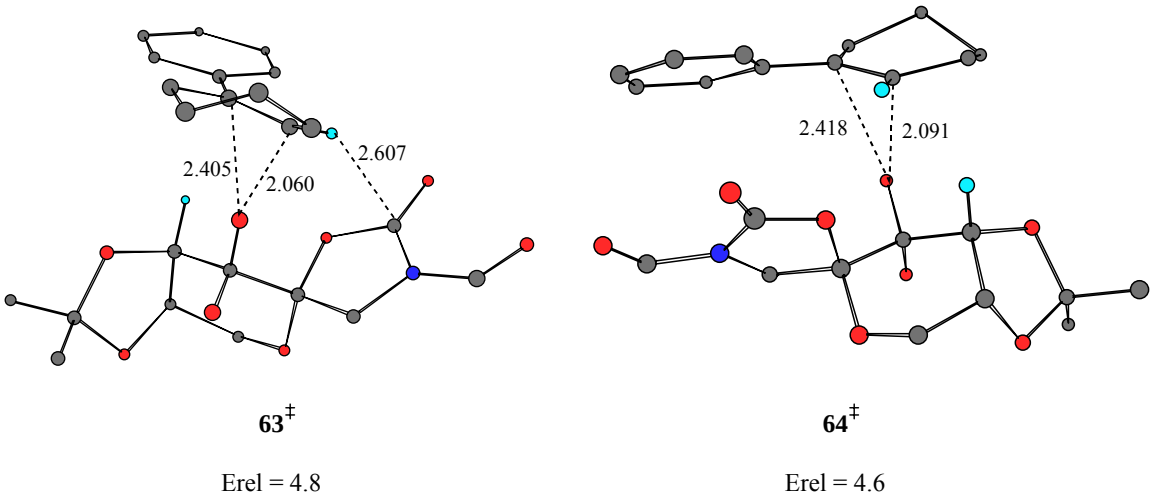
Another factor that appears to be contributing to the preference for **56** and the relatively low energy of **59** is a dipolar interaction. Epoxidation with dioxiranes is an electrophilic process, and there is a partial positive charge developed in the styrene moiety at the transition state. For example, the total Mulliken charge in the styrenyl part of **56** is 0.33. There is a dipole associated with the oxazolidinone ring, and this dipole would be oriented so as to stabilize **56** and **59** relative to **57** and **58**. In **59** in particular, the partially positive phenyl ring is approaching the partially negative oxazolidinone oxygens.

Consideration of the factors affecting the stability of **56-59** aids in the understanding of enantioselectivity in related reactions. Shi has made the interesting observation that 1-phenylcyclohexene (**60**) affords high selectivity for the (*R*, *R*) product **61** with **25** as catalyst but low selectivity for the opposite enantiomer **62** with **26a** as catalyst.[55] Additionally, substituents on the oxazolidinone nitrogen have a significant impact on the enantioselectivity. With **25**, a transition structure similar to **34** should be heavily favored, as was true with **55** above. With **26a** as catalyst, however, transition structures analogous to **56** and **57** would be precluded because they place the cyclohexenyl ring in an unfavorable position toward the pyran. The expected lowest-energy transition structures would be analogs of **58** and **59**.



61 **60** **62**

Based on this prescription, transition structures **63** and **64** were located for the epoxidation of phenylcyclohexene catalyzed by **26b**. The calculated structures and the relative energies are shown in Figure 31. The preferred transition structure **64** would afford **63**, and the small preference for **64** over **63** of 0.2 kcal/mol is well consistent with experimental observations. The structures of **63** and **64** support the ideas discussed with **56-59**. Although the phenyl group of **63** is well positioned to avoid steric interactions, the asynchronicity of the transition structure appears to push the olefinic hydrogen of **63** too close to the oxazolidinone. In contrast, the asynchronicity of **64** minimizes steric interactions between the phenyl group and the oxazolidinone. An additional interesting effect in **64** is that the phenyl group is twisted away from of conjugation with the olefin by 28°, compared with 0°–10° with **56-59**. It would seem that for the epoxidation of this trisubstituted alkene, activation by conjugation with the phenyl group is of decreased importance, allowing the phenyl group to twist so as to minimize steric interactions. Because the phenyl group in **64** is still pushed up against the oxazolidinone ring, the relatively large effect of substituents on the nitrogen is understandable. It should be noted that aside from the impact of asynchronicity on steric interactions, the basic analysis here is quite similar to the qualitative analysis described by Shi.[55]



63‡ Erel = 4.8 **64**‡ Erel = 4.6

Figure 31. Calculated transition structures **29** and **30** for the epoxidation of 1-phenylcyclohexane by the dioxirane derived from **26b**. Most hydrogens have been removed for clarity. Energies are B3LYP/6-311+G**//B3LYP/6-31G* + zpe reaction barriers in kcal/mol.

Conclusions

The potential energy surface for the epoxidation of alkenes with dioxiranes is thought to be very soft.[60] Under these circumstances, even very high level calculations cannot unambiguously decide between synchronous and asynchronous transition states for reactions of simple alkenes with simple dioxiranes, and the adequacy of a DFT method applied to a large enantioselective reaction cannot be assured theoretically. However, the calculated ^{13}C KIEs for diverse epoxidation transition structures suggest that the observed isotope effects should be a very sensitive measure of the transition state geometry. The experimental KIEs match well with those predicted for the lowest-energy theoretical transition structure **34**. This supports the approximate accuracy of **34**

and by implication supports the applicability of B3LYP/6-31G* calculations to these reactions. Multi-reference methods appear unnecessary here for geometrically accurate transition structures.[60, 63]

The transition state for epoxidation of *trans*-β-methylstyrene catalyzed by **25** is asynchronous with a shorter incipient C_β--O bond at the transition state. This asynchronicity approximates that in an unstrained model, and the asynchronicity of such unsymmetrical reactants is expected to have consequences. High enantioselectivity should be promoted when the major enantiomer can arise by a transition state for which the catalyst allows the natural asynchronicity. In contrast, when the natural asynchronicity of the epoxidation is hindered by the catalyst, as in the case of **53**, the enantioselectivity will likely be lowered.

The asynchronicity of transition states for unsymmetrical reactants has a significant impact on steric interactions at the transition state. Asynchronicity in the "wrong" direction, as in **57**, **58**, and **63**, increases steric interactions, while asynchronicity in the right direction decreases them, as in **56**, **59**, and **64**. The consideration of such an effect of asynchronicity is necessary to understand the significant preference for π-conjugating substituents to be proximal to the oxazolidinone of **26a** in literature observations. Overall, the asynchronicity of transition states for epoxidations by dioxiranes must be considered carefully in efforts to understand enantioselectivity in these reactions.

CHAPTER V

DYNAMIC CONTROL OF PRODUCT SELECTIVITY IN A DIELS-ALDER REACTION

Introduction

Transition state theory, as one of the fundamental ideas in chemistry, ubiquitously implicitly assumed in explaining the rates and selectivities of organic reactions. This is true, for example, whenever organic chemists discuss reactions in terms of a two-dimensional potential energy profile of the kind shown in Figure 32.

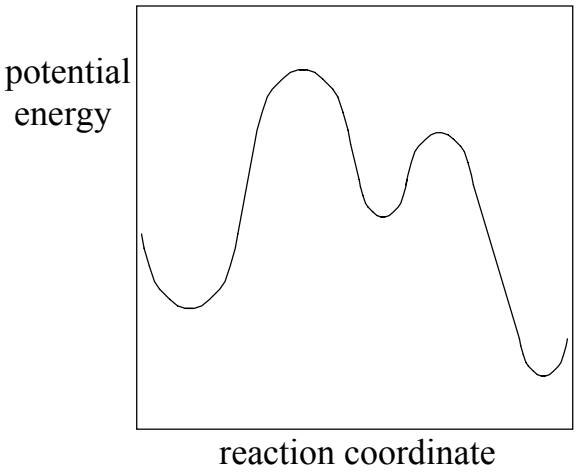


Figure 32. A typical potential energy profile.

Such graphs have been helpful in understanding the thermochemistry and kinetics of reactions. However, they can be misleading in some circumstances. The principal

problem comes from compressing the structural changes that occur during a reaction into a single reaction coordinate. In reality, a unimolecular reaction of an N-atom nonlinear reactant has 3N-6 degrees of freedom, thus requires 3N-6 geometrical coordinates to fully describe the structural changes during the reaction. So a 3N-5 dimensional hypersurface is needed to depict the potential energy as a function of molecular structure. However, it is impossible to draw the 3N-5 dimensional hypersurface. Thus physical organic chemists choose the one most important structural change and depict potential energy surface in a 2-dimensional way, as shown in Figure 32. This misses some important possible complications. By depicting the potential energy surface in a 3-dimensional way, like in Figure 33, we will be able to understand these complications.

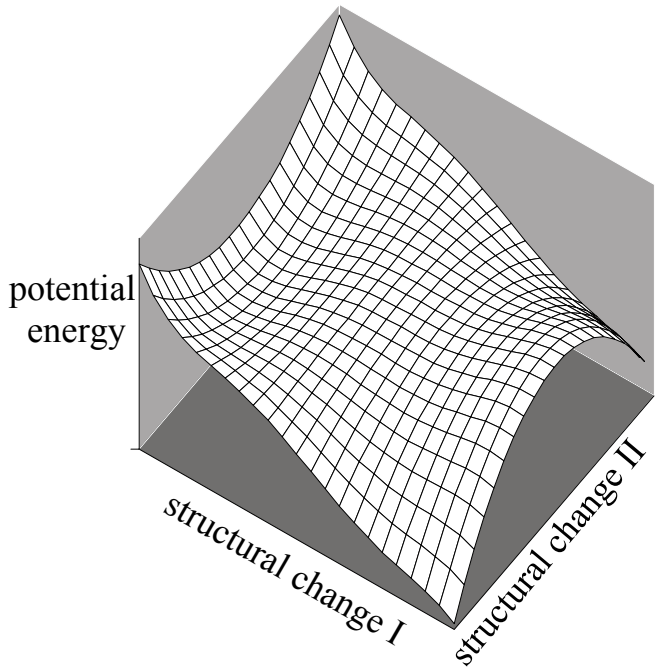


Figure 33. An example of 3-dimensional potential energy surface.

The 2-dimensional reaction coordinate paradigm governs the usual understanding of organic selectivity. If a reaction produces two products, the ratio of those products would be explained in terms of differing energetic barriers along their respective mechanistic pathways. Even when there is no enthalpic barrier, reactivity and selectivity can be discussed in terms of free-energy barriers. Complications such as tunneling,[19] recrossing [66] and variational transition state[67] effects are well recognized, but the control of rates and selectivity by barriers is employed as an intrinsic assumption in the interpretation of experimental observations.

Dynamic effects are the exceptions. For some reactions, the products ratio or stereochemistry is difficult to explain in terms of energetic barriers. Most of those cases occur when the intermediate is formed with kinetic energy that far exceeds the energy needed to traverse the barrier to products, or when a high-energy intermediate, such as a biradical, resides on an energy plateau in the potential energy profile. In such cases, explicit consideration of the detailed motions and momenta of the atoms aids in understanding the experimental results.[68] Figure 34 shows some examples of reactions which have been explained to have dynamic effects.[69-72] Most of those reactions involve high-energy biradical intermediates and the stereochemistry and the product distribution are explained as the results from a non-statistical distribution of atomic motions.

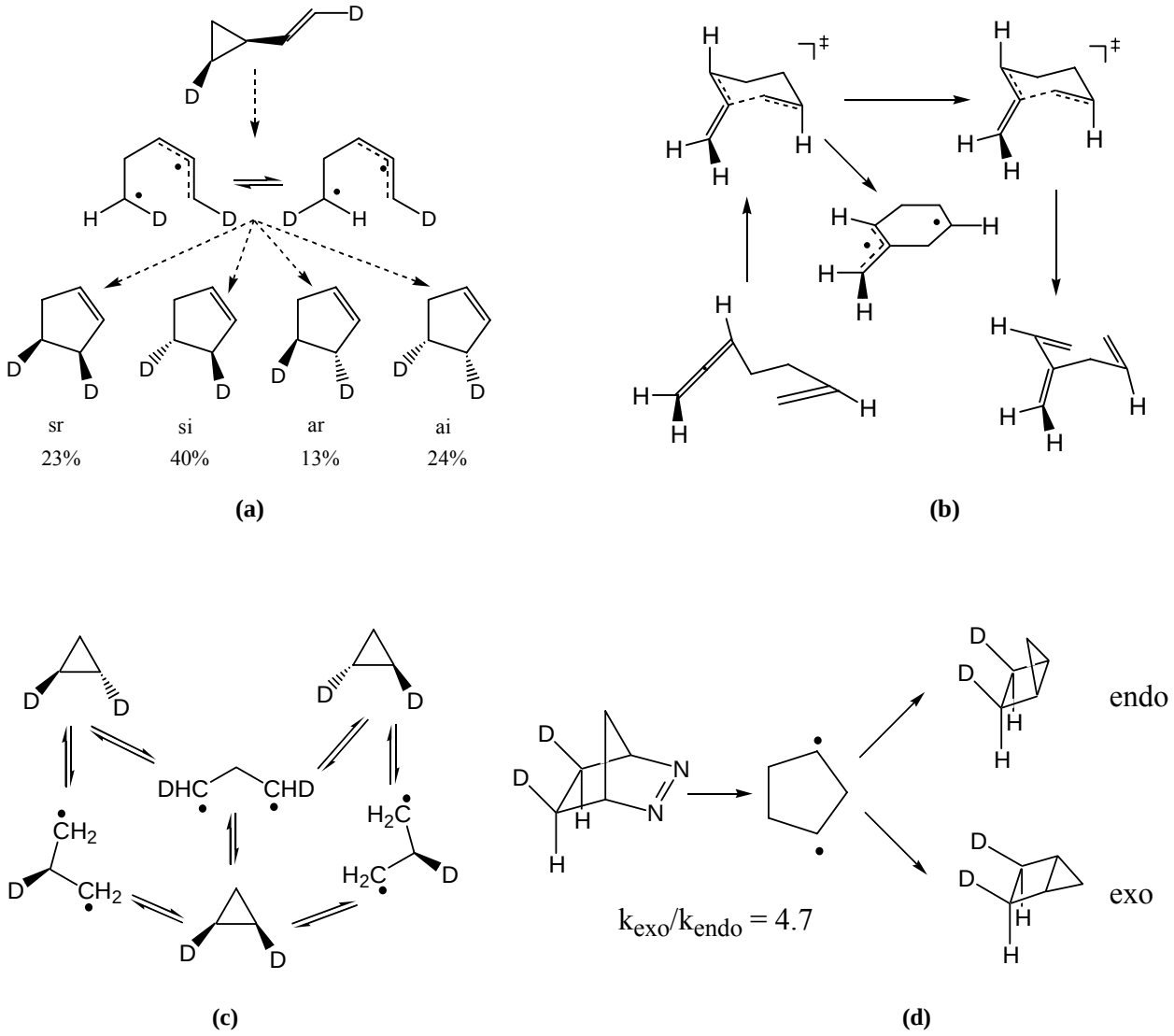


Figure 34. Some examples of reactions proposed to involve dynamic effects.

Dynamic effects can not only affect reactions involving high-energy intermediates, but also can play an important role in ordinary organic reactions in solution.[73] The circumstance of such dynamic effects is when a reaction involves a bifurcating energy surface.

Stationary points are usually the places of the interest when potential energy surfaces are investigated. A stationary point is a place where the partial first derivatives of the potential energy with respect to all geometrical coordinates are simultaneously zero. Two common classes of features on the potential energy surface meet this criterion: minima and transition states. While the minima have all of the partial second derivatives positive, the transition states has one and only one partial second derivative negative and all other partial second derivatives positive.

The potential energy surface in the vicinity of a transition state usually follows the steepest descent path down to a single reactant in one direction and a single product or an intermediate in the other direction. However, a transition state may sometimes be shared by more than one reactants or products; for an example, when there is a valley-ridge inflection point (VRI). [74] A VRI point is adjacent to two transition states and the partial second derivative for VRI is zero. On such a surface with a VRI point, reactants that pass through a rate-limiting transition state can proceed to two distinguishable products without barrier, even though there is an energetic barrier for the conversion of one product to another. However, transition state theory cannot predict the product ratio in a reaction that occurs via a VRI. Thus dynamic trajectory studies are needed.

If the surface is symmetrical, the minimum-energy path (MEP) bifurcates to afford equally two equivalent products. If the energy surface is not symmetrical, the MEP may not bifurcate but there may still be trajectories that lead to each product. Figure 35 illustrates the symmetrical and the unsymmetrical potential energy surfaces.

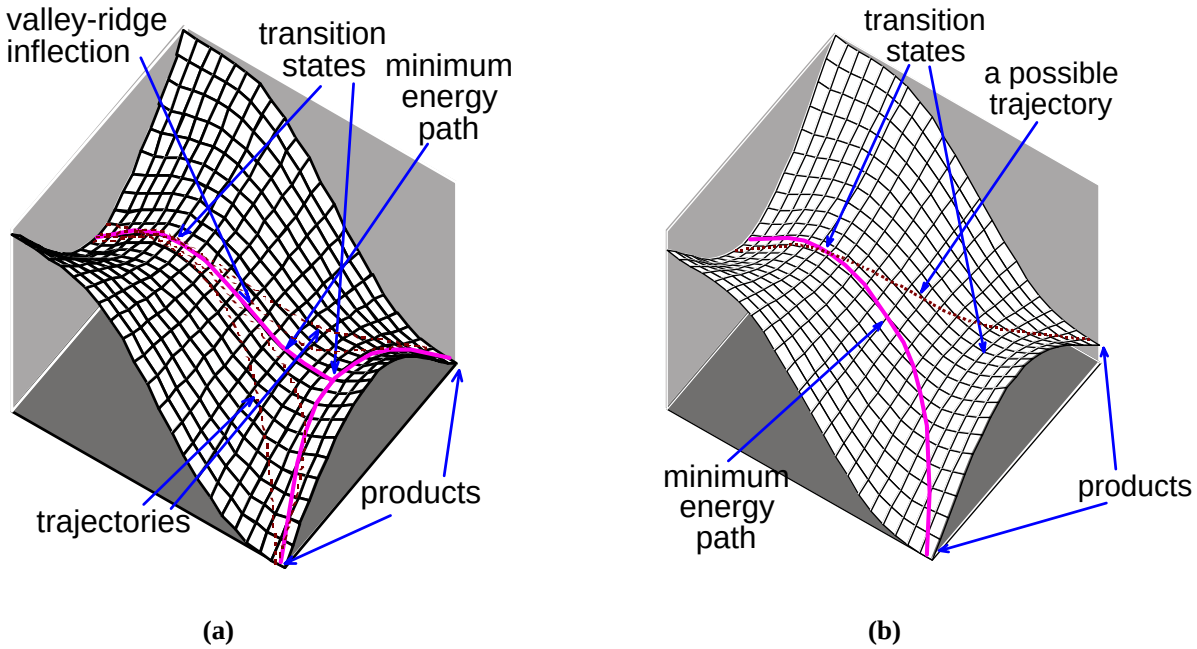
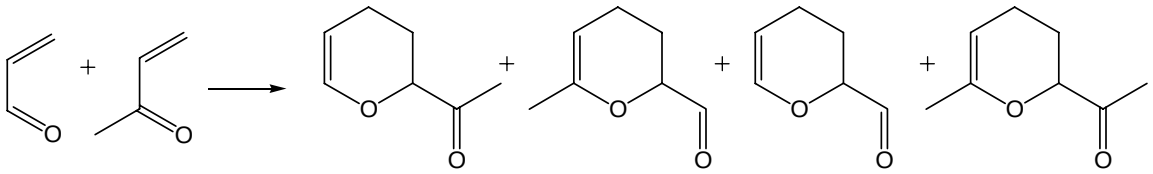


Figure 35. Bifurcating surfaces in which dynamic effects would control selectivity. (a) The surface is symmetrical and the MEP bifurcates at a second transition state. Real trajectories would tend to diverge from the MEP in the area of the VRI. (b) The surface is unsymmetrical and the MEP does not bifurcate. However, some possible trajectories afford a product not on the MEP.

We discuss here the effect of dynamic effects on such a surface in understanding the role selectivity of a Diels-Alder reaction.

The 77-year old Diels-Alder reactions are among the most important ring-forming process in chemistry, [75] and the regio-, stereo- and enantioselectivity have been extensively studied. When a Diels-Alder reaction is carried out between two components that have similar 4-electron π systems, role selectivity, the selection of which component

acts as the diene versus dienophile in the reaction, can be an important consideration. The reaction we chose here is the Diels-Alder reaction between acrolein (**65**) and methyl vinyl ketone (**66**), as shown in Figure 36,[76] which gives two cross products **67** and **68**, as well as two dimerization products **69** and **70**. In product **67**, acrolein acts as a diene, while in **68**, methyl vinyl ketone acts as a diene.



65 **66** **67** **68** **69** **70**

Figure 36. Diels-Alder reaction between acrolein and methyl vinyl ketone.

The normal assumption would be that the role selectivity would be controlled by the energetic difference between the two separate transition state leading to **67** and **68** respectively. However, theoretical studies by Caramella and coworkers suggested that for the regiospecific dimerization of methacrolein the 4+2 and 2+4 cycloaddition paths merge, the transition structure has a C_2-symmetry and the energy surface looks like that of figure 35(a). [77] At the rate-limiting transition state, it has not decided yet which molecule would act as the diene and which as dienophile in the product. However, in the dimerization of methacrolein, the two products are identical and not experimentally differentiatable. Thus we turn our attention to the less symmetrical reaction, reaction between **65** and **66**.

Results and Discussion

Kinetic studies and simulations. The reaction between acrolein and methyl vinyl ketone goes very slowly at temperatures even as high as 100 °C. Taking into consideration the low boiling points of the reactants, all the reactions for kinetic studies were done in sealed tubes at temperatures between 100 and 220 °C. The concentration of the products was determined with NMR and GC, by comparing to the internal standard 1,2-dimethoxyethane. With the assumption that all Diels-Alder reactions occur in second order and the rearrangement from minor cross product to major cross product is first order, kinetic simulation was then done to determine the rate constants since the formation of the four products affect one another and minor cross product **68** converts to major cross product **67** under thermal conditions, which makes it impractical to measure the individual rate constants separately. Due to the fact that all the four products have a similar structural frame, which leads to similar chemical shifts and partial overlap in NMR, the concentrations and derived rates are subject to considerable uncertainty.

Seven independent sets of kinetic studies and simulations at different temperature in the range between 100 and 220 °C shows the ratio between the rate constant of the formation of major cross product and the rate constant of the formation of minor cross product at 3.0 ± 0.5

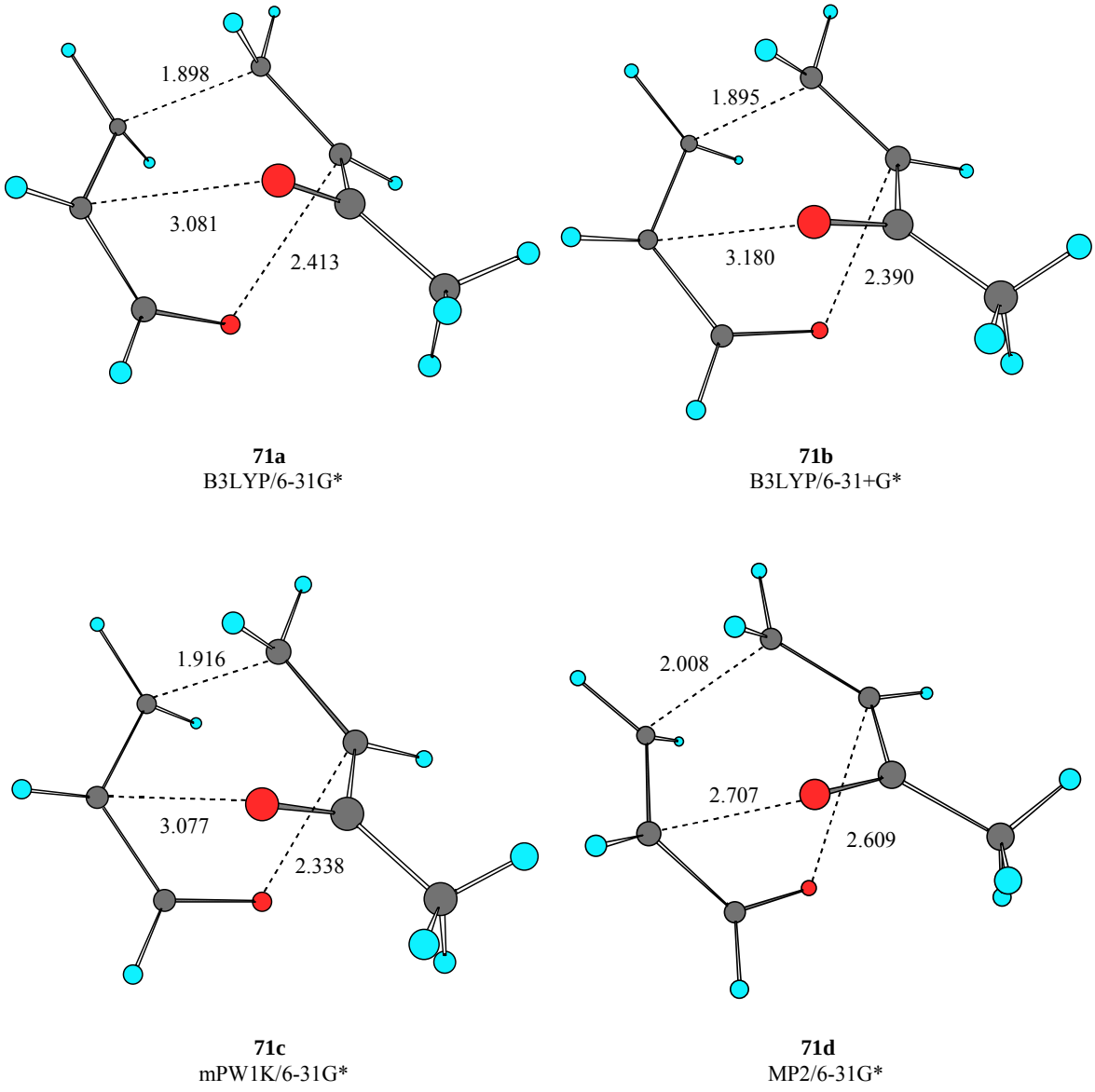
Theoretical studies. Calculational studies by Caramella and coworkers have suggested a bifurcating energy surface and the possible influence of dynamic effects in the dimerization of methacrolein. [77] To investigate the similar Diels-Alder reaction

between acrolein and methyl vinyl ketone, a thorough theoretical investigation was carried out.

A variety of transition structures were located for cycloaddition of acrolein and methyl vinyl ketone. First, both acrolein and methyl vinyl ketone can act as diene. Second, the dienophile can adopt s-*cis* or s-*trans* geometry. And both *endo* and *exo* approach need to be considered. Thus eight transition structures were expected. However, only seven transition structures were located, and the relative energies are listed in Table 8. Among those transition structures, the *endo* transition structure with acrolein as diene and s-*cis* methyl vinyl ketone as dienophile (**71**) has lowest energy. Most of other transition structures are considerably higher in energy than **71** and not likely to contribute in the formation of product. Only the *exo* one with acrolein as diene and s-*cis* methyl vinyl ketone is in an energetic range that could slightly contribute to the formation of products, however, this transition structure leads to the same inclination in role selectivity.

A key intriguing result was that even though there are two cross products formed in the reaction, only one low-energy cycloaddition transition structure could be found. Geometries of this transition structure **71** at different theoretical levels are illustrated in Figure 37. As shown in all the cases, the formation of C-$O_{acrolein}$ bond is more developed than the formation of C-O_{mvk} bond. However, the difference in the degree of bond formation varies with the method used in the calculation. Structures from B3LYP and mPW1K calculations are all considerably unsymmetrical, with the difference between C-$O_{acrolein}$ distance and C-O_{mvk} distance at 0.668, 0.790, and 0.739 Å respectively. On the

contrary, MP2 geometry is only slightly unsymmetrical, with the difference between C-$O_{acrolein}$ distance and C-O_{mvk} distance at 0.098 Å.



71a
B3LYP/6-31G*

71b
B3LYP/6-31+G*

71c
mPW1K/6-31G*

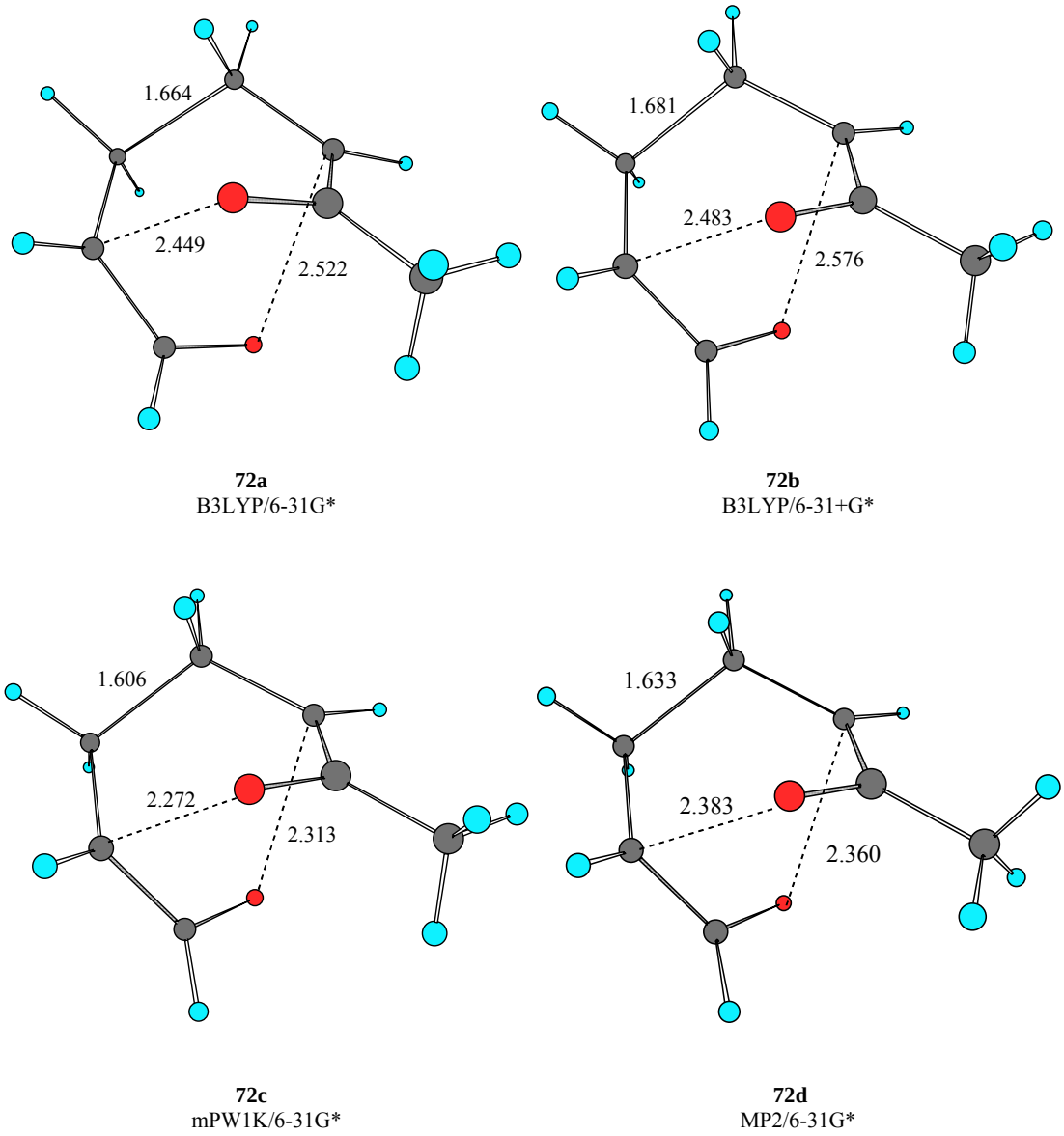
71d
MP2/6-31G*

Figure 37. Calculational geometries of transition structure **71** using different calculational methods.

Table 8. Relative energies of possible combinations for the Diels-Alder transition structures in kcal/mol.

	B3LYP/6-31G*	CCSD(T)/6-31G*
TS **71**, Ac as diene, MVK *cis, endo*	0.0	0.0
Ac as diene, MVK *cis, exo*	1.3	2.5
Ac as diene, MVK *trans, endo*	5.6	6.9
Ac as diene, MVK *trans, exo*	5.8	7.2
MVK as diene, Ac *cis, exo*	3.2	4.5
MVK as diene, Ac *trans, endo*	4.8	7.0
MVK as diene, Ac *trans, exo*	5.7	7.8

Another important geometry is the transition structure in the step that converts the minor cross product to the major cross product. This is formally a [3,3]-sigmatropic rearrangement and similar to Cope rearrangement. Geometries of transition structure for this conversion (**72**) are shown in Figure 38. The relative energies of all chemically important species at various calculational levels are listed in Table 9.



72a
B3LYP/6-31G*

72b
B3LYP/6-31+G*

72c
mPW1K/6-31G*

72d
MP2/6-31G*

Figure 38. Calculational geometries of transition structure **72** using different calculational methods.

Table 9. Relative energies of chemically important species in Diels-Alder reaction between acrolein and methyl vinyl ketone in kcal/mol.

	B3LYP /6-31G*	B3LYP /6-31+G*	CCSD(T)/ 6-31G*	mPW1K/ 6-31G*	MP2/ 6-31G*
Starting materials	0.0	0.0	0.0	0.0	0.0
TS **71**	19.5	22.7	17.7	20.8	10.6
Product **67**	-30.7	-15.0	-28.3	-31.0	-25.9
Product **68**	-28.8	-13.2	-26.0	-28.9	-24.2
TS **72**	8.2	23.8	16.1	21.1	7.4

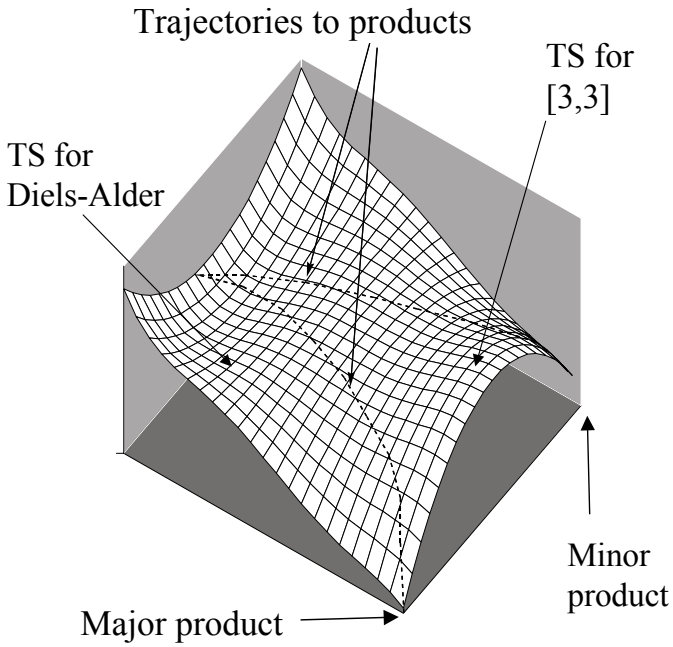


Figure 39. Qualitative B3LYP/6-31G* energy surface in Diels-Alder reaction between acrolein and methyl vinyl ketone.

To get a full view of the energy surface, series of calculations were carried out with an array of fixed C-C distance between the two carbon atoms that close the ring in the products. For each C-C distance, a second array of C-$O_{acrolein}$ distance is fixed. A qualitative 3-dimensional energy surface (Figure 39) was obtained form the resulting energy values.

Theoretical studies: dynamics. It has been reported before that a single transition state could give rise to two compounds in organic reactions. [69e, 78] Since only one transition structure is involved in the formation of both products in the Diels-Alder reaction between acrolein and methyl vinyl ketone, the selectivity between the two products cannot be explained with energetic difference in the reaction pathways. Thus the ratio of products is not associated with barrier but determined by momenta of atoms and dynamic calculations are needed to understand the role selectivity in the reaction.

Structure **71** was used as the starting point for quasiclassical direct dynamic trajectories on the B3LYP/6-31G* energy surface. The trajectories were initiated by giving each mode a random sign for its initial velocity, along with an initial energy based on a random Boltzmann sampling of vibrational levels at 353.15 K, including zero-point energy. One-fs steps were taken until either product or starting material was formed. The formation of product was judged by a C-$O_{acrolein}$ or C-O_{mvk} distance less than 1.6 Å, while the formation of starting material was judged by a C-C distance larger than 2.2 Å.

Dynamic calculations on the B3LYP/6-31G* energy surface gives a ratio of 214:14 between the major and the minor cross product. This is not surprising due to the large difference between C-$O_{acrolein}$ distance and C-O_{mvk} distance at 0.668Å. However, it is far from the experimental observation of a ratio of 3.0 ± 0.5, which indicates B3LYP/6-31G* energy surface may not be able to represent the reality in the reaction. The B3LYP/6-31+G* and mPW1K/6-31G* transition structures are expected to give similar results in dynamic calculations since they also have large difference in C-O distances.

As mentioned above, the MP2 calculational structures are considerably different from the B3LYP and mPW1K calculational structures. The MP2 calculation predicted much lower barrier for cycloaddition and a [3,3]-sigmatropic transition structure lower in energy than the Diels-Alder transition structure. The MP2 calculation has been proved to provide better prediction in the Clainsen rearrangement,[79] which has similarity with the [3,3]-sigmatropic rearrangement here. The MP2 Diels-Alder transition structure is only slightly unsymmetrical, which could rationally lead to much smaller ratio between the major and the minor cross product. However, the full exploration of MP2 energy surface is precluded due to the limited calculational capacity. Thus a qualitative surface is built with the relative energies of all the chemically important species involved, as shown in Figure 40. Dynamic calculations on the MP2/6-31G* energy surface showed a ratio of 45:14 (3.2:1), which is in good agreement with the experimental observation of 3.0 ± 0.5 and verifies the reflection of reality by MP2 calculations.

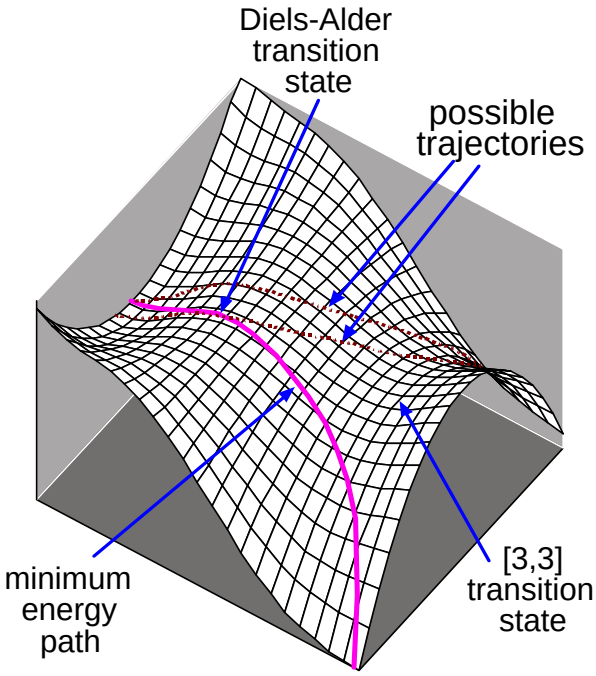


Figure 40. MP2/6-31G* energy surface in Diels-Alder reaction between acrolein and methyl vinyl ketone.

An unexpected experimental observation is the high rate constants and the low activation energy in the conversion of minor cross product to the major product. Kinetic studies and simulations suggest an activation energy of about 15 kcal/mol, which is just about the half of the calculational barrier of 31.6 kcal/mol. This could be the result of some unpredicted catalytic process or the further reaction of the minor product with components in the reaction system.

Conclusion

Diels-Alder reaction between acrolein and methyl vinyl ketone provides two cross products, one with acrolein as diene, the other with methyl vinyl ketone as diene, in a ratio of 3.0 ± 0.5. Theoretical studies show that only one low-energy transition structure

is involved in the formation of both products and that the role selectivity cannot be explained by energetic barriers. Dynamic calculations on B3LYP energy surface predict a product ratio of 214:14, indicating that B3LYP calculation may not reflect the reality in the reaction. Dynamic calculations on MP2 surface give a prediction of a product ratio of 45:14 (3.2:1), which is in good agreement with the experimental observation. Overall, dynamic effects successfully predicted the role selectivity in the Diels-Alder reaction between acrolein and methyl vinyl ketone, which cannot be explained with transition state theory.

CHAPTER VI

EXPERIMENTAL SECTION

General Procedures

Proton NMR spectra were recorded on Varian XL-300 or Mercury 300 spectrometer. ^{13}C spectra for KIE determinations were recorded on Varian-400, Unity 500, or Inova 500 spectrometer. T1 values for each sample were determined by the inversion-recovery method to avoid integration errors from paramagnetic impurities in the sample. ^{13}C integrations were determined numerically using a constant region for each peak that was about 5 times the peak width at half height on either side of the peak. A zero-order baseline was generally applied but in no case was a first order correction employed. KIEs and errors were calculated using equation 33-36 based on the isotopic enrichment and reaction conversion.

$$KIE_{calcd} = \frac{\ln(1-F)}{\ln[(1-F)R/R_0]} \quad . \quad (33)$$

$$\Delta KIE_F = \frac{\partial KIE}{\partial F}\Delta F = \frac{-\ln(R/R_0)}{(1-F)\ln^2[(1-F)R/R_0]}\Delta F \quad . \quad (34)$$

$$\Delta KIE_R = \frac{\partial KIE}{\partial (R/R_0)}\Delta(R/R_0) = \frac{-\ln(1-F)}{(R/R_0)\ln^2[(1-F)R/R_0]}\Delta(R/R_0) \quad . \quad (35)$$

$$\Delta KIE = KIE*((\Delta KIE_R/KIE)^2 + (\Delta KIE_F/KIE)^2)^{1/2} \quad (36)$$

All calculational structures and energies were obtained using standard procedures in Gaussian98[80] or Gaussian03.[81] Vibrational frequency analyses were carried out on all stationary points. The structures were all first located by density functional theory calculations employed Becke3LYP[82] method implemented in Gaussian with 6-31G* basis set. B3LYP calculations with larger basis sets, mPW1K calculations, [32] CCSD(T) single point energy calculations, and MP2 calculations were carried out when necessary, starting with B3LYP/6-31G* calculated structures. Semiclassical trajectory calculations were carried out according previously described method.[73a]

Fragmentation of Epoxy Inimo-1,3,4-oxadiazolines

Epoxy imino-1,3,4-oxadizoline diastereomers were synthesized by literature method.[28] The diastereomers were separated by flash column eluted with 6:4 mixture of dichloromethane/hexanes. A 10 x 5 cm column and 3 L of eluting solvents were used for the separation of 1 g of diastereomers. Column chromatography was then followed by a recrystallization in 5:1 hexanes/dichloromethane to yield pure major isomer. The structure of major diastereomer was determined by X-ray crystalgraphy.

To 2.00 g (7 mmol) of α,β-epoxy phenylinimo-1,3,4-oxadiazoline (**2**), 50 mL of diphenyl ether, and 1.00 g (5 mmol) of dibenzyl ether (internal standard) were added and stirred at 145 – 150 °C for 1 h. A conversion at 65 ± 1% was determined with NMR by comparing the signal of tertiary proton on the epoxide ring at 2.70 ppm to the methylene signal in the internal standard at 4.55 ppm. Unreacted α,β-epoxy phenylinimo-1,3,4-oxadiazoline was then recovered by a flash column eluted with a 1:1 mixture of

hexane/dichloromethane, followed by recyrstallization at –20 °C from 5:1 hexane/dichloromethane. By analogous procedure, two other reactions were taken to conversions of 70 ± 1%, and 84 ± 1% respectively.

NMR Measurements. All samples were prepared using a constant 150 mg of 2-phenylimino-Δ^3-1,3,4-oxidiazoline (**2**) in 5 mm NMR tubes filled with $CDCl_3$ to a constant height of 5.0 cm. The ^{13}C spectra were recorded at 125.70 MHz using inverse gated decoupling, 60 s delays between calibrated $\pi/2$ pulses, and a 6.560 s acquisition time to collect 262 144 points. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but no first-order correction was applied. Four or five spectra were recorded for each sample of recovered 2-phenylimino-Δ^3-1,3,4-oxidiazoline along with samples of 2-phenylimino-Δ^3-1,3,4-oxidiazoline which were not subjected to the reaction conditions.

For the ^{13}C spectra of α,β-epoxy 2-phenylinimo-1,3,4-oxadiazoline the integrations of the oxirane substitutent methyl carbons (C_8) were set at 1000. The average integrations and standard deviations (in parentheses) for the other carbons are shown in Table 10 along with the number of spectra recorded for each sample (n).

The values for R/R_O, calculated as the ratio of average integrations in Table 10 relative to the standard sample, are shown in Table 11. The standard deviations were calculated from the formula:

$$\Delta R / R_0 = R / R_0 \times ((\Delta \text{IntSample} / \text{IntSample})^2 + (\Delta \text{IntStandard} / \text{IntStandard})^2)^{1/2}$$

Table 10. Average ^{13}C integrations for α,β-epoxy phenylinimo-1,3,4-oxadiazoline, with standard deviations (in parentheses).

% conversion	C_1	C_2	C_3	C_4	C_5	C_6	C_7	n
Standard	1043.4 (5.6)	1040.3 (2.3)	1037.9 (2.9)	1032.5 (3.1)	1042.0 (5.7)	985.9 (3.6)	1015.4 (5.0)	5
Samp1 65 ± 1 %	1068.7 (2.0)	1057.6 (3.4)	1048.4 (5.1)	1038.1 (2.5)	1042.8 (3.7)	994.6 (4.9)	1016.5 (4.2)	5
Standard	1088.9 (3.5)	1053.1 (0.9)	1063.7 (5.1)	1050.5 (2.1)	1058.0 (3.6)	999.3 (3.4)	1029.3 (3.5)	4
Samp2 70 ± 1 %	1134.2 (5.7)	1064.6 (1.7)	1066.5 (5.2)	1041.9 (5.1)	1065.4 (4.2)	998.5 (3.3)	1031.8 (3.5)	4
Standard	1088.9 (3.5)	1053.1 (0.9)	1063.7 (5.1)	1050.5 (2.1)	1058.0 (3.6)	999.3 (3.4)	1029.3 (3.5)	4
Samp3 84 ± 1 %	1125.8 (3.5)	1073.4 (1.8)	1072.6 (1.3)	1049.1 (1.8)	1060.3 (3.6)	998.3 (3.3)	1029.4 (2.3)	4
% conversion	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	n
Standard	1000	1029.8 (4.4)	987.3 (1.4)	959.2 (5.0)	2079.3 (5.9)	2065.7 (9.2)	1016.2 (2.5)	5
Samp1 65 ± 1 %	1000	1026.1 (4.4)	984.7 (4.2)	977.2 (4.8)	2088.7 (11.5)	2101.5 (9.2)	1019.2 (2.9)	5
Standard	1000	1009.6 (4.8)	1006.6 (2.8)	1044.3 (3.9)	2106.2 (7.2)	2125.5 (5.4)	1036.8 (3.6)	4
Samp2 70 ± 1 %	1000	1010.8 (2.8)	1010.4 (5.2)	1046.6 (3.9)	2100.1 (9.3)	2143.4 (4.3)	1037.5 (2.0)	4
Standard	1000	1009.6 (4.8)	1006.6 (2.8)	1044.3 (3.9)	2106.2 (7.2)	2125.5 (5.4)	1036.8 (3.6)	4
Samp3 84 ± 1 %	1000	1012.5 (2.0)	1006.2 (4.6)	1044.8 (3.9)	2098.2 (4.3)	2130.9 (2.2)	1031.6 (3.1)	4

Table 11. R/R_O for ^{13}C for α,β-epoxy phenylinimo-1,3,4-oxadiazoline.

	C_1	C_2	C_3	C_4	C_5	C_6	C_7
65 ± 1 % R/R_O	1.024	1.017	1.010	1.005	1.001	1.009	1.001
Stand dev	0.006	0.004	0.006	0.004	0.007	0.006	0.006
70 ± 1 % R/R_O	1.042	1.011	0.999	0.992	1.007	0.999	1.002
Stand dev	0.006	0.002	0.007	0.005	0.005	0.005	0.005
84 ± 1 % R/R_O	1.034	1.029	1.005	0.999	1.002	0.999	1.000
Stand dev	0.005	0.002	0.005	0.003	0.005	0.005	0.004
	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	
65 ± 1 % R/R_O	0.996	0.997	1.019	1.005	1.017	1.003	
Stand dev	0.006	0.004	0.007	0.006	0.006	0.004	
70 ± 1 % R/R_O	1.001	1.004	1.002	0.997	1.008	1.001	
Stand dev	0.006	0.006	0.005	0.006	0.003	0.004	
84 ± 1 % R/R_O	1.003	1.000	1.000	0.996	1.003	0.995	
Stand dev	0.005	0.005	0.005	0.004	0.003	0.005	

The ^{13}C KIEs for α,β-epoxy 2-phenylinimo-1,3,4-oxadiazoline were then calculated from eq. 33, with the standard deviations calculated from eq. 34, 35, and 36 and the results are listed in Table 12.

Table 12. ^{13}C KIEs for α,β-epoxy phenylinimo-1,3,4-oxadiazoline**.**

	C_1	C_2	C_3	C_4	C_5	C_6	C_7
65 ± 1 % R/R_O	1.023(6)	1.016(4)	1.010(5)	1.005(4)	1.001(6)	1.008(6)	1.001(6)
70 ± 1 % R/R_O	1.035(5)	1.009(2)	1.002(6)	0.993(4)	1.006(4)	0.999(4)	1.002(4)
84 ± 1 % R/R_O	1.019(3)	1.011(1)	1.005(3)	0.999(1)	1.001(3)	0.999(3)	1.000(2)
	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	
65 ± 1 % R/R_O	0.997(6)	0.998(4)	1.018(7)	1.004(6)	1.017(6)	1.003(4)	
70 ± 1 % R/R_O	1.001(5)	1.003(5)	1.002(4)	0.998(5)	1.007(3)	1.001(3)	
84 ± 1 % R/R_O	1.002(3)	1.000(3)	1.000(3)	0.998(2)	1.001(2)	0.997(2)	

Deoxygenation of Epoxides with Dichlorocarbene

A mixture of 7.20 g (60 mmol) of styrene oxide, 120 mL of benzene, 0.32 g (1.2 mmol) of 18-crown-6 and 1.00 g (5 mmol) of dibenzyl ether (internal standard) was mechanically stirred at 40 °C for 10 min. Then 96 mL of $CHCl_3$ was added dropwise over a 2-h period in which 112 g of powdered solid KOH was added in three portions. The reaction mixture was stirred at 40 °C for another 18 h before being quenched by addition of 1 L of water. The resulting mixture was then extracted with three 100-mL portions of hexane and the combined organic layers were washed with three 30-mL portions of brine. The solvent was removed under vacuum to give a colorless liquid. A conversion at 72±1% was determined with NMR by comparing the tertiary proton on the epoxide ring at 3.84 ppm to the methylene signal in the internal standard at 4.55 ppm.

Unreacted styrene oxide was recovered by a chromatography on a 30 x 2.5 cm silica gel column eluted with a 9:1 mixture of hexane/dichloromethane followed by a microdistillation.

By this general procedure, three other reactions were taken to conversions of, 80±1%, 78±1%, and 80±1% respectively.

NMR Measurements. All samples were prepared using a constant 730 mg of styrene oxide **18** in 5 mm NMR tubes filled with $CDCl_3$ to a constant height of 5.0 cm. The ^{13}C spectra were recorded at 100.58 MHz using inverse gated decoupling, 110 s delays between calibrated $\pi/2$ pulses, and a 10.073 s acquisition time to collect 262 144 points. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but no first-order correction was applied. Six spectra were recorded for each sample of recovered styrene oxide along with samples of styrene oxide, which were not subjected to the reaction conditions.

For the ^{13}C spectra of styrene oxide the integrations of the *para* aromatic carbons (C6) were set at 1000. The average integrations and standard deviations (in parentheses) for the other carbons are shown in Table 13 along with the number of spectra recorded for each sample (n).

Table 13. Average ^{13}C integrations for styrene oxide, with standard deviations (in parentheses).

% conversion	C_1	C_2	C_3	$C_{4,8}$	$C_{5,7}$	C_6	n
Standard	981.4 (2.1)	970.7 (2.5)	988.4 (0.5)	2005.9 (3.5)	1992.3 (2.1)	1000	6
Samp1 80 $\pm$ 1 %	969.5 (0.6)	993.2 (0.8)	991.7 (1.5)	2003.1 (3.1)	1993.0 (4.1)	1000	6
Standard	1024.1 (1.6)	976.6 (2.3)	1049.9 (3.8)	1967.8 (2.5)	1973.7 (7.9)	1000	6
Samp2 72 $\pm$ 1 %	1018.3 (1.9)	999.1 (2.5)	1055.6 (3.7)	1977.1 (5.3)	1969.4 (4.9)	1000	6
Standard	973.1 (2.0)	975.3 (2.0)	931.3 (1.4)	1989.0 (2.7)	1976.5 (4.8)	1000	6
Samp3 78 $\pm$ 1 %	963.6 (2.2)	995.8 (3.5)	930.0 (4.0)	1985.2 (3.5)	1989.7 (3.5)	1000	6
Standard	983.1 (2.5)	985.6 (1.2)	942.9 (1.0)	2017.4 (1.7)	2012.3 (2.1)	1000	6
Samp4 82 $\pm$ 1 %	977.0 (1.4)	1013.9 (0.9)	939.0 (1.2)	2005.3 (1.4)	2025.6 (1.6)	1000	6

Table 14. R/R_O for ^{13}C for styrene oxide.

	C_1	C_2	C_3	$C_{4,8}$	$C_{5,7}$
80 $\pm$ 1 % R/R_O	0.988	1.023	1.003	0.999	1.000
72 $\pm$ 1 % R/R_O	0.994	1.023	1.005	1.005	0.998
78 $\pm$ 1 % R/R_O	0.990	1.021	0.999	0.998	1.007
82 $\pm$ 1 % R/R_O	0.991	1.031	0.996	0.994	1.007

The values for R/R_O, calculated as the ratio of average integrations in Table 13 relative to the standard sample, are shown in Table 14. The standard deviations were calculated using the same equation as shown before.

The ^{13}C KIEs for styrene oxide were then calculated from eq. 33, with the standard deviations calculated from eq. 34, 35, and 36 and the results are listed in Table 15.

Table 15. ^{13}C KIEs for styrene oxide**.**

	C_1	C_2	C_3	$C_{4,8}$	$C_{5,7}$
Samp1 80 $\pm$ 1 %	0.993(1)	1.014(2)	1.002(1)	0.999(1)	1.000(1)
Samp2 72 $\pm$ 1 %	0.996(2)	1.018(3)	1.004(4)	1.004(2)	0.998(4)
Samp3 78 $\pm$ 1 %	0.994(2)	1.014(3)	0.999(3)	0.999(1)	1.004(2)
Samp4 82 $\pm$ 1 %	0.995(2)	1.018(1)	0.998(1)	0.997(1)	1.004(1)

Shi Epoxidation of Trans-β-methylstyrene

All glassware used for the reaction was placed in a newly made base bath for at least 12 h, then rinsed with double distilled water for ten times and 4 x 10^{-3} M Na_2(EDTA) solution for three times. A mixture of 3.54 g (30 mmol) of trans-β-methylstyrene (**27**), 0.41 g (3 mmol) of 1,4-dimethoxybenzene (internal standard), 450 mL of 1:2 mixture of acetonitrile and dimethoxymethane, 300 mL of buffer solution (0.05 M solution of $Na_2B_4O_7 \bullet 10H_2O$ in 4 x 10^{-3} M aqueous Na_2(EDTA)), 0.34 g (1

mmol) of tetrabutylammonium hydrogen sulfate (phase transfer catalyst), and 1.55 g (6 mmol) of **25** was cooled in an ice bath, and solutions of 50 g (81 mmol) of Oxone™ in 390 mL of 4 x 10^{-3} M aqueous Na_2(EDTA) and 390 mL of 0.89 M K_2CO_3 were added dropwise separately and simultaneously over a period of 1.5 h. The reaction mixture was then stirred for another 30 min before the reaction was quenched by addition of 1 L of water. The resulting mixture was extracted with three portions of 100 mL of pentane and the combined organic layers were washed with three portions of 100 mL of brine, and dried over Na_2SO_4. The solvent was removed under vacuum and a conversion at 83±1% was determined based on the ^{1}H NMR integration of olefin protons in trans-β-methylstyrene (at δ 6.15 and δ 6.37) versus the methoxy signal in the internal standard. The unreacted **27** was then recovered by chromatography on a 40 x 4 cm silica gel column eluted with a 95:5 mixture of hexane/dichloromethane, affording 495 mg of **27**. By this procedure, another analogous reaction was taken to 93±1% conversion, and afforded 220 mg of recovered **27**.

NMR Measurements. All samples were prepared using a constant 220 mg of **27** in 5 mm NMR tubes filled with $CDCl_3$ to a constant height of 5.0 cm. The ^{13}C spectra were recorded at 125.70 MHz using inverse gated decoupling, 110 s delays between calibrated π/2 pulses, and a 6.560 s acquisition time to collect 262 144 points. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but no first-order correction was applied. Six spectra were recorded for each sample of recovered trans-β-methylstyrene along with samples of trans-β-methylstyrene, which were not subjected to the reaction conditions.

For the ^{13}C spectra of trans-β-methylstyrene, the integrations of the *meta* aromatic carbons (C_{meta}) were set at 2000. The average integrations and standard deviations (in parentheses) for the other carbons are shown in Table 16 along with the number of spectra recorded for each sample (n).

Table 16. Average ^{13}C integrations for trans-β–methylstyrene, with standard deviations (in parentheses).

% conversion	C_α	C_β	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	C_{methyl}	n
Standard	983.7 (1.5)	1012.0 (1.5)	954.2 (1.8)	2014.4 (2.4)	2000	1007.1 (1.5)	948.7 (1.6)	6
83 $\pm$ 1 %	993.0 (2.0)	1051.8 (1.9)	952.6 (2.0)	2019.2 (2.7)	2000	1004.0 (2.6)	952.0 (2.7)	6
Standard	976.9 (3.1)	1042.1 (1.7)	945.2 (3.1)	2011.7 (5.0)	2000	999.1 (3.6)	944.1 (2.1)	6
93 $\pm$ 1 %	992.6 (3.2)	1096.6 (2.5)	948.0 (3.3)	2019.5 (6.4)	2000	1001.4 (3.8)	947.8 (3.6)	6

The values for R/R_O, calculated as the ratio of average integrations in Table 16 relative to the standard sample, are shown in Table 17. The standard deviations were calculated using the same equation as shown before.

The ^{13}C KIEs for trans-β-methylstyrene were then calculated from eq. 33, with the standard deviations calculated from eq. 34, 35, and 36 and the results are listed in Table 18.

Table 17. R/R_O for ^{13}C for trans-β-methylstyrene.

	C_α	C_β	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	C_{methyl}
83 ± 1 % R/R_O	1.009	1.039	0.998	1.002	1	0.997	1.004
Stand dev	0.003	0.002	0.003	0.002	0.000	0.001	0.003
93 ± 1 % R/R_O	1.016	1.052	1.003	1.004	1	1.002	1.004
Stand dev	0.004	0.003	0.004	0.003	0.000	0.004	0.004

Table 18. ^{13}C KIEs for trans-β-methylstyrene**.**

	C_α	C_β	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	C_{methyl}
83 ± 1 %	1.005(1)	1.022(2)	0.999(2)	1.001(1)	1	0.998(2)	1.002(2)
93 ± 1 %	1.006(2)	1.020(2)	1.001(2)	1.001(2)	1	1.001(2)	1.001(2)

Diels-Alder Reaction between Acrolein and Methyl Vinyl Ketone

Diels-Alder reactions between acrolein and methyl vinyl ketone were carried out at 100 °C in sealed tubes. A solution containing 2.5 ml (2.1 g, 37 mmol) of acrolein, 1.2 ml (1.0 g, 14 mmol) of methyl vinyl ketone, 1.5 ml (1.3 g, 14 mmol) of ethylene glycol dimethyl ether and 1.5 ml of benzene was divided into 20 portions in sealed tubes. Fifteen tubes were placed in a oil bath to start and three tubes were taken out of the oil bath and the concentration of products were measured by NMR and GC at 4 h, 8 h, 16 h,

32 h, and 64 h respectively. Similar reactions at 120 °C, 140 °C, 160 °C, 180 °C, 200 °C, and 220 °C were carried out in analogous way but with shorter reaction time.

Kinetic simulations were done with an Excel spreadsheet by numerically integrating assumed rate equations with bimolecular kinetics in the cycloadditions and unimolecular kinetics in the [3,3]-sigmatropic rearrangement. The rate constants were adjusted to get a least-squares best fit of the predicted concentration of products and reactants to the measured values. Due to the fact that all the four products have a similar structural frame, which leads to similar chemical shifts and partial overlap in NMR, the concentrations and derived rates are subject to considerable uncertainty. The resulting rate constants are listed in Table 19.

Table 19. Rate constants in Diels-Alder reaction between acrolein and methyl vinyl ketone.

T (°C)	k_{major} (s^{-1})	k_{minor} (s^{-1})	k_{Cope} (s^{-1})	$k_{acdimer}$ (s^{-1})	$k_{mvkdimer}$ (s^{-1})
100	6.2×10^{-7}	2.7×10^{-7}	6.8×10^{-6}	1.3×10^{-7}	2.7×10^{-7}
120	2.4×10^{-6}	1.0×10^{-6}	1.5×10^{-5}	6.3×10^{-7}	1.1×10^{-6}
140	7.1×10^{-6}	3.0×10^{-6}	2.9×10^{-5}	1.6×10^{-6}	4.1×10^{-6}
160	2.3×10^{-5}	7.9×10^{-6}	6.2×10^{-5}	5.3×10^{-6}	9.0×10^{-6}
180	9.6×10^{-5}	2.7×10^{-5}	1.4×10^{-4}	7.9×10^{-6}	6.3×10^{-5}
200	2.3×10^{-4}	8.5×10^{-5}	4.5×10^{-4}	1.6×10^{-5}	2.0×10^{-4}
220	4.3×10^{-4}	1.5×10^{-4}	6.2×10^{-4}	3.5×10^{-5}	3.2×10^{-4}

Calculational studies on the B3LYP/6-31G* energy surface. Series of calculations were carried out with the C-C distance between the two carbon atoms that close the ring in the products fixed at 1.7 to 2.6 Å. For each C-C distance, a second array of $C\text{-}O_{acrolein}$ distance is fixed at 1.4 to 3.0 Å. The resulting energies are listed in Table 20.

Table 20. Relative energies in kcal/mol of geometries with fixed distance.

	C-C distance (Å)				
$C\text{-}O_{acrolein}$ distance	1.7	1.8	1.9	2.0	2.1
3.0	42.9	36.3	16.7	18.2	20.5
2.9	41.9		16.8		20.4
2.8	40.6	16.4	16.9	18.3	20.3
2.7	38.9		17.0		20.0
2.6	36.8	16.6	17.0	18.0	19.6
2.5	34.1		16.9		19.0
2.4	30.9	17.0	16.8	17.2	18.2
2.3	26.9		16.8		17.2
2.2	22.3	18.3	16.9	16.1	16.0
2.1	17.0		17.3		14.7
2.0	11.2	21.4	18.2	15.4	13.6
1.9	5.4		19.8		12.9
1.8	0.0	27.8	22.4	17.3	13.1

Table 20. Continued

	C-C distance (Å)				
$C\text{-}O_{acrolein}$ distance	1.7	1.8	1.9	2.0	2.1
1.7	38.7		25.7		14.2
1.6	44.8	38.4	29.1		15.7
1.5	49.1		35.0		16.5
1.4	49.4		35.5		15.2
	C-C distance (Å)				
$C\text{-}O_{acrolein}$ distance	2.2	2.3	2.4	2.5	2.6
3.0	22.9	25.2	27.4	52.8	54.4
2.9		25.0		53.5	
2.8	22.6	24.7	26.8	52.1	53.6
2.7		24.2		51.4	
2.6	21.6	23.5	25.4	50.5	52.0
2.5		22.6		49.4	
2.4	19.7	21.4	22.9	47.8	49.1
2.3		19.7		45.8	
2.2	16.6	17.6	18.8	43.3	44.3
2.1		15.1		40.3	
2.0	12.7	12.4	12.7	36.6	37.2
1.9		9.8		32.7	
1.8	9.8	7.5	6.1	28.8	28.3

Table 20. Continued

	C-C distance (Å)				
$C\text{-}O_{acrolein}$ distance	2.2	2.3	2.4	2.5	2.6
1.7		6.2		25.4	
1.6	10.2	5.6	2.0	22.8	20.8
1.5		5.0		20.4	
1.4		2.5		16.5	

CHAPTER VII

CONCLUSIONS

Kinetic isotope effects (KIEs) can be used as a subtle probe in the mechanistic studies of organic reactions. Several reactions that potentially involve coarctate transition states have been investigated by KIEs combined with theoretical studies.

In the thermal fragmentation of Δ-1,3,4-oxadiazolines, the KIEs and theoretical predictions supported a stepwise mechanism. At the stage of reactant, where the concerted reaction would be very complicated, the stepwise process is favored. At the stage of the diazo epoxide, the stepwise process again appears to be favored. The preference for a stepwise mechanism going on from diazo expoxide is less pronounced and less certain, but there is still no sign of a transition state aromaticity effect favoring a concerted coarctate process. The last step in the mechanism, going on from carbene, is a concerted coarctate reaction, but this may be viewed as being enforced by the necessity to avoid high-energy intermediates. Overall, the example here does not appear to demonstrate any special stabilization in coarctate transition states.

In the deoxygenation of epoxides with dichlorocarbene, the stabilization from the transition state aromaticity in coarctate transition state is not great enough to compete with the preference for asynchronous bonding changes. The theoretically predicted and KIE-supported mechanism suggests that the reaction occurs in a concerted manner but with a highly asynchronous early transition state with much more C_α-O bond breaking

than C_β-O bond breaking. The reaction pathway is not influenced by transition state aromaticity.

In the Shi epoxidations, the observation of a large β olefinic ^{13}C isotope effect and small α carbon isotope effect is indicative of an asynchronous transition state with more advanced formation of the C–O bond to the β olefinic carbon. By varying the catalyst conformation and alkene orientation, diverse transition structure geometries were located calculationally, and the lowest-energy structure leads to an accurate prediction of the isotope effects. Given this support for the accuracy of the calculations employed, the nature of enantioselectivity in this and related epoxidations is considered. The lowest-energy transition structures are generally those in which the differential formation of the incipient C–O bonds, the "asynchronicity," resembles that of an unhindered model, and the imposition of greater or less asynchronicity leads to higher barriers. In reactions of *cis*-disubstituted and terminal alkenes using Shi's oxazolidinone catalyst, the asynchronicity of the epoxidation transition state leads to increased steric interaction with the oxazolidinone when a π-conjugating substituent is distal to the oxazolidinone but decreased steric interaction when the π-conjugating substituent is proximal to the oxazolidinone. Overall, the asynchronicity of the transition state must be considered carefully to understand the enantioselectivity.

Diels-Alder reaction between acrolein and methyl vinyl ketone provides two cross products, one with acrolein as diene, the other with methyl vinyl ketone as diene, in a ratio of 3.0 ± 0.5. Theoretical studies show that only one low-energy transition structure is involved in the formation of both products and that the role selectivity cannot be

explained by energetic barriers. Dynamic calculations on B3LYP energy surface predict a product ratio of 214:14, indicating that B3LYP calculation may not reflect the reality in the reaction. Dynamic calculations on MP2 surface give a prediction of a product ratio of 45:14 (3.2:1), which is in good agreement with the experimental observation. Overall, dynamic effects successfully predicted the role selectivity in the Diels-Alder reaction between acrolein and methyl vinyl ketone, which cannot be explained with transition state theory.

REFERENCES

1. For recent development in the study of reactive intermediates, see: Moss, R. A.; Platz, M. S.; Jones, M. Jr., Eds., *Reactive Intermediate Chemistry*, John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004.

2. For recent examples of KIE applications on mechanistic studies, see: (a) Yip, V. L. Y.; Varrot, A.; Davies, G. J.; Rajan, S. S.; Yang, X.; Thompson, J.; Anderson, W. F.; Withers, S. G. *J. Am. Chem. Soc.* **2004,** *126*, 8354. (b) Lloyd-Jones, G. C.; Slatford, P. A. *J. Am. Chem. Soc.* **2004,** *126*, 2690. (c) Kumar, D.; de Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2005,** *127*, 8204. (d) Klain, O.; Agnuilar-Parrila, F.; Lopes, J. M.; Jagerovic, N.; Elguero, J.; Limbach, H. *J. Am. Chem. Soc.* **2004,** *126*, 11718. (e) Humphry,T.; Forconi, M.; Williams, N. H.; Hengge, A. C. *J. Am. Chem. Soc.* **2004,** *126*, 11864. (f) Fan, F.; Gadda, G. *J. Am. Chem. Soc.* **2005,** *127*, 2067. (g) Cohen, R.; Graves, C. R.; Nguyen, S. T.; Martin, J. M. L.; Ratner, M. A. *J. Am. Chem. Soc.* **2004,** *126*, 14796. (h) Casey, C. P.; Johnson, J. B. *J. Am. Chem. Soc.* **2005,** *127*, 1883. (i) Onyido, I.; Swierczek, K.; Purcell, J.; Hengge, A. C. *J. Am. Chem. Soc.* **2005,** *127*, 7703. (j) Dahlen, A.; Hilmersson, G. *J. Am. Chem. Soc.* **2005,** *127*, 8340.

3. (a). Houk, K. N.; Gustafson, S. M.;Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565. (b). Storer, J. W.; Raimondi, L.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 9675. (c). Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336. (d). Wiest, O.; Houk, K. N.; Black, K. A.; Thomas B. *J. Am. Chem. Soc.* **1995**, *117*, 8594.

4. Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357.

5. (a). Beno, B. R.; Houk, K. N.; Singleton, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 9984. (b). Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385. (c). DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907. (d). Singleton, D. A.; Szymanski, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9455. (e). Singleton, D. A.; Hang, C. *J. Am. Chem. Soc.* **1999**, *121*, 11885. (f). Merrigan, S. R.; Singleton, D. A. *Org. Lett*. **1999**, *1*, 327. (g). Singleton, D. A.; Merrigan, S. R.; Kim, B. J.; Beak, P.; Phillips, L. M.; Lee, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 3296. (h). Singleton, D. A.; Merrigan, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 11035. (i). Saettel, N. J.; Wiest, O.; Singleton, D. A.; Meyer, M. P. *J. Am. Chem. Soc.* **2002**, *124*, 11552. (j). Singleton, D. A.; Nowlan, D. T., III; Jahed, N.; Matyjaszewski, K. *Macromolecules*, **2003**, *36*, 8609. (k). Vo, L. K.; Singleton, D. A. *Org. Lett*. **2004**, *6*, 2496. (l). Ussing, B. R.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 2888. (m). Nowlan, D. T., III; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 6190.

6. (a). Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys*. **1947**, 261. (b). Bigeleisen, J. *J. Chem. Phys*. **1949**, 675

7. Stern, M. J.; Wolfsberg, M. *J. Chem. Phys.*, **1966**, *45*, 2618.

8. (a). Wolfsberg, M. *Acc. Chem. Res*. **1972**, *5*, 225.

9. (a). Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117. (b). Wolfsberg, M.; Stern, M. *Pure Appl. Chem*. **1964**, *8*, 225. (c). Wolfsberg, M.; Stern, M. *Pure Appl. Chem*. **1964**, *8*, 235. (d). Goldstein, M. J.; Thayer, G. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1933. (e). Seltzer, S.; Myonakis, S. M. Jr. *J. Am. Chem. Soc.* **1967**, *89*, 6584. (f). Stern, M.; Wolfsberg, M. *J. Chem. Phys*. **1966**,

45, 4105. (g). Gwinn, W. D. *J. Chem. Phys*. **1971**, *55*, 477. (h). Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002.

10. Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989.

11. Bell, R. P. *The Tunnel Effect in Chemistry*, Chapman & Hall: London, 1980, pp 60-63.

.

12. Neame, K. D.; Homewood, C. A. *Liquid Scintillation Counting*, Wiley-Halsted: New York, 1974.

13. (a). Hasan, T.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.* **1983**, *105*, 3967. (b). Shine, H. J.; Kupczyk-Subotkowska, L.; Subotkowski, W. *J. Am. Chem. Soc.* **1985**, *107*, 6674. (c). Kupczyk-Subotkowska, L.; Saunders, W. H. Jr.; Shine, H. J.; Subotkowski, W. *J. Am. Chem. Soc.* **1993**, *115*, 5957.

14. Coleman, D. C.; Fry, B. Eds., *Carbon Isotope Techniques*, Academic Press, Inc.: San Diego, California, 1991, pp 155-171.

15. (a). Rao, M.; Barlow, P. N.; Pryor, A. N.; Paneth, P.; O'Leary, M. H.; Quinn, D. M.; Huskey, W. P. *J. Am. Chem. Soc.* **1993**, *115*, 11676. (b). Paneth, P.; O'Leary, M. H. *J. Am. Chem. Soc.* **1991**, *113*, 1691. (c). Marlier, J. F.; Dopke, N. C.; Johustone, K. R.; Wirdzig, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 4356.

16. Pascal, R. A., Jr.; Baum, M. W.; Wagner, C. K.; Rodgers, L. R.; Huang, D. S. *J. Am. Chem. Soc.* **1986**, *108*, 6477.

17. Zhang, B. L. *Magn. Reson. Chem*. **1988**, *26*, 955.

18. For more details and other types of KIE analysis, see: Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980, pp 95-102.

19. Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980, pp 319-322.

20. (a). Herges, R. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 255. (b). Herges, R. *J. Chem. Comput. Sci.* **1994**, *34*, 91.

21. Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325.

22. Birney, D. M. *J. Am. Chem. Soc.* **2000**, *122*. 10917.

23. (a). Herges, R.; Papafilippopoulos, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4671. (b). Herges, R.; Geuenich, D. *J. Phys. Chem. A* **2001,** *105*, 3214.(c). Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 13463.

24. Cárdenas, C.; Chamorro, E.; Notario, R. *J. Phys. Chem. A* **2005**, *109*, 4352.

25. (a). Deubel, D. V.; Sundermeyer, J.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 10101. (b). Deubel, D. V. *J. Phys. Chem. A* **2001,** *105*, 4765. (c). Kimball, D. B.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 1572. (d). Shirtcliff, L. D.; Weakley, T. J. R.; Haley, M. M. *J. Org. Chem.* **2004**, *69*, 6979.

26. (a). Berger, C.; Bresler, C.; Dilger, U.; Geuenich, D.; Herges, R.; Röttele, H.; Schröder, G. *Angew. Chem., Int. Ed.* **1998,** *37*, 1850. (b). Berger, C.; Dieterich, S.; Dilger, U.; Geuenich, D.; Helios, H.; Herges, R.; Kirchmer, P.; Röttele, H.;

Schröder, G. *Angew. Chem., Int. Ed.* **1998,** *37*, 1854. (c). Herges, R.; Geuenich, D.; Bucher, G.; Tönshoff, C. *Chem. Eur. J.* **2000**, *6*, 1224.

27. Freccero, M.; Gandolfi, R.; Sarzi-Amadè.; Rastelli, A. *J. Org. Chem.* **2004**, *69*, 7479.

28. MacAlpine, G. A.; Warkentin, *J. Can. J. Chem*. **1978**, *56*, 308.

29. (a). Gil, S.; Lázaro, M. A.; Mestres, R.; Millan, F.; Parra, M. *Syn. Commun*. **1995**, *25*, 351. (b). Fehr, C.; Ohloff G. *Helv. Chim. Acta* **1979**, *62*, 2655. (c). Boar. R. B.; Jones, S.; Patel, A. C. *J. Chem. Soc. Perkin I* **1982**, 513.

30. Paine, A. J.; Warkentin, J. *J. Can. J. Chem*. **1979**, *57*, 2681.

31. This methyl group was chosen because its signal was at the upfield end of the spectrum, well separated from the remaining carbons.

32. Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.

33. For the fragmentation of cyclopropyl carbene to afford ethylene plus acetylene, B3LYP calculations again appear to underpredict the barrier. The predicted B3LYP/6-31+G(d,p) (+ zpe) barrier in this case is 12.6 kcal/mol, while the CCSD(T)/6-311+G(d,p)//B3LYP/6-31+G(d,p) barrier is 17.5 kcal/mol.

34. Jackson, J. E.; Mock, G. B.; Tetef, M. L.; Zheng, G. X.; Jones, Jr., M. *Tetrahedron* **1985**, *41*, 1453.

35. (a). Fujisawa, T.; Sugimoto, K.; Ohta, H. *Chem. Lett*. **1974**, *8*, 883. (b). Gladysz, J. A.; Fulcher, J. G.; Togashi, S. *J. Org. Chem.* **1976**, *41*, 3647. (c). Alper, H.; Des Roches, D. *Tetrahedron Lett.* **1977**, *48*, 4155. (d). Matsubara, S.; Nonaka, T.; Okuta, Y.; Kanemoto, S.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jap*. **1985**, *58*, 1480. (e). Moloy, K. G. *Inorg. Chem*. **1988**, *27*, 677.

36. Guruduff, K. N.; Ravindranath, B. *Tetrahedron Lett.* **1980**, *51*, 1173.

37. (a). Whinnery, L. L., Jr.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**,*113*, 7575. (b). Rosenblum, M.; Saidi, M. R.; Madhavarao, M. *Tetrahedron Lett.* **1975**, *46*, 4009.

38. (a). Sharpless, K. B.; Teranichi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b). Bäckvall, J. E.; Böckman, F.; Blomberg, M. R. A. *J. Am. Chem. Soc.* **1992**,*114*, 534.

39. (a). RajanBabu, T. V.; Nugent, W. A.; Beattie, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 6408 (b). Mahesh, M.; Murphy, J. A.; Wessel, H. P. *J. Org. Chem.* **2005**, *70*, 4118.

40. Yamada, K.; Goto, S.; Nagase, H.; Kyotani, Y.; Hirata, Y. *J. Org. Chem.* **1978**, *43*, 2076.

41. Arterbum, J. B.; Liu, M.; Perry, M. C. *Helv. Chim. Acta* **2002**, *85*, 3225.

42. Tabushi, I.; Kuroda, Y. *Tetrahedron* **1976**, *32*, 977.

43. (a). Wittig, G.; Schlosser, M. *Tetrahedron* **1962**, *18*, 1023. (b). Mannfov, G. G.; Berdnikov, E. A.; Samuilov, Y. D. *Russ. J. Org. Chem.* **2001**, *37*, 339.

44. Shields, C. J.; Schuster, G. B. *Tetrahedron Lett.* **1987**, *28*, 853.

45. Su, M. D.; Chu, S. Y. *Chem. Eur. J*. **2000**, *6*, 3777.

46. Su, M. D. *J. Phys. Chem. A* **2002**, *106*, 9563.

47. Hata, Y.; Watanabe, M. *Tetrahedron Lett*. **1972**, *13*, 3827.

48. (a). More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274. (b). Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705.

49. . (a). Curci, R.; Detomaso, A.; Prencipe, T.; Carpenter, G. B. *J. Am. Chem. Soc*. **1994**, *116*, 8112. (b). Yan, D.; Wong, M. K.; Yip, Y. C.; Wang, X. C.; Tang, M. W.; Zheng, J. H.; Cheung, K. K. *J. Am. Chem. Soc*. **1998**, *120*, 5943.

50. Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc*. **1997**, *119*, 10147.

51. Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estévez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem. A* **1997**, *101*, 6092.

52. Bravo, A.; Fontana, F.; Fronza, G.; Minichi, F.; Zhao, L. *J. Org. Chem.* **1998**, *63*, 254.

53. Liu, J.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 8565.

54. (a) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (b) Denmark, S. E.; Wu, Z. *Synlett* **1999**, 847. (c) Bonini,

C.; Righi, G. *Tetrahedron* **2002**, *58*, 4981. (d) Yang, D. *Accounts Chem. Res.* **2004**, *37*, 497.

55. Shi, Y. *Accounts Chem. Res.* **2004**, *37*, 488.

56. (a) Tu, Y.; Wang, Z. -X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806. (b) Wang, Z. –X.; Tu, Y.; Frohn, M.; Zhang, J. –R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

57. Tian, H.; She, Z.; Shu, L.; Yu, H.; Shi, Y. *J. Am. Chem. Soc.* **2000**, *122*, 11551.

58. Tian, H.; She, Z.; Xu, J.; Shi, Y. *Org. Lett.* **2001**, *3*, 1929.

59. (a) Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estevez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem. A* **1997**, *101*, 6092. (b) Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 10147. (c) Crehuet, R.; Anglada, J. M.; Cremer, D.; Bofill, J. M. *J. Phys. Chem. A* **2002**, *106*, 3917. (d) Bach, R. D.; Dmitrenko, O.; Adam, W.; Schambony, S. *J. Am. Chem. Soc.* **2003**, *125*, 924.

60. Dmitrenko, O.; Bach, R. D. *J. Phys. Chem. A* **2004**, *108*, 6886.

61. For a study of epoxidations with fluorinated dioxiranes, see: Armstrong, A.; Washington, I.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 6297.

62. (a) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311. (b) Yang, D.; Wang, X. –C.; Wong, M. –K.; Yip, Y. –C.; Tang, M. –W. *J. Am. Chem. Soc.* **1996**, *118*, 11311.

63. (a) Okovytyy, S.; Gorb, L.; Leszczynski, J. *Tetrahedron Lett.* **2002**, *43*, 4215. (b) For a strong countering study, see: Bach, R. D.; Dmitrenko, O. *J. Phys. Chem. A* **2003**, *107*, 4300.

64. The *meta* carbon of **27** is more separate from other peaks in the ^{13}C NMR than the *para* carbon, and its use as standard gives lower variance in the isotope effects than when the *para* carbon is used as standard. Both *meta* and *para* carbons are calculationally predicted to exhibit a ^{13}C KIE of unity, and each exhibit ^{13}C KIEs within experimental error of unity relative to the other.

65. Of course, the observed ee depends equally on the facility of formation of the minor enantiomer, but this is less obviously affected by the substitution patterns in **53-55**.

66. (a). Yarkony, D. R. *Acc. Chem. Res.* **1998**, *31*, 511. (b). Klessinger, M. *Pure Appl. Chem.* **1997**, *69*, 773. (c). Bernardi F.; Olivucci M.; Robb, M. A. *Chem. Soc. Rev*. **1996**, 321. (d). Robb, M. A.; Bernardi F.; Olivucci M. *Pure Appl. Chem.* **1995**, *67*, 783.

67. (a). Truhlar, D G.; Garrett, B. C. *Annu. Rev. Phys. Chem*. **1984**, *35*, 159. (b). Pechukas, P. *Annu. Rev. Phys. Chem*. **1981**, *32*, 159. (c). Truhlar, D G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440. (d). Miller, W. H. *J. Chem. Phys.* **1976**, *65*, 2216.

68. (a). Carpenter, B. K. *Angew. Chem. Int. Ed.* **1998**, *37*, 3340. (b) Carpenter, B. K. *Acc. Chem. Res.* **1992**, *25*, 520.

69. (a). Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336. (b). Reyes, M. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **2000**, *122*, 10163. (c). Reyes, M. B.;

Lobkovsky, E. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **2002**, *124*, 641. (d). Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118,* 10329. (e). Debbert, S. L.; Carpenter, B. K.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 7896.

70. (a). Doubleday, C. Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 5251. (b). Doubleday, C.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M. *J. Am. Chem. Soc.* **1999**, *121*, 4720. (c). Doubleday, C. *J. Chem. Phys*. **2001**, *105*, 6333. (d). Doubleday, C. Jr.; Bolton, K.; Hase, W. L. *J. Chem. Phys*. *A* **1998**, *102*, 3648. (e). Doubleday, C.; Li, G.; Hase, W. L. *Phys. Chem. Chem. Phys*. **2002**, *4*, 304.

71. Jarz, A. A.; Gajewski, J.; Davidson, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 6928.

72. Kless, A.; Nendel, M.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4524.

73. (a). Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E. *J. Am. Chem. Soc.* **2003**, *125*, 1176. (b). Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 9216. (c). Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319. (d). Ussing, B. R.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 2888.

74. Metiu, H.; Ross, J.; Silbey, R.; George, T. F. *J. Chem. Phys*. **1974**, *61*, 3200

75. For some recent examples of applications of Diels-Alder reaction in total synthesis, see: (a). Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005** *44*, 4442. (b). Nicolaou, K. C.; Safina, B. S.; Zak, M.; Lee, S. H.;

Nevalainen, M.; Bella, M.; Estrada, A. A.; Funke, C.; Zecri, F. J.; Bulat, S. *J. Am. Chem. Soc.* **2005**, *127*, 11159. (c). Hamasaki, A.; Zimpleman, J. M.; Hwang, I.; Boger, D. L. *J. Am. Chem. Soc.* **2005**, *127*, 10767. (d). Hong, R.; Chen, Y.; Deng, L. *Angew. Chem., Int. Ed.* **2005** *44*, 3478. (e). Padwa, A.; Ginn, J. D. *J. Org. Chem.* **2005**, *70*, 5197. (f). Sammakia, T.; Johns, D. M.; Kim, G.; Berliner, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 6504. (g). Nattrass, G. L.; Diez, E.; McLachlan, M. M.; Dixon, D. J.; Ley, S. V. *Angew. Chem., Int. Ed.* **2005** *44*, 580. (h). Gao, X.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 1628.

76. Ibrahim, N.; Eggimann, T.; Dixon, E. A.; Wieser, H. *Tetrahedron*, **1990**, *46*, 1603.

77. Toma, L.; Romano, S.; Quadrelli, P.; Caramella, P. *Tetrahedron Lett.* **2001**, *42*, 5077.

78. (a). Yamataka, H.; Aida, M.; Dupuis, M. *Chem. Phys. Lett*. **1999**, *300*, 583. (b). Bakken, V.; Danovich, D.; Shaik, S.; Schlegel, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 130. (c). Yanai, T.; Taketsugu, T.; Hirao, K. *J. Chem. Phys*. **1997**, *107*, 1137.

79. Meyer, M. P.; DelMonte, A. J.; Singleton, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 10865.

80. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.;

Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

81. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2003.

82. (a). Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (b). Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37,* 785.

APPENDIX

CALCULATIONAL STRUCTURES AND ENERGIES

Terms:

B3: Becke 3-parameter exchange model
RB: Restricted Becke
HF: Hartree-Fock
LYP: Lee-Yang-Parr gradient-corrected functionals
mPW1K: modified Perdew-Wang 1-parameter model for kinetics
RmPW: Restricted modified Perdew-Wang model
PW91: Perdew-Wang 1991 gradient-corrected functionals
MP2: Möller-Plesset second-order perturbation
RHF: Restricted Hartree-Fock

HN=C=O

B3LYP/6-31G*
E(RB+HF-LYP) = -168.677509863

Zero-point correction= 0.021292 (Hartree/Particle)
Thermal correction to Energy= 0.024548
Thermal correction to Enthalpy= 0.025493
Thermal correction to Gibbs Free Energy= -0.001627
Sum of electronic and zero-point Energies= -168.656217
Sum of electronic and thermal Energies= -168.652961
Sum of electronic and thermal Enthalpies= -168.652017
Sum of electronic and thermal Free Energies= -168.679137

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	15.404	8.864	57.078

O,0,0.9780834162,0.4888365542,0.5359351196
C,0,0.0363674869,-0.0027937876,0.0353549526
N,0,-0.9420835709,-0.3802117309,-0.5859671133
H,0,-1.4482872544,-1.2324475919,-0.3978408793

mPW1K/6-31G*

E(RmPW+HF-PW91) = -168.613933554

Zero-point correction= 0.021960 (Hartree/Particle)
Thermal correction to Energy= 0.025198
Thermal correction to Enthalpy= 0.026142
Thermal correction to Gibbs Free Energy= -0.000887
Sum of electronic and zero-point Energies= -168.591973
Sum of electronic and thermal Energies= -168.588736
Sum of electronic and thermal Enthalpies= -168.587792
Sum of electronic and thermal Free Energies= -168.614820

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	15.812	8.795	56.887

O,0,0.9685220358,0.4884830058,0.5270704241
C,0,0.0372377087,0.0027748025,0.0322569898
N,0,-0.931377396,-0.3858306946,-0.5717167144
H,0,-1.4519607664,-1.2236979994,-0.4080883306

B3LYP/6-31+G**
E(RB+HF-LYP) = -168.691277783

Zero-point correction= 0.021194 (Hartree/Particle)
Thermal correction to Energy= 0.024462
Thermal correction to Enthalpy= 0.025406
Thermal correction to Gibbs Free Energy= -0.001711
Sum of electronic and zero-point Energies= -168.670084
Sum of electronic and thermal Energies= -168.666816
Sum of electronic and thermal Enthalpies= -168.665872
Sum of electronic and thermal Free Energies= -168.692988

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	15.350	8.936	57.072

O,0,0.9784866175,0.4934970962,0.5325546707
C,0,0.036652203,-0.0025613361,0.035727573
N,0,-0.9413068648,-0.3856501816,-0.5811015929
H,0,-1.4586581042,-1.233057481,-0.4070916532

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -168.620197115

Zero-point correction= 0.021994 (Hartree/Particle)
Thermal correction to Energy= 0.025235
Thermal correction to Enthalpy= 0.026179
Thermal correction to Gibbs Free Energy= -0.000857
Sum of electronic and zero-point Energies= -168.598203
Sum of electronic and thermal Energies= -168.594962
Sum of electronic and thermal Enthalpies= -168.594018
Sum of electronic and thermal Free Energies= -168.621054

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	15.835	8.807	56.902

O,0,0.968320719,0.4872418636,0.5278460824
C,0,0.0370041647,0.0030620124,0.0318179864
N,0,-0.9313974763,-0.3847971856,-0.5725405418
H,0,-1.4488084068,-1.2227266842,-0.4058927844

N_2

B3LYP/6-31G*
E(RB+HF-LYP) = -109.524125196

Zero-point correction= 0.005599 (Hartree/Particle)
Thermal correction to Energy= 0.007960
Thermal correction to Enthalpy= 0.008904
Thermal correction to Gibbs Free Energy= -0.012851
Sum of electronic and zero-point Energies= -109.518530
Sum of electronic and thermal Energies= -109.516170
Sum of electronic and thermal Enthalpies= -109.515225
Sum of electronic and thermal Free Energies= -109.536980

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	4.995	4.970	45.786

N,0,0.2884086738,-0.4410356919,-0.1668572068
N,0,-0.2884086738,0.4410356919,0.1668572068

mPW1K/6-31G*
E(RmPW+HF-PW91) = -109.478692485

Zero-point correction= 0.005886 (Hartree/Particle)
Thermal correction to Energy= 0.008247
Thermal correction to Enthalpy= 0.009191
Thermal correction to Gibbs Free Energy= -0.012541
Sum of electronic and zero-point Energies= -109.472806
Sum of electronic and thermal Energies= -109.470445
Sum of electronic and thermal Enthalpies= -109.469501
Sum of electronic and thermal Free Energies= -109.491234

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	5.175	4.969	45.740

N,0,0.2788177839,0.445524735,-0.1493046612
N,0,-0.2788177839,-0.445524735,0.1493046612

B3LYP/6-31+G**
E(RB+HF-LYP) = -109.529779364

Zero-point correction= 0.005592 (Hartree/Particle)
Thermal correction to Energy= 0.007952
Thermal correction to Enthalpy= 0.008896
Thermal correction to Gibbs Free Energy= -0.012858
Sum of electronic and zero-point Energies= -109.524188
Sum of electronic and thermal Energies= -109.521827
Sum of electronic and thermal Enthalpies= -109.520883
Sum of electronic and thermal Free Energies= -109.542637

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	4.990	4.970	45.785

N,0,0.2883175468,-0.4408961494,-0.1668040904
N,0,-0.2883175468,0.4408961494,0.1668040904

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -109.479999058

Zero-point correction= 0.005886 (Hartree/Particle)
Thermal correction to Energy= 0.008246
Thermal correction to Enthalpy= 0.009190
Thermal correction to Gibbs Free Energy= -0.012542
Sum of electronic and zero-point Energies= -109.474113
Sum of electronic and thermal Energies= -109.471753

Sum of electronic and thermal Enthalpies= -109.470809
Sum of electronic and thermal Free Energies= -109.492541

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	5.175	4.969	45.740

N,0,0.2850920806,-0.4359637559,-0.1649380196
N,0,-0.2850920806,0.4359637559,0.1649380196

Iminooxadiazoline oxirane 4

B3LYP/6-31G*
E(RB+HF-LYP) = -626.094322624

Zero-point correction= 0.194236 (Hartree/Particle)
Thermal correction to Energy= 0.205143
Thermal correction to Enthalpy= 0.206087
Thermal correction to Gibbs Free Energy= 0.157689
Sum of electronic and zero-point Energies= -625.900087
Sum of electronic and thermal Energies= -625.889180
Sum of electronic and thermal Enthalpies= -625.888235
Sum of electronic and thermal Free Energies= -625.936633

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	128.729	43.142	101.862

C,0,-2.2026532843,-0.1645723845,-1.4319531441
C,0,-2.0433888879,-0.3946051645,0.0698771057
C,0,-0.7305753666,-0.1983974616,0.7209914886
C,0,0.4981033643,0.1838342353,-0.085476159
C,0,0.137646016,0.8642464091,-1.4074396192
C,0,-0.8748422515,0.0160071437,-2.189119801
O,0,1.3596502506,1.0158239488,0.7051757789
C,0,2.5239036688,0.3302217604,0.893032801
N,0,2.4202330304,-0.9492498565,0.2143852731
N,0,1.3048671274,-1.040914711,-0.3319634503
N,0,3.556684036,0.6770197107,1.528084384
O,0,-1.7339162736,0.811663494,0.8147145095
C,0,-3.0720687097,-1.284745049,0.7315323055
H,0,-0.5070577556,-0.7192845172,1.6541121781
H,0,-4.0833688177,-0.9129710047,0.5283199565

H,0,-2.9275912239,-1.3065567546,1.8155145117
H,0,-3.0041230561,-2.3084456761,0.3459929833
H,0,1.055911302,1.0157242406,-1.9850390462
H,0,-0.2765398635,1.8482316356,-1.1645868053
H,0,-1.0657444363,0.4797748838,-3.1633056336
H,0,-0.4297376827,-0.9656054682,-2.3876906441
H,0,-2.7582328665,-1.0035672527,-1.8668665492
H,0,-2.8351521156,0.7246301293,-1.5515527791
H,0,3.4365280484,1.6082473057,1.9337662082

mPW1K/6-31G*
E(RmPW+HF-PW91) = -625.921783278

Zero-point correction= 0.201226 (Hartree/Particle)
Thermal correction to Energy= 0.211765
Thermal correction to Enthalpy= 0.212709
Thermal correction to Gibbs Free Energy= 0.164963
Sum of electronic and zero-point Energies= -625.720557
Sum of electronic and thermal Energies= -625.710019
Sum of electronic and thermal Enthalpies= -625.709074
Sum of electronic and thermal Free Energies= -625.756820

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	132.884	41.373	100.490

C,0,-2.1798519812,-0.1580531934,-1.4157602864
C,0,-2.0224909572,-0.3869708948,0.0713429278
C,0,-0.7216763411,-0.2003221709,0.7172117799
C,0,0.4956638453,0.1812999024,-0.0818143583
C,0,0.1359172358,0.855133224,-1.3900161867
C,0,-0.8637957132,0.0120250185,-2.1639022108
O,0,1.3462296073,0.9993785701,0.6958507505
C,0,2.4955849717,0.3283987264,0.8791517561
N,0,2.3927287964,-0.9355974032,0.2070346137
N,0,1.2893885669,-1.0234892293,-0.3262041199
N,0,3.5173934922,0.676076689,1.5072710815
O,0,-1.7097593503,0.7927176288,0.8065011405
C,0,-3.0431885475,-1.2709343871,0.7229049686
H,0,-0.5031802721,-0.7196816889,1.6447156944
H,0,-4.0474150329,-0.9012800596,0.5160450646
H,0,-2.9036901267,-1.2926496913,1.8011820756
H,0,-2.9704654906,-2.2875183515,0.33892405
H,0,1.0495377715,1.0082820212,-1.9634715079

H,0,-0.2766757863,1.8335025263,-1.1481538715
H,0,-1.049946757,0.4694803662,-3.1349119276
H,0,-0.4237598783,-0.966274981,-2.357249098
H,0,-2.7376578264,-0.9896001684,-1.8457273255
H,0,-2.8036868559,0.7298084777,-1.5338938944
H,0,3.4016271343,1.5967742121,1.9123042452

B3LYP/6-31+G**
E(RB+HF-LYP) = -626.133702369

Zero-point correction= 0.193107 (Hartree/Particle)
Thermal correction to Energy= 0.204057
Thermal correction to Enthalpy= 0.205001
Thermal correction to Gibbs Free Energy= 0.156525
Sum of electronic and zero-point Energies= -625.940595
Sum of electronic and thermal Energies= -625.929645
Sum of electronic and thermal Enthalpies= -625.928701
Sum of electronic and thermal Free Energies= -625.977177

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	128.048	43.425	102.027

C,0,-2.2074428431,-0.1569660792,-1.4301756936
C,0,-2.0459760621,-0.3957845751,0.0695600368
C,0,-0.7302740288,-0.2039341886,0.7192967681
C,0,0.4981878655,0.1789251934,-0.088848333
C,0,0.1426117973,0.8541142934,-1.4150063293
C,0,-0.8813890425,0.0156170584,-2.1927012566
O,0,1.3592474816,1.0170658571,0.7012804543
C,0,2.5254376581,0.336570159,0.895268638
N,0,2.4251110146,-0.9465375756,0.2218786307
N,0,1.3107156383,-1.0439701831,-0.3245993713
N,0,3.5549191971,0.6918114112,1.5316158294
O,0,-1.7326145454,0.8079197843,0.8212673438
C,0,-3.0742489827,-1.288813882,0.7269074038
H,0,-0.5062069078,-0.7284295546,1.649782487
H,0,-4.0841936432,-0.914239996,0.5252655443
H,0,-2.9291502623,-1.318078782,1.8099206365
H,0,-3.0050471551,-2.3088010065,0.3334619662
H,0,1.0610576057,0.9909619395,-1.9951486893
H,0,-0.2579375815,1.8445797191,-1.1766743849
H,0,-1.0733992945,0.485963895,-3.1629191073
H,0,-0.4467347344,-0.9686491714,-2.3992396968

H,0,-2.7703305266,-0.9904695479,-1.8645084509
H,0,-2.8337534506,0.7371776771,-1.543026347
H,0,3.4359733405,1.6226062532,1.9346306312

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -625.945153322

Zero-point correction= 0.200546 (Hartree/Particle)
Thermal correction to Energy= 0.211105
Thermal correction to Enthalpy= 0.212049
Thermal correction to Gibbs Free Energy= 0.164271
Sum of electronic and zero-point Energies= -625.744608
Sum of electronic and thermal Energies= -625.734049
Sum of electronic and thermal Enthalpies= -625.733104
Sum of electronic and thermal Free Energies= -625.780882

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	132.470	41.518	100.557

C,0,-2.178934828,-0.1602255333,-1.4160947156
C,0,-2.0224688683,-0.3873519164,0.0712547612
C,0,-0.7218126482,-0.2000899981,0.7179225868
C,0,0.495413393,0.1815117791,-0.0816890893
C,0,0.1351894659,0.8566442826,-1.3889412789
C,0,-0.8630155662,0.0126373203,-2.1637240658
O,0,1.3465669126,0.998758106,0.6963901681
C,0,2.4962143892,0.3278601584,0.8790698255
N,0,2.392457234,-0.9362241942,0.2057152159
N,0,1.288814418,-1.0234342383,-0.3269785957
N,0,3.5175899634,0.6755779752,1.5068567095
O,0,-1.7101443377,0.7933210691,0.8050918043
C,0,-3.0439114543,-1.269671656,0.7235992177
H,0,-0.502616767,-0.7202470128,1.6446363869
H,0,-4.0465343954,-0.8989813972,0.5153944129
H,0,-2.9041365364,-1.2884502926,1.8010089201
H,0,-2.9712132552,-2.2859368876,0.3411190971
H,0,1.0484668946,1.0119984757,-1.9610479102
H,0,-0.2795912454,1.832672683,-1.1436117729
H,0,-1.0493189299,0.4698144061,-3.1339603031
H,0,-0.4211592235,-0.9643335842,-2.3565750509
H,0,-2.7341511465,-0.9933328474,-1.8445172284
H,0,-2.8046774501,0.7256653465,-1.5335524672
H,0,3.4014768497,1.5951742903,1.9117133805

Alternative structure A of Iminooxadiazoline oxirane (with methyl group on imine)

B3LYP/6-31G*

E(RB+HF-LYP) = -665.404972724
Zero-point correction= 0.221898 (Hartree/Particle)
Thermal correction to Energy= 0.234647
Thermal correction to Enthalpy= 0.235591
Thermal correction to Gibbs Free Energy= 0.182576
Sum of electronic and zero-point Energies= -665.183075
Sum of electronic and thermal Energies= -665.170326
Sum of electronic and thermal Enthalpies= -665.169381
Sum of electronic and thermal Free Energies= -665.222396

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.243	48.750	111.579

C,3.5673822404,-1.7025080962,0.6532676923
C,2.1455372404,0.157286903 8,0.8172796923
N,0.6335452404,1.7642339038,0.8005376923
N,3.2479982404,-0.3652600962,1.1222926923
N,1.7640292404, 1.4857939038,1.2460436923
C,-1.1545677596,0.0781439038,0.6451166923
C,-3.1719417596,-1.5203030962,0.4303726923
O,1.1240412404,-0.3671250962 0.0638186923
C,-2.2501477596,-0.4846440962,-0.1747333077
C,-0.1409757596,1.0804819038,-.4513343077
C,0.1005822404,0.6364289038,-0.0077763077
C,-0.7897977596,-0.0552630962,-2.2527183077
O,-2.3476997596,0.8271259038,0.4362916923
C,-2.1708907596,-0.4489670962,-1.7000253077
H,3.7420192404,-2.3446600962,1.5249796923
H,4.5117182404,-1.6601000962,0.0980706923
H,2.7996862404,-2.1634700962,0.0199596923
H,-0.9988347596,-0.2872820962,1.6623096923
H,-4.1838787596,-1.4140120962,0.0214046923
H,-3.2288987596,-1.4035020962,1.5164516923
H,-2.8206297596,0.5333850962,0.2026146923
H,0.8199052404,1.3748809038,-1.8870203077
H,-0.7853987596,1.9650579038,-1.4258963077
H,-0.8838167596,0.2409189038,-3.3034873077
H,-0.1211797596,-0.9242750962,-2.2286833077

H,-2.4572157596,-1.4294580962,-2.0984983077
H,-2.9342977596,0.2619699038,-2.0419023077

Alternative structure B of Iminooxadiazoline oxirane (with methyl group on imine)

B3LYP/6-31G*
E(RB+HF-LYP) = -665.405558882

Zero-point correction= 0.221869 (Hartree/Particle)
Thermal correction to Energy= 0.234672
Thermal correction to Enthalpy= 0.235617
Thermal correction to Gibbs Free Energy= 0.182364
Sum of electronic and zero-point Energies= -665.183690
Sum of electronic and thermal Energies= -665.170886
Sum of electronic and thermal Enthalpies= -665.169942
Sum of electronic and thermal Free Energies= -665.223194

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.259	48.789	112.079

C,3.3129314808,1.7996617308,2.0123448558
C,2.2469404808,0.1617277308,0.7159238558
N,1.0255414808,1.2051582692,0.5097611442
N,3.2756114808,0.5046337308,1.3538568558
N,2.1411364808,-1.1130682692,0.0382428558
C,-1.0076385192,-0.3593762692,0.5446258558
C,-3.3485115192,-1.4489252692,0.5591988558
O,1.0806694808,0.8554907308,0.5237998558
C,-2.3212125192,-0.5579992692,-0.1038041442
C,-0.1438785192,0.7007167308,0.5855391442
C,0.2206954808,0.0228357308,-0.2631671442
C,-1.1565795192,-0.1484452692,-2.3650721442
O,-2.0130375192,0.6491907308,0.6391908558
C,-2.4831665192,-0.3300052692,-1.6058991442
H,4.1507874808,2.3753507308,1.6011558558
H,3.5279654808,1.6426657308,3.0758688558
H,2.3933084808,2.3891697308,1.9163978558
H,-0.7828575192,-0.8794732692,1.4780298558
H,-4.3604175192,-1.0784452692,0.3560528558
H,-3.2035875192,-1.4698182692,1.6431958558
H,-3.2797725192,-.4729382692,0.1744718558
H,0.7734164808,0.8515117308,-2.1650841442

H,-0.5575255192,1.6854627308,-1.3442291442
H,-1.3496835192,0.3146977308,-3.3392021442
H,-0.7107555192,-1.1297372692,-2.5636711442
H,-3.0384875192,-1.1702722692,-2.0390691442
H,-3.1169545192,0.5583807308,-1.7258831442

Alternative structure C of Iminooxadiazoline oxirane (with methyl group on imine)

B3LYP/6-31G*
E(RB+HF-LYP) = -665.403876161

Zero-point correction= 0.221625 (Hartree/Particle)
Thermal correction to Energy= 0.234420
Thermal correction to Enthalpy= 0.235364
Thermal correction to Gibbs Free Energy= 0.182106
Sum of electronic and zero-point Energies= -665.182251
Sum of electronic and thermal Energies= -665.169456
Sum of electronic and thermal Enthalpies= -665.168512
Sum of electronic and thermal Free Energies= -665.221770

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	147.101	48.861	112.092

C,3.3307831538,-2.5826944327,0.280720875
C,2.2947381538,-0.4785264327,0.352262875
N,1.0871391538,1.3680435673,0.324487875
N,3.3260011538,-1.1610364327,0.579533875
N,2.2175311538,0.9400925673,0.625417875
C,-0.9391218462,0.0275595673,0.730768875
C,-3.4314718462,-0.6166184327,0.998475875
O,1.0929721538,-0.8858364327,-0.174165125
C,-2.3453518462,0.1653705673,0.294580875
C,-0.1697098462,0.5669565673,-1.664092125
C,0.2399491538,0.2643365673,-0.215303125
C,-1.4648078462,1.3820045673,-1.751657125
O,-1.7022058462,1.1763465673,1.101286875
C,-2.6368788462,0.6122925673,-1.128774125
H,3.5885621538,-3.1296894327,1.195209875
H,4.1287171538,-2.7837684327,-0.444081125
H,2.3845621538,-2.9721364327,-0.114317125
H,-0.6931498462,-0.6471674327,1.552757875
H,-4.3547208462,-0.0271664327,1.045798875

H,-3.1326228462,-0.8647564327,2.021080875
H,-3.6518708462,-1.5470394327,0.462243875
H,-0.3057838462,-0.4022734327,0.159397125
H,0.6591811538,1.0774795673,-2.166708125
H,-1.6835728462,1.6010505673,-2.802548125
H,-1.3377698462,2.3407325673,-1.238762125
H,-2.8687798462,-0.2763934327,-1.733102125
H,-3.5423528462,1.2332625673,-1.123124125

First Transition structure (5)

B3LYP/6-31G*
E(RB+HF-LYP) = -626.035765075

Zero-point correction= 0.190091 (Hartree/Particle)
Thermal correction to Energy= 0.201948
Thermal correction to Enthalpy= 0.202893
Thermal correction to Gibbs Free Energy= 0.151791
Sum of electronic and zero-point Energies= -625.845674
Sum of electronic and thermal Energies= -625.833817
Sum of electronic and thermal Enthalpies= -625.832873
Sum of electronic and thermal Free Energies= -625.883974

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	126.725	44.870	107.553

N,0,1.4305985721,-0.777053454,-0.1205443126
C,0,0.3360160937,-0.0724070911,-0.2602260008
O,0,1.6429380517,1.4331241944,1.028218644
C,0,2.6784580835,0.7807340292,1.1630779159
N,0,2.5189193909,-0.7523146457,0.3673581412
C,0,0.0535390876,0.6524438952,-1.5440622429
C,0,-1.0297451779,-0.1104618393,-2.3357214635
C,0,-2.3441651749,-0.2768646754,-1.5479577395
C,0,-2.1764246073,-0.5409861439,-0.0507836274
C,0,-0.8304756678,-0.4199486198,0.5878001745
O,0,-1.7923743148,0.6295301412,0.6965045523
C,0,-3.2303717738,-1.3963842768,0.6153683318
N,0,3.8560854829,0.7670446216,1.6585575587
H,0,-0.6111282021,-0.9636858115,1.5059857477
H,0,-4.226419269,-0.9720434878,0.4409720542
H,0,-3.0658323636,-1.4455936245,1.6955003069

H,0,-3.2201504091,-2.4139233392,0.2087936037
H,0,0.9721405076,0.7666934937,-2.1246767784
H,0,-0.2995671962,1.6503562702,-1.2599422164
H,0,-1.2276451256,0.4122942161,-3.277942583
H,0,-0.6307554523,-1.0975115523,-2.6013705328
H,0,-2.930046994,-1.0894169722,-1.9926776443
H,0,-2.9537486557,0.6318178326,-1.6351305554
H,0,4.0084339648,1.6592909676,2.1401312274

mPW1K/6-31G*
E(RmPW+HF-PW91) = -625.846411684

Zero-point correction= 0.196772 (Hartree/Particle)
Thermal correction to Energy= 0.208229
Thermal correction to Enthalpy= 0.209173
Thermal correction to Gibbs Free Energy= 0.158816
Sum of electronic and zero-point Energies= -625.649640
Sum of electronic and thermal Energies= -625.638182
Sum of electronic and thermal Enthalpies= -625.637238
Sum of electronic and thermal Free Energies= -625.687596

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	130.666	43.275	105.987

N,0,-1.5172177315,-0.3151075821,0.2762917242
C,0,-0.365741837,0.1813242279,0.0102443754
O,0,-0.9775392647,-1.1312463217,-1.980487653
C,0,-2.064399151,-1.5404674772,-1.608889054
N,0,-2.4212895489,-0.9801033619,-0.0823331202
C,0,-0.2241200445,1.5779497756,-0.4809366695
C,0,0.386423121,2.4311290141,0.6291614843
C,0,1.7477748141,1.9200011896,1.090283666
C,0,1.8844981223,0.4125033388,1.1509101424
C,0,0.8282257361,-0.458317987,0.5917315368
O,0,2.0074797732,-0.1941371773,-0.1220402696
C,0,2.7968993115,-0.1397606975,2.2037031161
N,0,-3.0628916203,-2.247591955,-1.94637158
H,0,0.7048304357,-1.4719301199,0.9513260648
H,0,3.7859273395,0.3091188688,2.1127126612
H,0,2.9021112859,-1.2167579887,2.0978458829
H,0,2.4146049023,0.0811417657,3.1990386044
H,0,-1.186860778,1.9630265852,-0.8046210594
H,0,0.4334027969,1.5295967752,-1.3492818392

H,0,0.4783272947,3.4598075665,0.2834150065
H,0,-0.3061859433,2.4463156401,1.472030465
H,0,1.9744168602,2.3368228317,2.0709621799
H,0,2.5300088399,2.2707632283,0.4149622608
H,0,-2.897675232,-2.611385173,-2.8785275994

B3LYP/6-31+G**
E(RB+HF-LYP) = -626.078064245

Zero-point correction= 0.189050 (Hartree/Particle)
Thermal correction to Energy= 0.200905
Thermal correction to Enthalpy= 0.201850
Thermal correction to Gibbs Free Energy= 0.150799
Sum of electronic and zero-point Energies= -625.889015
Sum of electronic and thermal Energies= -625.877159
Sum of electronic and thermal Enthalpies= -625.876215
Sum of electronic and thermal Free Energies= -625.927266

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	126.070	45.069	107.446

N,0,1.4257859175,-0.7648010217,-0.1012288513
C,0,0.3260698666,-0.0741304071,-0.2586866796
O,0,1.6758432857,1.4531976199,1.0285050033
C,0,2.6988795783,0.7739474291,1.1562833376
N,0,2.5166151907,-0.7317773645,0.3845297578
C,0,0.0519189072,0.6439209863,-1.5476728865
C,0,-1.0363958773,-0.1144497824,-2.3380706989
C,0,-2.3515444181,-0.276643803,-1.5509165895
C,0,-2.1875272861,-0.5458729183,-0.0547194053
C,0,-0.8418183726,-0.4236052515,0.5886039958
O,0,-1.8078419248,0.6236563072,0.6982469902
C,0,-3.2393046881,-1.4087283659,0.6042252719
N,0,3.878654998,0.7637158235,1.6549779992
H,0,-0.623155419,-0.9673171835,1.5064124881
H,0,-4.2354701808,-0.988684744,0.4240450946
H,0,-3.0804993577,-1.4599207845,1.6843531184
H,0,-3.2192581053,-2.4239857944,0.1939828199
H,0,0.9723056165,0.7470075302,-2.1262206491
H,0,-0.2929027125,1.6465145613,-1.2696731756
H,0,-1.2315248253,0.4121934527,-3.2780368852
H,0,-0.642367312,-1.102190589,-2.6066239929
H,0,-2.9392024649,-1.0867300969,-1.9960093517

H,0,-2.9579829619,0.6339991217,-1.6356592837
H,0,4.0369878325,1.6576937249,2.1271834563

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -625.870002715

Zero-point correction= 0.196081 (Hartree/Particle)
Thermal correction to Energy= 0.207565
Thermal correction to Enthalpy= 0.208509
Thermal correction to Gibbs Free Energy= 0.158111
Sum of electronic and zero-point Energies= -625.673921
Sum of electronic and thermal Energies= -625.662438
Sum of electronic and thermal Enthalpies= -625.661493
Sum of electronic and thermal Free Energies= -625.711892

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	130.249	43.431	106.073

N,0,1.4061968811,-0.7083676281,-0.0820853932
C,0,0.3046808061,-0.0763034288,-0.2622753364
O,0,1.7042346736,1.4575038506,1.0443789557
C,0,2.7014089748,0.7639892544,1.1512914811
N,0,2.489353066,-0.7012008365,0.3818245043
C,0,0.0306562201,0.6465361139,-1.5321640956
C,0,-1.0295757695,-0.1224921423,-2.3180994335
C,0,-2.3334254443,-0.2949064464,-1.5452144975
C,0,-2.175965219,-0.5474551869,-0.0599984902
C,0,-0.8510551733,-0.4207817692,0.5853658897
O,0,-1.8047116851,0.6058677112,0.6717270706
C,0,-3.221551712,-1.3990732664,0.5934021158
N,0,3.8746720454,0.7232457557,1.6314978531
H,0,-0.6333822287,-0.9520840457,1.5028403417
H,0,-4.2108672145,-0.9877417213,0.398074018
H,0,-3.0737801149,-1.4321831419,1.6692158116
H,0,-3.1916344982,-2.4133062007,0.2006032339
H,0,0.9473476684,0.769486193,-2.1004031966
H,0,-0.3295430701,1.6339232217,-1.244013142
H,0,-1.2247919098,0.3917453002,-3.2572669692
H,0,-0.6230561482,-1.1006365838,-2.5769932057
H,0,-2.9061137495,-1.1102829997,-1.9839105452
H,0,-2.9474109056,0.601967725,-1.6368049398
H,0,4.0544582175,1.5993199502,2.1073058325

Alternative structure A of First Transition structure (with methyl group on imine)

B3LYP/6-31G*
E(RB+HF-LYP) = -665.342943246

Zero-point correction= 0.215691 (Hartree/Particle)
Thermal correction to Energy= 0.230193
Thermal correction to Enthalpy= 0.231137
Thermal correction to Gibbs Free Energy= 0.173362
Sum of electronic and zero-point Energies= -665.127252
Sum of electronic and thermal Energies= -665.112750
Sum of electronic and thermal Enthalpies= -665.111806
Sum of electronic and thermal Free Energies= -665.169581

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	144.448	52.625	121.597

C,0,-2.2836919666,-0.4441042007,-1.7530938594
C,0,-2.3280035728,-0.5486048787,-0.2265979408
C,0,-1.1499718654,-0.1238101465,0.5831256589
C,0,0.0885188045,0.3186785737,-0.1186755701
C,0,-0.1069717325,0.8878804625,-1.5039104624
C,0,-0.8901260759,-0.1450035519,-2.3413664288
O,0,1.1647866507,-0.3585649105,0.1467414156
C,0,2.3951494132,0.2369010792,0.9636091165
N,0,1.5012273418,2.0672996641,1.4014440449
N,0,0.4681246705,2.0543050842,0.91649765
N,0,3.4242721822,-0.3818386255,1.1184929544
C,0,3.8756758936,-1.6814678668,0.6749438656
O,0,-2.2913909137,0.7269493815,0.4450472445
C,0,-3.3166269401,-1.5341636556,0.3562526007
H,0,4.1033739729,-2.300976306,1.5482916638
H,0,4.799810532,-1.5656874525,0.0998356526
H,0,3.120811203,-2.1837816911,0.0579164349
H,0,-0.9938899707,-0.5578683853,1.5718338965
H,0,-4.3290023308,-1.3175915825,-0.0066702956
H,0,-3.3263051806,-1.4732547117,1.4484161055
H,0,-3.0656462186,-2.5599601862,0.0621033729
H,0,0.871010828,1.0939528626,-1.9494042535
H,0,-0.6685518639,1.8256422605,-1.4423186638
H,0,-0.9952880488,0.2139727348,-3.371839489
H,0,-0.3044426165,-1.0721549547,-2.3889430259

H,0,-2.6687918005,-1.3738412799,-2.188927337
H,0,-2.9893355113,0.3482751728,-2.0353677689

Alternative structure B of First Transition structure (with methyl group on imine)

B3LYP/6-31G*
E(RB+HF-LYP) = -665.343751231

Zero-point correction= 0.215645 (Hartree/Particle)
Thermal correction to Energy= 0.230087
Thermal correction to Enthalpy= 0.231031
Thermal correction to Gibbs Free Energy= 0.173978
Sum of electronic and zero-point Energies= -665.128106
Sum of electronic and thermal Energies= -665.113664
Sum of electronic and thermal Enthalpies= -665.112720
Sum of electronic and thermal Free Energies= -665.169773

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	144.382	52.674	120.078

C,0,-2.3954044245,-0.0996172962,-1.61770275
C,0,-2.3974684089,-0.4779296261,-0.1336655449
C,0,-1.1648942895,-0.3160444722,0.6694020291
C,0,0.0742271912,0.2008904659,0.0383033452
C,0,-0.0084633998,0.7903781772,-1.3455463632
C,0,-0.9918182948,0.0190874998,-2.237237948
O,0,1.0223418899,0.5804562636,0.842071953
C,0,2.4687363633,0.1269635021,0.7287463806
N,0,2.0437424888,-1.7346791752,-0.2192578996
N,0,0.9383868752,-1.718085426,-0.4883978285
N,0,3.4159111613,0.7790750078,1.1316598767
C,0,3.4523137825,2.1229262814,1.6760635428
O,0,-2.2382858035,0.6528978672,0.7518897852
C,0,-3.4456692407,-1.4750458941,0.3100166732
H,0,4.1516524556,2.7293395076,1.0916279607
H,0,3.8286048402,2.0815086736,2.7033563689
H,0,2.4617100417,2.595444842,1.6699193165
H,0,-1.0154748458,-0.9104715229,1.5705672461
H,0,-4.447670776,-1.1166058522,0.0448231935
H,0,-3.4104997418,-1.620550189,1.3936460047
H,0,-3.2916165748,-2.4430554619,-0.1806133999
H,0,0.9980888243,0.8065782314,-1.7823376291

H,0,-0.3238870268,1.8403521243,-1.246367965
H,0,-1.0617268073,0.5084908142,-3.2154115919
H,0,-0.5892629499,-0.9843392205,-2.4120137851
H,0,-2.9744463053,-0.8403643776,-2.1816227412
H,0,-2.933559175,0.8530147114,-1.7055721124

Alternative structure C of First Transition structure (with methyl group on imine)

B3LYP/6-31G*
E(RB+HF-LYP) = -665.344590800

Zero-point correction= 0.215503 (Hartree/Particle)
Thermal correction to Energy= 0.229911
Thermal correction to Enthalpy= 0.230856
Thermal correction to Gibbs Free Energy= 0.173470
Sum of electronic and zero-point Energies= -665.129088
Sum of electronic and thermal Energies= -665.114679
Sum of electronic and thermal Enthalpies= -665.113735
Sum of electronic and thermal Free Energies= -665.171121

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	144.272	52.664	120.779

C,0,-2.607883764,0.4654142403,-1.2150927232
C,0,-2.4362422615,0.1214733326,0.2582810931
C,0,-1.0562453344,-0.0614073802,0.7826355934
C,0,0.1110615022,-0.0189914597,-0.1450086979
C,0,-0.1021238363,0.3716674143,-1.5916314385
C,0,-1.3836634751,1.1908097499,-1.7941738429
O,0,1.0645036264,-0.86307158,0.128776562
C,0,2.5289547034,-0.4585226157,0.4094699841
N,0,2.1480346745,1.5809888635,0.7489253472
N,0,1.0459262486,1.7539105314,0.5176589654
N,0,3.4547082368,-1.244169143,0.3722138016
C,0,3.5082186773,-2.6449356419,0.0104555291
O,0,-1.7917841055,1.1516786944,1.0242214821
C,0,-3.6015846579,-0.5587872878,0.9410999857
H,0,3.8293312725,-3.2280188468,0.8797388481
H,0,4.2546861842,-2.7863349659,-0.7775480615
H,0,2.5346814105,-3.01442342,-0.3358531091
H,0,-0.8934402025,-0.67841532,1.6666530051
H,0,-4.4960932117,0.0733456377,0.885902687

H,0,-3.3796310267,-0.7437794654,1.9961300559
H,0,-3.8340896829,-1.5151100302,0.4581346427
H,0,-0.1628468244,-0.5625693351,-2.1716673867
H,0,0.7807535749,0.9053740562,-1.9635410489
H,0,-1.5353534318,1.3739468802,-2.8636263688
H,0,-1.2782932081,2.1643771266,-1.3062641254
H,0,-2.8011804205,-0.4629288576,-1.7719504798
H,0,-3.5039140424,1.0902457509,-1.3278927077

First Intermediate –diazoalkane (6)

B3LYP/6-31G*
E(RB+HF-LYP) = -457.403329352

Zero-point correction= 0.165871 (Hartree/Particle)
Thermal correction to Energy= 0.175075
Thermal correction to Enthalpy= 0.176019
Thermal correction to Gibbs Free Energy= 0.131590
Sum of electronic and zero-point Energies= -457.237458
Sum of electronic and thermal Energies= -457.228255
Sum of electronic and thermal Enthalpies= -457.227310
Sum of electronic and thermal Free Energies= -457.271739

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.861	35.108	93.508

C,0,0.0991549163,-0.4848322367,0.7902794023
C,0,0.9621042994,-0.4559594891,-0.4089386944
C,0,0.7876876853,0.6437142775,-1.4340183447
C,0,-0.7126279834,0.8962950669,-1.6518562294
C,0,-1.4438913516,1.2687839477,-0.3493274975
C,0,-1.1261925452,0.3454825146,0.8313682526
N,0,1.927209033,-1.3140371668,-0.5140050227
N,0,2.7646229848,-2.0935596848,-0.6337458685
O,0,0.0490706821,0.7301670573,1.5816560433
C,0,-2.2990342728,-0.0816003041,1.6871704349
H,0,0.136873743,-1.4010838506,1.3808673415
H,0,-2.8185081612,0.798168885,2.0868845243
H,0,-1.9629308004,-0.6906905989,2.5316471092
H,0,-3.0218520149,-0.6613059578,1.1007045873
H,0,1.2689964753,0.3613072518,-2.3766296091
H,0,1.2708343073,1.5694353249,-1.087311047

H,0,-0.8488873451,1.6964601483,-2.3892432906
H,0,-1.1625427481,-0.0106120109,-2.076736374
H,0,-2.5253112701,1.2701962634,-0.5316762933
H,0,-1.1752662549,2.2886633862,-0.0455629999

mPW1K/6-31G*
E(RmPW+HF-PW91) = -457.274114863

Zero-point correction= 0.171118 (Hartree/Particle)
Thermal correction to Energy= 0.180063
Thermal correction to Enthalpy= 0.181007
Thermal correction to Gibbs Free Energy= 0.137028
Sum of electronic and zero-point Energies= -457.102997
Sum of electronic and thermal Energies= -457.094052
Sum of electronic and thermal Enthalpies= -457.093107
Sum of electronic and thermal Free Energies= -457.137087

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	112.991	33.917	92.563

C,0,0.5489174834,0.2911814898,0.6861376883
C,0,0.6381058753,-0.9225992044,-0.1354015612
C,0,-0.1777089154,-1.0438700641,-1.3879161379
C,0,-1.5642287,-0.4714510521,-1.1332075134
C,0,-1.5152523818,0.9836625482,-0.683102008
C,0,-0.5391084143,1.24440531,0.448564862
N,0,1.489420598,-1.8279387011,0.1845179452
N,0,2.2180480029,-2.6495438448,0.4740052507
O,0,0.7886305509,1.5281266277,0.0235034525
C,0,-1.0327411469,2.1125312858,1.5673976874
H,0,0.9838512922,0.22729325,1.6770603319
H,0,-1.3563049941,3.0788178555,1.179178403
H,0,-0.2459859408,2.2866543316,2.2980422215
H,0,-1.8816173345,1.6497295304,2.0700082189
H,0,-0.2466637464,-2.0880985592,-1.6898728156
H,0,0.300273449,-0.4994132498,-2.2072695162
H,0,-2.1674037644,-0.5516669076,-2.0379098387
H,0,-2.0569993561,-1.0732793389,-0.367034649
H,0,-2.5130085604,1.2994057587,-0.3774697227
H,0,-1.2253684595,1.6247602489,-1.5172607285

B3LYP/6-31+G**
E(RB+HF-LYP) = -457.432551526

Zero-point correction= 0.164676 (Hartree/Particle)
Thermal correction to Energy= 0.173930
Thermal correction to Enthalpy= 0.174874
Thermal correction to Gibbs Free Energy= 0.130349
Sum of electronic and zero-point Energies= -457.267876
Sum of electronic and thermal Energies= -457.258622
Sum of electronic and thermal Enthalpies= -457.257678
Sum of electronic and thermal Free Energies= -457.302202

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	109.142	35.395	93.710

C,0,0.0907813809,-0.495952166,0.7816731236
C,0,0.9552572403,-0.4597671102,-0.4158778702
C,0,0.7734693116,0.6254734495,-1.4565956552
C,0,-0.7269216246,0.8926142488,-1.6534068237
C,0,-1.4350095393,1.2790491714,-0.3418582691
C,0,-1.1290466446,0.3421000757,0.8307265615
N,0,1.9442841569,-1.2943091705,-0.5006979397
N,0,2.8051066756,-2.0504932304,-0.6053844436
O,0,0.0458288133,0.7113528031,1.5949100388
C,0,-2.3100628561,-0.0888130325,1.6726014142
H,0,0.1236075474,-1.4167588564,1.3641496492
H,0,-2.8270424396,0.7901148466,2.0757726153
H,0,-1.9847248013,-0.7088721766,2.5123114263
H,0,-3.0288725485,-0.6575827233,1.0716920048
H,0,1.234180432,0.319622488,-2.4016673583
H,0,1.2735877014,1.5505390415,-1.1339872671
H,0,-0.8635865817,1.691780248,-2.3910442297
H,0,-1.1942407651,-0.0097509726,-2.0684454589
H,0,-2.5174415021,1.3048296984,-0.5116418419
H,0,-1.1386369861,2.2906449672,-0.0374180535

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -457.292209439

Zero-point correction= 0.170425 (Hartree/Particle)
Thermal correction to Energy= 0.179391
Thermal correction to Enthalpy= 0.180335
Thermal correction to Gibbs Free Energy= 0.136321
Sum of electronic and zero-point Energies= -457.121784
Sum of electronic and thermal Energies= -457.112819

Sum of electronic and thermal Enthalpies= -457.111875
Sum of electronic and thermal Free Energies= -457.155888

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.569	34.051	92.634

C,0,0.0962186883,-0.4836011234,0.7842863132
C,0,0.9553047186,-0.4461200331,-0.4061147034
C,0,0.7761949123,0.6371210579,-1.4273913927
C,0,-0.7112843101,0.8809854689,-1.6344370525
C,0,-1.4211859503,1.2625994175,-0.3409635627
C,0,-1.1146209553,0.3422108033,0.8252814243
N,0,1.913884326,-1.2932975416,-0.5073203078
N,0,2.7470808111,-2.0564664625,-0.6228409228
O,0,0.0438198038,0.7039973574,1.5679300507
C,0,-2.2828173265,-0.0818949847,1.6644937181
H,0,0.1275096444,-1.3993041304,1.3633433837
H,0,-2.8003363209,0.7932544671,2.0562933269
H,0,-1.9534269027,-0.6866093775,2.5053522407
H,0,-2.9930722339,-0.6581480647,1.0737273871
H,0,1.2490871089,0.3484072963,-2.3642710938
H,0,1.2569379852,1.5589931822,-1.0897835659
H,0,-0.8557413564,1.6683411865,-2.3735658935
H,0,-1.1612746344,-0.0255465997,-2.0423614158
H,0,-2.4969952577,1.2776238448,-0.5122892026
H,0,-1.136861084,2.271553726,-0.0396854238

Second Transition structure for loss of N2 (7)

B3LYP/6-31G*
E(RB+HF-LYP) = -457.352516673

Zero-point correction= 0.161553 (Hartree/Particle)
Thermal correction to Energy= 0.171308
Thermal correction to Enthalpy= 0.172252
Thermal correction to Gibbs Free Energy= 0.126417
Sum of electronic and zero-point Energies= -457.190963
Sum of electronic and thermal Energies= -457.181209
Sum of electronic and thermal Enthalpies= -457.180265
Sum of electronic and thermal Free Energies= -457.226099

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	107.497	36.022	96.467

C,0,-1.1746910102,0.4072936954,0.8170178113
C,0,-0.003480668,-0.5412627311,0.6903663775
C,0,0.5369325262,-0.7007131272,-0.6418946632
C,0,0.6950378054,0.5941882439,-1.3753814593
C,0,-0.7781866485,1.0052223533,-1.655618552
C,0,-1.5500342109,1.3106368163,-0.3611171802
O,0,0.0586419631,0.7378772433,1.4301811263
N,0,2.3844349448,-1.3435832124,-0.3348759007
N,0,3.0947773925,-2.1787593039,-0.5321670642
C,0,-2.2971469839,0.0495426446,1.7697279903
H,0,-0.0022712686,-1.3987821444,1.3612868474
H,0,-2.7672613305,0.9643960798,2.1516341817
H,0,-1.915238946,-0.5189733123,2.6220326626
H,0,-3.0695806734,-0.5407838815,1.263919989
H,0,1.2191684346,0.4623705422,-2.3280143673
H,0,1.1805116777,1.3975971765,-0.803593779
H,0,-0.7859047243,1.8736070652,-2.3237792677
H,0,-1.2727264056,0.184954305,-2.1906630846
H,0,-2.6278547261,1.2395207745,-0.5490836039
H,0,-1.353048964,2.3400256911,-0.0344897814

mPW1K/6-31G*
E(RmPW+HF-PW91) = -457.221023635

Zero-point correction= 0.166959 (Hartree/Particle)
Thermal correction to Energy= 0.176426
Thermal correction to Enthalpy= 0.177371
Thermal correction to Gibbs Free Energy= 0.132159
Sum of electronic and zero-point Energies= -457.054065
Sum of electronic and thermal Energies= -457.044597
Sum of electronic and thermal Enthalpies= -457.043653
Sum of electronic and thermal Free Energies= -457.088865

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	110.709	34.802	95.156

C,0,-0.6208398187,1.293400495,0.2864663846
C,0,0.3282276677,0.2561131165,0.7733119536
C,0,0.1347149512,-1.0821439698,0.2482877668
C,0,-0.1344964234,-1.0917550318,-1.2158657653

C,0,-1.5407973456,-0.4790271962,-1.2927757242
C,0,-1.5507482106,0.9831529213,-0.8685187652
O,0,0.734995946,1.3506194238,-0.0678517345
N,0,1.9110073384,-1.8303959555,0.3837319456
N,0,2.5689085101,-2.6245283081,0.7606788102
C,0,-1.0799151358,2.3598008269,1.2372902377
H,0,0.682171386,0.3581844784,1.791173949
H,0,-1.3005337257,3.2759554126,0.6885138326
H,0,-0.3082299808,2.5796603968,1.9707338448
H,0,-1.9853311656,2.0507041218,1.7576553806
H,0,-0.1612529979,-2.1052464276,-1.6122749502
H,0,0.5484003157,-0.486154803,-1.8163120113
H,0,-1.9204010904,-0.5840450152,-2.3086314743
H,0,-2.2072962312,-1.0517122864,-0.6454403307
H,0,-2.5649935571,1.2833050324,-0.6055061246
H,0,-1.2387855694,1.6216165734,-1.6971500583

B3LYP/6-31+G**
E(RB+HF-LYP) = -457.383910436

Zero-point correction= 0.160588 (Hartree/Particle)
Thermal correction to Energy= 0.170353
Thermal correction to Enthalpy= 0.171297
Thermal correction to Gibbs Free Energy= 0.125506
Sum of electronic and zero-point Energies= -457.223323
Sum of electronic and thermal Energies= -457.213558
Sum of electronic and thermal Enthalpies= -457.212614
Sum of electronic and thermal Free Energies= -457.258404

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	106.898	36.231	96.374

C,0,-1.1749648654,0.3997585338,0.8164499408
C,0,-0.0108048873,-0.5551590381,0.6860532068
C,0,0.53937809,-0.7070111301,-0.644301599
C,0,0.6928492244,0.5815030067,-1.3903553822
C,0,-0.7795985787,1.0028650986,-1.6576321958
C,0,-1.542622864,1.3100731202,-0.3580348177
O,0,0.0633046786,0.7215775326,1.4340634103
N,0,2.3657182324,-1.326680983,-0.3285334312
N,0,3.112828412,-2.1318907657,-0.513884304
C,0,-2.3006354421,0.0478062914,1.7666305896
H,0,-0.0087138388,-1.4153929683,1.3520155615

H,0,-2.7620659587,0.9656542889,2.1500941529
H,0,-1.925109831,-0.5274684883,2.6163345049
H,0,-3.0752651493,-0.5337608584,1.2554120512
H,0,1.2044378289,0.4361760458,-2.3468192455
H,0,1.1921551561,1.383740625,-0.8298328602
H,0,-0.7826389438,1.8749955372,-2.320241296
H,0,-1.2839762714,0.1909510132,-2.1955825311
H,0,-2.6209745554,1.2472749579,-0.5416710449
H,0,-1.3357164384,2.3361965332,-0.028150884

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -457.239168770

Zero-point correction= 0.166231 (Hartree/Particle)
Thermal correction to Energy= 0.175724
Thermal correction to Enthalpy= 0.176668
Thermal correction to Gibbs Free Energy= 0.131401
Sum of electronic and zero-point Energies= -457.072937
Sum of electronic and thermal Energies= -457.063445
Sum of electronic and thermal Enthalpies= -457.062501
Sum of electronic and thermal Free Energies= -457.107767

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.268	34.944	95.272

C,0,-1.1646861227,0.3813452642,0.7993581429
C,0,-0.0353904071,-0.5776733188,0.6604829387
C,0,0.5109701775,-0.7300565042,-0.6748915072
C,0,0.6807241621,0.5712919747,-1.3775379907
C,0,-0.7734512846,0.9892931857,-1.6417473441
C,0,-1.5227503954,1.2972625987,-0.3527772545
O,0,0.0775404134,0.6591326302,1.3883948319
N,0,2.323162191,-1.286472943,-0.3098725569
N,0,3.1250751329,-2.0231196018,-0.4515949631
C,0,-2.2719585376,0.0635072636,1.7608877095
H,0,-0.0493687356,-1.4452378504,1.3073655801
H,0,-2.7028932438,0.9870852413,2.1463521784
H,0,-1.8960159877,-0.5138803519,2.600656351
H,0,-3.062002361,-0.4994425527,1.2677401477
H,0,1.1986685548,0.4495292483,-2.3264582793
H,0,1.1717152527,1.3509884427,-0.791351023
H,0,-0.7811984213,1.8538244478,-2.3035532311
H,0,-1.2776284531,0.1801566707,-2.1720353229

H,0,-2.5963244369,1.248910003,-0.530120886
H,0,-1.3036822964,2.3123306901,-0.0181296979

Second Intermediate —epoxy carbene (8)

B3LYP/6-31G*
E(RB+HF-LYP) = -347.833879396

Zero-point correction= 0.152967 (Hartree/Particle)
Thermal correction to Energy= 0.160567
Thermal correction to Enthalpy= 0.161512
Thermal correction to Gibbs Free Energy= 0.121677
Sum of electronic and zero-point Energies= -347.680913
Sum of electronic and thermal Energies= -347.673312
Sum of electronic and thermal Enthalpies= -347.672368
Sum of electronic and thermal Free Energies= -347.712203

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	100.758	29.767	83.840

C,0,-0.7629215913,1.0153064475,-0.4451467575
C,0,-0.7226981863,-0.1916744625,0.4859346257
C,0,0.4851877498,-1.1761246482,0.368243525
C,0,1.1336000735,-1.014235164,-0.8638186827
C,0,1.5134140307,0.3562001506,-1.2963274762
C,0,0.6568474577,1.5204132178,-0.7232535361
O,0,0.2705444159,-0.125204279,1.4511130875
C,0,-2.0521925794,-0.792217947,0.8920361537
H,0,0.3209159926,-2.1579748645,0.8037205503
H,0,-2.6579011392,-0.0297887463,1.3976982851
H,0,-1.9083431324,-1.627954186,1.5811806363
H,0,-2.6094944547,-1.1407874501,0.0159932719
H,0,2.5670279968,0.4629920022,-0.979947683
H,0,1.5437774867,0.4001884962,-2.3937478275
H,0,0.6346815221,2.3582621673,-1.4293623254
H,0,1.0851289661,1.8842702221,0.2138256608
H,0,-1.288193545,0.7519061489,-1.372857695
H,0,-1.359376748,1.7945148768,0.0485853155

mPW1K/6-31G*
E(RmPW+HF-PW91) = -347.743673370

Zero-point correction= 0.158337 (Hartree/Particle)
Thermal correction to Energy= 0.165649
Thermal correction to Enthalpy= 0.166593
Thermal correction to Gibbs Free Energy= 0.127233
Sum of electronic and zero-point Energies= -347.585336
Sum of electronic and thermal Energies= -347.578024
Sum of electronic and thermal Enthalpies= -347.577080
Sum of electronic and thermal Free Energies= -347.616440

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	103.946	28.328	82.840

C,0,-0.766674477,0.9961394827,-0.4536145794
C,0,-0.7214414233,-0.2008452316,0.4654999122
C,0,0.461086052,-1.1609691203,0.3626183513
C,0,1.1288053462,-1.0057556179,-0.8722814216
C,0,1.5061461653,0.3673425603,-1.2602066503
C,0,0.6399816367,1.5094619533,-0.7035029824
O,0,0.2964586789,-0.1448487268,1.3935272085
C,0,-2.0329518979,-0.7687142041,0.919281251
H,0,0.2981116962,-2.148226171,0.7723901263
H,0,-2.606012469,0.0018565809,1.4349205034
H,0,-1.8788418013,-1.5966934014,1.6052329768
H,0,-2.6187739405,-1.114521662,0.0698380644
H,0,2.5420753636,0.4548924193,-0.9030083567
H,0,1.5801508027,0.4302306239,-2.3470915366
H,0,0.6218600588,2.3420395462,-1.4053581836
H,0,1.0453882891,1.8776906721,0.2345796128
H,0,-1.2694463977,0.7283551626,-1.3844497057
H,0,-1.3758894448,1.763207109,0.027965546

B3LYP/6-31+G**
E(RB+HF-LYP) = -347.863414143

Zero-point correction= 0.151980 (Hartree/Particle)
Thermal correction to Energy= 0.159627
Thermal correction to Enthalpy= 0.160571
Thermal correction to Gibbs Free Energy= 0.120651
Sum of electronic and zero-point Energies= -347.711434
Sum of electronic and thermal Energies= -347.703788
Sum of electronic and thermal Enthalpies= -347.702843
Sum of electronic and thermal Free Energies= -347.742763

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	100.167	30.017	84.017

C,0,-0.7670940927,1.0124717928,-0.4446827518
C,0,-0.7270818737,-0.193161075,0.4866289566
C,0,0.4764028888,-1.1839125049,0.3555415008
C,0,1.141180903,-1.008818097,-0.8673501101
C,0,1.5216638419,0.3614991244,-1.2869149737
C,0,0.6503609549,1.5233080022,-0.7271684657
O,0,0.2788307379,-0.1346017357,1.4420510949
C,0,-2.0550474047,-0.7861369923,0.9049270251
H,0,0.3164168437,-2.1672202155,0.7859869698
H,0,-2.6434444958,-0.0229038468,1.4280000149
H,0,-1.9100597576,-1.6313338706,1.5809510957
H,0,-2.6256297429,-1.1176559166,0.0317773421
H,0,2.5673263376,0.4652899919,-0.94286015
H,0,1.5821750596,0.4072747868,-2.3814720934
H,0,0.6212657715,2.3481938451,-1.4472409545
H,0,1.0758584201,1.9074969969,0.2028106923
H,0,-1.2933609187,0.7458071027,-1.3701376489
H,0,-1.3635047264,1.7903635105,0.0498888862

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -347.767618098

Zero-point correction= 0.157382 (Hartree/Particle)
Thermal correction to Energy= 0.164723
Thermal correction to Enthalpy= 0.165667
Thermal correction to Gibbs Free Energy= 0.126264
Sum of electronic and zero-point Energies= -347.610236
Sum of electronic and thermal Energies= -347.602895
Sum of electronic and thermal Enthalpies= -347.601951
Sum of electronic and thermal Free Energies= -347.641354

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	103.365	28.526	82.930

C,0,-0.7697874244,0.9939323271,-0.4537094803
C,0,-0.7247925623,-0.201577487,0.4657876704
C,0,0.4547791101,-1.165803961,0.354368684
C,0,1.1367546038,-1.00124305,-0.8726160574

C,0,1.5106086192,0.3710686097,-1.2535148484
C,0,0.6350766623,1.5106960995,-0.7061875584
O,0,0.3016296886,-0.1509568769,1.3863832324
C,0,-2.0343528548,-0.7645602225,0.9278738598
H,0,0.2950015318,-2.1547663205,0.7588408065
H,0,-2.5950071336,0.0057340074,1.4562031543
H,0,-1.8794107524,-1.6001271128,1.6032745355
H,0,-2.6293645277,-1.0971222961,0.0803354318
H,0,2.5414112132,0.4554595705,-0.8796618022
H,0,1.6054195678,0.4329957005,-2.3376911946
H,0,0.6130035293,2.3350465653,-1.4169506552
H,0,1.0386344373,1.8917305999,0.227484754
H,0,-1.2734221368,0.723235046,-1.3827374227
H,0,-1.3790201612,1.7603953606,0.0278229158

CCSD(T)/6-31+G//B3LYP/6-31+G****
CCSD(T)= -0.34691039238D+03

Third Transition structure (9)

B3LYP/6-31G*
E(RB+HF-LYP) = -347.827893912

Zero-point correction= 0.152236 (Hartree/Particle)
Thermal correction to Energy= 0.159653
Thermal correction to Enthalpy= 0.160598
Thermal correction to Gibbs Free Energy= 0.120928
Sum of electronic and zero-point Energies= -347.675658
Sum of electronic and thermal Energies= -347.668240
Sum of electronic and thermal Enthalpies= -347.667296
Sum of electronic and thermal Free Energies= -347.706966

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	100.184	28.733	83.492

C,0,-0.8072350057,1.0152277282,-0.376955898
C,0,-0.4261396097,0.0812581001,0.796876441
C,0,0.6435280724,-1.107836797,0.4802526272
C,0,1.0251842768,-1.1467300497,-0.7976447172
C,0,1.2508295396,0.0809518589,-1.586078244
C,0,-0.1916908373,0.6581455609,-1.7366962303
O,0,0.6925202007,0.3939885284,1.449542903

C,0,-1.6080131524,-0.4073849153,1.6293205899
H,0,0.6447608647,-1.8721363444,1.2424787605
H,0,-2.1209126346,0.4639135046,2.0563531674
H,0,-1.2629980635,-1.0354299608,2.4545844767
H,0,-2.3287875912,-0.9628439104,1.0201652519
H,0,1.6565753628,-0.1182578657,-2.5838102003
H,0,1.8855555053,0.8178448834,-1.074047229
H,0,-0.1563039596,1.5373660744,-2.3901893323
H,0,-0.8121686961,-0.093007482,-2.2394728317
H,0,-1.8981426301,1.0596483497,-0.4734098965
H,0,-0.4665194649,2.0092056069,-0.0634428028

mPW1K/6-31G*
E(RmPW+HF-PW91) = -347.733312400

Zero-point correction= 0.156564 (Hartree/Particle)
Thermal correction to Energy= 0.163912
Thermal correction to Enthalpy= 0.164856
Thermal correction to Gibbs Free Energy= 0.125260
Sum of electronic and zero-point Energies= -347.576749
Sum of electronic and thermal Energies= -347.569401
Sum of electronic and thermal Enthalpies= -347.568456
Sum of electronic and thermal Free Energies= -347.608053

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	102.856	28.181	83.337

C,0,-0.747084684,1.040448633,-0.3604685344
C,0,-0.4096481445,0.1082290653,0.8078327878
C,0,0.675708859,-1.1152621471,0.4931893488
C,0,1.0403371493,-1.1006681367,-0.7583665634
C,0,1.2151852435,0.0710743699,-1.6149206994
C,0,-0.2191586669,0.6231003407,-1.7209456723
O,0,0.6449536218,0.4143530121,1.505581477
C,0,-1.6096320575,-0.4462786629,1.5405280506
H,0,0.6839886803,-1.8416864463,1.2802646501
H,0,-2.1651392517,0.3902635635,1.9671382927
H,0,-1.2975222832,-1.0936048949,2.3550257627
H,0,-2.2708998227,-0.9904516058,0.8691833747
H,0,1.5794389911,-0.1805759299,-2.6088220646
H,0,1.8685250673,0.8250511493,-1.169608815
H,0,-0.2282203116,1.469445001,-2.4076739076
H,0,-0.8578529762,-0.1476982409,-2.1532092405

H,0,-1.8280796065,1.167668026,-0.4163907432
H,0,-0.3181136545,2.0029045086,-0.0816514319

B3LYP/6-31+G**
E(RB+HF-LYP) = -347.862165110

Zero-point correction= 0.150981 (Hartree/Particle)
Thermal correction to Energy= 0.158352
Thermal correction to Enthalpy= 0.159296
Thermal correction to Gibbs Free Energy= 0.119904
Sum of electronic and zero-point Energies= -347.711184
Sum of electronic and thermal Energies= -347.703813
Sum of electronic and thermal Enthalpies= -347.702869
Sum of electronic and thermal Free Energies= -347.742261

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	99.367	28.937	82.907

C,0,0.683018594,1.5006816727,-0.7505567499
C,0,-0.7361670391,1.0057313062,-0.4575073376
C,0,-0.7108636063,-0.1655430868,0.525899055
C,0,0.5028644806,-1.2111856825,0.3623335838
C,0,1.1474516936,-1.0022946012,-0.8072177224
C,0,1.5272934679,0.3285660724,-1.3261347309
O,0,0.17109991,-0.0399612176,1.5430335959
C,0,-2.0534906774,-0.8134162687,0.8192562435
H,0,0.3577837334,-2.1408524666,0.8926808327
H,0,-2.7155494749,-0.0632599629,1.268160092
H,0,-1.9396682303,-1.6360261545,1.5282792015
H,0,-2.523719787,-1.1829918699,-0.0968233441
H,0,2.5901042062,0.4590508626,-1.0628802926
H,0,1.5016866974,0.3217250663,-2.4231939275
H,0,0.6634833949,2.3317291962,-1.4639380148
H,0,1.1258549335,1.8636186456,0.1803104246
H,0,-1.2591283543,0.7118559426,-1.3765156834
H,0,-1.330287879,1.7996040085,0.0132178957

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -347.757005022

Zero-point correction= 0.155560 (Hartree/Particle)
Thermal correction to Energy= 0.162838
Thermal correction to Enthalpy= 0.163782

Thermal correction to Gibbs Free Energy= 0.124583
Sum of electronic and zero-point Energies= -347.601445
Sum of electronic and thermal Energies= -347.594167
Sum of electronic and thermal Enthalpies= -347.593223
Sum of electronic and thermal Free Energies= -347.632422

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	102.183	28.372	82.503

C,0,0.7003379186,1.475850017,-0.7375368262
C,0,-0.7084470866,1.0002747178,-0.4465264811
C,0,-0.692379035,-0.1399128815,0.5538899783
C,0,0.517727664,-1.2372483231,0.3510074407
C,0,1.1269683185,-0.9783984347,-0.7797931996
C,0,1.4933338402,0.3168443429,-1.3560208392
O,0,0.1122871295,0.0051754762,1.5762347137
C,0,-2.0189906268,-0.8246622358,0.7696562435
H,0,0.378871732,-2.1195384135,0.9426637224
H,0,-2.7240906564,-0.0905842875,1.1593848519
H,0,-1.9220128361,-1.6211341178,1.5005374101
H,0,-2.416060692,-1.2243488372,-0.1597631731
H,0,2.5652037503,0.4415285745,-1.177016804
H,0,1.3788130646,0.2881709729,-2.4401523873
H,0,0.6929423031,2.3280794991,-1.415271468
H,0,1.1602508185,1.7878229163,0.1968259045
H,0,-1.2259388056,0.6966754777,-1.3576158131
H,0,-1.297581672,1.7954411903,0.012472148

CCSD(T)/6-31+G//B3LYP/6-31+G****
CCSD(T)= -0.34688712875D+03

6-Heptyn-2-one (10)

B3LYP/6-31G*
E(RB+HF-LYP) = -347.916334560

Zero-point correction= 0.151611 (Hartree/Particle)
Thermal correction to Energy= 0.161022
Thermal correction to Enthalpy= 0.161967
Thermal correction to Gibbs Free Energy= 0.116855
Sum of electronic and zero-point Energies= -347.764723
Sum of electronic and thermal Energies= -347.755312

Sum of electronic and thermal Enthalpies= -347.754368
Sum of electronic and thermal Free Energies= -347.799480

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	101.043	33.251	94.946

C,0,-0.536652931,1.3800804218,-0.2776259155
C,0,-0.6356452665,0.6625168666,1.0697884251
C,0,1.5485822828,-2.081463196,0.0559044593
C,0,1.2973656855,-1.2054118012,-0.7370236177
C,0,0.9922422816,-0.1566589389,-1.7119129277
C,0,-0.3922301466,0.5086495891,-1.5389822648
O,0,0.0470105509,1.0130759593,2.0129793183
C,0,-1.6643990566,-0.4493510097,1.2029688026
H,0,1.7804620606,-2.8394170835,0.7692989548
H,0,-2.6176619598,-0.1771298536,0.7339078736
H,0,-1.8194513214,-0.6714098411,2.2609337973
H,0,-1.2956471471,-1.3523600863,0.70295906
H,0,1.0509792162,-0.5840610059,-2.7222060417
H,0,1.7698762406,0.6185429852,-1.6637441231
H,0,-0.5559241431,1.1485116952,-2.4145804795
H,0,-1.1735611947,-0.2599737901,-1.5677122803
H,0,-1.4615932633,1.9686444479,-0.3778787251
H,0,0.2908600101,2.0938732671,-0.2035143511

mPW1K/6-31G*
E(RmPW+HF-PW91) = -347.820550704

Zero-point correction= 0.156236 (Hartree/Particle)
Thermal correction to Energy= 0.165389
Thermal correction to Enthalpy= 0.166334
Thermal correction to Gibbs Free Energy= 0.121728
Sum of electronic and zero-point Energies= -347.664315
Sum of electronic and thermal Energies= -347.655161
Sum of electronic and thermal Enthalpies= -347.654217
Sum of electronic and thermal Free Energies= -347.698823

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.783	32.186	93.881

C,0,-0.4985429001,1.3646511003,-0.2627417309
C,0,-0.6309073934,0.6470256309,1.0623240804

C,0,1.5605576744,-2.0309633404,0.0722676244
C,0,1.2892685928,-1.184089883,-0.7345949947
C,0,0.963032087,-0.1630137703,-1.7203810823
C,0,-0.3969954906,0.5053291949,-1.5177732678
O,0,0.01558718,0.9946714409,2.0185894405
C,0,-1.6503727293,-0.4541364355,1.1625113143
H,0,1.8084903412,-2.7647621074,0.7993812958
H,0,-2.5810216875,-0.1827677506,0.664159611
H,0,-1.8406156636,-0.6756708397,2.2081154445
H,0,-1.2666026785,-1.3508505952,0.67708541
H,0,0.9918045219,-0.6165377015,-2.7123370189
H,0,1.7448262994,0.5990190379,-1.7082891883
H,0,-0.5730130394,1.1457404536,-2.3823474663
H,0,-1.1827092556,-0.2503005877,-1.5324239635
H,0,-1.3933360488,1.988758776,-0.3473594432
H,0,0.3512407265,2.0411848061,-0.184371866

B3LYP/6-31+G**
E(RB+HF-LYP) = -347.947256200

Zero-point correction= 0.150716 (Hartree/Particle)
Thermal correction to Energy= 0.160160
Thermal correction to Enthalpy= 0.161104
Thermal correction to Gibbs Free Energy= 0.115801
Sum of electronic and zero-point Energies= -347.796540
Sum of electronic and thermal Energies= -347.787096
Sum of electronic and thermal Enthalpies= -347.786152
Sum of electronic and thermal Free Energies= -347.831456

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	100.502	33.336	95.349

C,0,-0.5323558473,1.3775166048,-0.2745225754
C,0,-0.6518602347,0.6737845961,1.075996724
C,0,1.5806163842,-2.1052979319,0.02691321
C,0,1.3155670072,-1.2191133153,-0.7537738803
C,0,0.9983359871,-0.1593615533,-1.7130383322
C,0,-0.3894052854,0.4978644701,-1.5312512455
O,0,0.016266474,1.0390708879,2.0283972694
C,0,-1.677049773,-0.4377658318,1.2111430192
H,0,1.8233737473,-2.86959918,0.7296429385
H,0,-2.6210425514,-0.1740129688,0.7206514111
H,0,-1.8496062822,-0.6449368433,2.268637643

H,0,-1.297918132,-1.3457297957,0.7294341487
H,0,1.057420213,-0.5780994863,-2.7258934617
H,0,1.7738458072,0.6162750453,-1.6559918194
H,0,-0.5602195096,1.1341505077,-2.4073460526
H,0,-1.1667847704,-0.2741182275,-1.5542558429
H,0,-1.4518872719,1.9724155097,-0.3805451496
H,0,0.2995975293,2.085326104,-0.2003134882

mPW1K/6-31+G**
E(RmPW+HF-PW91) = -347.838719034

Zero-point correction= 0.155572 (Hartree/Particle)
Thermal correction to Energy= 0.164739
Thermal correction to Enthalpy= 0.165683
Thermal correction to Gibbs Free Energy= 0.121050
Sum of electronic and zero-point Energies= -347.683147
Sum of electronic and thermal Energies= -347.673980
Sum of electronic and thermal Enthalpies= -347.673036
Sum of electronic and thermal Free Energies= -347.717669

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	103.375	32.299	93.938

C,0,-0.496134965,1.3641221776,-0.2633846944
C,0,-0.6341467417,0.6505347357,1.0629717303
C,0,1.5622116313,-2.0365342147,0.0691342317
C,0,1.2899922127,-1.1878433231,-0.7360886182
C,0,0.9645569837,-0.1653733727,-1.720032454
C,0,-0.3950080817,0.5040465482,-1.5176712507
O,0,0.0029687631,1.0079213553,2.0222298705
C,0,-1.6457564784,-0.4569733309,1.1621369343
H,0,1.8096864584,-2.7720254867,0.7933191268
H,0,-2.5764478736,-0.1907345191,0.6629911295
H,0,-1.8336000725,-0.6784953365,2.2071989786
H,0,-1.2542292499,-1.3491179034,0.6761700249
H,0,0.9944386377,-0.6191425783,-2.7110883146
H,0,1.747538301,0.594502594,-1.7050696301
H,0,-0.5711402112,1.1431856267,-2.3822597355
H,0,-1.1804510789,-0.2510571059,-1.5314918082
H,0,-1.3887993276,1.9900298658,-0.3480748999
H,0,0.3549669463,2.0376086806,-0.1819291093

Alternative fragmentation transition structure (11)

B3LYP/6-31+G**
E(RB+HF-LYP) = -626.068994355

Zero-point correction=	0.185761 (Hartree/Particle)
Thermal correction to Energy=	0.198466
Thermal correction to Enthalpy=	0.199411
Thermal correction to Gibbs Free Energy=	0.147057
Sum of electronic and zero-point Energies=	-625.883234
Sum of electronic and thermal Energies=	-625.870528
Sum of electronic and thermal Enthalpies=	-625.869584
Sum of electronic and thermal Free Energies=	-625.921937

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.539	47.865	110.186

C,0,-1.9868643559,-0.8236275511,-0.4532576827
C,0,-2.018276312,-1.180152942,1.0439266418
C,0,-0.6824435148,-0.9854586175,1.7659675477
C,0,0.3616623324,-0.1270220589,1.1589974395
C,0,0.1137379145,0.5230600695,-0.1475923484
C,0,-1.267344865,0.5034156626,-0.7371452852
O,0,-0.471250607,0.3660344828,2.2403441342
C,0,-0.2775308713,-2.0625028481,2.7477377725
O,0,0.9554263709,1.4574262683,-0.4975966576
C,0,1.5470252168,1.5987676791,-1.840277108
N,0,1.8595553931,2.6615675337,-2.3781076256
H,0,1.6172732974,3.5499128443,-1.9361632324
N,0,1.6269552193,-0.540850036,-2.2494136463
N,0,1.0151663152,-1.0353399055,-1.4312913661
H,0,1.4097731522,-0.2673952885,1.419482062
H,0,-1.060771666,-2.1990680173,3.5021692445
H,0,0.6498471631,-1.7940679099,3.2604745959
H,0,-0.1317297726,-3.0175731345,2.2313683495
H,0,-1.1945907776,0.6993064444,-1.8144527823
H,0,-1.829241473,1.3450717718,-0.304788305
H,0,-3.0100805244,-0.7738224625,-0.8404599616
H,0,-1.4774626302,-1.6216870235,-1.0032210325
H,0,-2.3391955878,-2.2215261723,1.1565618798
H,0,-2.7587590541,-0.5633565676,1.5685959717

Ring-flipped alternative structure

E(RB+HF-LYP) = -626.068741464

Zero-point correction=	0.185711 (Hartree/Particle)
Thermal correction to Energy=	0.198487
Thermal correction to Enthalpy=	0.199431
Thermal correction to Gibbs Free Energy=	0.146378
Sum of electronic and zero-point Energies=	-625.883031
Sum of electronic and thermal Energies=	-625.870254
Sum of electronic and thermal Enthalpies=	-625.869310
Sum of electronic and thermal Free Energies=	-625.922363

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	124.553	47.913	111.660

C,0,2.1991348097,-0.102909445,-1.288590731
C,0,1.597095015,-1.511329501,-1.3845888128
C,0,0.0788883891,-1.5111391101,-1.2713994421
C,0,-0.5693744949,-0.432081524,-0.5011407114
C,0,0.2581092647,0.6122503316,0.1615646082
C,0,1.7548219633,0.6246819006,-0.0042124402
O,0,-0.5665484482,-0.4101816344,-1.9552194797
C,0,-0.6095064852,-2.8485525344,-1.4228993775
O,0,-0.3222223316,1.7275018003,0.5163818546
C,0,-1.3247937765,1.9028062745,1.5745733496
N,0,-2.2556236408,2.7084945879,1.5639776217
H,0,-2.444940743,3.2625110089,0.7271859608
N,0,-0.6702740532,0.2294784358,2.8024243854
N,0,0.0358110483,-0.3685783339,2.1466678742
H,0,-1.5565913599,-0.5904102317,-0.0673252494
H,0,-0.3797279877,-3.2837343823,-2.4017814503
H,0,-1.6941247707,-2.7403556577,-1.3414531353
H,0,-0.2676392898,-3.5463513255,-0.6507532086
H,0,2.2099429246,0.1274238053,0.8637025355
H,0,2.1011885717,1.6625323364,0.0030151863
H,0,3.2921068444,-0.167835214,-1.3003284002
H,0,1.8974983369,0.4788298262,-2.1650124747
H,0,1.9989893518,-2.1540111466,-0.5893289002
H,0,1.8778227701,-1.9752815272,-2.3385476884

Dichlorocarbene

B3LYP/6-31G*
E(RB+HF-LYP) = -958.383063867

Zero-point correction= 0.003971 (Hartree/Particle)
Thermal correction to Energy= 0.007411
Thermal correction to Enthalpy= 0.008356
Thermal correction to Gibbs Free Energy= -0.021810
Sum of electronic and zero-point Energies= -958.379092
Sum of electronic and thermal Energies= -958.375652
Sum of electronic and thermal Enthalpies= -958.374708
Sum of electronic and thermal Free Energies= -958.404873

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	4.651	9.211	63.488

C,0,-0.7033044177,0.,-0.4973114503
Cl,0,-0.7014480463,0.,1.255279529
Cl,0,0.9496731349,0.,-1.0797578407

MPW1K/6-31G*
E(RmPW+HF-PW91) = -958.433234127

Zero-point correction= 0.004391 (Hartree/Particle)
Thermal correction to Energy= 0.007747
Thermal correction to Enthalpy= 0.008691
Thermal correction to Gibbs Free Energy= -0.021269
Sum of electronic and zero-point Energies= -958.428843
Sum of electronic and thermal Energies= -958.425487
Sum of electronic and thermal Enthalpies= -958.424543
Sum of electronic and thermal Free Energies= -958.454503

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	4.861	8.876	63.056

C,0,-0.6808091343,0.,-0.481404679
Cl,0,-0.6879175619,0.,1.2277238552
Cl,0,0.9282031387,0.,-1.0578163215

MP2/6-31G*
E(RHF) = -956.712219043

Zero-point correction= .004367 (Hartree/Particle)

Thermal correction to Energy= .007724
Thermal correction to Enthalpy= .008668
Thermal correction to Gibbs Free Energy= -.021307
Sum of electronic and zero-point Energies= -957.081945
Sum of electronic and thermal Energies= -957.078588
Sum of electronic and thermal Enthalpies= -957.077644
Sum of electronic and thermal Free Energies= -957.107619

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	4.847	8.893	63.088

C,0,-0.6845298912,0.,-0.484035651
Cl,0,-0.6912612265,0.,1.2338453796
Cl,0,0.9328600116,0.,-1.0630092675

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -958.460612255

Zero-point correction= 0.003986 (Hartree/Particle)
Thermal correction to Energy= 0.007421
Thermal correction to Enthalpy= 0.008365
Thermal correction to Gibbs Free Energy= -0.021762
Sum of electronic and zero-point Energies= -958.456626
Sum of electronic and thermal Energies= -958.453192
Sum of electronic and thermal Enthalpies= -958.452247
Sum of electronic and thermal Free Energies= -958.482375

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	4.657	9.198	63.408

C,0,-0.6946420667,0.,-0.4911860378
Cl,0,-0.6962270869,0.,1.2446536675
Cl,0,0.9413948751,0.,-1.0712938895

Styreneoxide (18)

B3LYP/6-31G*
E(RB+HF-LYP) = -384.846014992

Zero-point correction= 0.139241 (Hartree/Particle)
Thermal correction to Energy= 0.146439

Thermal correction to Enthalpy= 0.147383
Thermal correction to Gibbs Free Energy= 0.107103
Sum of electronic and zero-point Energies= -384.706774
Sum of electronic and thermal Energies= -384.699576
Sum of electronic and thermal Enthalpies= -384.698632
Sum of electronic and thermal Free Energies= -384.738912

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	91.892	27.825	84.777

C,0,-0.2143138858,-0.1342144713,0.2011319728
C,0,-0.3266268774,-0.0158454236,1.6844947156
O,0,0.8876253326,-0.0410869151,2.4484037785
C,0,0.1410399074,1.1777410473,2.4198412558
H,0,-1.1435836006,-0.5845640145,2.1334932993
H,0,0.5987850461,1.9942911669,1.8611317733
H,0,-0.3350984105,1.4584573024,3.3602167249
C,0,-1.3503744394,-0.4312972696,-0.5612811538
C,0,-1.2676049254,-0.5151774867,-1.9514196101
C,0,-0.0443186196,-0.3120315245,-2.5927057624
C,0,1.0948667092,-0.027959391,-1.835672813
C,0,1.0120105325,0.0601351592,-0.4466198845
H,0,-2.3039029511,-0.5971950704,-0.0640937953
H,0,-2.1569381252,-0.7451927237,-2.532269129
H,0,0.0224542038,-0.3820311346,-3.6750950747
H,0,2.0525208228,0.1189153085,-2.3283921821
H,0,1.8966899444,0.257910647,0.151165834

mPW1K/6-31G*
E(RmPW+HF-PW91) = -384.819700025

Zero-point correction= 0.142903 (Hartree/Particle)
Thermal correction to Energy= 0.149926
Thermal correction to Enthalpy= 0.150871
Thermal correction to Gibbs Free Energy= 0.110897
Sum of electronic and zero-point Energies= -384.676797
Sum of electronic and thermal Energies= -384.669774
Sum of electronic and thermal Enthalpies= -384.668829
Sum of electronic and thermal Free Energies= -384.708804

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	94.080	26.868	84.133

C,0,-0.2031820304,-0.1497613357,0.2045077179
C,0,-0.2986826172,-0.0452731874,1.6787076841
O,0,0.9048513562,0.0269344695,2.4003496603
C,0,0.090955191,1.1730254547,2.3853083527
H,0,-1.056227302,-0.6674948682,2.1390508319
H,0,0.471824211,2.0049516276,1.8083808203
H,0,-0.3786742952,1.4223977561,3.3272949595
C,0,-1.3394995768,-0.4099013383,-0.5467011444
C,0,-1.2645408202,-0.4846530391,-1.9249454471
C,0,-0.0500734849,-0.3085726193,-2.563866335
C,0,1.0879305542,-0.0611894985,-1.8166795506
C,0,1.0137333803,0.0166607652,-0.4385785321
H,0,-2.2879993715,-0.5555886478,-0.0502934815
H,0,-2.1546180917,-0.6859258774,-2.5007160782
H,0,0.0100408431,-0.3710357733,-3.6392145088
H,0,2.0397839426,0.0647716658,-2.3092003277
H,0,1.8972156382,0.1904371512,0.15538403

MP2/6-31G*

E(RHF) = -382.417874747

Zero-point correction= .139896 (Hartree/Particle)
Thermal correction to Energy= .147253
Thermal correction to Enthalpy= .148197
Thermal correction to Gibbs Free Energy= .107686
Sum of electronic and zero-point Energies= -383.473745
Sum of electronic and thermal Energies= -383.466388
Sum of electronic and thermal Enthalpies= -383.465444
Sum of electronic and thermal Free Energies= -383.505955

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	92.403	28.435	85.264

C,0,-0.2144320398,-0.1537943058,0.207950705
C,0,-0.3214986325,-0.0350987263,1.6853579887
O,0,0.9159323993,-0.0133169291,2.4283587755
C,0,0.1157107497,1.1821270023,2.3885763292
H,0,-1.1017657433,-0.6347966151,2.1577836668
H,0,0.5326036003,1.997650176,1.8004920121
H,0,-0.3477154569,1.4629856647,3.3327028554
C,0,-1.3574149976,-0.4247626044,-0.5535223311
C,0,-1.2730909581,-0.4981434963,-1.9443101369

C,0,-0.04626388,-0.3005020471,-2.582495946
C,0,1.0965534273,-0.0379162111,-1.8228842509
C,0,1.0154141441,0.0376392338,-0.4322125859
H,0,-2.3132522147,-0.5858223745,-0.0569205136
H,0,-2.1644311532,-0.7105067099,-2.5299586948
H,0,0.0203407761,-0.3613555398,-3.6660208264
H,0,2.0557695653,0.1040725997,-2.3153758091
H,0,1.9011245541,0.2170151605,0.1716684721

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -384.960406846

Zero-point correction= 0.138184 (Hartree/Particle)
Thermal correction to Energy= 0.145434
Thermal correction to Enthalpy= 0.146378
Thermal correction to Gibbs Free Energy= 0.105915
Sum of electronic and zero-point Energies= -384.822223
Sum of electronic and thermal Energies= -384.814973
Sum of electronic and thermal Enthalpies= -384.814028
Sum of electronic and thermal Free Energies= -384.854492

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	91.261	28.022	85.163

C,0,-0.2099004981,-0.1262570501,0.1977666417
C,0,-0.3282138254,-0.0096104002,1.6772819265
O,0,0.8778788683,-0.0523672112,2.4526695369
C,0,0.1408403919,1.1735586344,2.4198576734
H,0,-1.1498288085,-0.5707071339,2.1174646474
H,0,0.6143480777,1.9817318144,1.8696013771
H,0,-0.339962339,1.4498798117,3.3542930513
C,0,-1.3419945245,-0.428323618,-0.5604734451
C,0,-1.2620676982,-0.516891344,-1.9459236487
C,0,-0.0446154239,-0.3149215333,-2.5878314407
C,0,1.0908456899,-0.0269635631,-1.8357400872
C,0,1.0103960503,0.0669124914,-0.4513189084
H,0,-2.2917596066,-0.5965439665,-0.0636640122
H,0,-2.1490277603,-0.7506384325,-2.5229263445
H,0,0.0209743011,-0.3896239614,-3.6667346783
H,0,2.0446726046,0.1186588564,-2.3292077843
H,0,1.8958116119,0.2711589982,0.1381051794

Transition state 20

B3LYP/6-31G*

E(RB+HF-LYP) = -1343.22740266

Zero-point correction= 0.144582 (Hartree/Particle)
Thermal correction to Energy= 0.155851
Thermal correction to Enthalpy= 0.156795
Thermal correction to Gibbs Free Energy= 0.104803
Sum of electronic and zero-point Energies= -1343.082821
Sum of electronic and thermal Energies= -1343.071551
Sum of electronic and thermal Enthalpies= -1343.070607
Sum of electronic and thermal Free Energies= -1343.122600

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	97.798	41.196	109.427

C,0,0.8258701492,1.1221197311,-2.1236965298
C,0,-0.2746169014,0.7387050151,-1.3371007161
C,0,-1.3925505609,0.1613526883,-1.9637564801
C,0,-1.4164904711,-0.017611719,-3.344422058
C,0,-0.3190736288,0.3686644616,-4.1162621732
C,0,0.8018320138,0.935365631,-3.5021401491
C,0,-0.3131599148,0.9204456869,0.1143588413
C,0,0.6835277903,1.6187229059,0.9374676459
O,0,0.8819972273,0.187600262,0.9477285889
H,0,-1.2423742646,0.6817826929,0.6217504511
H,0,1.5152064511,2.1452514883,0.4753179304
H,0,0.3591795312,2.0196550807,1.8949611338
H,0,-2.2428703399,-0.1462170782,-1.3606761972
H,0,-2.2878747308,-0.4620921176,-3.8162480665
H,0,-0.3343268521,0.226767958,-5.1931599932
H,0,1.6587829663,1.2313197042,-4.1002502443
H,0,1.7074013534,1.5539986338,-1.6597500358
C,0,0.8714847961,-0.618999148,2.3498533098
Cl,0,0.5394326777,-2.2964393012,1.7122673846
Cl,0,-0.7153174758,-0.0637877561,3.1977570957

MPW1K/6-31G*
E(RmPW+HF-PW91) = -1343.24912618

Zero-point correction= 0.149190 (Hartree/Particle)

Thermal correction to Energy= 0.159885
Thermal correction to Enthalpy= 0.160829
Thermal correction to Gibbs Free Energy= 0.110443
Sum of electronic and zero-point Energies= -1343.099936
Sum of electronic and thermal Energies= -1343.089241
Sum of electronic and thermal Enthalpies= -1343.088297
Sum of electronic and thermal Free Energies= -1343.138683

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	100.329	39.399	106.046

C,0,0.7999714815,1.1483747373,-2.1021315685
C,0,-0.2844753286,0.7455254853,-1.3238667728
C,0,-1.373551443,0.1355415389,-1.945519514
C,0,-1.3835407102,-0.0580004487,-3.310254112
C,0,-0.3017445019,0.3469569625,-4.0727900966
C,0,0.788868983,0.9476939507,-3.4654751125
C,0,-0.3348626857,0.9386879827,0.1037287279
C,0,0.7046524689,1.5288934257,0.9333580998
O,0,0.877279179,0.1251944816,0.9895142498
H,0,-1.2568328629,0.7143968838,0.6150612396
H,0,1.5531646463,2.0125543839,0.4730397328
H,0,0.4032958586,1.9644350359,1.8747942063
H,0,-2.2109186484,-0.1885917494,-1.3467440354
H,0,-2.2317928073,-0.5296878824,-3.7799104662
H,0,-0.305752695,0.1923698922,-5.1402143575
H,0,1.633526691,1.2589937595,-4.0591348517
H,0,1.659062116,1.6110665255,-1.643573496
C,0,0.8258183838,-0.6052904912,2.2507023048
Cl,0,0.4709420871,-2.2635131563,1.706311749
Cl,0,-0.6420482998,-0.0192745826,3.1574562682

MP2/6-31G*
E(RHF) = -1339.11237527

Zero-point correction= .146314 (Hartree/Particle)
Thermal correction to Energy= .157173
Thermal correction to Enthalpy= .158117
Thermal correction to Gibbs Free Energy= .107948
Sum of electronic and zero-point Energies= -1340.558955
Sum of electronic and thermal Energies= -1340.548097
Sum of electronic and thermal Enthalpies= -1340.547152
Sum of electronic and thermal Free Energies= -1340.597321

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	98.627	40.842	105.589

C,0,0.8802375502,1.2704387559,-2.1173798676
C,0,-0.1153030539,0.736801887,-1.2878702301
C,0,-1.1606114805,-0.0079791852,-1.8527889676
C,0,-1.2160470086,-0.20791734,-3.2310505326
C,0,-0.2222361506,0.3260598174,-4.0544996388
C,0,0.8229499751,1.0655312099,-3.4952470188
C,0,-0.099444859,0.898026788,0.1783689765
C,0,0.9457477957,1.5761226126,0.9576596744
O,0,0.9712039333,0.1173006845,0.8988496206
H,0,-1.0532176573,0.7816574562,0.6911332834
H,0,1.8105710843,2.0202698106,0.4764286685
H,0,0.6794815583,1.9719292126,1.9334819987
H,0,-1.9269998458,-0.4319106518,-1.2067518365
H,0,-2.0296598922,-0.786152478,-3.6612209114
H,0,-0.263345204,0.1699429994,-5.1294979777
H,0,1.5962492274,1.4840956035,-4.1343150189
H,0,1.6960960494,1.8541502365,-1.6991500473
C,0,0.7089182153,-0.8182670483,2.3788591914
Cl,0,-0.0105904106,-2.2443093238,1.572556865
Cl,0,-0.6684726887,0.0657626974,3.1734893324

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1343.41351052

Zero-point correction= 0.143489 (Hartree/Particle)
Thermal correction to Energy= 0.154812
Thermal correction to Enthalpy= 0.155756
Thermal correction to Gibbs Free Energy= 0.103701
Sum of electronic and zero-point Energies= -1343.270021
Sum of electronic and thermal Energies= -1343.258699
Sum of electronic and thermal Enthalpies= -1343.257754
Sum of electronic and thermal Free Energies= -1343.309810

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	97.146	41.395	109.560

C,0,0.8312829272,1.1628245636,-2.1374096634
C,0,-0.2436862093,0.7470092669,-1.3414923144

C,0,-1.3456341518,0.1369968018,-1.9545713149
C,0,-1.3769877445,-0.0460353714,-3.3296171227
C,0,-0.3037878399,0.3713696756,-4.1105325526
C,0,0.7998240791,0.9735933676,-3.5108287951
C,0,-0.2724354498,0.9279162497,0.1078353695
C,0,0.7424187734,1.5957066269,0.924931737
O,0,0.8949901961,0.1594651485,0.9390022032
H,0,-1.2058267499,0.7218227153,0.6155589203
H,0,1.5873389643,2.0916052009,0.4609945662
H,0,0.431742135,2.0074331767,1.8789193
H,0,-2.1766855131,-0.197318173,-1.3444115122
H,0,-2.2354210694,-0.5181999754,-3.7912372833
H,0,-0.3248574395,0.2266085425,-5.1838741723
H,0,1.6373574892,1.2963425239,-4.117002496
H,0,1.6998132392,1.6261071458,-1.6866456691
C,0,0.8288297419,-0.6352326973,2.3648382652
Cl,0,0.4768335696,-2.3046581956,1.7505318598
Cl,0,-0.7434410626,-0.0444602305,3.1657480855

Alternative transition state 21

B3LYP/6-31G*
E(RB+HF-LYP) = -1343.21908262

Zero-point correction= 0.144873 (Hartree/Particle)
Thermal correction to Energy= 0.156048
Thermal correction to Enthalpy= 0.156992
Thermal correction to Gibbs Free Energy= 0.105646
Sum of electronic and zero-point Energies= -1343.074210
Sum of electronic and thermal Energies= -1343.063034
Sum of electronic and thermal Enthalpies= -1343.062090
Sum of electronic and thermal Free Energies= -1343.113437

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	97.922	41.078	108.068

C,0,1.2755248459,0.7160454526,-3.5163944678
C,0,1.002540191,1.0148709068,-2.1882432398
C,0,-0.2430189624,0.6618847355,-1.6210281445
C,0,-1.1998198615,0.0036001444,-2.4273801134
C,0,-0.9253027252,-0.2809258653,-3.7585499099
C,0,0.3135500205,0.0720796744,-4.303452967

C,0,-0.5877585411,0.9489242317,-0.25890356
O,0,0.3882996898,0.0848374873,1.0618922952
C,0,-0.5464914161,-0.3057742549,2.1767359958
Cl,0,0.4858115243,0.2138718474,3.6672499388
C,0,0.2759604771,1.506319318,0.7821606133
Cl,0,-0.4537476655,-2.1339990364,2.0530793849
H,0,-1.5843698308,0.6964071427,0.0904368116
H,0,1.246400085,1.9114591832,0.5047219453
H,0,-0.2043667885,2.0523064244,1.5908926027
H,0,-2.1548752806,-0.2778827847,-1.9925425653
H,0,-1.6676893073,-0.7838077426,-4.3706534537
H,0,0.5317220096,-0.1560397715,-5.3428971673
H,0,2.2365172079,0.9844997898,-3.9445955192
H,0,1.7540746171,1.5143740126,-1.5857647588

MPW1K/6-31G*
E(RmPW+HF-PW91) = -1343.23934014

Zero-point correction= 0.149193 (Hartree/Particle)
Thermal correction to Energy= 0.159898
Thermal correction to Enthalpy= 0.160842
Thermal correction to Gibbs Free Energy= 0.110515
Sum of electronic and zero-point Energies= -1343.090147
Sum of electronic and thermal Energies= -1343.079442
Sum of electronic and thermal Enthalpies= -1343.078498
Sum of electronic and thermal Free Energies= -1343.128825

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	100.337	39.417	105.922

C,0,1.2747221494,0.7222447785,-3.5174479169
C,0,1.0091138157,1.0081637462,-2.1985332263
C,0,-0.2180125358,0.6411116423,-1.6327586949
C,0,-1.1646739753,-0.0178550633,-2.4275221086
C,0,-0.8983330134,-0.2889739244,-3.7497426308
C,0,0.322390379,0.0781383436,-4.2936840473
C,0,-0.550452254,0.9072461402,-0.2781543965
O,0,0.4046002486,0.0271077427,1.078093077
C,0,-0.4900131815,-0.3128705148,2.134016035
Cl,0,0.3784712098,0.2811192743,3.6280458537
C,0,0.3221839741,1.4209123373,0.7565763466
Cl,0,-0.4542102364,-2.0956858843,2.1212523015
H,0,-1.5294327346,0.6328348446,0.0848303747

H,0,1.2971115422,1.7865472877,0.4711095497
H,0,-0.1316713268,1.9971851274,1.5491888454
H,0,-2.1054704828,-0.3116708151,-1.9884753557
H,0,-1.6324333448,-0.793475592,-4.3567571369
H,0,0.5353737671,-0.1406115471,-5.3283201765
H,0,2.2227898142,1.0005629873,-3.9485147365
H,0,1.7529420802,1.5106932244,-1.6023707796

MP2/6-31G*
E(RHF) = -1339.08695704

Zero-point correction= .146195 (Hartree/Particle)
Thermal correction to Energy= .157249
Thermal correction to Enthalpy= .158193
Thermal correction to Gibbs Free Energy= .106969
Sum of electronic and zero-point Energies= -1340.532706
Sum of electronic and thermal Energies= -1340.521651
Sum of electronic and thermal Enthalpies= -1340.520707
Sum of electronic and thermal Free Energies= -1340.571931

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	98.675	40.921	107.811

C,0,1.2956378626,0.7609371554,-3.5888394994
C,0,1.0445472074,1.0516924055,-2.2511625368
C,0,-0.1703590102,0.648348669,-1.6570017508
C,0,-1.1218035214,-0.039748194,-2.4428264535
C,0,-0.8668193128,-0.307027175,-3.7828646112
C,0,0.3452701515,0.0852829357,-4.3605069545
C,0,-0.4856903742,0.8849222074,-0.2783740196
O,0,0.4438860941,-0.0677468299,1.1149113899
C,0,-0.4474887412,-0.3389020357,2.147098702
Cl,0,0.2889503759,0.3432399547,3.6421785589
C,0,0.4089735732,1.3977932159,0.7281626324
Cl,0,-0.5503912691,-2.1042283649,2.2047364974
H,0,-1.4714917297,0.6185272437,0.0944577111
H,0,1.4200496387,1.6701499095,0.4391299228
H,0,0.0214718949,1.9920651786,1.5494321889
H,0,-2.0566026788,-0.3572172416,-1.985243754
H,0,-1.6076698224,-0.8339014597,-4.378836869
H,0,0.5474618648,-0.1326696134,-5.4062077365
H,0,2.2365021588,1.0697568435,-4.0375209641
H,0,1.7900780963,1.5922716451,-1.6741706277

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1343.40699403

Zero-point correction= 0.143843 (Hartree/Particle)
Thermal correction to Energy= 0.155045
Thermal correction to Enthalpy= 0.155989
Thermal correction to Gibbs Free Energy= 0.104617
Sum of electronic and zero-point Energies= -1343.263151
Sum of electronic and thermal Energies= -1343.251949
Sum of electronic and thermal Enthalpies= -1343.251005
Sum of electronic and thermal Free Energies= -1343.302377

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	97.292	41.244	108.121

C,0,1.2692914803,0.7154474373,-3.4965524301
C,0,0.9925954914,1.0161628823,-2.1746889758
C,0,-0.2509088476,0.6671902266,-1.6139677661
C,0,-1.2014961389,0.0091958348,-2.418690352
C,0,-0.9228395296,-0.2783809751,-3.7433092617
C,0,0.3134738877,0.0720536803,-4.282472278
C,0,-0.5986541096,0.956284204,-0.2557321911
O,0,0.375923084,0.0948583949,1.051701235
C,0,-0.5332346984,-0.2989074759,2.1808086342
Cl,0,0.527404061,0.1782843576,3.6474902877
C,0,0.2626050119,1.5189413012,0.7779906541
Cl,0,-0.4744676883,-2.1195354103,2.0423661204
H,0,-1.5958698133,0.7097932314,0.0870928671
H,0,1.2279019635,1.9244549451,0.4966924203
H,0,-0.2145236539,2.0577122626,1.5892121212
H,0,-2.1550533588,-0.2716473585,-1.9875719182
H,0,-1.6603630436,-0.7818115321,-4.3555342625
H,0,0.5349715585,-0.1585322855,-5.3175763192
H,0,2.2293893594,0.980678843,-3.9211205751
H,0,1.7412486981,1.5138299376,-1.5726793535

Alternative transition state 22

B3LYP/6-31G*
E(RB+HF-LYP) = -1343.21882592

Zero-point correction= 0.144312 (Hartree/Particle)
Thermal correction to Energy= 0.155679
Thermal correction to Enthalpy= 0.156624
Thermal correction to Gibbs Free Energy= 0.104188
Sum of electronic and zero-point Energies= -1343.074514
Sum of electronic and thermal Energies= -1343.063146
Sum of electronic and thermal Enthalpies= -1343.062202
Sum of electronic and thermal Free Energies= -1343.114638

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	97.690	41.403	110.360

C,0,-0.5413907667,0.2067825727,-3.5017958563
C,0,0.3842537162,1.0014205439,-2.8202010861
C,0,0.1991873741,1.2938691308,-1.4723245785
C,0,-0.9190748041,0.7928029211,-0.7857791314
C,0,-1.8504997576,0.0049839465,-1.4849527487
C,0,-1.6606821709,-0.2912105554,-2.8314571277
C,0,-1.2091799191,1.1134480478,0.6170379253
C,0,-0.3082841673,1.7490556617,1.5902432714
O,0,-0.4747774856,0.3435171812,1.8505262203
C,0,0.8221823845,-0.681231621,2.2085175926
Cl,0,0.1420087605,-2.2455211337,1.5702205958
Cl,0,2.2042765028,-0.186445549,1.0591103467
H,0,-2.2566299728,1.071733161,0.8986750031
H,0,0.6984572684,2.0112152198,1.2718511036
H,0,-0.7145367471,2.3827532495,2.3769971154
H,0,-2.7212939518,-0.3813724483,-0.9614137163
H,0,-2.384261457,-0.9074602557,-3.3569913966
H,0,-0.3913261924,-0.0210031385,-4.5533909607
H,0,1.2533470194,1.3932415427,-3.340412232
H,0,0.9285431071,1.9066649381,-0.9538802655

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1343.40471203

Zero-point correction= 0.143149 (Hartree/Particle)
Thermal correction to Energy= 0.154578
Thermal correction to Enthalpy= 0.155522
Thermal correction to Gibbs Free Energy= 0.102990
Sum of electronic and zero-point Energies= -1343.261563
Sum of electronic and thermal Energies= -1343.250134
Sum of electronic and thermal Enthalpies= -1343.249190

Sum of electronic and thermal Free Energies= -1343.301722

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	96.999	41.647	110.562

C,0,-0.5637856652,0.1922312153,-3.4929730378
C,0,0.3724988271,0.9594460713,-2.8042861394
C,0,0.1828735673,1.2549533608,-1.4630162788
C,0,-0.9507433625,0.7861482344,-0.7890812507
C,0,-1.8920991047,0.0257207592,-1.4960876463
C,0,-1.6985548962,-0.2737489107,-2.8361950082
C,0,-1.2413134238,1.1047302697,0.6083847745
C,0,-0.3452481554,1.7317406465,1.5826437632
O,0,-0.4929051568,0.3258067041,1.8500274568
C,0,0.8373729741,-0.6849733177,2.2003672057
Cl,0,0.2245094179,-2.2448717363,1.5255542573
Cl,0,2.2200699802,-0.1388467089,1.1076857787
H,0,-2.2844359478,1.0535325915,0.8924828524
H,0,0.6547457475,2.0034682441,1.2613189922
H,0,-0.7549561519,2.360910292,2.3668627703
H,0,-2.7753545308,-0.3379254413,-0.9835068295
H,0,-2.4301771861,-0.8693631783,-3.3680436376
H,0,-0.4089955283,-0.0396909185,-4.5398283788
H,0,1.254650849,1.3257687582,-3.3147102248
H,0,0.9239096718,1.8425696148,-0.9384141032

Styrene

B3LYP/6-31G*
E(RB+HF-LYP) = -309.648258855

Zero-point correction= 0.133731 (Hartree/Particle)
Thermal correction to Energy= 0.140501
Thermal correction to Enthalpy= 0.141445
Thermal correction to Gibbs Free Energy= 0.102256
Sum of electronic and zero-point Energies= -309.514528
Sum of electronic and thermal Energies= -309.507758
Sum of electronic and thermal Enthalpies= -309.506814
Sum of electronic and thermal Free Energies= -309.546003

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	88.166	26.029	82.481

C,0,0.7709302491,-0.1931408146,-1.9063976365
C,0,-0.458630052,-0.0606152387,-1.2622047616
C,0,-0.5413889633,0.0483680005,0.1364373714
C,0,0.6580361081,0.0203260366,0.8718023219
C,0,1.886119592,-0.1118103329,0.2311675372
C,0,1.9500215061,-0.2194140999,-1.1617171594
C,0,-1.8671843589,0.185673576,0.761710571
C,0,-2.1498511944,0.2949503875,2.0659223979
H,0,0.629494604,0.1030866742,1.9544659593
H,0,2.7996841265,-0.1309695447,0.8198555178
H,0,2.9107153378,-0.3223952302,-1.6589337131
H,0,0.8066672599,-0.2757023676,-2.9895454103
H,0,-2.6983479437,0.1962505784,0.0562245392
H,0,-3.1759007699,0.3915240728,2.4074396825
H,0,-1.3859949297,0.2929832399,2.8388679468
H,0,-1.3746350051,-0.0408025096,-1.8486983729

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -309.739345231

Zero-point correction= 0.132747 (Hartree/Particle)
Thermal correction to Energy= 0.139546
Thermal correction to Enthalpy= 0.140491
Thermal correction to Gibbs Free Energy= 0.101229
Sum of electronic and zero-point Energies= -309.606599
Sum of electronic and thermal Energies= -309.599799
Sum of electronic and thermal Enthalpies= -309.598855
Sum of electronic and thermal Free Energies= -309.638116

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	87.567	26.162	82.632

C,0,0.7692492571,-0.1923779671,-1.9001893769
C,0,-0.4566635767,-0.0603982382,-1.2581073768
C,0,-0.5392749393,0.0480268138,0.1357370506
C,0,0.6559938281,0.0199839588,0.8686649903
C,0,1.879834563,-0.1115544344,0.2303143321
C,0,1.9438814401,-0.2186107231,-1.1580588338
C,0,-1.8629561721,0.1850285196,0.7602635415
C,0,-2.1432567766,0.2943478758,2.0593379549
H,0,0.6293329762,0.1021031999,1.9482443333

H,0,2.7911026857,-0.1308091042,0.8166666371
H,0,2.9018140299,-0.3211929069,-1.6536620129
H,0,0.8057458036,-0.2745762455,-2.9801252747
H,0,-2.6932489305,0.1952491587,0.0584613225
H,0,-3.1667428109,0.3903534612,2.3984840919
H,0,-1.379157593,0.2928069189,2.8275213198
H,0,-1.369691902,-0.0406093141,-1.8433641087

Phosgene

B3LYP/6-31G*
E(RB+HF-LYP) = -1033.71437719

Zero-point correction= 0.010503 (Hartree/Particle)
Thermal correction to Energy= 0.014455
Thermal correction to Enthalpy= 0.015399
Thermal correction to Gibbs Free Energy= -0.017458
Sum of electronic and zero-point Energies= -1033.703875
Sum of electronic and thermal Energies= -1033.699922
Sum of electronic and thermal Enthalpies= -1033.698978
Sum of electronic and thermal Free Energies= -1033.731835

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	9.071	11.837	69.153

C,0,-0.3898664893,0.,-0.3164925357
Cl,0,-0.546825253,0.,1.4424045499
Cl,0,1.2993605549,0.,-0.8314239494
O,0,-1.3067376495,0.,-1.0609643744

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1033.81206656

Zero-point correction= 0.010389 (Hartree/Particle)
Thermal correction to Energy= 0.014361
Thermal correction to Enthalpy= 0.015306
Thermal correction to Gibbs Free Energy= -0.017579
Sum of electronic and zero-point Energies= -1033.801677
Sum of electronic and thermal Energies= -1033.797705
Sum of electronic and thermal Enthalpies= -1033.796761
Sum of electronic and thermal Free Energies= -1033.829646

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	9.012	11.904	69.212

C,0,-0.393279468,0.,-0.3192978655
Cl,0,-0.5457815551,0.,1.4401076677
Cl,0,1.297312974,0.,-0.8299296426
O,0,-1.3020446642,0.,-1.0571549042

(2,2-Dichlorocyclopropyl)benzene (19)

B3LYP/6-31G*
E(RB+HF-LYP) = -1268.12975277

Zero-point correction= 0.144292 (Hartree/Particle)
Thermal correction to Energy= 0.153996
Thermal correction to Enthalpy= 0.154941
Thermal correction to Gibbs Free Energy= 0.107150
Sum of electronic and zero-point Energies= -1267.985461
Sum of electronic and thermal Energies= -1267.975756
Sum of electronic and thermal Enthalpies= -1267.974812
Sum of electronic and thermal Free Energies= -1268.022602

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	96.634	36.795	100.583

C,0,3.0734732101,0.7308725402,-1.9289101277
C,0,1.8910435136,0.6426024704,-2.6656729841
C,0,0.6594172422,0.6556002325,-2.0134932663
C,0,0.5840459083,0.7539004869,-0.6157594249
C,0,1.7772542361,0.8458605758,0.1120453683
C,0,3.0111293479,0.8327952862,-0.5386912781
C,0,-0.7692019285,0.7655353305,0.0194359543
C,0,-1.0329446508,1.0148787028,1.5004599763
H,0,1.7513052688,0.930552153,1.1940781699
H,0,3.9251695428,0.9062803731,0.044392453
H,0,4.0352465408,0.7235372591,-2.4344103936
H,0,1.9261327916,0.5662122682,-3.7491046466
H,0,-1.544924063,1.1496098607,-0.6391356066
H,0,-1.8871423464,1.6289968981,1.7694214056
H,0,-0.1845797241,1.1009847315,2.1726794108
H,0,-0.2581908756,0.5881110732,-2.5932142182

C,0,-1.2975584879,-0.3356473607,0.9224610802
Cl,0,-0.2480062476,-1.6900201854,1.387947912
Cl,0,-2.9956977219,-0.8413135912,0.6993486549

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1268.28298072

Zero-point correction= 0.143048 (Hartree/Particle)
Thermal correction to Energy= 0.151918
Thermal correction to Enthalpy= 0.152862
Thermal correction to Gibbs Free Energy= 0.108025
Sum of electronic and zero-point Energies= -1268.139933
Sum of electronic and thermal Energies= -1268.131063
Sum of electronic and thermal Enthalpies= -1268.130119
Sum of electronic and thermal Free Energies= -1268.174956

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	95.330	35.067	94.367

C,0,3.0815684166,0.7120092619,-1.8734987243
C,0,1.9022615348,0.5566946023,-2.5946699956
C,0,0.677866313,0.592181881,-1.9418204743
C,0,0.6076352497,0.7778441882,-0.5577671786
C,0,1.796101013,0.9376308159,0.1536192205
C,0,3.0235715202,0.9042163184,-0.4986965042
C,0,-0.7393940175,0.8080779351,0.0843192811
C,0,-0.9822032614,0.9465834978,1.5802570799
H,0,1.7724546199,1.09646102,1.2243580144
H,0,3.9364367039,1.0323125251,0.0708657492
H,0,4.038500088,0.6868490225,-2.3808836439
H,0,1.9357719834,0.410221697,-3.6677734152
H,0,-1.49904825,1.2750415911,-0.5324647903
H,0,-1.8072745528,1.5667494021,1.9040831103
H,0,-0.1297412605,0.9372687374,2.2457634365
H,0,-0.2380242865,0.4720780045,-2.5099157134
C,0,-1.3025486897,-0.334914645,0.8969850645
Cl,0,-0.3014222631,-1.7580726696,1.2371322856
Cl,0,-3.0161202968,-0.7642170441,0.6542559873

Loose epoxide-CCl_2 complex

B3LYP/6-31G*
E(RB+HF-LYP) = -1343.23654742

Zero-point correction= 0.144799 (Hartree/Particle)
Thermal correction to Energy= 0.157029
Thermal correction to Enthalpy= 0.157973
Thermal correction to Gibbs Free Energy= 0.102538
Sum of electronic and zero-point Energies= -1343.091749
Sum of electronic and thermal Energies= -1343.079518
Sum of electronic and thermal Enthalpies= -1343.078574
Sum of electronic and thermal Free Energies= -1343.134009

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	98.537	42.643	116.673

C,0,1.2387105664,0.451012252,-3.5106089094
C,0,0.9687490856,0.5931165192,-2.1505234469
C,0,-0.3415352407,0.4569764738,-1.6740808986
C,0,-1.3719377642,0.1652987604,-2.5757421913
C,0,-1.1013384743,0.0303850831,-3.9377268532
C,0,0.2046754515,0.1740812627,-4.4084258496
C,0,-0.664795851,0.635854666,-0.2306724062
O,0,0.42813537,0.4894387815,0.712875609
C,0,-0.4974716984,-0.3882241105,2.6171989453
Cl,0,0.7613993274,0.1426070054,3.7513545621
C,0,-0.191199895,1.782075929,0.566580015
Cl,0,-0.2400834426,-2.1048710597,2.2542900619
H,0,-1.5801476184,0.1574531654,0.1156675676
H,0,0.4463792086,2.530728774,0.1000761871
H,0,-0.7679351879,2.1008388015,1.4325871836
H,0,-2.38916101,0.0443419212,-2.2100357798
H,0,-1.909472737,-0.1942293502,-4.6285020948
H,0,0.4175380387,0.0633272051,-5.4681731974
H,0,2.2593413492,0.5511463958,-3.8700524807
H,0,1.7728678748,0.7859107433,-1.4465212957

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1343.42455768

Zero-point correction= 0.143214 (Hartree/Particle)
Thermal correction to Energy= 0.155831
Thermal correction to Enthalpy= 0.156775
Thermal correction to Gibbs Free Energy= 0.099201

Sum of electronic and zero-point Energies= -1343.281344
Sum of electronic and thermal Energies= -1343.268727
Sum of electronic and thermal Enthalpies= -1343.267782
Sum of electronic and thermal Free Energies= -1343.325357

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	97.786	43.008	121.175

C,0,3.6097639954,-0.5208339198,-1.2654327898
C,0,2.2922561303,-0.7010653513,-0.8623333816
C,0,1.8217297294,-0.0889554578,0.3006708818
C,0,2.6868997328,0.715702981,1.0429808711
C,0,4.0070688328,0.8906489357,0.6423171169
C,0,4.4724768267,0.2712735905,-0.5126758866
C,0,0.4243615058,-0.2854880381,0.7725699432
O,0,-0.5425753369,-0.7612673379,-0.1843273769
C,0,-2.7791343808,0.3205773591,0.5656229005
Cl,0,-3.8407498907,-0.8522954491,-0.1732074613
C,0,-0.1901161475,-1.6151329649,0.9139857156
Cl,0,-2.7030781194,1.7397747404,-0.4455981246
H,0,0.0344419329,0.497740734,1.4173537193
H,0,0.3868902045,-2.4923813104,0.6375549241
H,0,-0.9789544754,-1.7627542905,1.6451025403
H,0,2.325262641,1.2090029761,1.9388882018
H,0,4.6694211395,1.5164735139,1.2286272538
H,0,5.4989586446,0.4115768883,-0.8296797599
H,0,3.9633745367,-0.9953558199,-2.1732414702
H,0,1.614446893,-1.3016747462,-1.4565236591

Epoxide of cis-2-butene

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -232.504089410

Zero-point correction= 0.112931 (Hartree/Particle)
Thermal correction to Energy= 0.118792
Thermal correction to Enthalpy= 0.119736
Thermal correction to Gibbs Free Energy= 0.084326
Sum of electronic and zero-point Energies= -232.391158
Sum of electronic and thermal Energies= -232.385297
Sum of electronic and thermal Enthalpies= -232.384353
Sum of electronic and thermal Free Energies= -232.419763

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	74.543	20.496	74.527

C,0,-0.4273190138,-0.3339860421,-0.736021202
C,0,-0.4262363086,-0.3355953367,0.7358915204
C,0,0.7658783234,-0.0313769644,1.6002240691
C,0,0.763634982,-0.0280385755,-1.6013559688
O,0,-1.0121934224,0.7550634059,0.0015081963
H,0,0.4483471709,0.4966383172,2.5029178668
H,0,1.2534429509,-0.9599186724,1.9109868263
H,0,1.4967801364,0.5918258832,1.0868267476
H,0,0.4446711472,0.4998640913,-2.5036074375
H,0,1.4941382689,0.5959682309,-1.088363321
H,0,1.2521294126,-0.9558564366,-1.9128308182
H,0,-1.1747225534,-0.9662259639,-1.2149962863
H,0,-1.1729870523,-0.9688211848,1.2145703397

Transition structure 23

B3LYP/6-31G*
E(RB+HF-LYP) = -1190.80836503

Zero-point correction= 0.119149 (Hartree/Particle)
Thermal correction to Energy= 0.128998
Thermal correction to Enthalpy= 0.129943
Thermal correction to Gibbs Free Energy= 0.082991
Sum of electronic and zero-point Energies= -1190.689216
Sum of electronic and thermal Energies= -1190.679367
Sum of electronic and thermal Enthalpies= -1190.678422
Sum of electronic and thermal Free Energies= -1190.725374

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	80.948	33.598	98.818

C,0,1.5932644364,1.6478224545,-1.6412134097
C,0,0.3333460791,1.3395988514,-0.9112118019
O,0,0.5446501257,0.1336901082,0.3551807079
C,0,-0.2520109641,-1.0417609173,0.728765104
Cl,0,-2.0397664344,-0.7087880075,0.3111398861
C,0,0.1011165419,1.5228554643,0.5309880715

Cl,0,0.3354420406,-2.2977913447,-0.461503226
H,0,-0.5320474616,1.0171573169,-1.4814894965
C,0,1.0058487033,2.3142550731,1.4399762575
H,0,-0.9483669063,1.5526065057,0.8193608433
H,0,1.4865787181,2.6109661225,-2.1641974232
H,0,1.7970364015,0.8862475465,-2.3999688527
H,0,2.4567975333,1.7213409834,-0.9762996095
H,0,0.8807812552,1.9697924873,2.4707101548
H,0,2.0586610874,2.2141744881,1.1668723956
H,0,0.7274842816,3.3734171167,1.3959177753

B3LYP/6-311++G(2d,p)
E(RB+HF-LYP) = -1190.95586317

Zero-point correction= 0.117924 (Hartree/Particle)
Thermal correction to Energy= 0.127814
Thermal correction to Enthalpy= 0.128758
Thermal correction to Gibbs Free Energy= 0.081716
Sum of electronic and zero-point Energies= -1190.837939
Sum of electronic and thermal Energies= -1190.828049
Sum of electronic and thermal Enthalpies= -1190.827105
Sum of electronic and thermal Free Energies= -1190.874147

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	80.204	33.820	99.008

C,0,1.5898182257,1.6449662168,-1.6290107539
C,0,0.3385358176,1.3249366943,-0.8995380953
O,0,0.5548225251,0.131734763,0.3580942393
C,0,-0.2594922527,-1.041074114,0.725420219
Cl,0,-2.0288147127,-0.703102448,0.2935796814
C,0,0.1072667757,1.519159201,0.5371312096
Cl,0,0.32065414,-2.2992225598,-0.4545851287
H,0,-0.5263697974,1.0050763358,-1.4663253377
C,0,1.005538108,2.3212899335,1.4343038968
H,0,-0.9397539622,1.5431856934,0.8234655371
H,0,1.4822362682,2.6254625429,-2.1117620191
H,0,1.7775248945,0.9139828183,-2.4160665878
H,0,2.4580105766,1.6891809254,-0.9734083958
H,0,0.8798925036,1.9944021758,2.4671486738
H,0,2.0559529358,2.223259646,1.1649284207
H,0,0.7226560688,3.375429302,1.3745195398

Alternative transition structure 24

B3LYP/6-31G*
E(RB+HF-LYP) = -1190.79290751

Zero-point correction= 0.118919 (Hartree/Particle)
Thermal correction to Energy= 0.128776
Thermal correction to Enthalpy= 0.129720
Thermal correction to Gibbs Free Energy= 0.082705
Sum of electronic and zero-point Energies= -1190.673989
Sum of electronic and thermal Energies= -1190.664131
Sum of electronic and thermal Enthalpies= -1190.663187
Sum of electronic and thermal Free Energies= -1190.710202

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	80.808	33.632	98.951

C,0,2.0711834237,-1.5792710378,1.7275198937
C,0,0.7780516321,-1.5773845264,1.0086744848
O,0,0.3931713987,0.0266838422,0.0696038675
C,0,-0.9750682762,0.4066024601,0.1962663067
Cl,0,-1.5164168466,0.6931112982,-1.5662646396
C,0,0.5710552145,-1.3748765817,-0.4244334459
C,0,1.6905532511,-1.446202316,-1.4291846881
Cl,0,-0.8676817963,2.000825324,1.0619819736
H,0,2.1003047338,-0.7697684033,2.4691906641
H,0,2.1559907087,-2.5183807741,2.2952400096
H,0,2.9373980446,-1.4960280126,1.068846811
H,0,1.375704043,-0.950592991,-2.3514769579
H,0,2.5996823623,-0.9594170948,-1.0677439725
H,0,1.9155088014,-2.4949207472,-1.6550113711
H,0,-0.3793855202,-1.7411265138,-0.8064901657
H,0,-0.1355489051,-1.6533667672,1.5903640575

Trans-β-methylstyrene (27)

B3LYP/6-31G*
E(RB+HF-LYP) = -348.968043718

Zero-point correction= 0.161954 (Hartree/Particle)
Thermal correction to Energy= 0.170303
Thermal correction to Enthalpy= 0.171247

Thermal correction to Gibbs Free Energy= 0.127992
Sum of electronic and zero-point Energies= -348.806090
Sum of electronic and thermal Energies= -348.797741
Sum of electronic and thermal Enthalpies= -348.796797
Sum of electronic and thermal Free Energies= -348.840052

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	106.867	31.343	91.038

C,0,0.8762098441,1.006259444,0.6186028698
C,0,1.0354987319,1.0142054004,1.9504502609
C,0,1.8996482582,1.986932795,2.6972311738
C,0,0.0513864756,0.0909500988,-0.185531929
H,0,0.5161205147,0.2771812322,2.5630567299
H,0,1.4127286489,1.7595829161,0.0394349774
H,0,1.3130028758,2.5635649367,3.4258830335
H,0,2.6816905761,1.4681524138,3.2689554315
H,0,2.3883854934,2.6947263955,2.0192584707
C,0,0.0239079132,0.2541383495,-1.5818481315
C,0,-0.7388324287,-0.5825009934,-2.3955029505
C,0,-1.496486147,-1.6078420142,-1.8295065391
C,0,-1.4815687346,-1.7852355727,-0.4426298833
C,0,-0.7195731503,-0.9490438657,0.3677401315
H,0,0.6120074203,1.05142835,-2.0312262153
H,0,-0.7404288561,-0.4322792493,-3.4720674635
H,0,-2.0926185841,-2.2625572009,-2.4593589351
H,0,-2.068224036,-2.5809832434,0.0094547361
H,0,-0.7238086277,-1.1059984005,1.442579219

B3LYP/6-31+G**
E(RB+HF-LYP) = -348.996549701

Zero-point correction= 0.161254 (Hartree/Particle)
Thermal correction to Energy= 0.169587
Thermal correction to Enthalpy= 0.170531
Thermal correction to Gibbs Free Energy= 0.127697
Sum of electronic and zero-point Energies= -348.835296
Sum of electronic and thermal Energies= -348.826963
Sum of electronic and thermal Enthalpies= -348.826019
Sum of electronic and thermal Free Energies= -348.868852

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total	106.417	31.482	90.151

C,0,0.8776665082,1.0079336552,0.6186635853
C,0,1.0372196014,1.0162209327,1.952398851
C,0,1.9015154242,1.9888958836,2.7002187015
C,0,0.0516324279,0.0911879207,-0.1856847512
H,0,0.5172490426,0.2789746498,2.5636987989
H,0,1.4140851567,1.760864747,0.0395947377
H,0,1.3134382973,2.5635389538,3.4278862867
H,0,2.6816157323,1.4683126427,3.2711664062
H,0,2.3905689705,2.6966866661,2.0234561724
C,0,0.0238478402,0.2543046539,-1.5832362097
C,0,-0.7400418117,-0.5835420648,-2.397904661
C,0,-1.4985163575,-1.6100304134,-1.8314334634
C,0,-1.4830160493,-1.7870983272,-0.4427704376
C,0,-0.7199180956,-0.9497183484,0.3682132193
H,0,0.6112228046,1.0508865111,-2.0336031819
H,0,-0.7417760023,-0.4334618279,-3.4739082371
H,0,-2.0944308702,-2.2644904314,-2.4607294861
H,0,-2.0692408539,-2.5823709657,0.0093462088
H,0,-0.7250692042,-1.1078642993,1.442303289

Cis-β-methylstyrene

E(RB+HF-LYP) = -348.963675765

Zero-point correction= 0.162382 (Hartree/Particle)
Thermal correction to Energy= 0.170490
Thermal correction to Enthalpy= 0.171435
Thermal correction to Gibbs Free Energy= 0.129243
Sum of electronic and zero-point Energies= -348.801294
Sum of electronic and thermal Energies= -348.793185
Sum of electronic and thermal Enthalpies= -348.792241
Sum of electronic and thermal Free Energies= -348.834433

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	106.984	31.052	88.800

C,0,0.5654023694,1.2828633604,0.89245624
C,0,0.008671306,0.4707563178,-0.1134065692
C,0,0.5605415802,-0.80949664,-0.3029761999
C,0,1.6010584549,-1.2688837315,0.5042891275

C,0,2.1218791624,-0.4588584757,1.51460575
C,0,1.6016550169,0.8239014934,1.7019300847
C,0,-1.0872657166,1.0132331247,-0.938256248
C,0,-2.1319310374,0.3719626492,-1.4898437489
C,0,-2.506193326,-1.0793995084,-1.3781188424
H,0,-3.5897291665,-1.1805304423,-1.2389728146
H,0,-2.2572399091,-1.6345142788,-2.2942633128
H,0,-2.0071464896,-1.5751047348,-0.5411294084
H,0,0.1670909983,2.2838413372,1.0425825983
H,0,2.0071054981,1.4689684895,2.4772289113
H,0,2.9337231935,-0.8180847781,2.1413273852
H,0,2.013788985,-2.2601254638,0.3344606261
H,0,0.1961123038,-1.4360315597,-1.1102641178
H,0,-2.8226176091,0.9820382223,-2.0721174214
H,0,-1.0439946623,2.0930716689,-1.0829300083

Styrene

E(RB+HF-LYP) = -309.648271016

Zero-point correction= 0.133718 (Hartree/Particle)
Thermal correction to Energy= 0.140502
Thermal correction to Enthalpy= 0.141446
Thermal correction to Gibbs Free Energy= 0.102109
Sum of electronic and zero-point Energies= -309.514553
Sum of electronic and thermal Energies= -309.507769
Sum of electronic and thermal Enthalpies= -309.506825
Sum of electronic and thermal Free Energies= -309.546162

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	88.166	26.031	82.791

C,0,-1.0751480168,0.,-1.5714576142
C,0,-1.0783422225,0.,-0.1798993656
C,0,0.1273824495,0.,0.545548821
C,0,1.331290702,0.,-0.1797904339
C,0,1.3370209296,0.,-1.5741414443
C,0,0.1322440143,0.,-2.2769899247
C,0,0.1854747248,0.,2.0170600015
C,0,-0.8410661494,0.,2.8764437845
H,0,-0.6705965413,0.,3.9486122711
H,0,-1.8797033981,0.,2.5571597144

H,0,1.1958388217,0.,2.4265283772
H,0,2.2742844354,0.,0.3624769654
H,0,2.2825035922,0.,-2.1102299519
H,0,0.1308723801,0.,-3.3636259791
H,0,-2.0191162884,0.,-2.110378929
H,0,-2.0272215908,0.,0.3488145855

Shi's original catalyst ketone (25)

E(RB+HF-LYP) = -919.433549646

Zero-point correction= 0.299586 (Hartree/Particle)
Thermal correction to Energy= 0.316585
Thermal correction to Enthalpy= 0.317529
Thermal correction to Gibbs Free Energy= 0.255639
Sum of electronic and zero-point Energies= -919.133963
Sum of electronic and thermal Energies= -919.116965
Sum of electronic and thermal Enthalpies= -919.116020
Sum of electronic and thermal Free Energies= -919.177911

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	198.660	66.574	130.259

O,0,-0.1977930939,2.6713951744,-0.1804751089
C,0,-0.2396746584,1.687948108,0.8465842803
C,0,-1.2743934297,0.7088050373,0.263470203
O,0,-2.2016828418,1.5607436839,-0.3706124438
C,0,-1.5224538751,2.790030813,-0.7185853357
C,0,1.141115811,1.0999178824,1.1051574021
O,0,1.5928934581,0.2127156119,0.0802547242
C,0,0.711959724,-0.8716530785,-0.1753205657
C,0,-0.6007891842,-0.2683031416,-0.7109076418
C,0,1.4220868003,-1.8631166743,-1.1125385027
O,0,1.3509947511,-3.1128439771,-0.4366010984
C,0,1.1629335877,-2.853476818,0.9443293647
O,0,0.3986018475,-1.6210582912,0.9810278018
C,0,0.3084886072,-3.9608399142,1.5365124608
C,0,2.4974673862,-2.6596447674,1.6686665815
O,0,-1.0272960778,-0.5090169351,-1.8179609164
C,0,-1.4153556485,2.9322412669,-2.2307811464
C,0,-2.2755760893,3.9425815677,-0.0574666005
H,0,0.8365964132,-4.9163086635,1.4650879216

H,0,0.0933656806,-3.7564759153,2.589594029
H,0,-0.6312521755,-4.0326698428,0.9833834369
H,0,3.088554814,-3.579242641,1.6126349085
H,0,3.0688140938,-1.8453896474,1.2142987449
H,0,2.3271327653,-2.4156402199,2.7222663003
H,0,-2.4144292578,3.0174724091,-2.6687558299
H,0,-0.8419944521,3.8297772314,-2.4840015567
H,0,-0.9209417117,2.0564951052,-2.6552206519
H,0,-3.3146075734,3.9576852758,-0.4007850018
H,0,-2.2758328369,3.8268164493,1.0307372346
H,0,-1.8058125669,4.898028877,-0.3108799127
H,0,2.4561698529,-1.5340502922,-1.2691585111
H,0,0.90849444,-1.9553800818,-2.0707031869
H,0,-1.7865997571,0.1251029254,1.0375641386
H,0,-0.6171384952,2.1226195847,1.7864184533
H,0,1.1276152351,0.5763405105,2.0687287464
H,0,1.8812670004,1.9023951145,1.1490040718

Dioxirane isomer # 1 (lowest energy) (29a-chair)

B3LYP/6-31G*
E(RB+HF-LYP) = -994.546993362

Zero-point correction= 0.303460 (Hartree/Particle)
Thermal correction to Energy= 0.321067
Thermal correction to Enthalpy= 0.322011
Thermal correction to Gibbs Free Energy= 0.258893
Sum of electronic and zero-point Energies= -994.243534
Sum of electronic and thermal Energies= -994.225926
Sum of electronic and thermal Enthalpies= -994.224982
Sum of electronic and thermal Free Energies= -994.288101

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	201.473	69.619	132.844

O,0,-1.1419555603,-1.1721053463,-1.0980721715
C,0,-1.1324062204,-0.1350970098,-0.1392803524
C,0,-2.5022306893,-0.2301367168,0.5393958985
O,0,-3.3103821727,-0.8473810668,-0.4547949218
C,0,-2.4855729033,-1.7227315978,-1.2038110184
C,0,0.0748356381,-0.3462485857,0.7722646395
C,0,1.4301470511,-0.2145965724,0.0697790518

C,0,1.4481472252,0.9722536183,-0.9096999686
C,0,0.1196848175,1.2759352837,-1.5914721938
O,0,-1.0060481973,1.1466492296,-0.7240983207
O,0,2.4829384632,0.0760033636,0.9622463127
C,0,2.7796538611,1.4934625821,0.8847909503
O,0,1.841691072,2.0342149246,-0.0490005359
C,0,2.556298239,2.1564925948,2.2353874682
C,0,4.2128249877,1.6458277115,0.3747594051
O,0,-0.0759638515,0.1490115179,2.0650660087
O,0,-0.0284362762,-1.3279310678,1.7566430337
C,0,-2.4686111317,-3.1305514957,-0.6083482991
C,0,-2.931504721,-1.6811914057,-2.6571484945
H,0,-2.9115156868,0.7560780033,0.7591068631
H,0,-2.4456132576,-0.8283812427,1.4550286292
H,0,1.6285837397,-1.1700561726,-0.4283962324
H,0,2.209708413,0.8012873976,-1.6871682363
H,0,0.0023711013,0.6109463272,-2.455459256
H,0,0.1117734061,2.311905207,-1.9378615116
H,0,3.2469977535,1.7393629885,2.9743473275
H,0,2.7328850417,3.2339646269,2.1574718531
H,0,1.5332223472,1.9809349881,2.5718268044
H,0,4.9070638687,1.1375773048,1.0509548413
H,0,4.3199125149,1.2023676735,-0.6199889347
H,0,4.4854275399,2.7044865769,0.319032129
H,0,-3.470244661,-3.569191897,-0.6536924355
H,0,-1.7772261961,-3.7711972892,-1.164856965
H,0,-2.1431421409,-3.0995393085,0.4357709219
H,0,-3.9529489099,-2.0636667996,-2.7466181128
H,0,-2.907929738,-0.6491662464,-3.0162615775
H,0,-2.2716698775,-2.2959150152,-3.2768538682

B3LYP/6-31+G**
E(RB+HF-LYP) = -994.603951790

Zero-point correction= 0.301298 (Hartree/Particle)
Thermal correction to Energy= 0.318992
Thermal correction to Enthalpy= 0.319936
Thermal correction to Gibbs Free Energy= 0.256686
Sum of electronic and zero-point Energies= -994.302654
Sum of electronic and thermal Energies= -994.284960
Sum of electronic and thermal Enthalpies= -994.284015
Sum of electronic and thermal Free Energies= -994.347265

E (Thermal) CV S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	200.171	70.136	133.121

O,1.8328611443,-0.4220659422,0.6060677086
C,1.05071957,0.0691682649,0.4638467299
C,2.0338584903,0.8833874677,1.3088978971
O,3.287803676,0.272866433,1.0137000509
C,3.2473810469,-0.1931921992,-0.3270170443
C,-0.1291578213,0.8461207644,-0.1240907255
C,-1.11541686,-0.007800808,-0.9301079505
C,-1.3924034912,-1.3610899246,-0.2511646373
C,-0.2297592687,-1.9472540083,0.5387880538
O,0.5156426129,-0.9681429539,1.2669062422
O,-2.3959975573,0.5780643885,-1.0341539539
C,-3.2920544923,-0.0679944836,-0.0900792237
O,-2.4854951122,-1.0295822491,0.6005173412
C,-3.8176238465,0.9399598719,0.9194224184
C,-4.4033317853,-0.7511814671,-0.885927585
O,-0.6176328414,1.867595378,0.6892623485
O,0.1241586832,2.1315368397,-0.6009697472
C,3.7630293219,0.8589415317,-1.3075441264
C,3.9981183769,-1.5129828703,0.4059255617
H,1.8372056705,0.7750844461,2.3749833871
H,2.0154512593,1.9397331888,1.022219455
H,-0.6901329307,-0.1260218479,-1.9327264426
H,-1.7063511803,-2.0973306252,-1.007294533
H,0.436288727,-2.4814377577,-0.148943868
H,-0.6074778526,-2.6483270713,1.2857414166
H,-4.4148583255,1.7002987047,0.4085334891
H,-4.4470046209,0.4334173547,1.6570411062
H,-2.9859566107,1.4288924919,1.4284453536
H,-4.9384463616,-0.01144333,-1.4880698623
H,-3.990363126,-1.5067115565,-1.5601941309
H,-5.1111809911,-1.2339823046,0.2058062836
H,4.8230520919,1.0527100454,0.1199791377
H,3.6443369413,0.5073446637,-2.3366161329
H,3.2083142721,1.7942986,-1.1959762635
H,5.0514032505,-1.3555933063,-0.1567574817
H,3.5695997694,-2.2238951032,0.3040468441
H,3.9352397291,-1.9257045811,-1.4167929694

Dioxirane isomer # 2 (29b)

E(RB+HF-LYP) = -994.546649805

Zero-point correction= 0.303495 (Hartree/Particle)
Thermal correction to Energy= 0.321110
Thermal correction to Enthalpy= 0.322054
Thermal correction to Gibbs Free Energy= 0.259163
Sum of electronic and zero-point Energies= -994.243155
Sum of electronic and thermal Energies= -994.225540
Sum of electronic and thermal Enthalpies= -994.224596
Sum of electronic and thermal Free Energies= -994.287487

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	201.499	69.612	132.365

C,0,0.7649184074,2.7964851576,-1.4549544649
O,0,0.7218854127,1.7654125242,-0.4365156858
C,0,-0.1847058211,0.7672987446,-0.8510998474
C,0,-0.4096957791,1.0329854601,-2.3524045935
O,0,0.4532871208,2.1195437955,-2.6606352381
C,0,0.4295741734,-0.5871225443,-0.5006111958
C,0,0.6504140993,-0.7998831755,0.9989692134
C,0,-0.5788146244,-0.3452468282,1.8074239028
C,0,-1.3422506698,0.8429417685,1.2332522966
O,0,-1.438440688,0.8400942609,-0.1928592611
O,0,0.78976301,-2.1602434176,1.3441753682
C,0,-0.4687989341,-2.634037902,1.8866590121
O,0,-1.3698807073,-1.527375689,1.7928597156
O,0,-0.0179919041,-1.6534857135,-1.2741504496
O,0,1.3850079602,-1.1037161384,-1.3707202624
C,0,-1.0140284648,-3.776498213,1.043681563
C,0,-0.2327830066,-3.02943772,3.344750962
C,0,2.1894428321,3.3165870454,-1.5427774414
C,0,-0.2638389964,3.8849102228,-1.139345983
H,0,2.2672457142,4.0523229927,-2.3487159083
H,0,2.4818170597,3.7934862239,-0.6024760656
H,0,2.8678396054,2.4861431738,-1.7532640406
H,0,-0.2531639567,4.6462972374,-1.9256391517
H,0,-1.2690176413,3.4588120893,-1.075645446
H,0,-0.0303054741,4.3647902653,-0.1833482175
H,0,-0.325144659,-4.6258429092,1.0774160822
H,0,-1.986287668,-4.0968042048,1.4314388114
H,0,-1.1250186604,-3.4540357896,0.0073752326
H,0,0.5341755978,-3.8078858963,3.4012112201

H,0,0.1103851385,-2.1707217162,3.9297561713
H,0,-1.1572433923,-3.4114126033,3.7892960762
H,0,-1.4650251946,1.2825914946,-2.5130351782
H,0,-0.131748262,0.1819442988,-2.9744711194
H,0,1.5599327055,-0.2568155516,1.2773213725
H,0,-0.2759081677,-0.0960645981,2.8367949437
H,0,-0.8571565276,1.7678034296,1.5672310587
H,0,-2.3710171494,0.8296629915,1.600260121

Dioxirane isomer # 3 (29c-boat)

E(RB+HF-LYP) = -994.543903031

Zero-point correction= 0.303172 (Hartree/Particle)
Thermal correction to Energy= 0.320873
Thermal correction to Enthalpy= 0.321817
Thermal correction to Gibbs Free Energy= 0.258192
Sum of electronic and zero-point Energies= -994.240731
Sum of electronic and thermal Energies= -994.223030
Sum of electronic and thermal Enthalpies= -994.222086
Sum of electronic and thermal Free Energies= -994.285711

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	201.351	69.636	133.910

O,0,-1.6228477543,-1.251015353,-0.8534441928
C,0,-0.7422199057,-0.3798070819,-0.2033293497
C,0,-1.4823612849,0.0289285314,1.0955461929
O,0,-2.6144461897,-0.816959208,1.1423167279
C,0,-2.9063042932,-1.2148470958,-0.1921281545
C,0,0.5886953514,-1.114729732,0.0488674454
C,0,1.8158618418,-0.2281528633,0.1023593309
C,0,1.9179747972,0.6239632628,-1.1892238849
C,0,0.5615193347,0.6881649111,-1.9003126172
O,0,-0.4949849802,0.8045816259,-0.9453470473
O,0,1.6552282641,0.7328892299,1.1312252471
C,0,2.2704789399,1.95805071,0.7098532467
O,0,2.3113735551,1.9071659108,-0.7223051489
C,0,1.382859196,3.1125407578,1.1515901351
C,0,3.6979708736,2.0450642837,1.2496412959
O,0,0.5499328811,-2.2184738109,0.8932777287
O,0,0.8027949931,-2.3391300951,-0.5863333543

C,0,-3.4652618848,-2.626806227,-0.1613825957
C,0,-3.8192039177,-0.205607664,-0.8913732363
H,0,-1.7523369731,1.0898672027,1.0194277527
H,0,-0.8888068497,-0.1266843232,1.9985969057
H,0,2.6960366311,-0.8611763548,0.266798316
H,0,2.6829341975,0.240340264,-1.8752457453
H,0,0.412225691,-0.1959096828,-2.5367376059
H,0,0.5128779009,1.5823360116,-2.5253447374
H,0,1.8103479623,4.0634664612,0.8195903287
H,0,0.3910277692,2.9918355888,0.7095493673
H,0,1.2947235801,3.1292861326,2.2423513681
H,0,4.1890015783,2.9473251094,0.8720998649
H,0,3.6915954988,2.0770912651,2.3436476886
H,0,4.2814094014,1.1763243453,0.9282866768
H,0,-4.4064720255,-2.6444272424,0.396486163
H,0,-3.6509173376,-2.9850819698,-1.1781914726
H,0,-2.7449200043,-3.2875669146,0.3265878822
H,0,-4.7846316256,-0.1517149142,-0.378215143
H,0,-3.3630571973,0.7884253967,-0.8954053577
H,0,-3.9874986415,-0.5067735301,-1.930048788

Dioxirane isomer # 4 (29d)

E(RB+HF-LYP) = -994.543071975

Zero-point correction= 0.302979 (Hartree/Particle)
Thermal correction to Energy= 0.320773
Thermal correction to Enthalpy= 0.321718
Thermal correction to Gibbs Free Energy= 0.257487
Sum of electronic and zero-point Energies= -994.240093
Sum of electronic and thermal Energies= -994.222299
Sum of electronic and thermal Enthalpies= -994.221354
Sum of electronic and thermal Free Energies= -994.285585

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	201.288	69.729	135.185

O,0,-1.6329778479,-1.2272114858,-0.8206501475
C,0,-0.7391348375,-0.3765134467,-0.1618667385
C,0,-1.4960837847,0.0394902699,1.1125334641
O,0,-2.8560610131,-0.0661505811,0.7284225096
C,0,-2.9573390301,-1.0964259187,-0.2487034694

C,0,0.5746732247,-1.1379515346,0.1077041251
C,0,1.8219784934,-0.2800349462,0.1331621767
C,0,1.9406167841,0.5366816958,-1.1787535347
C,0,0.5796440147,0.6287260327,-1.8799036111
O,0,-0.4642955375,0.7924367143,-0.920156601
O,0,1.6853073801,0.7083334579,1.138604703
C,0,2.3223481358,1.912251234,0.685625486
O,0,2.3863593534,1.8136362588,-0.7431962071
C,0,1.445072498,3.0927951661,1.0772794434
C,0,3.7430843066,1.9973561035,1.2426722026
O,0,0.5158387276,-2.2173326632,0.9837912431
O,0,0.7552574547,-2.3862288062,-0.4927864893
C,0,-3.3280302468,-2.4337566033,0.3894265213
C,0,-3.9295062866,-0.6390653929,-1.3259192638
H,0,-1.2842425817,1.0703075617,1.3947141355
H,0,-1.2532502872,-0.63222808,1.9469609616
H,0,2.6876103031,-0.9292592253,0.3116059457
H,0,2.6865096659,0.1125543707,-1.8616829159
H,0,0.4004718848,-0.2622878163,-2.4993306201
H,0,0.5531093988,1.5118738102,-2.5218309151
H,0,1.8959190537,4.027069664,0.7291716113
H,0,0.4608135309,2.9777160072,0.6171706272
H,0,1.3352272749,3.1412398289,2.1652461112
H,0,4.2519768373,2.8800058833,0.843018902
H,0,3.7221063487,2.0653769246,2.3348206327
H,0,4.3180429299,1.1105155308,0.9576682182
H,0,-3.3522636322,-3.2220656966,-0.3693042267
H,0,-2.5864384747,-2.710917415,1.1443168381
H,0,-4.3126574234,-2.3660997739,0.8626874836
H,0,-3.9938325701,-1.3871945731,-2.1217305475
H,0,-4.9260913404,-0.4949501787,-0.8968817413
H,0,-3.5823786862,0.307164061,-1.7483933981

Dioxirane isomer # 5 (29e)

E(RB+HF-LYP) = -994.539936043

Zero-point correction= 0.303006 (Hartree/Particle)
Thermal correction to Energy= 0.320901
Thermal correction to Enthalpy= 0.321845
Thermal correction to Gibbs Free Energy= 0.257652
Sum of electronic and zero-point Energies= -994.236930
Sum of electronic and thermal Energies= -994.219035

Sum of electronic and thermal Enthalpies= -994.218091
Sum of electronic and thermal Free Energies= -994.282284

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	201.368	69.960	135.105

O,0,-1.1548578941,-1.0126450103,-0.9555250293
C,0,-1.2441335293,-0.3565686455,0.3008646191
C,0,-2.3780643896,-1.0935089543,1.0396474521
O,0,-2.7071954475,-2.1914407302,0.2035036791
C,0,-2.3194267366,-1.8545039327,-1.1206256645
C,0,0.1503551272,-0.472641875,0.9187347007
C,0,1.2219289089,0.1239816363,0.0125211551
C,0,0.6864194249,1.4093633298,-0.6725165607
C,0,-0.5237114264,1.9542766371,0.091783358
O,0,-1.5989948335,1.0045290717,0.1679347975
O,0,2.3400004567,0.5674311607,0.7492499909
C,0,2.8805220769,1.6977339655,0.0632094684
O,0,1.759311736,2.3351618708,-0.5765488001
C,0,3.4672318915,2.6462157225,1.0961686727
C,0,3.8928658083,1.2588823533,-0.9971966048
O,0,0.2334211203,-0.2756813234,2.2937698782
O,0,0.4475885759,-1.6215440977,1.6392481486
C,0,-1.8952477192,-3.1251428302,-1.8367455911
C,0,-3.4180713297,-1.0791573077,-1.8514811204
H,0,-3.21856096,-0.4010821492,1.1683093494
H,0,-2.0628020644,-1.4759579568,2.0114106643
H,0,1.4934568701,-0.6390715013,-0.7280396717
H,0,0.4246771757,1.2249181651,-1.7195400287
H,0,-0.1997140005,2.2399422659,1.101830346
H,0,-0.9344990994,2.8389113534,-0.4000519994
H,0,2.6989872029,2.9142342256,1.8256981937
H,0,3.8308763487,3.5552548234,0.6082010367
H,0,4.3014062079,2.1680573448,1.6180583586
H,0,4.7418751307,0.7537838313,-0.5261579559
H,0,3.4318834139,0.5700957773,-1.7124956532
H,0,4.2599870158,2.1288199297,-1.5503280034
H,0,-1.52694995,-2.893581181,-2.8406236877
H,0,-2.7472654324,-3.8059799928,-1.9235280845
H,0,-1.1041265516,-3.617893868,-1.2660630344
H,0,-3.0787483321,-0.7958682753,-2.8528449138
H,0,-4.3151531775,-1.6994280365,-1.9448650738
H,0,-3.6735281493,-0.1652228825,-1.3082144709

Dioxirane isomer # 6 (highest energy, 29f)

E(RB+HF-LYP) = -994.538803139

Zero-point correction=	0.302737 (Hartree/Particle)
Thermal correction to Energy=	0.320767
Thermal correction to Enthalpy=	0.321711
Thermal correction to Gibbs Free Energy=	0.255990
Sum of electronic and zero-point Energies=	-994.236066
Sum of electronic and thermal Energies=	-994.218036
Sum of electronic and thermal Enthalpies=	-994.217092
Sum of electronic and thermal Free Energies=	-994.282813

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	201.284	70.044	138.321

O,0,-0.5325244096,-1.7676488006,0.1738674192
C,0,-0.699064249,-0.5918365056,0.9460022051
C,0,-0.9899354828,-1.1239995236,2.3550218929
O,0,-1.5958920054,-2.3848970934,2.1038692971
C,0,-1.0363380183,-2.9128770718,0.9098113139
C,0,0.5969965716,0.2037941157,0.7812736584
C,0,0.8688256175,0.5753358485,-0.6714945199
C,0,-0.4475681856,1.0077682885,-1.3743629286
C,0,-1.5310460528,1.3013779818,-0.3353519185
O,0,-1.8067405455,0.1620996766,0.4877798773
O,0,1.7077118076,1.70421218,-0.7699023451
C,0,1.301990923,2.4418680248,-1.9251487718
O,0,-0.1093969563,2.2064199602,-2.0563681588
C,0,1.5318226483,3.919385946,-1.6526817555
C,0,2.0293315646,1.936177626,-3.1732940676
O,0,0.884425093,1.1202446203,1.79031888
O,0,1.6786011791,-0.1480110322,1.5796127869
C,0,0.1417661261,-3.8387632033,1.209443321
C,0,-2.1491175987,-3.5750079482,0.1109892643
H,0,-1.7035107287,-0.4946299319,2.8868827529
H,0,-0.064154753,-1.2195008925,2.9342626605
H,0,1.3087286746,-0.3063421605,-1.1557914855
H,0,-0.793760358,0.2407824074,-2.0762658
H,0,-2.4776882292,1.562849845,-0.8134378963
H,0,-1.20839375,2.1552286876,0.2773701145
H,0,2.5990700696,4.1173354014,-1.5167691662

H,0,1.1659973096,4.5175082882,-2.4923822219
H,0,0.9977015684,4.2107902877,-0.7449889376
H,0,3.1082527304,2.0905488047,-3.0738059187
H,0,1.8447361871,0.8674498725,-3.3239562028
H,0,1.6746149219,2.4715358326,-4.0593137927
H,0,-0.1999370299,-4.7107719111,1.7755975298
H,0,0.6046985279,-4.1817608165,0.2786655747
H,0,0.8992472486,-3.3114873816,1.7975546545
H,0,-2.573715015,-4.4088162572,0.6787507562
H,0,-2.9349853046,-2.8422998623,-0.0883492181
H,0,-1.7623585569,-3.9571177734,-0.8386916179

Dioxirane model for Shi's oxazolidinone catalyst for cis and terminal alkenes (dioxirane derived from 26)

E(RB+HF-LYP) = -1083.41839519

Zero-point correction=	0.251102 (Hartree/Particle)
Thermal correction to Energy=	0.268498
Thermal correction to Enthalpy=	0.269442
Thermal correction to Gibbs Free Energy=	0.205751
Sum of electronic and zero-point Energies=	-1083.167293
Sum of electronic and thermal Energies=	-1083.149897
Sum of electronic and thermal Enthalpies=	-1083.148953
Sum of electronic and thermal Free Energies=	-1083.212644

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.485	66.757	134.050

C	-1.929444	1.000294	-0.709751
C	-0.836408	0.039584	-0.226121
O	-1.476550	-0.803423	0.740145
C	-2.855850	-0.721126	0.637423
N	-3.141172	0.318864	-0.256185
O	-0.371655	-0.697197	-1.320439
C	0.503361	-1.782098	-0.974240
C	1.709464	-1.354562	-0.148522
C	1.440758	-0.278492	0.921457
C	0.356709	0.700771	0.461328
O	2.680182	-0.700704	-0.954907
C	3.515966	0.055068	-0.072716
O	2.691791	0.344130	1.088521
O	0.092907	1.801439	1.270722

O	0.722397	1.920697	-0.096502
C	3.918814	1.344555	-0.769814
C	4.713449	-0.771373	0.394598
O	-3.598301	-1.433134	1.243191
C	-4.423174	0.712820	-0.646584
O	-5.457607	0.204636	-0.295317
H	4.531557	1.953943	-0.098999
H	4.501002	1.117854	-1.668523
H	3.030447	1.913558	-1.048652
H	5.281247	-0.214830	1.146245
H	4.385907	-1.713322	0.845085
H	5.371640	-0.996018	-0.450435
H	-1.892049	1.087868	-1.797047
H	-1.822696	1.984259	-0.246986
H	1.111673	-0.705902	1.875170
H	2.136563	-2.250815	0.327242
H	-0.060123	-2.544687	-0.425912
H	0.835525	-2.199813	-1.926351
H	-4.369674	1.571644	-1.343199

Trihydroxy substituted dimethyldioxirane (starting oxidant for structure 52)

E(RB+HF-LYP) = -493.892195472

Zero-point correction= 0.103061 (Hartree/Particle)
Thermal correction to Energy= 0.111688
Thermal correction to Enthalpy= 0.112632
Thermal correction to Gibbs Free Energy= 0.069839
Sum of electronic and zero-point Energies= -493.789135
Sum of electronic and thermal Energies= -493.780507
Sum of electronic and thermal Enthalpies= -493.779563
Sum of electronic and thermal Free Energies= -493.822356

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	70.085	30.543	90.066

O,0,-1.2858958718,0.5476136673,0.9912352827
C,0,-0.3027474815,0.0304153287,0.1351942501
C,0,1.0486097971,-0.2632537554,0.7777265562
O,0,1.8838131197,0.823101911,0.5352000797
C,0,-0.3281623918,0.5504477077,-1.2892422866
O,0,-1.6354759689,0.6442270603,-1.8023203481

O,0,-1.2883724246,-0.8840961803,0.5183334602
O,0,1.6255681483,-1.4099742207,0.1770426527
H,0,0.8790920316,-0.4358085112,1.8533626019
H,0,0.2013840659,1.5154363182,-1.2942680464
H,0,0.236001367,-0.1381843075,-1.9255987642
H,0,1.1922146908,-2.194295714,0.5518397584
H,0,-2.1905226783,1.0144941138,-1.0956486952
H,0,2.7785349589,0.5657245141,0.8123130079

Transition structure A (Structure 34)

B3LYP/6-31G*
E(RB+HF-LYP) = -1343.49880272

Zero-point correction= 0.466153 (Hartree/Particle)
Thermal correction to Energy= 0.492971
Thermal correction to Enthalpy= 0.493916
Thermal correction to Gibbs Free Energy= 0.409013
Sum of electronic and zero-point Energies= -1343.032650
Sum of electronic and thermal Energies= -1343.005831
Sum of electronic and thermal Enthalpies= -1343.004887
Sum of electronic and thermal Free Energies= -1343.089790

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.344	105.146	178.693

C,0,-0.1507830347,3.0443105882,-0.7990448169
C,0,-0.72190297,2.9132813291,0.4861898114
C,0,-2.0481752319,3.3541415719,0.6739575103
C,0,-2.7789290832,3.897860928,-0.3774760039
C,0,-2.1996678394,4.0162209756,-1.6428815238
C,0,-0.8841518813,3.5867147784,-1.8484144247
C,0,0.0039564909,2.3814544305,1.6246613032
C,0,1.229578541,1.7450186196,1.6202008452
C,0,2.0762033842,1.5808959903,2.8477657067
O,0,1.9542004122,-0.3941024239,-0.7414790199
C,0,1.3380747395,-1.3935104621,0.0647691338
C,0,2.4313953125,-1.7955543961,1.0735245166
O,0,3.5649197052,-0.9948894551,0.7248041101
C,0,3.3854598443,-0.576426774,-0.6193927182
C,0,0.0203914713,-0.9026433586,0.7193724274
C,0,-1.0384995911,-0.5363450746,-0.3435201949

C,0,-1.1573723199,-1.6137484023,-1.4324809792
C,0,0.1448851298,-2.3152626989,-1.7935740273
O,0,1.0067948319,-2.5561699704,-0.6834230446
O,0,-2.34723153,-0.481857112,0.195228648
C,0,-3.0323214613,-1.7149406167,-0.1178851238
O,0,-2.0973554667,-2.5098317298,-0.8542955967
C,0,-3.403711449,-2.4605425736,1.1552633302
C,0,-4.2459787322,-1.3697461127,-0.984535096
O,0,-0.3380911021,-1.7094037112,1.7244169345
O,0,0.1553494004,0.0755542958,1.7652747243
C,0,4.0778101239,0.7628141099,-0.8206749143
C,0,3.8856373195,-1.6335635236,-1.6112372229
H,0,5.1610394913,0.6352048518,-0.7352852643
H,0,3.8525328648,1.1598963566,-1.8150772818
H,0,3.7571219856,1.4818705772,-0.0632987482
H,0,4.9608950039,-1.7877297824,-1.4749191017
H,0,3.3673260681,-2.5825021846,-1.4610832223
H,0,3.707341102,-1.3018475996,-2.6396495867
H,0,-4.1243320976,-1.8738781488,1.7343315731
H,0,-3.8576323429,-3.4255552841,0.9062437844
H,0,-2.5046999311,-2.6157267145,1.7530911353
H,0,-4.9087132726,-0.684721115,-0.4461731977
H,0,-3.9322895744,-0.8812565553,-1.912505596
H,0,-4.805481601,-2.2767526444,-1.2354990315
H,0,2.6452588832,-2.8649123542,0.9756932528
H,0,2.1411804049,-1.5698309133,2.098660223
H,0,-0.7899723827,0.440602556,-0.7683264252
H,0,-1.5721853856,-1.1699620053,-2.3532761786
H,0,0.6693430099,-1.7105324367,-2.5447383069
H,0,-0.0705944371,-3.297481301,-2.2214421838
H,0,2.7419251698,0.7211857559,2.7399375044
H,0,2.7044925005,2.4715461564,2.9914173816
H,0,1.4601831409,1.4501138896,3.7423267577
H,0,-2.5024694165,3.2544373137,1.6561321336
H,0,-3.8008767658,4.2268870914,-0.2121662167
H,0,-2.767213449,4.4435949774,-2.4648729541
H,0,-0.4283102653,3.6831026857,-2.8299760232
H,0,0.8722451059,2.7250222165,-0.9716613078
H,0,1.7269007466,1.5888788089,0.6697200277
H,0,-0.4830971393,2.5033706843,2.5906575736

B3LYP/6-31+G**
E(RB+HF-LYP) = -1343.58260590

Zero-point correction= 0.462895 (Hartree/Particle)
Thermal correction to Energy= 0.489945
Thermal correction to Enthalpy= 0.490889
THERMAL CORRECTION TO GIBBS FREE ENERGY= 0.405921
Sum of electronic and zero-point Energies= -1343.119711
Sum of electronic and thermal Energies= -1343.092661
Sum of electronic and thermal Enthalpies= -1343.091717
Sum of electronic and thermal Free Energies= -1343.176685

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	307.445	105.985	178.830

C,0.9955366892,-2.7924590253,-0.955514423
C,1.5731607869,-2.5101718243,0.3027565047
C,2.9801925271,-2.4419090208,0.3912420751
C,3.7806302915,-2.643453368,-0.7306835374
C,3.192277621,-2.9199360755,-1.9684282761
C,1.7975541353,-2.9929487422,-2.074996739
C,0.7918231934,-2.3210319918,1.513077508
C,-0.5799490558,-2.2025536285,1.6265211689
C,-1.3091025019,-2.3881318914,2.9230630627
O,-1.811079123,-0.2811947605,-0.8703584632
C,-1.7036420576,0.8109567378,0.0374866626
C,-2.9615511619,0.6942128737,0.9198137149
O,-3.6807638926,-0.4262300205,0.3860687027
C,-3.2124264796,-0.6457136103,-0.9378833082
C,-0.360721409,0.7974671405,0.8146873802
C,0.8459046926,0.9274415192,-0.1424986781
C,0.6494825978,2.0433642946,-1.1811936237
C,-0.7844193537,2.2542314149,-1.6477930718
O,-1.7684785681,2.066625665,0.6290715289
O,2.0337429843,1.3211780288,0.5249126389
C,2.2471250722,2.7396157168,0.3236592773
O,1.1535492055,3.1828581349,0.4906693867
C,2.2000133937,3.4860209149,1.6481255089
C,3.5757866562,2.9160206273,-0.414186629
O,-0.4116155985,1.6057170478,1.8824198678
O,-0.2048599453,-0.2359463975,1.8049244172
C,-3.3264528846,-2.1252993168,-1.2689690916
C,-3.9611639559,0.2255731112,-1.9535417757
H,-4.3803393937,-2.4152720519,-1.293871432
H,-2.8869719542,-2.3289516316,-2.2495454457
H,-2.8224258526,-2.7313007461,-0.5135308992

H,-5.0177704004,-0.0578955302,-1.9676226943
H,-3.8805569174,1.2828962168,-1.6966783052
H,-3.5456878213,0.0788016285,-2.9555151673
H,3.028556359,3.1629350096,2.2857473349
H,2.291642811,4.5621815922,1.4710433958
H,1.2563765344,3.2717116022,2.1508793953
H,4.3894548191,2.480842776,0.1736132182
H,3.5477731861,2.4141584016,-1.3856822654
H,3.7821206993,3.9791190217,-0.5705350218
H,-3.5463363024,1.6162716632,0.8512993662
H,-2.7128630546,0.4887013638,1.9600329951
H,1.0158712679,-0.0404500124,0.6218833856
H,1.2700290702,1.838171739,-2.0687926941
H,-0.985777098,1.5696907278,-2.481641466
H,-0.911382496,3.2819130495,-1.9955311644
H,-2.2118522463,-1.7739154898,2.9526676799
H,-1.6174016174,-3.4372756883,3.0274089723
H,-0.6767603034,-2.128617983,3.7763432925
H,3.4377462405,-2.214075235,1.3497190321
H,4.8610081316,-2.581294959,-0.6418537266
H,3.8140848734,-3.0803129721,-2.8442769235
H,1.3371742672,-3.2113590909,-3.0340763952
H,-0.0824279714,-2.8552727333,-1.0547384161
H,-1.1827160935,-2.2299107074,0.7258248849
H,1.3651179831,-2.2733266823,2.4369235926

Transition structure B (Structure 35)

B3LYP/6-31G*
E(RB+HF-LYP) = -1343.49715905

Zero-point correction= 0.466330 (Hartree/Particle)
Thermal correction to Energy= 0.493021
Thermal correction to Enthalpy= 0.493965
Thermal correction to Gibbs Free Energy= 0.410261
Sum of electronic and zero-point Energies= -1343.030829
Sum of electronic and thermal Energies= -1343.004138
Sum of electronic and thermal Enthalpies= -1343.003194
Sum of electronic and thermal Free Energies= -1343.086898

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.375	105.114	176.170

O,0,-3.1460413688,-1.9607588585,-1.3813884403
C,0,-2.786288604,-1.6751096494,-0.0360359545
C,0,-1.2519191149,-1.7455228885,-0.1014440467
O,0,-1.0182803488,-2.7666827114,-1.053835475
C,0,-2.2069256676,-2.924270169,-1.8678995091
C,0,-3.3611354306,-0.3479578251,0.4536526418
O,0,-2.6100530989,0.8100649592,0.0902281084
C,0,-1.2212001159,0.7279222344,0.3874816439
C,0,-0.6612560681,-0.3855606939,-0.527274252
C,0,-0.6122239419,2.1256483097,0.1760332977
O,0,-0.1295903104,2.5142209307,1.4696799933
C,0,-0.8016944456,1.7097178025,2.4308420433
O,0,-0.9798474052,0.4450927313,1.7618405927
C,0,0.0987967367,1.5054643083,3.6391716405
C,0,-2.1513099613,2.3234685425,2.8230328883
O,0,-0.7248167753,-0.0538006757,-1.8105789224
O,0,0.7825187434,-0.3687092649,-0.736874746
C,0,-1.8996686764,-2.6123832899,-3.3243528177
C,0,-2.7326557001,-4.3460318432,-1.6570847601
C,0,2.4287234023,0.0089606732,0.648117697
C,0,2.259648502,-1.2993052049,0.2313622658
H,0,0.3032245964,2.4687363936,4.1160132338
H,0,-0.390168713,0.8529981361,4.3686688601
H,0,1.0489435193,1.0534939762,3.3447991759
H,0,-1.9906733423,3.2959711273,3.2996529715
H,0,-2.7856849172,2.4585578355,1.9448345915
H,0,-2.6733218942,1.6697609029,3.529770485
H,0,-1.1848501483,-3.3420313813,-3.7188844321
H,0,-2.8171031867,-2.6651818771,-3.9200278407
H,0,-1.4705718234,-1.611974494,-3.3896285192
H,0,-1.9661320046,-5.0752629783,-1.9382546244
H,0,-2.9931159009,-4.5125069224,-0.6070355876
H,0,-3.6225470675,-4.517014055,-2.2713441832
H,0,-1.3818607066,2.8140374201,-0.1872942157
H,0,0.2276357847,2.1032256294,-0.517804457
H,0,-0.8306846597,-2.044369026,0.8602644053
H,0,-3.1647173034,-2.4688809413,0.6298231832
H,0,-3.4476211223,-0.3975213092,1.5466734395
H,0,-4.3576898593,-0.201580856,0.0297391882
H,0,1.9226763187,0.3048653691,1.5619415583
C,0,3.2287016572,1.0364621742,-0.000984688
H,0,2.7520630313,-1.6219821174,-0.6808809424
C,0,1.7543848226,-2.399478136,1.111524023

C,0,3.1137302645,2.3680478163,0.4481482278
C,0,3.8725439866,3.3819359102,-0.1297419339
C,0,4.7641790065,3.0876435395,-1.1635685866
C,0,4.889861709,1.7713378803,-1.6191528596
C,0,4.133272265,0.7558764326,-1.0453857125
H,0,2.3947103539,2.6018876704,1.2281747898
H,0,3.7647155734,4.4037178512,0.2234482611
H,0,5.3586636541,3.8780739871,-1.6135476699
H,0,5.5830742247,1.5377222598,-2.4224603544
H,0,4.2522583296,-0.2620256776,-1.4031090348
H,0,2.6109125055,-2.9634830335,1.5079410247
H,0,1.1845897604,-2.012805746,1.9619269468
H,0,1.1367717528,-3.1030405723,0.5453833711

B3LYP/6-31+G**
E(RB+HF-LYP) = -1343.58073657

Zero-point correction= 0.462995 (Hartree/Particle)
Thermal correction to Energy= 0.490008
Thermal correction to Enthalpy= 0.490952
Thermal correction to Gibbs Free Energy= 0.405879
Sum of electronic and zero-point Energies= -1343.117741
Sum of electronic and thermal Energies= -1343.090728
Sum of electronic and thermal Enthalpies= -1343.089784
Sum of electronic and thermal Free Energies= -1343.174857

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	307.485	105.992	179.051

O,-3.8840754221,-0.3154889727,-0.785352618
C,-3.2045858289,0.5543549248,0.1149149125
C,-2.0390845189,-0.3299945716,0.5902892784
O,-2.6081985113,-1.6283051444,0.6027544637
C,-3.7775929967,-1.6435120133,-0.257348405
C,-2.8081219369,1.8729674914,-0.5428981312
O,-1.5852461217,1.8368452316,-1.2829147786
C,-0.4803283763,1.2820901438,-0.576963653
C,-0.8239348735,-0.2112002727,-0.3548385889
C,0.7922374029,1.5551421339,-1.3994120205
O,1.60284065,2.3847279504,-0.5512528912
C,0.7433029817,2.9726644583,0.4186178953
O,-0.2483243393,1.9495269774,0.6595510771

C,1.5202258232,3.217211853,1.7021985554
C,0.096658643,4.2583432096,-0.1109189456
O,-0.8523720213,-0.8962528967,-1.4958317311
O,0.3018744257,-1.0760997491,-0.0281288087
C,-3.5812114773,-2.6128472647,-1.4120616821
C,-4.9929707654,-1.9819688115,0.6079167676
C,2.0664083501,-0.8212581485,1.2890408919
C,1.0790188965,-1.6739653349,1.7469770699
H,2.3277570662,3.9301517275,1.5143167182
H,0.8607054453,3.6322633985,2.4693166402
H,1.9533576987,2.2873724477,2.0754212672
H,0.8723851997,5.0061692043,-0.3012885314
H,-0.4485467626,4.0696660707,-1.0371933812
H,-0.6034887717,4.6601131104,0.6282012294
H,-3.4975181542,-3.634255332,-1.0283644783
H,-4.4398782102,-2.5619422308,-2.0888432553
H,-2.6691077692,-2.3525309053,-1.9499411432
H,-4.8500343274,-2.9547681227,1.0877593985
H,-5.1339536992,-1.2309807167,1.3906645311
H,-5.8952439581,-2.0219735077,0.009606228
H,0.5298219453,2.0699179224,-2.3283896863
H,1.3411798702,0.6397592601,-1.6168416292
H,-1.7330827487,-0.0627971946,1.6035840649
H,-3.8601999298,0.789912021,0.9691995698
H,-2.7346221468,2.6391322432,0.2391053187
H,-3.5783142257,2.1709181318,-1.2578764609
H,2.0239523559,0.2104210555,1.6258262093
C,3.1842918075,-1.1577418491,0.420409708
H,1.1054103836,-2.7155025383,1.4427539221
C,0.1767332662,-1.3641239523,2.8999353064
C,4.0386111574,-0.1204402977,-0.0087844718
C,5.1355380855,-0.3893218401,-0.8248620634
C,5.401566252,-1.7004036104,-1.2300574531
C,4.5606724444,-2.7407424143,-0.815578234
C,3.4654184704,2.4755415511,0.000548985
H,3.8159326957,0.9017412627,0.2821641007
H,5.7781088057,0.4234639352,-1.1500029077
H,6.2557168195,-1.9122601917,-1.8665111263
H,4.7613592596,-3.7600226711,-1.1318641341
H,2.8248853229,-3.2944891607,0.3099484501
H,0.587979519,-1.8299039586,3.8062499685
H,0.0956221788,-0.2889340174,3.0824552466
H,-0.8192899839,-1.788542112,2.7464042911

Transition structure EA (Structure 36)

E(RB+HF-LYP) = -1343.49417539

Zero-point correction= 0.465352 (Hartree/Particle)
Thermal correction to Energy= 0.492535
Thermal correction to Enthalpy= 0.493479
Thermal correction to Gibbs Free Energy= 0.407620
Sum of electronic and zero-point Energies= -1343.028823
Sum of electronic and thermal Energies= -1343.001640
Sum of electronic and thermal Enthalpies= -1343.000696
Sum of electronic and thermal Free Energies= -1343.086556

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.070	105.583	180.707

C,0,-0.3269567393,2.8348642482,-0.7745468189
C,0,-1.076970799,2.6042724679,0.4002927737
C,0,-2.4656818317,2.8480528589,0.3646846318
C,0,-3.0827734167,3.3155120338,-0.7910970196
C,0,-2.3253936274,3.5435345789,-1.9421176825
C,0,-0.9480281261,3.296418923,-1.9293784729
C,0,-0.4880312793,2.1604407179,1.6499362601
C,0,0.8275477904,1.8282318525,1.8984394446
C,0,1.3889141094,1.7347045998,3.286164654
H,0,0.7377198918,2.6282197951,-0.7872354657
H,0,-3.0563142614,2.6600879979,1.2571532666
H,0,-4.1536772407,3.497602881,-0.7969416977
H,0,-2.8041311746,3.9087760605,-2.8465324865
H,0,-0.3577891986,3.4656184942,-2.8256654474
H,0,-1.1752785509,2.0980149461,2.4918199672
H,0,1.5450705599,1.8822590044,1.0886375456
H,0,2.1543203108,0.9556049056,3.3441437821
H,0,1.8572000827,2.6881113957,3.5679160878
H,0,0.6086205508,1.5057990233,4.0179818965
O,0,2.0485007839,0.2099671173,-0.5628497825
C,0,1.5568394628,-1.0489339828,-0.1591072879
C,0,2.7277814606,-1.6132861391,0.6477929096
O,0,3.8685706968,-1.0810138012,-0.0213001143
C,0,3.48894172,0.1130430843,-0.6993490558
C,0,0.2234592471,-0.9479642992,0.6395620804
C,0,-0.960337836,-0.7741193666,-0.3255136588
C,0,-1.0576896348,-2.0038402493,-1.2534300038

C,0,0.273124795,-2.7622779,-1.2917135346
O,0,1.3455569491,-1.8193128461,-1.3510338864
O,0,-2.208472678,-0.7299965345,0.3349795231
C,0,-2.9250181626,-1.9583171105,0.1191485139
O,0,-2.0655805331,-2.8015478755,-0.6535288999
C,0,-3.1903341451,-2.6415803929,1.4541855592
C,0,-4.1985066193,-1.6397803161,-0.6662119187
C,0,4.1187486154,1.3267227732,-0.0197500104
C,0,3.8721916704,-0.0108739134,-2.1715331606
H,0,2.7772651616,-2.7028302624,0.6149430468
H,0,2.6745995458,-1.2820495389,1.691876666
H,0,-0.8219121312,0.1495312709,-0.8963801241
H,0,-1.3533834112,-1.6949911857,-2.2667269571
H,0,0.370740032,-3.3825422756,-2.1857080096
H,0,0.3433288612,-3.4048072326,-0.404850511
H,0,-3.8548559873,-2.0246135825,2.0678885586
H,0,-3.6652063951,-3.6149619096,1.2933293796
H,0,-2.2402203904,-2.7754132339,1.9749341148
H,0,-4.8244133295,-0.9378571172,-0.1057450674
H,0,-3.9456300637,-1.1842126622,-1.6289734715
H,0,-4.7720950607,-2.5540622914,-0.8494156935
H,0,5.2072768349,1.2838215892,-0.1232325822
H,0,3.7652229536,2.2581379745,-0.475397377
H,0,3.8758254168,1.3328136099,1.0469458739
H,0,4.9544185951,-0.149110388,-2.263827297
H,0,3.361630336,-0.8720553487,-2.6061680684
H,0,3.5856448349,0.8924790616,-2.7203547615
O,0,0.1146108264,-1.9196991087,1.5679444008
O,0,0.223696868,-0.0904366753,1.7741432108

Transition structure DA (Structure 37)

E(RB+HF-LYP) = -1343.49414673

Zero-point correction= 0.465574 (Hartree/Particle)
Thermal correction to Energy= 0.492786
Thermal correction to Enthalpy= 0.493730
Thermal correction to Gibbs Free Energy= 0.407317
Sum of electronic and zero-point Energies= -1343.028573
Sum of electronic and thermal Energies= -1343.001360
Sum of electronic and thermal Enthalpies= -1343.000416
Sum of electronic and thermal Free Energies= -1343.086830

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.228	105.546	181.873

C,0,1.1052237427,-2.6074528871,-1.0075153345
C,0,1.593180386,-2.4024750507,0.3015808533
C,0,2.9890990296,-2.3770990949,0.4958854892
C,0,3.8657699041,-2.5502814461,-0.5701811691
C,0,3.36606005,-2.7505904286,-1.8587434645
C,0,1.983534691,-2.7756710962,-2.0720985542
C,0,0.7286155427,-2.2555014226,1.4596839835
C,0,-0.6443552264,-2.1592105406,1.4762710698
C,0,-1.4785458329,-2.3495993032,2.7074049248
H,0,0.0357499293,-2.6307077359,-1.1902505804
H,0,3.3783741008,-2.2127565129,1.4971508927
H,0,4.9381507797,-2.5264807832,-0.3981018285
H,0,4.0480533519,-2.8882180671,-2.6933068419
H,0,1.5911840636,-2.9326334942,-3.0730772949
H,0,1.237807128,-2.2286025059,2.4217736156
H,0,-1.1755073566,-2.1639391604,0.5321703105
H,0,-2.3990590729,-1.7639210026,2.6375504875
H,0,-1.7646000518,-3.4064021719,2.8083013267
H,0,-0.9353449422,-2.0551465748,3.6102135417
O,0,-1.9860273432,-0.3221081863,-0.8268619962
C,0,-1.8164046071,0.8475530309,-0.0406658393
C,0,-3.0500251586,0.841940391,0.8944795373
O,0,-3.8187302588,-0.2944234655,0.4938899279
C,0,-3.3957839861,-0.6425423083,-0.8166197382
C,0,-0.4552974221,0.8329913122,0.7089604412
C,0,0.6893505508,0.9584349515,-0.3052787474
C,0,0.5564995972,2.3029341313,-1.0584326641
C,0,-0.8115775934,2.9473942304,-0.804576548
O,0,-1.8613292201,1.9826224174,-0.9121685511
O,0,1.9639293634,1.0002756896,0.29906741
C,0,2.5398256832,2.3070404971,0.1704890381
O,0,1.5722419193,3.1211350072,-0.5005981208
C,0,2.786315869,2.8951170903,1.5547856838
C,0,3.8064509753,2.1961871696,-0.6789760778
C,0,-3.5725346558,-2.1407151383,-1.0128829408
C,0,-4.1445405344,0.1621383781,-1.8857532549
H,0,-3.6120205815,1.7732550417,0.7655450061
H,0,-2.7653064265,0.7241960489,1.940231925
H,0,0.6439199641,0.1090865925,-0.99484285
H,0,0.7210298341,2.1605031669,-2.1356443099

H,0,-0.7970362178,3.4162874684,0.1862302749
H,0,-1.0434844321,3.710093104,-1.5519750105
H,0,1.8514131251,2.8729443722,2.1187504553
H,0,3.1438739653,3.9265977768,1.4707747262
H,0,3.5392880891,2.3047819216,2.0871481517
H,0,4.5256269517,1.522991057,-0.2014795231
H,0,3.5615354421,1.7962221488,-1.6680400286
H,0,4.2712880922,3.1797526017,-0.8017464558
H,0,-3.141091424,-2.4515013659,-1.9692610703
H,0,-4.638405078,-2.3872430504,-1.0178308062
H,0,-3.0977328949,-2.6978869033,-0.2021459082
H,0,-3.7730476197,-0.0983290887,-2.8821624884
H,0,-5.2139326562,-0.067588045,-1.8362742782
H,0,-4.0007916144,1.2341208898,-1.7407159072
O,0,-0.4411225112,1.6718561766,1.766752977
O,0,-0.3008495089,-0.1472364544,1.7216826457

Transition structure EB (Structure 38)

E(RB+HF-LYP) = -1343.49441751

Zero-point correction= 0.466189 (Hartree/Particle)
Thermal correction to Energy= 0.493123
Thermal correction to Enthalpy= 0.494068
Thermal correction to Gibbs Free Energy= 0.409189
Sum of electronic and zero-point Energies= -1343.028229
Sum of electronic and thermal Energies= -1343.001294
Sum of electronic and thermal Enthalpies= -1343.000350
Sum of electronic and thermal Free Energies= -1343.085229

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	309.440	105.300	178.642

O,0,-0.1397808007,1.9487730159,0.8031809682
C,0,-0.4030080094,1.443350613,-0.5042255978
C,0,0.910780291,1.72311721,-1.2694294903
O,0,1.7556920424,2.3973039863,-0.3291714303
C,0,0.901115582,2.9332783582,0.6779235037
C,0,-0.8177936035,-0.0470992952,-0.4199137197
C,0,-2.0670068514,-0.1304498079,0.470845904
C,0,-3.2059507186,0.6692129949,-0.2059883139
C,0,-2.6914304869,1.5038583726,-1.3898011439

O,0,-1.4689699695,2.1874445406,-1.0901627665
O,0,-2.5721236057,-1.4393367573,0.6248363467
C,0,-3.8113128516,-1.5898100466,-0.0858387024
O,0,-4.0937312995,-0.3252260784,-0.6943988694
C,0,-3.6472888994,-2.6326567682,-1.1849890499
C,0,-4.9067510242,-1.93336503,0.9232821522
C,0,1.6611815506,3.0259532762,1.991899334
C,0,0.3319903717,4.2946968687,0.25893833
H,0,0.7024766612,2.3522947134,-2.1408606371
H,0,1.4019524279,0.8013863206,-1.5832062824
H,0,-1.8323666494,0.2833998721,1.4542975155
H,0,-3.7146251219,1.3105085728,0.5268174491
H,0,-3.4004167794,2.2910699948,-1.6581791379
H,0,-2.5622022599,0.8343608928,-2.246767072
H,0,-3.4553055976,-3.6172627799,-0.7460404648
H,0,-4.5576290697,-2.689868233,-1.7905102428
H,0,-2.8008792501,-2.3505925523,-1.8146829276
H,0,-4.6700748084,-2.8696933901,1.4389450977
H,0,-4.9942006645,-1.1363717559,1.6685110614
H,0,-5.8698920249,-2.0457646747,0.4153457794
H,0,2.5054662173,3.7129715773,1.881844764
H,0,1.0043857013,3.4055114513,2.7801958577
H,0,2.0443851796,2.0492477648,2.2956435638
H,0,1.1467900916,5.0189481645,0.1567858834
H,0,-0.2035032027,4.2218830434,-0.689058871
H,0,-0.36961938,4.6572076776,1.0169669182
O,0,-0.8768563412,-0.6575178095,-1.6112248534
O,0,0.2372639947,-0.9885213684,-0.1745982146
C,0,1.9849771301,-0.8745592573,1.1751639514
C,0,0.9546963744,-1.658412982,1.6498006058
C,0,3.0859952642,-1.2925956272,0.3190297157
C,0,0.0381964405,-1.254552448,2.761196819
C,0,3.9245502672,-0.3006762665,-0.229057831
C,0,4.9970718423,-0.6478813529,-1.0458917726
C,0,5.2567952742,-1.9908913477,-1.3276208648
C,0,4.434754257,-2.9858579009,-0.7887916952
C,0,3.3619031599,-2.6432214837,0.0265996834
H,0,1.9896138264,0.1690735953,1.4712535327
H,0,0.9147818313,-2.7044149715,1.3600803263
H,0,0.3807826153,-1.7149454308,3.6993419847
H,0,0.0246491757,-0.1695857891,2.8993869541
H,0,-0.9790067678,-1.6123466168,2.5764903326
H,0,3.7029245463,0.744755447,-0.0312490997
H,0,5.6287873317,0.129837838,-1.4660618177

H,0,6.0950248825,-2.2632721141,-1.9631435135
H,0,4.6346273822,-4.0318627859,-1.0042560616
H,0,2.7403293826,-3.428460541,0.4456287561

Transition structure D (Structure 39)

E(RB+HF-LYP) = -1343.49437390

Zero-point correction= 0.466324 (Hartree/Particle)
Thermal correction to Energy= 0.493082
Thermal correction to Enthalpy= 0.494026
Thermal correction to Gibbs Free Energy= 0.409960
Sum of electronic and zero-point Energies= -1343.028049
Sum of electronic and thermal Energies= -1343.001291
Sum of electronic and thermal Enthalpies= -1343.000347
Sum of electronic and thermal Free Energies= -1343.084413

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.414	104.987	176.932

O,0,-2.6740989201,-2.1275664876,-0.8457298065
C,0,-1.4122778501,-1.6501662115,-1.3003142701
C,0,-1.2406944174,-0.3847308913,-0.4519628389
O,0,-2.5648170256,0.1133676394,-0.3426382548
C,0,-3.4878470016,-0.9805917003,-0.589735822
C,0,-0.3016038022,-2.6839960805,-1.1408970671
O,0,0.2273800344,-2.7877220432,0.1776629966
C,0,0.6723337109,-1.5489997309,0.7344540303
C,0,-0.6064641704,-0.6984597923,0.9130837161
C,0,1.4129732966,-1.8730354092,2.042806845
O,0,2.7684741967,-1.495300827,1.802373935
C,0,2.940055568,-1.2997410561,0.4075883936
O,0,1.6347117416,-0.9062760281,-0.0723341119
C,0,3.9017007805,-0.1425304468,0.1948863762
C,0,3.4011748602,-2.5890821406,-0.2803476146
O,0,-1.3592998499,-1.2165307723,1.9009076591
O,0,-0.5101540489,0.4205755926,1.7956844336
C,0,-4.3336437404,-1.251468313,0.6448644708
C,0,-4.3198318702,-0.6184308109,-1.8214252548
C,0,0.5263682445,2.5486195305,1.0301817222
C,0,-0.7515608311,2.2977499433,1.5019938541
H,0,4.8930834186,-0.4088907106,0.5738468125

H,0,3.9822175233,0.1003551318,-0.8686916236
H,0,3.5387129493,0.7329395361,0.7368902763
H,0,4.3750544536,-2.893261173,0.1168588617
H,0,2.6809094347,-3.3915604942,-0.1053280449
H,0,3.4968374462,-2.4333021806,-1.3603755087
H,0,-4.973940285,-0.3888909039,0.8569311727
H,0,-4.9706995749,-2.1260050837,0.4768245352
H,0,-3.6747810565,-1.4319861519,1.4952776439
H,0,-4.8614694999,0.3170943257,-1.6485140948
H,0,-3.6776482125,-0.4850719112,-2.6976618787
H,0,-5.0452490492,-1.4098683847,-2.0350690811
H,0,1.3242407331,-2.941998663,2.2622167505
H,0,1.0275893457,-1.2896366587,2.8795801029
H,0,-0.6167664034,0.3564534846,-0.9590862646
H,0,-1.4741728214,-1.3797507499,-2.3674137363
H,0,0.5023717232,-2.4285107104,-1.8432429918
H,0,-0.683170954,-3.6774001945,-1.3900459974
H,0,1.315636881,2.6431846005,1.7739456134
C,0,-1.1465892421,2.5929859143,2.9211652307
H,0,-1.5754686389,2.245250974,0.7959131386
H,0,-1.9322731051,1.9060761992,3.2448282653
H,0,-0.2946815059,2.4986959516,3.6012331865
H,0,-1.5322083101,3.6188356073,2.9898698168
C,0,0.9227983991,2.7706590711,-0.3457510115
C,0,2.2779965603,3.0548997826,-0.6236499281
C,0,2.7073805915,3.3338359961,-1.9164701759
C,0,1.7923093259,3.3345325876,-2.9723934071
C,0,0.443624151,3.0646313331,-2.7187907055
C,0,0.009527684,2.7927482225,-1.4260583429
H,0,2.9920429127,3.0616978041,0.1954992983
H,0,3.755446563,3.5519375331,-2.1022089671
H,0,2.1245897801,3.551411036,-3.9837232489
H,0,-0.2747756237,3.0756438158,-3.5338908257
H,0,-1.0453786333,2.6056025938,-1.2512472231

Transition structure BD (Structure 40)

E(RB+HF-LYP) = -1343.49416342

Zero-point correction= 0.466150 (Hartree/Particle)
Thermal correction to Energy= 0.492993
Thermal correction to Enthalpy= 0.493937
Thermal correction to Gibbs Free Energy= 0.409405

Sum of electronic and zero-point Energies= -1343.028014
Sum of electronic and thermal Energies= -1343.001171
Sum of electronic and thermal Enthalpies= -1343.000226
Sum of electronic and thermal Free Energies= -1343.084758

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.358	105.056	177.913

O,0,1.2229450328,-1.2701686665,-0.5479930923
C,0,0.0635100323,-1.8152109978,0.0434374049
C,0,0.6106763684,-2.8603730184,1.0102374443
O,0,1.8430422977,-3.2617843246,0.4145876223
C,0,2.270567388,-2.266804672,-0.5104078934
C,0,-0.8248139811,-0.7325743701,0.6958925149
C,0,-1.3143791924,0.2832337031,-0.3515243311
C,0,-1.8974851668,-0.4032459505,-1.5910523132
C,0,-1.1950644651,-1.6951003081,-1.9935867374
O,0,-0.7650559652,-2.495281179,-0.8980985961
O,0,-2.3936314483,1.0755777113,0.1171047835
C,0,-3.6297823399,0.5181910765,-0.4040940597
O,0,-3.2471372004,-0.6130545174,-1.1901956297
C,0,-4.5191120648,0.0397500782,0.7331141069
C,0,-4.2906703693,1.5873992897,-1.276071119
C,0,3.5429746072,-1.5950200395,-0.0054434552
C,0,2.4381255734,-2.9137600283,-1.8836629351
H,0,-0.0491362374,-3.7250411131,1.0871984854
H,0,0.76862722,-2.4204544851,2.0005274573
H,0,-0.475356795,0.9336458455,-0.6145708906
H,0,-1.862323783,0.2860417603,-2.450926095
H,0,-0.3360130509,-1.431505049,-2.624715
H,0,-1.8764621343,-2.322250529,-2.5741775302
H,0,-4.8309099479,0.8903575403,1.3480782316
H,0,-5.4135862965,-0.445530403,0.3290082093
H,0,-3.9614453376,-0.6668987614,1.3492524576
H,0,-4.489527981,2.4864631041,-0.6839698008
H,0,-3.6385659565,1.8641710887,-2.1104415486
H,0,-5.2380427447,1.2156231409,-1.6792033073
H,0,4.3501719144,-2.3309745033,0.0615630101
H,0,3.8502764078,-0.7905432954,-0.6805291494
H,0,3.3657690036,-1.176469958,0.9894685541
H,0,3.2090653027,-3.6900007204,-1.8399718545
H,0,1.4940665664,-3.3745726821,-2.1836345519
H,0,2.7330846723,-2.1675436348,-2.628998091

O,0,-1.7028742452,-1.315165635,1.5331775412
O,0,-0.3249155986,-0.1386520738,1.8972778797
C,0,1.4114429161,1.6304550951,1.7947570532
C,0,0.1297415234,1.6741515827,2.3183517089
C,0,-0.1344157983,1.5303426998,3.7902488564
C,0,1.8653092541,2.1982841552,0.5412128987
C,0,3.221435103,2.0459107076,0.1774655529
C,0,3.72528268,2.6167756634,-0.9860900038
C,0,2.8856932689,3.3567578182,-1.8229298633
C,0,1.5416718181,3.5286881833,-1.4770846879
C,0,1.0363379766,2.9654294696,-0.3103685611
H,0,2.1780402535,1.1624180943,2.4098337412
H,0,-0.6546416673,2.1738818596,1.756828717
H,0,-1.1165461058,1.0807361527,3.9550058662
H,0,0.6235873125,0.9067802104,4.2737640083
H,0,-0.1216183457,2.5204641266,4.2648686377
H,0,3.878076693,1.4731461573,0.826511662
H,0,4.7733113264,2.4868698588,-1.2416111611
H,0,3.276424442,3.8035584633,-2.7328166253
H,0,0.8869494225,4.1141754471,-2.1166997452
H,0,-0.0045279263,3.1320009389,-0.0509372407

Transition structure DD (Structure 41)

E(RB+HF-LYP) = -1343.49267341

Zero-point correction= 0.465809 (Hartree/Particle)
Thermal correction to Energy= 0.492805
Thermal correction to Enthalpy= 0.493749
Thermal correction to Gibbs Free Energy= 0.408585
Sum of electronic and zero-point Energies= -1343.026864
Sum of electronic and thermal Energies= -1342.999869
Sum of electronic and thermal Enthalpies= -1342.998925
Sum of electronic and thermal Free Energies= -1343.084089

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	309.240	105.275	179.243

O,0,1.5672715027,-1.0954421547,-0.2803306105
C,0,0.3457876838,-1.7686849109,-0.1441918547
C,0,0.724397723,-3.0118721544,0.6651370812
O,0,2.0496495392,-3.2831013492,0.2198083766

C,0,2.6506827512,-2.0481189061,-0.1494233823
C,0,-0.7321401461,-0.879652535,0.5374325655
C,0,-1.3216797265,0.0909591522,-0.4924300619
C,0,-2.034171252,-0.7040681472,-1.602593951
C,0,-1.5086640916,-2.1441499416,-1.6549558966
O,0,-0.0933005449,-2.1310774287,-1.4650883014
O,0,-2.3261671695,0.9378671647,0.0359469862
C,0,-3.6254144269,0.4890766596,-0.4100506489
O,0,-3.397981408,-0.6748738988,-1.2063201591
C,0,-4.4724996075,0.0903159756,0.790408914
C,0,-4.2475329715,1.6009381344,-1.2552429469
C,0,3.5834455987,-1.5581032679,0.9568953764
C,0,3.3430033414,-2.2276985582,-1.4952598228
H,0,0.0970911338,-3.8748269236,0.4375360979
H,0,0.6843922172,-2.8006179728,1.7403057863
H,0,-0.5106090725,0.7032129368,-0.8982310603
H,0,-1.8992715391,-0.2081649649,-2.5746253275
H,0,-2.0207145954,-2.7378276741,-0.8862405718
H,0,-1.6774298771,-2.6091342373,-2.6290222792
H,0,-3.9292475156,-0.6575868926,1.3713748439
H,0,-5.4281158222,-0.3259132514,0.4554363066
H,0,-4.6729724717,0.9643011061,1.4189064894
H,0,-4.3539521425,2.5158029008,-0.6632078659
H,0,-3.6142290049,1.819578222,-2.1210643183
H,0,-5.2366638191,1.2973131325,-1.6124270758
H,0,4.0210796981,-0.5900830131,0.692770189
H,0,4.3935100235,-2.2782264424,1.1082049375
H,0,3.0265505528,-1.4512522967,1.8926201669
H,0,3.7906170056,-1.2841006544,-1.8233741777
H,0,4.1305589908,-2.9843078433,-1.4166381259
H,0,2.6076606994,-2.5514498238,-2.2353262512
O,0,-1.5912849014,-1.6146994349,1.2835762918
O,0,-0.3653263974,-0.3351401608,1.7877943225
C,0,1.2732372452,1.5953120611,1.6832960692
C,0,0.0534334623,1.507597631,2.3253756975
C,0,-0.0584827267,1.2163371567,3.7944468427
C,0,1.5597887198,2.2673590487,0.4315416635
C,0,2.8919288849,2.2865635621,-0.0355449144
C,0,3.2387920025,2.9645912751,-1.1985175203
C,0,2.259348194,3.6405046792,-1.930886665
C,0,0.933359141,3.6339064291,-1.4861270837
C,0,0.583640018,2.9620125797,-0.3199227497
H,0,2.129486251,1.1503132068,2.1864743365
H,0,-0.8165170354,1.9727798649,1.8722213708

H,0,-0.9713740551,0.6516924562,4.0005212469
H,0,0.799203805,0.6414379928,4.1567853912
H,0,-0.1038964757,2.1591351248,4.3557805913
H,0,3.6559050076,1.7658672639,0.53537824
H,0,4.2713672309,2.9666891493,-1.5362443123
H,0,2.5265368317,4.1708535789,-2.8406431287
H,0,0.1687855747,4.1600254312,-2.0510516768
H,0,-0.452195465,2.9674721858,0.004364657

Transition structure AA (42)

E(RB+HF-LYP) = -1343.49168309

Zero-point correction= 0.465694 (Hartree/Particle)
Thermal correction to Energy= 0.492558
Thermal correction to Enthalpy= 0.493503
Thermal correction to Gibbs Free Energy= 0.408650
Sum of electronic and zero-point Energies= -1343.025989
Sum of electronic and thermal Energies= -1342.999125
Sum of electronic and thermal Enthalpies= -1342.998181
Sum of electronic and thermal Free Energies= -1343.083033

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.085	105.256	178.587

C,0,-2.6782024338,-2.0461799999,1.1842101219
C,0,-2.7058095348,-1.8988149126,-0.2195319122
C,0,-3.8527634059,-1.3233568296,-0.8067033928
C,0,-4.9125565243,-0.8788874319,-0.0222830688
C,0,-4.8585260482,-1.014067718,1.3677919331
C,0,-3.7408860184,-1.6049630191,1.9658755154
C,0,-1.632838285,-2.3656394247,-1.0791018396
C,0,-0.3233862209,-2.6581325611,-0.7271912153
C,0,0.5518811244,-3.5554870577,-1.5496392176
H,0,-1.8302367199,-2.5325196629,1.6568397965
H,0,-3.8945437473,-1.2168254756,-1.8877503699
H,0,-5.7821144761,-0.4288735562,-0.492830535
H,0,-5.6868852748,-0.6715860497,1.9814005007
H,0,-3.7043390669,-1.7303636474,3.0443721024
H,0,-1.8965212827,-2.5143296253,-2.1246250354
H,0,0.0023741931,-2.4960434838,0.2959964426
H,0,1.5909926611,-3.2293171854,-1.4772049515

H,0,0.4828015331,-4.5868801835,-1.1763145749
H,0,0.2511079706,-3.5492391265,-2.6012994287
O,0,2.0506561863,-1.1375621681,0.3418577548
C,0,1.6850500107,0.2016805588,0.0721249714
C,0,3.0384108072,0.8675177515,-0.2003021758
O,0,3.9277277702,0.1476957279,0.6473887599
C,0,3.4331613044,-1.177666616,0.7774888345
C,0,0.7085616881,0.2651835192,-1.1552541039
C,0,-0.3757615277,1.3372182897,-0.9734340904
C,0,-1.0878163035,1.3215453138,0.3947264976
C,0,-0.2427961408,0.5858896196,1.4357570772
O,0,1.1431499814,0.8247800689,1.2282875826
O,0,0.2815316682,2.6006254629,-0.986104052
C,0,-0.4502740635,3.5073325983,-0.1638464994
O,0,-1.2299000905,2.7002433869,0.7300710455
C,0,0.5447297061,4.339770329,0.6355777467
C,0,-1.3980476865,4.3536598428,-1.0164077708
C,0,4.1864085797,-2.1321397061,-0.1472738895
C,0,3.4997899473,-1.5700186869,2.248823046
H,0,3.0489482714,1.9179224296,0.0895017344
H,0,3.3017967003,0.7594682645,-1.2580687737
H,0,-1.0738473822,1.2453487134,-1.8142754921
H,0,-2.0860973429,0.8751951523,0.3402769892
H,0,-0.4571453228,-0.4902356259,1.4127605632
H,0,-0.4773614565,0.9628184042,2.4344654392
H,0,0.0135413245,5.0327909974,1.2956268644
H,0,1.1656796478,3.6734389191,1.2392281752
H,0,1.1848365057,4.9182286997,-0.0382510324
H,0,-2.0137093735,4.9943978186,-0.3769410073
H,0,-0.8300882011,4.9843876179,-1.7077749588
H,0,-2.0623409113,3.7070836609,-1.5986272837
H,0,3.7774855131,-3.1455625367,-0.0743908524
H,0,4.0979618988,-1.792699328,-1.1835221832
H,0,5.2455219435,-2.1623766509,0.1273883345
H,0,3.1013195812,-2.5791290665,2.397249033
H,0,4.537394435,-1.5490313494,2.5973620787
H,0,2.912998283,-0.8588293196,2.8350055453
O,0,1.2925908384,0.2601749244,-2.346698759
O,0,0.1280556769,-1.0039451477,-1.6228068977

Transition structure G (43)

E(RB+HF-LYP) = -1343.49216932

Zero-point correction= 0.466269 (Hartree/Particle)
Thermal correction to Energy= 0.492954
Thermal correction to Enthalpy= 0.493899
Thermal correction to Gibbs Free Energy= 0.410508
Sum of electronic and zero-point Energies= -1343.025900
Sum of electronic and thermal Energies= -1342.999215
Sum of electronic and thermal Enthalpies= -1342.998271
Sum of electronic and thermal Free Energies= -1343.081661

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.334	105.155	175.509

O,0,0.8930008106,3.1989853979,-0.5939211544
C,0,0.3779270185,2.0602371612,-1.2703275105
C,0,0.6983916618,0.9286422369,-0.2821416417
O,0,1.925374485,1.347907621,0.2923174689
C,0,2.0680079581,2.7734833193,0.1022502046
C,0,-1.0978179249,2.216214029,-1.6151180621
O,0,-1.9881644613,1.9696044765,-0.5302999263
C,0,-1.8126046828,0.7080633769,0.106303306
C,0,-0.4167325493,0.7590784711,0.7840967423
C,0,-2.9914686677,0.5279275145,1.0795446084
O,0,-3.7188397214,-0.5993133716,0.5739152348
C,0,-3.334669856,-0.778150861,-0.7831347421
O,0,-1.949361198,-0.3739904923,-0.8114649809
C,0,-3.4270583543,-2.2549248704,-1.1370051371
C,0,-4.1853694995,0.086348852,-1.7217604546
O,0,-0.4255614218,1.6304934447,1.7909119578
O,0,-0.1120263438,-0.2890907808,1.7420227111
C,0,2.1243455517,3.4905734568,1.4427328878
C,0,3.3142266129,3.0093081931,-0.7560106825
H,0,-4.467047011,-2.5874205852,-1.0682734592
H,0,-3.0757605412,-2.4224629859,-2.1598084999
H,0,-2.8273797386,-2.8549202268,-0.4484042176
H,0,-5.2329780668,-0.2262741742,-1.6625792912
H,0,-4.1119226512,1.1405966531,-1.4490246564
H,0,-3.84397191,-0.0287412642,-2.7560635065
H,0,3.0227493377,3.1875790945,1.9909165833
H,0,2.1594520991,4.5741085996,1.2869871086
H,0,1.2391926951,3.2233902008,2.0209515683
H,0,4.1973267622,2.5956214663,-0.2583345966
H,0,3.2113617539,2.5207999177,-1.7302642493

H,0,3.4702098138,4.0813406003,-0.914686222
H,0,-3.6078255391,1.432244078,1.085909017
H,0,-2.6526329363,0.3064786121,2.090983403
H,0,0.8618565285,-0.0172939898,-0.8033266466
H,0,0.9297628486,1.899899918,-2.2124809214
H,0,-1.3308145095,1.5371370742,-2.4460029007
H,0,-1.296071937,3.2421796908,-1.9354721597
C,0,-0.0987008901,-2.0353490418,1.8523599979
C,0,0.2699960303,-2.3716403415,0.54285829
C,0,-1.4460225462,-2.4085397632,2.4157435263
H,0,0.7028050583,-2.0612543133,2.5858699403
C,0,1.6064276345,-2.4361695227,0.0169259267
H,0,-0.5324585637,-2.5575580926,-0.1670053162
C,0,1.8009665038,-3.0097286049,-1.2621156968
C,0,3.0766700893,-3.1464771378,-1.7958322388
C,0,4.1840356519,-2.6869473828,-1.076748595
C,0,4.0075693132,-2.083837657,0.1748095371
C,0,2.7382861319,-1.9582551825,0.7210580488
H,0,0.9364928369,-3.3612968291,-1.8196478278
H,0,3.2104689623,-3.6022712117,-2.7726333476
H,0,5.1816643993,-2.7838479656,-1.49597586
H,0,4.8661766349,-1.6989381362,0.7170049595
H,0,2.6039093137,-1.4405857216,1.6643908135
H,0,-1.6226348287,-1.8503023442,3.3391851744
H,0,-2.2581539418,-2.1849946346,1.7202285735
H,0,-1.4675851869,-3.4791212662,2.658776163

Transition structure CA (44)

E(RB+HF-LYP) = -1343.49137261

Zero-point correction= 0.465751 (Hartree/Particle)
Thermal correction to Energy= 0.492595
Thermal correction to Enthalpy= 0.493539
Thermal correction to Gibbs Free Energy= 0.409098
Sum of electronic and zero-point Energies= -1343.025622
Sum of electronic and thermal Energies= -1342.998777
Sum of electronic and thermal Enthalpies= -1342.997833
Sum of electronic and thermal Free Energies= -1343.082274

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.108	105.241	177.721

C,0,1.0503621231,-2.8865208276,-1.8755286836
C,0,1.6631781706,-2.8115557003,-0.6057971387
C,0,3.0719627849,-2.7473103786,-0.5490290836
C,0,3.8353147193,-2.7204820852,-1.7119945104
C,0,3.2096621274,-2.7739149277,-2.9607051569
C,0,1.8160611318,-2.8637403273,-3.0366132074
C,0,0.9094451716,-2.8578703107,0.6337399776
C,0,-0.4427982375,-2.6077132149,0.823472877
C,0,-1.2009342913,-3.1413659638,2.0019503404
H,0,-0.0282482732,-2.9896397932,-1.9460902286
H,0,3.5589987665,-2.7045631589,0.4219213378
H,0,4.9179918598,-2.6601144439,-1.646882946
H,0,3.8043788831,-2.7574588666,-3.8695653516
H,0,1.3275613644,-2.9266759745,-4.0049342232
H,0,1.4762676074,-3.1359591298,1.5203149802
H,0,-1.0502471721,-2.2946878073,-0.0206767676
H,0,-1.9927266318,-2.4443687821,2.2813209801
H,0,-1.6596427998,-4.1060032537,1.7432650484
H,0,-0.5421851314,-3.2927573183,2.8619141236
O,0,-2.3050377548,-0.2389648823,0.5546282533
C,0,-1.3881906968,0.8337051608,0.4950432782
C,0,-2.1505305435,2.0168768662,1.1432401787
O,0,-3.4139012717,1.4852528561,1.5202895944
C,0,-3.6269828166,0.2995703907,0.7752051062
C,0,-0.0787049898,0.4600239833,1.2773327875
C,0,1.1764788644,1.041796324,0.6110002062
C,0,1.2755308053,0.8050242095,-0.910283433
C,0,-0.0980556669,0.4790993791,-1.4973412302
O,0,-1.1199670643,1.2240901674,-0.8460788648
O,0,1.0831356993,2.4596980785,0.7152129553
C,0,1.7472987945,3.044279968,-0.4024599248
O,0,1.7703758829,2.0391562298,-1.4261576189
C,0,0.9256902415,4.2357674817,-0.8780123017
C,0,3.1871874578,3.4109088988,-0.0361890271
C,0,-4.407898675,-0.6763137762,1.6411963094
C,0,-4.3081076731,0.5926125887,-0.5658995452
H,0,-2.2525201194,2.8217609041,0.4066316491
H,0,-1.6513188912,2.3889116337,2.0382358117
H,0,2.0482885463,0.6604470844,1.1560928891
H,0,1.9872561131,0.012416743,-1.1635711963
H,0,-0.3004366577,-0.5967082096,-1.4287037437
H,0,-0.1274081829,0.7692141482,-2.5506279289
H,0,1.3938769447,4.6920028288,-1.7558903687

H,0,-0.0779560604,3.8943358574,-1.1423891935
H,0,0.8537325242,4.9887510821,-0.0867892268
H,0,3.7180009169,3.7895073988,-0.9156436274
H,0,3.1992790371,4.1797565186,0.7429655277
H,0,3.7199632062,2.529519793,0.3348680661
H,0,-5.39938656,-0.2682266118,1.8598549202
H,0,-4.5309150541,-1.6350406266,1.1276698455
H,0,-3.8751102453,-0.8304942522,2.5828970901
H,0,-5.295428765,1.034104653,-0.3954172001
H,0,-3.7042867658,1.2846962698,-1.1577244698
H,0,-4.4311566487,-0.3319893168,-1.1399761339
O,0,-0.1440832649,0.6271613642,2.5902708972
O,0,0.1191734461,-0.954894289,1.6309552117

Transition structure H (45)

E(RB+HF-LYP) = -1343.49177120

Zero-point correction= 0.466361 (Hartree/Particle)
Thermal correction to Energy= 0.492971
Thermal correction to Enthalpy= 0.493915
Thermal correction to Gibbs Free Energy= 0.410271
Sum of electronic and zero-point Energies= -1343.025410
Sum of electronic and thermal Energies= -1342.998800
Sum of electronic and thermal Enthalpies= -1342.997856
Sum of electronic and thermal Free Energies= -1343.081501

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.344	105.070	176.045

O,0,-3.741984794,-1.1172129746,-0.677175909
C,0,-3.3071399304,-0.1005606772,0.2155316252
C,0,-1.9623902646,-0.6664264063,0.7073092312
O,0,-2.1969042235,-2.0630640444,0.733877926
C,0,-3.3180686021,-2.3672480456,-0.1247831814
C,0,-3.2383155602,1.2604708058,-0.4685414422
O,0,-2.0823388185,1.4606043995,-1.2798518729
C,0,-0.856243889,1.2337037824,-0.6008349022
C,0,-0.809208054,-0.2756624454,-0.2471487879
C,0,0.2882183742,1.6830421602,-1.5288532622
O,0,0.986254735,2.6896539079,-0.7849015804
C,0,0.0540711009,3.2188643159,0.1506845153

O,0,-0.7255087008,2.0701252432,0.5474355311
C,0,0.8039934513,3.7571818937,1.3588788177
C,0,-0.8378559894,4.2892375303,-0.4907640201
O,0,-0.6559686628,-1.011482658,-1.337635732
O,0,0.5141617855,-0.7564528176,0.1586501131
C,0,-2.8893901463,-3.2801342806,-1.2639060344
C,0,-4.4230460175,-2.9743909184,0.7440838183
C,0,1.49495079,-0.0017185765,1.6386255919
C,0,2.4190795223,-1.0286870391,1.4942626088
H,0,1.427217797,4.6050459496,1.0591976457
H,0,0.0960982499,4.0979265046,2.1201791153
H,0,1.4474756682,2.9892973708,1.7938072594
H,0,-0.2230927409,5.1282743033,-0.8325974758
H,0,-1.3878071891,3.8798867706,-1.3403368523
H,0,-1.5635406779,4.6619691774,0.2396716231
H,0,-2.5637760482,-4.2461982126,-0.8645311213
H,0,-3.729635447,-3.4483367675,-1.9458879383
H,0,-2.061507111,-2.8139493785,-1.7990753297
H,0,-4.0561890518,-3.8791701539,1.2391289226
H,0,-4.7402625662,-2.2674801623,1.5173960116
H,0,-5.2907969462,-3.2362131176,0.1299158948
H,0,-0.1261766353,2.0841499898,-2.4597900963
H,0,0.9739106161,0.8661598426,-1.7477391729
H,0,-1.7341716718,-0.3322912704,1.7218838384
H,0,-4.0079095233,-0.0162786648,1.0634992819
H,0,-3.2840589678,2.0390295677,0.3040482489
H,0,-4.0952713082,1.3785441669,-1.136409018
C,0,0.6249535508,0.0718866188,2.8650356068
H,0,1.6952375609,0.9412414639,1.1453873491
C,0,3.4877681252,-1.0974750085,0.5339068558
H,0,2.2847933395,-1.9098389105,2.1209685332
H,0,1.2089686224,0.4610344067,3.7108400776
H,0,-0.2100490118,0.7560342991,2.7063254769
H,0,0.2400285804,-0.913850685,3.1452254777
C,0,4.3058597099,-2.2497733398,0.5114843173
C,0,5.358482841,-2.3621365527,-0.3886929011
C,0,5.6123295222,-1.3269407334,-1.2926802654
C,0,4.8090014308,-0.1798132997,-1.2899060835
C,0,3.7602988896,-0.058651849,-0.3885814006
H,0,4.0989497917,-3.0564427349,1.2102156708
H,0,5.9773284419,-3.2547532561,-0.3924619784
H,0,6.4321139652,-1.4130015331,-2.0005565746
H,0,5.0046819018,0.620435515,-1.9977762001
H,0,3.141656665,0.8327994624,-0.4043807214

Transition structure E (46)

E(RB+HF-LYP) = -1343.49073403

Zero-point correction= 0.466386 (Hartree/Particle)
Thermal correction to Energy= 0.493015
Thermal correction to Enthalpy= 0.493959
Thermal correction to Gibbs Free Energy= 0.410249
Sum of electronic and zero-point Energies= -1343.024348
Sum of electronic and thermal Energies= -1342.997719
Sum of electronic and thermal Enthalpies= -1342.996775
Sum of electronic and thermal Free Energies= -1343.080485

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.371	104.956	176.182

O,0,2.7607388106,0.6623802515,-1.109361647
C,0,1.909942182,-0.3928686223,-0.6594276136
C,0,0.5426977977,0.272714795,-0.3623450804
C,0,0.6657918751,1.3019948951,0.7847981427
C,0,1.8414559982,2.262305881,0.5545341851
C,0,3.0612123061,1.6372256776,-0.1159407085
O,0,1.2387132943,3.2685924196,-0.2500064899
C,0,-0.1044909962,3.4256596263,0.2100240473
O,0,-0.4551370124,2.1712528315,0.8487094262
C,0,-0.9999893094,3.6811746502,-0.9925705206
C,0,-0.1903425468,4.5276371023,1.2685686186
O,0,2.4581153128,-1.0722525644,0.4562889067
C,0,3.207688164,-2.2024618454,-0.0511308789
O,0,2.5035621443,-2.6043168964,-1.2133574162
C,0,1.8616872274,-1.4546219337,-1.7702669039
C,0,4.645240119,-1.7882871172,-0.3857168875
C,0,3.1514280372,-3.3283375714,0.9696683452
H,0,5.1612365881,-1.4362068764,0.5141401854
H,0,5.1919567343,-2.6470714792,-0.7886106277
H,0,4.6483080687,-0.9861633055,-1.1266839647
H,0,3.6029219161,-3.0127653727,1.9153107262
H,0,2.1141813285,-3.6217691267,1.1430457455
H,0,3.7022195588,-4.1952713332,0.5924403084
H,0,2.3892258527,-1.0880623503,-2.6567424054
H,0,0.8351450284,-1.7150994404,-2.0293767374
H,0,3.6871686993,1.1887371828,0.6667892142

H,0,3.6390051518,2.4140403306,-0.6232552145
H,0,2.1679229712,2.6942694576,1.5154531056
H,0,0.7625618597,0.780845125,1.7420166819
H,0,0.5056128074,4.3313367767,2.0901692328
H,0,0.053505427,5.4989219866,0.8262409918
H,0,-1.2027109775,4.5741524507,1.6825971611
H,0,-0.675901726,4.588368639,-1.5131142249
H,0,-2.0361254692,3.8197249551,-0.6655059704
H,0,-0.9407652196,2.8249988215,-1.6657907901
O,0,-0.0136888664,0.6749077918,-1.500023687
O,0,-0.6013761486,-0.6167998286,-0.2067530669
C,0,-1.1901705999,-1.2323452324,1.5075882028
C,0,-2.196253004,-1.9879456617,0.9075802923
H,0,-2.0419869777,-3.0645574629,0.8414059177
C,0,-3.3945112835,-1.4788306262,0.3025489365
H,0,-1.4400264138,-0.2279270617,1.8338042658
C,0,-0.1006510844,-1.9219566061,2.2850730119
H,0,0.8685314711,-1.438439787,2.1519211396
H,0,-0.3460782718,-1.9066952572,3.3558752731
H,0,0.0051385708,-2.9663239743,1.9751498765
C,0,-4.3942987258,-2.391345516,-0.1084329966
C,0,-5.5811291387,-1.9412787839,-0.671369808
C,0,-5.7844660137,-0.569807328,-0.8576667728
C,0,-4.7942520833,0.3456439268,-0.4820002772
C,0,-3.6106848347,-0.0938795982,0.0962741733
H,0,-4.2273598489,-3.4565535234,0.0320713821
H,0,-6.3446297118,-2.6525809991,-0.9729748352
H,0,-6.7088580819,-0.2152142087,-1.3054930451
H,0,-4.9465278491,1.4075983193,-0.6517438029
H,0,-2.8265162797,0.6152548042,0.3381551566

Transition structure C (47)

E(RB+HF-LYP) = -1343.48975459

Zero-point correction= 0.465680 (Hartree/Particle)
Thermal correction to Energy= 0.492585
Thermal correction to Enthalpy= 0.493529
Thermal correction to Gibbs Free Energy= 0.408591
Sum of electronic and zero-point Energies= -1343.024074
Sum of electronic and thermal Energies= -1342.997170
Sum of electronic and thermal Enthalpies= -1342.996226
Sum of electronic and thermal Free Energies= -1343.081164

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	309.102	105.325	178.767

O,0,2.8187181735,0.7638809969,-0.6512546764
C,0,1.4578054795,0.8711036356,-1.0678935906
C,0,0.6206680607,0.2475339649,0.0855611258
C,0,0.9650951242,-1.2444008229,0.2886499545
C,0,2.4797655474,-1.4782899353,0.3506332665
C,0,3.3041477034,-0.5711029414,-0.5556222943
O,0,-0.8223869584,0.4811312957,0.022147269
O,0,0.6327402619,1.0714789234,1.1223687359
O,0,1.245797884,0.2696896139,-2.3343583009
C,0,1.4209471117,1.3030199284,-3.3362396722
O,0,0.9634176849,2.4879647482,-2.7106980968
C,0,1.1682811196,2.3639523854,-1.3013579131
C,0,0.5172373344,1.0007737068,-4.5224201222
C,0,2.8949039548,1.4170630289,-3.7410952658
O,0,0.5114923613,-1.7422512063,1.5382035629
C,0,1.6280889703,-1.747763495,2.4641942336
O,0,2.7496290733,-1.2533350286,1.7286494479
C,0,1.3607527091,-0.8048139544,3.6273786114
C,0,1.8631374046,-3.1952970005,2.9005492504
H,0,0.5050322049,-1.8303025544,-0.5138088219
H,0,2.7096625558,-2.5242823754,0.0861697175
H,0,4.3231451975,-0.4917670982,-0.1684147828
H,0,3.3426802029,-1.0262755514,-1.5543024335
H,0,1.1258088764,0.1845955706,3.2324751469
H,0,0.5159663273,-1.1706591914,4.2207948315
H,0,2.2425204519,-0.7501615529,4.2743350401
H,0,0.9619729065,-3.5977533166,3.3743345354
H,0,2.1063059971,-3.8242525581,2.0382946129
H,0,2.6891348469,-3.246465266,3.6170982354
H,0,2.0202004392,2.9626568408,-0.9640841453
H,0,0.2640333398,2.6837890403,-0.7836609797
H,0,3.2434948872,0.4791055357,-4.1869497269
H,0,3.0131347214,2.2187699372,-4.4772944377
H,0,3.5132932986,1.6416075598,-2.8697529375
H,0,0.6373305866,1.7782461362,-5.2828365249
H,0,-0.5273042463,0.9890962242,-4.2023629165
H,0,0.7747196481,0.0351619501,-4.9686761603
C,0,-2.1964521124,-0.3726978399,-1.3553947467
C,0,-2.4107031889,-0.7546187773,-0.0416500503

C,0,-3.2856631092,-0.1129714414,0.9361061727
C,0,-1.5950357978,-1.2860718503,-2.375727408
C,0,-3.1463562782,-0.4660843701,2.2905507454
C,0,-3.9635416756,0.1084456128,3.2588710614
C,0,-4.9386490793,1.038291972,2.8881833526
C,0,-5.0895737115,1.3933334271,1.5450268849
C,0,-4.2700316086,0.8231748989,0.5749894596
H,0,-2.3663959994,-1.1684146902,2.57176506
H,0,-3.8395028373,-0.1644632883,4.3030205433
H,0,-5.5805375782,1.4842190605,3.6430642239
H,0,-5.8500385231,2.1126015958,1.2540137359
H,0,-4.4066161674,1.0924329475,-0.4681619441
H,0,-2.294776723,-1.4164268311,-3.212620933
H,0,-0.6662287604,-0.873898521,-2.7786586987
H,0,-1.3841317007,-2.2745396311,-1.9553284888
H,0,-1.9628936689,-1.691761725,0.2800957378
H,0,-2.614221877,0.5651862119,-1.708769355

Transition structure AD (48)

E(RB+HF-LYP) = -1343.48737507

Zero-point correction= 0.465261 (Hartree/Particle)
Thermal correction to Energy= 0.492281
Thermal correction to Enthalpy= 0.493225
Thermal correction to Gibbs Free Energy= 0.407643
Sum of electronic and zero-point Energies= -1343.022114
Sum of electronic and thermal Energies= -1342.995094
Sum of electronic and thermal Enthalpies= -1342.994150
Sum of electronic and thermal Free Energies= -1343.079732

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	308.911	105.371	180.123

O,0,-0.9265597202,1.3371790652,0.2865886106
C,0,0.4697590612,1.2022825927,0.1797541596
C,0,0.983600962,2.6056473737,0.5231531335
O,0,-0.0669016979,3.4546928708,0.0750257819
C,0,-1.2875119044,2.7337036679,0.18301961
C,0,0.97992203,0.0968119805,1.171088808
C,0,2.0745467573,-0.7847045209,0.5466259048
C,0,1.769717348,-1.2945603083,-0.8781944641

C,0,0.7087975563,-0.4208644908,-1.5528623336
O,0,0.8582036959,0.9375653545,-1.1655318868
O,0,3.2193861273,0.0385202343,0.3585902947
C,0,3.9428921149,-0.4236713616,-0.7810120783
O,0,3.0222128552,-1.2141081283,-1.5497386303
C,0,4.3804057748,0.7892469705,-1.5930073482
C,0,5.1069318822,-1.3153978616,-0.3470012908
C,0,-2.0335988575,3.1117910547,1.4621552058
C,0,-2.0910491879,2.9680396343,-1.090624597
H,0,1.8945790543,2.8553871036,-0.0211476671
H,0,1.1484726712,2.6913832319,1.6025917082
H,0,2.2912631684,-1.5999021113,1.2495100684
H,0,1.4524757194,-2.3459668578,-0.8883529889
H,0,-0.302874526,-0.7746921687,-1.3153662717
H,0,0.8417935088,-0.4554325528,-2.6375203495
H,0,4.9173364645,0.4700634437,-2.4918914522
H,0,3.4960669366,1.3607484976,-1.8844774947
H,0,5.0414281103,1.4266594878,-0.9970371111
H,0,5.6173628783,-1.7270172467,-1.223668664
H,0,5.826823505,-0.7411364607,0.2445499596
H,0,4.7385182682,-2.1475720736,0.2612218449
H,0,-2.9532522266,2.5246284975,1.5565655969
H,0,-1.4028551362,2.9075544785,2.3322603544
H,0,-2.2940979625,4.1749273334,1.4487571983
H,0,-3.0157025635,2.3831320453,-1.0734991276
H,0,-2.3434779636,4.0290321137,-1.1885008598
H,0,-1.4905456343,2.6644683628,-1.9516693524
O,0,1.2354485909,0.5154259926,2.4038708626
O,0,-0.0592192593,-0.7048054816,1.8351427409
C,0,-2.0073496052,-1.7918618265,1.3260449797
C,0,-0.7878486478,-2.4464834577,1.4137413962
C,0,-0.3320865269,-3.1500001724,2.6596975343
C,0,-2.7843652232,-1.4973950728,0.139019913
C,0,-3.8619551154,-0.5930512379,0.2409148861
C,0,-4.6687664294,-0.3138665293,-0.8567399133
C,0,-4.422374984,-0.9390126036,-2.0824996811
C,0,-3.3701529914,-1.8524608833,-2.1984634453
C,0,-2.5630089442,-2.1336038982,-1.1013252019
H,0,-2.4499439289,-1.477402691,2.2688606274
H,0,-0.3067853396,-2.7600037613,0.4895265015
H,0,0.7585746903,-3.1428096913,2.7366582765
H,0,-0.7418576467,-2.6694658757,3.5522592681
H,0,-0.6661982635,-4.1967406647,2.6440201741
H,0,-4.0492725686,-0.1040710482,1.1930205635

H,0,-5.4921282487,0.3880709616,-0.7589101788
H,0,-5.054217106,-0.7254972253,-2.9400126634
H,0,-3.1877768835,-2.3545716789,-3.1443775949
H,0,-1.7733041272,-2.8730670062,-1.1958636188

Transition structure CD (49)

E(RB+HF-LYP) = -1343.48733066

Zero-point correction= 0.465253 (Hartree/Particle)
Thermal correction to Energy= 0.492270
Thermal correction to Enthalpy= 0.493214
Thermal correction to Gibbs Free Energy= 0.407792
Sum of electronic and zero-point Energies= -1343.022077
Sum of electronic and thermal Energies= -1342.995061
Sum of electronic and thermal Enthalpies= -1342.994117
Sum of electronic and thermal Free Energies= -1343.079538

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	308.904	105.380	179.785

O,0,-1.6707329906,-0.1774074338,0.312431011
C,0,-0.9133412826,0.9142890808,-0.1484766237
C,0,-1.9334079257,2.0748527613,-0.2472170871
O,0,-3.1607212073,1.5305678826,0.2170930835
C,0,-3.0685655896,0.1172415793,0.1356355693
C,0,0.245369624,1.2100632096,0.8698628399
C,0,1.5499463325,1.6194812928,0.1664621349
C,0,1.9617496131,0.722442319,-1.0207594546
C,0,0.7636867598,-0.0725455651,-1.5431638759
O,0,-0.4253310292,0.703808734,-1.4706546143
O,0,1.3100999236,2.8802326159,-0.4480302483
C,0,2.1078075776,2.9816306258,-1.625742122
O,0,2.4474240162,1.6366566593,-1.9980960815
C,0,1.261291068,3.6164239841,-2.7220445496
C,0,3.3971348014,3.7505340138,-1.3329768577
C,0,-3.8334824125,-0.4763972886,1.3089568807
C,0,-3.5482210432,-0.3968300375,-1.2258304224
H,0,-2.0028379707,2.4008164771,-1.2916681687
H,0,-1.6643398162,2.9168375955,0.3913487125
H,0,2.3355121478,1.6987766641,0.9293961156
H,0,2.7810764842,0.0376757246,-0.7636299704

H,0,0.6419416185,-1.0099224639,-0.9868811535
H,0,0.9152857103,-0.3134071283,-2.5987170933
H,0,1.8334190707,3.6812471217,-3.6528559361
H,0,0.3726623832,3.0023552423,-2.8866162395
H,0,0.9529911131,4.6246929444,-2.4278855513
H,0,4.0406917227,3.7637419947,-2.2184604995
H,0,3.1690153198,4.7816828549,-1.0455146818
H,0,3.9451580507,3.2724284803,-0.5148286484
H,0,-4.8853076605,-0.1790188904,1.2569729166
H,0,-3.7783965456,-1.5694362881,1.2911745124
H,0,-3.4021512991,-0.104831882,2.2417094586
H,0,-4.6074031353,-0.1579052974,-1.3678617854
H,0,-2.9682177903,0.0617496477,-2.0308798412
H,0,-3.4181524027,-1.4823785595,-1.28701426
O,0,-0.0998397771,1.969985309,1.8987118913
O,0,0.47029551,0.1846652536,1.8992631036
C,0,0.6299430864,-2.0864490462,2.0370571505
C,0,1.738481314,-1.2507632147,2.0382308062
C,0,2.4061070268,-0.7887377632,3.3015175088
C,0,0.187019184,-2.9801433289,0.9855716945
C,0,-1.1213028467,-3.5040636813,1.0423539255
C,0,-1.5767647988,-4.3975082068,0.0792760024
C,0,-0.7306691,-4.7986786199,-0.9586432732
C,0,0.5763632818,-4.3059314117,-1.0207631347
C,0,1.0330029524,-3.4102263425,-0.0595574121
H,0,0.0285095641,-2.0860668109,2.9433536874
H,0,2.3505688671,-1.2112187346,1.1393223984
H,0,2.8679887264,0.1924100552,3.1620064397
H,0,1.6852937729,-0.7151849824,4.1203188442
H,0,3.1920828342,-1.4993154885,3.5926057302
H,0,-1.7790017908,-3.1861381352,1.8462166373
H,0,-2.5900315642,-4.784968882,0.1366980871
H,0,-1.0832318227,-5.5010616881,-1.7086737826
H,0,1.2430540145,-4.6309258292,-1.8145476872
H,0,2.0613790955,-3.0628120665,-0.0993316018

Transition structure AB (50)

E(RB+HF-LYP) = -1343.48585457

Zero-point correction= 0.465165 (Hartree/Particle)
Thermal correction to Energy= 0.492273
Thermal correction to Enthalpy= 0.493217

Thermal correction to Gibbs Free Energy= 0.407393
Sum of electronic and zero-point Energies= -1343.020690
Sum of electronic and thermal Energies= -1342.993582
Sum of electronic and thermal Enthalpies= -1342.992638
Sum of electronic and thermal Free Energies= -1343.078462

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	308.906	105.596	180.632

O,0.7647369571,1.1755739857,0.4447429905
C,-0.5879100429,1.0590159857,0.0687139905
C,-0.8696860429,2.3603729857,-0.7067330095
O,0.1161369571,3.2612299857,-0.2182730095
C,1.2630829571,2.4892449857,0.0945829905
C,-0.8075490429,-0.2215510143,-0.8184710095
C,-2.1534370429,-0.9082330143,-0.5251640095
C,-2.5028320429,-1.0823100143,0.9717399905
C,-1.6255050429,-0.1811770143,1.8413679905
O,-1.4272140429,1.0757749857,1.2181469905
O,-3.1612500429,-0.0166660143,-0.9932520095
C,-4.3250200429,-0.1773570143,-0.1874840095
O,-3.8696800429,-0.6943280143,1.0697939905
C,-4.9497260429,1.1939439857,0.0315399905
C,-5.2841310429,0.1844600143,0.8270440095
C,2.1876089571,2.3477899857,-1.1161240095
C,1.9365479571,3.1076729857,1.3109489905
H,-1.8557840429,2.7609199857,-0.4729840095
H,-0.7735050429,2.1911819857,-1.7842400095
H,-2.1780120429,-1.8539130143,-1.0816340095
H,-2.4167050429,-2.1238380143,1.3006479905
H,-0.6633890429,-0.6685820143,2.0579959905
H,-2.1301900429,0.0177479857,2.7905929905
H,-5.8376450429,1.1081849857,0.6655889905
H,-4.2208930429,1.8432839857,0.5225799905
H,-5.2426130429,1.6359979857,-0.9259090095
H,-6.1425760429,-1.3598670143,-0.1708480095
H,-5.6448460429,-0.8101260143,-1.7903530095
H,-4.7768830429,-2.1404360143,-0.9931450095
H,3.0664669571,1.7495869857,-0.8574850095
H,1.6598019571,1.8413989857,1.9291680095
H,2.5165949571,3.3358179857,1.4551570095
H,2.7996289571,2.5073349857,1.6146059905
H,2.2799189571,4.1202659857,1.0762879905

H,1.2201199571,3.1566939857,2.1350299905
O,-0.5304680429,-0.0750900143,-2.0971980095
O,0.3456499571,-1.1817250143,-0.8272890095
C,1.7570449571,-1.8453270143,0.7218409905
C,0.9652099571,-2.7681300143,0.0528549905
C,3.0426469571,-1.3256050143,0.2952569905
C,-0.1038230429,-3.5795290143,0.7186669905
C,3.8151759571,-0.6023580143,1.2254329905
C,5.0797149571,-0.1271780143,0.8892949905
C,5.5907969571,-0.3511820143,-0.3913300095
C,4.8270409571,-1.0505850143,-1.3324180095
C,3.5688569571,-1.5359900143,-0.9957150095
H,1.4162029571,-1.5121450143,1.6996629905
H,1.3431169571,-3.1902150143,-0.8730610095
H,0.2964959571,-4.5764460143,0.9496269905
H,-0.4413920429,-3.1313260143,1.6565759905
H,-0.9637670429,-3.7267570143,0.0579419905
H,3.4135189571,-0.4201510143,2.2188679905
H,5.6642859571,0.4212699857,1.6226089905
H,6.5751009571,0.0229529857,-0.6588000095
H,5.2142489571,-1.2112860143,-2.3346070095
H,2.9747559571,-2.0481220143,-1.7451520095

Transition structure CB (51)

E(RB+HF-LYP) = -1343.48491397

Zero-point correction= 0.465176 (Hartree/Particle)
Thermal correction to Energy= 0.492271
Thermal correction to Enthalpy= 0.493215
Thermal correction to Gibbs Free Energy= 0.407854
Sum of electronic and zero-point Energies= -1343.019738
Sum of electronic and thermal Energies= -1342.992643
Sum of electronic and thermal Enthalpies= -1342.991699
Sum of electronic and thermal Free Energies= -1343.077060

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
TOTAL	308.904	105.563	179.658

O,0,0.7597152554,1.2043513705,0.3171495928
C,0,-0.5973784244,1.0507095195,-0.0134597842
C,0,-0.9404653158,2.3208460431,-0.8310597994

O,0,0.2831370788,3.0312458727,-0.9426088433
C,0,1.1462190072,2.5743171125,0.0861605868
C,0,-0.7988242114,-0.2689412576,-0.8460567657
C,0,-2.1247532632,-0.9745213436,-0.5034591503
C,0,-2.4546093248,-1.0946877753,1.0032380113
C,0,-1.5857860329,-0.1423018511,1.8235177282
O,0,-1.4288722191,1.0937770435,1.1459055071
O,0,-3.158252767,-0.1259859248,-0.9954998998
C,0,-4.3087717054,-0.278922599,-0.1704543542
O,0,-3.8267980225,-0.7272274081,1.1036578952
C,0,-4.9636380199,1.0857215525,-0.0057162219
C,0,-5.2496339469,-1.3369535516,-0.7522199054
C,0,2.5703615806,2.5886750348,-0.4445399731
C,0,0.9663966276,3.3937584111,1.3687969571
H,0,-1.6985216187,2.8981236615,-0.2880212538
H,0,-1.2970293821,2.0836785723,-1.8335584488
H,0,-2.1346296045,-1.9427346242,-1.0202191925
H,0,-2.3437648574,-2.1200226977,1.3730115909
H,0,-0.6078387975,-0.5960217298,2.0408834646
H,0,-2.0797280087,0.0829274498,2.7724372695
H,0,-5.8359184916,1.0102425641,0.6508945841
H,0,-4.2405013911,1.7758672564,0.4354913891
H,0,-5.2866074934,1.4724712569,-0.9772731116
H,0,-6.0957849187,-1.503458849,-0.0779963559
H,0,-5.6305451525,-1.0155435436,-1.7267710487
H,0,-4.7206585379,-2.2868118493,-0.8816514646
H,0,2.8605510245,3.6125566231,-0.7005287375
H,0,3.2654060944,2.2002560602,0.3050739739
H,0,2.6248768464,1.9652010396,-1.3398546544
H,0,1.2257675768,4.4415903948,1.1851411032
H,0,-0.0687540725,3.3384132163,1.7158824762
H,0,1.6143827197,3.0052264239,2.161717232
O,0,-0.5520209853,-0.1593310388,-2.1326814492
O,0,0.3781946043,-1.1954620794,-0.8366521405
C,0,1.8178693245,-1.8145487909,0.7386840723
C,0,1.0287107401,-2.7329624388,0.0581026799
C,0,3.1003603233,-1.2887269664,0.313200631
C,0,-0.0285573621,-3.5613056473,0.7237361105
C,0,3.9241177323,-0.6694387182,1.2742350451
C,0,5.1947930702,-0.2115127175,0.9374825565
C,0,5.6574153073,-0.3419892514,-0.3739186482
C,0,4.8401140848,-0.9309952871,-1.345300727
C,0,3.5772428917,-1.4039604834,-1.0091298027
H,0,1.4778549987,-1.4952156431,1.7218789277

H,0,1.4233303894,-3.1579752323,-0.859587984
H,0,0.3886135991,-4.5496029773,0.9608911065
H,0,-0.3775012901,-3.1149747977,1.6584633595
H,0,-0.883626972,-3.7252822044,0.060906455
H,0,3.5612929422,-0.5619849017,2.2935004319
H,0,5.8212455473,0.2524185034,1.6942514814
H,0,6.6454273863,0.0218558136,-0.6419632374
H,0,5.1891337908,-1.0136845653,-2.3707289733
H,0,2.9356056197,-1.8220118719,-1.7774711602

Oxazolidinone + styrene transition structure A (56)

E(RB+HF-LYP) = -1393.06039948

Zero-point correction= 0.386073 (Hartree/Particle)
Thermal correction to Energy= 0.411025
Thermal correction to Enthalpy= 0.411969
Thermal correction to Gibbs Free Energy= 0.330684
Sum of electronic and zero-point Energies= -1392.674327
Sum of electronic and thermal Energies= -1392.649374
Sum of electronic and thermal Enthalpies= -1392.648430
Sum of electronic and thermal Free Energies= -1392.729715

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	257.922	96.504	171.079

C,0,-2.0491801084,3.5921548672,-0.1672754231
C,0,-0.9531920739,3.0715774351,-0.8908445755
C,0,0.2126929111,3.859899005,-1.0089376553
C,0,0.2823124905,5.119841128,-0.4214139267
C,0,-0.8121271909,5.6205208167,0.2867530221
C,0,-1.9769258893,4.852351553,0.4112610352
C,0,-0.9684555392,1.7639959177,-1.5175124723
C,0,-1.9609443381,0.8153844845,-1.4438984925
H,0,-2.9259970087,1.0227281849,-0.9979898639
O,0,-1.2712827237,0.0217417108,0.2645114724
C,0,-0.434330955,-1.120351215,0.3744244155
C,0,-0.7208247137,-2.2618263286,-0.6269396565
C,0,0.2659534921,-3.4292394385,-0.4608608313
C,0,1.6908604384,-3.0402720349,-0.0930092589
O,0,1.7841511383,-1.9421254608,0.8222253987
C,0,1.0755966034,-0.8004019217,0.4432826985

O,0,-1.9761457575,-2.8698919775,-0.4054013623
C,0,-1.7731506815,-4.0952182437,0.3431770006
O,0,-0.3611680376,-4.1837951163,0.5665924536
O,0,1.5231731648,-0.3287374288,-0.851025202
C,0,2.2170959439,0.8462249398,-0.7501472569
N,0,2.2172527851,1.232606306,0.5945185046
C,0,1.4209447253,0.32600566,1.4255798941
C,0,-2.47392212,-4.0217695458,1.6906275358
C,0,-2.2607596374,-5.258238635,-0.5221207404
O,0,-0.9748592662,-1.1796774681,1.6041531935
C,0,2.7808902477,2.4054266444,1.0909639444
O,0,3.3718682406,3.2405798514,0.4493089143
O,0,2.682337391,1.415229081,-1.7004273693
H,0,-3.5558580183,-3.945612958,1.5433812776
H,0,-2.2623584191,-4.9254617758,2.2714141797
H,0,-2.1245066621,-3.1423469793,2.2329240258
H,0,-3.3174919015,-5.1211301596,-0.7716804861
H,0,-1.6943407158,-5.3131957571,-1.456926696
H,0,-2.1457876014,-6.2051079973,0.01488905
H,0,2.0019170672,-0.077229834,2.2571120523
H,0,0.5133888496,0.8066767665,1.7940560224
H,0,-0.6905268335,-1.8566171306,-1.6435793127
H,0,0.3076816877,-4.01353284,-1.3945944311
H,0,2.2406174771,-2.7953816278,-1.0096636727
H,0,2.1880239748,-3.8758424443,0.4039708812
H,0,-0.0757486683,1.5081386652,-2.0838171368
H,0,-1.9196674371,-0.0606094373,-2.0795438991
H,0,2.6168737509,2.4825481951,2.1827323035
H,0,1.0728018119,3.4669241516,-1.5440511014
H,0,1.1940120111,5.702743082,-0.5099260312
H,0,-0.7605844937,6.6045235864,0.7447535993
H,0,-2.8272260917,5.2411952557,0.9644412017
H,0,-2.9557871025,3.0053708495,-0.0576870246

Oxazolidinone + styrene transition structure B (57)

E(RB+HF-LYP) = -1393.05531773

Zero-point correction= 0.385384 (Hartree/Particle)
Thermal correction to Energy= 0.410644
Thermal correction to Enthalpy= 0.411588
Thermal correction to Gibbs Free Energy= 0.327390
Sum of electronic and zero-point Energies= -1392.669933

Sum of electronic and thermal Energies= -1392.644674
Sum of electronic and thermal Enthalpies= -1392.643730
Sum of electronic and thermal Free Energies= -1392.727928

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	257.683	96.784	177.210

C,0,4.53159354,-0.817104176,-0.0353636485
C,0,3.3374030741,-1.5027199451,-0.3428323788
C,0,3.2044294012,-2.8441679803,0.0770785463
C,0,4.2303266285,-3.4699094783,0.7725743529
C,0,5.4116326604,-2.7764207032,1.0619716185
C,0,5.5598711499,-1.4479750607,0.6562729229
C,0,2.3072434887,-0.8011738992,-1.0768969951
C,0,1.0808472727,-1.2860154979,-1.4714069618
H,0,0.8309373758,-2.3371200211,-1.3882564549
O,0,0.3426167513,-0.7418130836,0.3023438704
C,0,-0.5958344669,0.3224124697,0.4447465331
C,0,0.0063908302,1.7298116638,0.2219379762
C,0,-1.0546731789,2.8383976949,0.3212971476
C,0,-2.4343466641,2.4738922979,-0.2076966725
O,0,-2.8316034606,1.1289009927,0.0800221032
C,0,-1.9217112757,0.1489743289,-0.3329005783
O,0,0.9336068361,2.0845210502,1.2275654883
C,0,0.2709453442,2.9436268674,2.1881022898
O,0,-1.0747771424,3.0857822472,1.7201780199
O,0,-1.6947472399,0.2438933456,-1.7583805939
C,0,-2.4224799825,-0.7058207299,-2.4429666705
N,0,-2.9910099346,-1.5638920296,-1.4923699823
C,0,-2.5806240115,-1.2187188291,-0.1291619114
C,0,0.2401095897,2.2877183567,3.5595428843
C,0,0.9907488383,4.2932292998,2.1827454623
O,0,-0.7233264589,-0.1507251384,1.6928491135
C,0,-3.8181187687,-2.6474634584,-1.7814693241
O,0,-4.1711491089,-3.0034066774,-2.8788656313
O,0,-2.4839194139,-0.7479208483,-3.6377514402
H,0,1.2604945036,2.1622788379,3.935463139
H,0,-0.3178429003,2.9150394574,4.2624162202
H,0,-0.2337036037,1.3085442557,3.4785885234
H,0,2.0452263236,4.156965549,2.4425292235
H,0,0.9399845782,4.7559448798,1.1920700459
H,0,0.5335402402,4.9705344578,2.911003233
H,0,-3.4362346243,-1.122577409,0.5407444127

H,0,-1.8653195068,-1.9364602245,0.2777719779
H,0,0.5111089462,1.7427512299,-0.7504867942
H,0,-0.7093957755,3.7335494957,-0.2219190142
H,0,-2.4553190825,2.6370102901,-1.2917932403
H,0,-3.1916233133,3.1071172759,0.2591737623
H,0,4.640734828,0.2190485298,-0.3451913163
H,0,6.4731588112,-0.9059433397,0.8835920302
H,0,6.2116686901,-3.2715099524,1.6052389249
H,0,4.113361823,-4.5005483975,1.0947380669
H,0,2.2897496751,-3.3891090486,-0.1321035052
H,0,0.4587838376,-0.6972420552,-2.1331675988
H,0,2.526508156,0.2407869494,-1.3025632497
H,0,-4.1248763618,-3.1591109815,-0.8483935058

Oxazolidinone + styrene transition structure C (58)

E(RB+HF-LYP) = -1393.05684109

Zero-point correction= 0.385877 (Hartree/Particle)
Thermal correction to Energy= 0.410945
Thermal correction to Enthalpy= 0.411889
Thermal correction to Gibbs Free Energy= 0.329744
Sum of electronic and zero-point Energies= -1392.670964
Sum of electronic and thermal Energies= -1392.645896
Sum of electronic and thermal Enthalpies= -1392.644952
Sum of electronic and thermal Free Energies= -1392.727097

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	257.872	96.620	172.889

C	0	2.09859	-2.08712	0.42443
C	0	0.92636	-1.38766	-0.27532
O	0	1.48391	-0.1604	-0.81026
C	0	2.84571	-0.12453	-0.68248
N	0	3.24559	-1.28401	-0.00978
O	0	0.48866	-2.21516	-1.31002
C	0	-0.50417	-1.63728	-2.16581
C	0	-1.71425	-1.08203	-1.42961
C	0	-1.41452	-0.37625	-0.09767
C	0	-0.25048	-1.05013	0.67053
O	0	-2.60004	-2.11333	-1.01677
C	0	-3.40892	-1.5688	0.03257

O	0	-2.64272	-0.47794	0.59647
O	0	0.13592	-0.3704	1.87691
C	0	0.14167	2.07323	1.99642
C	0	1.22205	1.22284	2.12752
O	0	-0.52729	-2.07602	1.47829
C	0	-3.64647	-2.65278	1.07262
C	0	-4.70587	-0.98616	-0.53236
O	0	3.51119	0.80244	-1.0595
C	0	4.56418	-1.62419	0.29076
O	0	5.54821	-0.9941	-0.00923
C	0	-0.19568	2.90355	0.86255
C	0	-1.42517	3.60063	0.88728
C	0	-1.79429	4.43562	-0.16074
C	0	-0.9413	4.59221	-1.25687
C	0	0.27971	3.90875	-1.29967
C	0	0.65581	3.07315	-0.25545
H	0	2.00583	1.1961	1.38146
H	0	-4.25972	-2.25753	1.88865
H	0	-4.17117	-3.49961	0.61817
H	0	-2.68707	-2.98169	1.474
H	0	-5.26828	-0.48492	0.26169
H	0	-4.49234	-0.25167	-1.31528
H	0	-5.32766	-1.78137	-0.95586
H	0	2.17202	-3.11874	0.07607
H	0	1.96971	-2.065	1.50813
H	0	-1.17662	0.68023	-0.24687
H	0	-2.22977	-0.38434	-2.11038
H	0	-0.04875	-0.8352	-2.75902
H	0	-0.81187	-2.4415	-2.83736
H	0	-2.08716	3.47175	1.73959
H	0	-2.74277	4.96356	-0.1259
H	0	-1.22519	5.24665	-2.07644
H	0	0.94277	4.03137	-2.15093
H	0	1.60592	2.55303	-0.31319
H	0	1.49199	0.86118	3.11124
H	0	-0.55866	2.10403	2.82815
H	0	4.5992	-2.57719	0.8531

Oxazolidinone + styrene transition structure D

E(RB+HF-LYP) = -1393.05644322

Zero-point correction= 0.386029 (Hartree/Particle)

Thermal correction to Energy= 0.411022
Thermal correction to Enthalpy= 0.411966
Thermal correction to Gibbs Free Energy= 0.330242
Sum of electronic and zero-point Energies= -1392.670415
Sum of electronic and thermal Energies= -1392.645421
Sum of electronic and thermal Enthalpies= -1392.644477
Sum of electronic and thermal Free Energies= -1392.726201

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	257.920	96.439	172.003

C,0,-0.1288383054,2.8387789147,0.7689670104
C,0,0.2037495219,1.599357616,-0.0736448051
O,0,-1.0806316763,1.0620290589,-0.4771483063
C,0,-2.1112608476,1.8830431108,-0.1133819841
N,0,-1.5741857074,2.9749469264,0.5727842062
O,0,0.9291671359,2.0189344385,-1.1903498722
C,0,1.2106861734,0.9916569616,-2.1466577183
C,0,1.8934123738,-0.2355826722,-1.560914744
C,0,1.3889472817,-0.6748289867,-0.1776148409
C,0,1.0078267202,0.5314778093,0.7124044032
O,0,3.2715306806,-0.0052545522,-1.3029826282
C,0,3.6876988439,-0.9939485689,-0.3539656285
O,0,2.485333294,-1.400877432,0.3447713601
O,0,0.4291387267,0.2008820589,1.9695544976
O,0,1.96604623,1.1240805069,1.4401715044
C,0,4.6780285605,-0.3564829015,0.6082815813
C,0,4.2524327033,-2.224128378,-1.0666123337
O,0,-3.264642602,1.6308490754,-0.3443136819
C,0,-2.3099771824,4.0371607589,1.0957927281
O,0,-3.5031158245,4.192177129,1.004222854
C,0,-0.7547098015,-1.213511029,2.4807949774
C,0,-1.7925794728,-1.1658746812,1.5677875015
C,0,-2.0106468941,-2.056162971,0.4506727188
C,0,-1.2845439489,-3.2593867496,0.2789288578
C,0,-1.554831997,-4.1006532272,-0.792409737
C,0,-2.5525241925,-3.7649508938,-1.7158270055
C,0,-3.2773732348,-2.5795536118,-1.5636365908
C,0,-3.0132563507,-1.7324264863,-0.4932923064
H,0,-0.0393971701,-2.0279591714,2.4769329116
H,0,5.0065784727,-1.0944793937,1.346977952
H,0,5.5543034536,0.0036474408,0.0593543798
H,0,4.1958588756,0.4746960868,1.1244943564

H,0,4.4715415953,-3.0112435157,-0.3382701095
H,0,3.5314933307,-2.6188281216,-1.789405683
H,0,5.1758102401,-1.9666874334,-1.5949969822
H,0,0.4150669171,3.7023526028,0.3817687006
H,0,0.1260315703,2.671529118,1.816349098
H,0,0.5282129693,-1.3439853889,-0.2601173231
H,0,1.7711462296,-1.0622264273,-2.2801119817
H,0,0.2773229087,0.6802825867,-2.6314524095
H,0,1.8570693599,1.4583046885,-2.8929901746
H,0,-2.5198321384,-0.3645376431,1.6777224748
H,0,-0.8709985596,-0.7005916668,3.4276481684
H,0,-1.6426075045,4.7483520221,1.6197195947
H,0,-3.5501898201,-0.7937678539,-0.3935961905
H,0,-4.0461720481,-2.3141779334,-2.2833894735
H,0,-2.762875677,-4.4280520219,-2.5505166999
H,0,-0.9944993406,-5.0239221986,-0.9083075131
H,0,-0.5206111328,-3.5398006137,0.9972591359

Oxazolidinone + styrene transition structure E (59)

E(RB+HF-LYP) = -1393.05692479

C,0,1.0282043093,-0.7936558384,3.2947049669
C,0,2.1311429831,-1.2434965747,2.5336909267
C,0,3.4330688441,-0.9470821753,2.9971042164
C,0,3.6242196308,-0.2084078938,4.1591464911
C,0,2.5191977654,0.2527579482,4.881308797
C,0,1.2209832896,-0.041737005,4.4460748527
C,0,1.9879508217,-1.9855509746,1.3038901183
C,0,0.8391228595,-2.2051278599,0.5732799234
O,0,1.156178369,-0.6968137886,-0.6795325831
C,0,0.0186702204,-0.1186142744,-1.3239118047
C,0,-0.9476159522,-1.1371564732,-1.9768456704
C,0,-2.1716333649,-0.445278061,-2.6010603975
C,0,-2.693615092,0.7726600948,-1.8510802136
O,0,-1.6696851223,1.5963488553,-1.280803046
C,0,-0.7508219882,0.9173223315,-0.4755425651
O,0,-0.3614347196,-1.8022245011,-3.0771316355
C,0,-0.816373458,-1.171144221,-4.2994856904
O,0,-1.6773155464,-0.1031988732,-3.8881333668
C,0,0.1497654966,1.9578298456,0.1952419149
N,0,-0.4207535067,2.0276638206,1.5443303291
C,0,-1.32720183,0.9876710735,1.7793089282

O,0,-1.4345680892,0.2588879004,0.6213368822
C,0,0.3570056167,-0.5807206858,-5.0657551642
C,0,-1.5931476327,-2.2146376776,-5.1042475008
O,0,0.9308479468,0.4844533811,-2.0946847338
O,0,-1.9087547725,0.703049241,2.7899478716
C,0,0.0099586914,2.9445215108,2.4986337574
O,0,-0.3456520822,2.9967564697,3.6518399716
H,0,0.852162887,-2.9416189077,-0.2202517908
H,0,2.9169404728,-2.3546218155,0.8713348358
H,0,-0.1333417005,-1.9280255074,0.9646241168
H,0,1.0319412884,-1.3806208591,-5.3863385365
H,0,-0.0043757225,-0.0507883225,-5.9531764206
H,0,0.9005985085,0.1077285776,-4.4176463711
H,0,-0.95022227,-3.0728960187,-5.3230985893
H,0,-2.4606178756,-2.5735358065,-4.5415661125
H,0,-1.9401132253,-1.784563553,-6.0491526674
H,0,0.0718587758,2.9116250397,-0.3282857486
H,0,1.1860999258,1.6149056702,0.2104231299
H,0,-1.2453967946,-1.8800664568,-1.2299241976
H,0,-3.0008697645,-1.166526995,-2.6883176148
H,0,-3.3736076759,0.4375915851,-1.0586816674
H,0,-3.2427574379,1.4232583989,-2.5348672437
H,0,0.7439073265,3.6464468428,2.0582551464
H,0,4.2899005081,-1.2932675361,2.4244577583
H,0,4.6310018995,0.0156724552,4.4997488041
H,0,2.6664900738,0.840582004,5.7829236733
H,0,0.3593219416,0.3275669124,4.9923921427
H,0,0.0161382735,-1.0314804662,2.9873848491

Oxizolidinone + cis-beta-methylstyrene transition structure A

E(RB+HF-LYP) = -1432.37549396

Zero-point correction= 0.413978 (Hartree/Particle)
Thermal correction to Energy= 0.440784
Thermal correction to Enthalpy= 0.441728
Thermal correction to Gibbs Free Energy= 0.355627
Sum of electronic and zero-point Energies= -1431.961516
Sum of electronic and thermal Energies= -1431.934710
Sum of electronic and thermal Enthalpies= -1431.933766
Sum of electronic and thermal Free Energies= -1432.019866

E (Thermal) CV S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	276.596	102.129	181.214
O	-4.15531	-0.6657	0.39866
C	-3.25696	-1.05814	-0.62995
C	-2.31839	0.15708	-0.69504
O	-3.18161	1.2441	-0.42985
C	-4.35759	0.74478	0.25724
C	-2.58621	-2.39096	-0.32683
O	-1.51419	-2.31182	0.61955
C	-0.53824	-1.35712	0.32288
C	-1.17132	0.0528	0.33619
C	0.6151	-1.52391	1.31993
N	1.67923	-2.07538	0.47743
C	1.33464	-2.06042	-0.87832
O	0.04373	-1.61032	-0.97851
O	-1.38124	0.48388	1.58704
O	-0.22397	1.11894	0.29714
C	-4.46901	1.36015	1.64324
C	-5.57265	1.03367	-0.6257
C	1.49997	1.32304	-1.27214
C	2.73059	1.4565	-0.50611
C	0.39782	2.1537	-1.36292
C	0.23602	3.57244	-0.90633
H	-4.61843	2.44133	1.55942
H	-5.3232	0.92945	2.17576
H	-3.55019	1.16727	2.1983
H	-5.65394	2.10939	-0.81035
H	-5.48154	0.52801	-1.592
H	-6.48881	0.69073	-0.13456
H	0.32166	-2.21828	2.10935
H	0.89623	-0.56002	1.74738
H	-1.88829	0.27459	-1.69494
H	-3.79379	-1.16317	-1.58698
H	-2.21101	-2.81962	-1.26386
H	-3.31066	-3.08072	0.11117
H	1.45943	0.4316	-1.89365
H	-0.36477	1.82483	-2.06388
O	2.00667	-2.33511	-1.8343
C	2.93053	-2.42466	0.98075
O	3.87507	-2.81361	0.33768
H	2.95342	-2.30156	2.08058
C	3.83088	0.6666	-0.90641
C	5.0479	0.74135	-0.23556

C	5.18691	1.59041	0.86446
C	4.09512	2.3483	1.30062
C	2.87841	2.28311	0.62961
H	3.71719	-0.02045	-1.74036
H	5.87904	0.12266	-0.56007
H	6.13377	1.64528	1.39455
H	4.1897	2.98203	2.1781
H	2.02645	2.82823	1.01699
H	-0.0358	4.19611	-1.76699
H	-0.58479	3.63649	-0.18411
H	1.13931	3.98826	-0.45881

Oxizolidinone + cis-beta-methylstyrene transition structure B

E(RB+HF-LYP) = -1432.37261342

Zero-point correction= 0.413953 (Hartree/Particle)
Thermal correction to Energy= 0.440592
Thermal correction to Enthalpy= 0.441536
Thermal correction to Gibbs Free Energy= 0.355872
Sum of electronic and zero-point Energies= -1431.958660
Sum of electronic and thermal Energies= -1431.932022
Sum of electronic and thermal Enthalpies= -1431.931077
Sum of electronic and thermal Free Energies= -1432.016741

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	276.476	102.085	180.295

O,0,-0.2433104925,3.6892762658,0.1381307606
C,0,-0.7867674801,2.8351016101,-0.8592232356
C,0,0.1098083706,1.5959536573,-0.7212104733
O,0,1.3738629645,2.1515637511,-0.4116293232
C,0,1.1724755903,3.480509242,0.140540031
C,0,-2.2747780848,2.5865198259,-0.6557898796
O,0,-2.5757093552,1.6392472021,0.3738262653
C,0,-1.9206188979,0.4078069562,0.2568533696
C,0,-0.3946061367,0.6282934577,0.3751782872
C,0,-2.4942035882,-0.5262850122,1.3273221337
N,0,-3.3835473682,-1.3828298612,0.5383683273
C,0,-3.1905114901,-1.2100788977,-0.839561504
O,0,-2.2465493982,-0.221572268,-1.0039943781
O,0,-0.0507384084,0.8329586043,1.6482215012

O,0,0.3860170416,-0.5704407696,0.4984742942
C,0,1.6691298971,3.5441384718,1.5760578336
C,0,1.8704341499,4.4791723978,-0.783344644
C,0,0.3694653948,-2.1461339659,-0.8937568856
C,0,0.1078774748,-3.3429043874,-0.0327103217
C,0,1.5749419256,-1.4994155029,-1.0895969963
C,0,2.8836904728,-1.77599205,-0.5036604676
C,0,3.3380820864,-3.0754085093,-0.2100954329
C,0,4.6144641725,-3.2756200896,0.3113165601
C,0,5.4509699346,-2.1852309847,0.5587318208
C,0,5.0117445021,-0.8897171871,0.2698603257
C,0,3.7457618691,-0.6855810508,-0.268319497
H,0,2.752584069,3.3895999832,1.6039690836
H,0,1.4456947011,4.5267425216,2.0042606
H,0,1.1800060585,2.7638413453,2.1605053834
H,0,2.9379334198,4.2468079137,-0.8506441873
H,0,1.4477769142,4.4378652107,-1.7919546767
H,0,1.7565198465,5.4963564966,-0.3956559906
H,0,-3.0435356465,0.0551199006,2.0691563803
H,0,-1.6991745283,-1.0958130285,1.8126129744
H,0,0.1793861388,1.0511165534,-1.6685000169
H,0,-0.6529818535,3.2809367499,-1.8585671598
H,0,-2.7090201551,2.245662098,-1.6034542036
H,0,-2.7699581784,3.5119270375,-0.354203233
H,0,-0.9212146514,-3.3213244001,0.3382576625
H,0,0.2130313806,-4.2684693788,-0.6163292329
H,0,0.7885136153,-3.3921183276,0.8201127345
H,0,3.3888040409,0.3204795993,-0.4721529521
H,0,5.6593988799,-0.0392975541,0.4634408922
H,0,6.4440241309,-2.3444899075,0.9699798865
H,0,4.9580191152,-4.2848127485,0.5205600953
H,0,2.7091444333,-3.9322852079,-0.4256018164
H,0,-0.4506100752,-1.8277053176,-1.5301206644
H,0,1.5565572274,-0.6547150071,-1.7728373334
O,0,-3.688587133,-1.7996700099,-1.7549932924
C,0,-4.2914481692,-2.2682528862,1.1171896711
O,0,-5.0342205874,-3.0147635941,0.5285058124
H,0,-4.2476563169,-2.1996595279,2.2215701922

Transition structure for trihydroxy dimethyldioxirane reacting with trans-β-methylstyrene (52)

E(RB+HF-LYP) = -842.841920744

Zero-point correction= 0.265259 (Hartree/Particle)
Thermal correction to Energy= 0.283270
Thermal correction to Enthalpy= 0.284214
Thermal correction to Gibbs Free Energy= 0.218299
Sum of electronic and zero-point Energies= -842.576662
Sum of electronic and thermal Energies= -842.558650
Sum of electronic and thermal Enthalpies= -842.557706
Sum of electronic and thermal Free Energies= -842.623621

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	177.755	66.296	138.730

C,0,-3.3075254437,2.1256127759,-0.9093299359
C,0,-1.9800420732,2.4629373789,-1.1909793337
C,0,-0.9522937598,2.0315348396,-0.3580140867
C,0,-1.2322064951,1.2463743235,0.7804531791
C,0,-2.5760519512,0.9126606526,1.0467787265
C,0,-3.6019714066,1.346652229,0.2130287909
C,0,-0.2092856524,0.796120733,1.7101985274
O,0,1.0087563392,-1.0700915421,1.0686635652
C,0,1.1593244368,0.8820202225,1.5720572481
C,0,2.1079611543,0.7132632174,2.7213864272
C,0,1.0552280069,-1.505178156,-0.2854443742
C,0,-0.2682107908,-1.4929862212,-1.0458396575
O,0,-1.2935298542,-2.0138010803,-0.2162553621
O,0,1.436383619,-2.6711921181,0.2776262812
C,0,2.2274275138,-0.8918569463,-1.0758045551
O,0,2.5910951261,-1.7577660807,-2.1347402895
H,0,0.0724959173,2.2966866885,-0.5947492018
H,0,-2.8034505035,0.2997618436,1.9147652195
H,0,-4.631082148,1.0796191942,0.4373581054
H,0,-4.1070588828,2.4701821655,-1.5595194309
H,0,-1.7462960332,3.0676136144,-2.0628824342
H,0,-0.5800929933,0.3489944867,2.6304613099
H,0,1.5717183364,1.3123676628,0.6630119793
H,0,3.021555438,0.2049561012,2.4002958393
H,0,2.3927736943,1.6956939162,3.1233996934
H,0,1.6551820932,0.1300374692,3.5285519461
H,0,3.0688702299,-0.7857502233,-0.3697292338
O,0,1.8764746878,0.3461679759,-1.638907972
H,0,-0.486441531,-0.468651782,-1.3734335205
H,0,-0.1148203804,-2.1046157578,-1.9486152365

H,0,2.7580516836,-2.6222352731,-1.7184981963
H,0,-2.1248330021,-1.9127589735,-0.7025305873
H,0,2.5658675047,0.5586313362,-2.2899217702

Transition Structure for reaction of oxazolidinone-derived dioxirane with 1-phenylcyclohexene, Isomer A, (Structure 63)

C---O distances 2.405, 2.060
E(RB+HF-LYP) = -1549.11709090

Zero-point correction= 0.480036 (Hartree/Particle)
Thermal correction to Energy= 0.508684
Thermal correction to Enthalpy= 0.509628
Thermal correction to Gibbs Free Energy= 0.419837
Sum of electronic and zero-point Energies= -1548.637055
Sum of electronic and thermal Energies= -1548.608407
Sum of electronic and thermal Enthalpies= -1548.607463
Sum of electronic and thermal Free Energies= -1548.697254

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	319.204	111.508	188.981

C,0,0.6049027792,2.8956908014,-0.7350336793
C,0,-0.3330471641,2.6409019488,0.2923181095
C,0,-1.6393082542,3.1533891964,0.1245826222
C,0,-1.9913171595,3.8783310282,-1.010211705
C,0,-1.050017091,4.1126309862,-2.0142405025
C,0,0.2475381243,3.6151960794,-1.8700993096
C,0,0.0301928281,1.905272826,1.5155258383
C,0,1.2363314417,1.2286069625,1.6407378174
O,0,0.14370026,-0.4905131237,1.3333582519
C,0,-0.2615064236,-1.2037522361,0.159620176
C,0,0.8984224482,-1.5352636088,-0.8095322135
O,0,0.4525443231,-2.3843995017,-1.8232844553
C,0,-0.58071677,-1.846014614,-2.6566433444
C,0,-1.7828247662,-1.3078980809,-1.8950382243
C,0,-1.4574179743,-0.5709210176,-0.5885408653
O,0,1.4211354855,-0.3039831841,-1.3683222966
C,0,2.7747807916,-0.2054852116,-1.2075854186
N,0,3.2122260528,-1.3451548882,-0.5221269176
C,0,2.0965011439,-2.2077245165,-0.1255818846
O,0,-2.6641190087,-0.6790913974,0.1448273355

C,0,-3.4228841671,-1.7993935249,-0.3728679588
O,0,-2.6340314455,-2.3491247141,-1.4343029715
O,0,3.4109652604,0.7457093006,-1.5744684548
C,0,4.5348345372,-1.6175368696,-0.1775603858
O,0,5.4955907167,-0.935526214,-0.4380892624
O,0,-0.4928643739,-2.2143466961,1.0031186142
C,0,-3.605506698,-2.8660947926,0.6959937958
C,0,-4.7490197964,-1.2573937897,-0.9096902347
H,0,1.9164480957,1.2208915099,0.7983316287
H,0,-4.2046350418,-2.4681231293,1.5213060243
H,0,-4.1233870818,-3.733807737,0.2742730713
H,0,-2.6279170921,-3.1655995626,1.0758010192
H,0,-5.2994999687,-0.7531634154,-0.1091280479
H,0,-4.5759188694,-0.5344314305,-1.712927769
H,0,-5.3642703762,-2.0751423209,-1.2982961574
H,0,2.2137216348,-3.2231072881,-0.5092582832
H,0,1.9587231356,-2.2305031881,0.9566727099
H,0,-1.243746438,0.4854821827,-0.7654344338
H,0,-2.3347435029,-0.6359581666,-2.5729020626
H,0,-0.1641660821,-1.0415863034,-3.274975351
H,0,-0.8863509953,-2.6683901706,-3.3069319701
H,0,-2.3932308768,2.9740339129,0.8817428387
H,0,-3.0044648189,4.2573045991,-1.1112244065
H,0,-1.3240588445,4.6785844152,-2.9003707841
H,0,0.9906855272,3.790515636,-2.6424200169
H,0,1.6239714546,2.5352250723,-0.6626645349
C,0,1.8434120629,0.8447832238,2.9675001039
C,0,-0.9330430731,1.9194320699,2.6831309044
H,0,4.5999236155,-2.5710504449,0.3816676489
H,0,2.8619402001,1.2551438862,3.0039145379
C,0,1.0206610547,1.3305556817,4.1684783945
H,0,1.9506134538,-0.2464908585,2.9963703233
H,0,-1.1081342212,2.9684456291,2.9665311353
H,0,-1.8994961961,1.5301320425,2.339645392
C,0,-0.4702711213,1.110100326,3.9038397865
H,0,-1.0695164658,1.4016453171,4.7740753042
H,0,-0.6560403493,0.046929921,3.7194200882
H,0,1.3402337662,0.8049743452,5.0752860542
H,0,1.2101837097,2.3998567979,4.3390794421

Transition Structure for reaction of oxazolidinone-derived dioxirane with 1-phenylcyclohexene, Isomer B, (Structure 64)

C----O distances 2.091, 2.417
E(RB+HF-LYP) = -1549.11870065

Zero-point correction= 0.480121 (Hartree/Particle)
Thermal correction to Energy= 0.508517
Thermal correction to Enthalpy= 0.509461
Thermal correction to Gibbs Free Energy= 0.421250
Sum of electronic and zero-point Energies= -1548.638580
Sum of electronic and thermal Energies= -1548.610184
Sum of electronic and thermal Enthalpies= -1548.609239
Sum of electronic and thermal Free Energies= -1548.697450

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	319.099	111.356	185.655

O,0,-3.9300734097,-1.6135321417,0.1999158082
C,0,-2.90964285,-1.6989493497,-0.7856891375
C,0,-2.239728952,-0.3209982639,-0.6556815898
O,0,-3.3232522788,0.5334892808,-0.3462744796
C,0,-4.4115254309,-0.2662972859,0.184202453
C,0,-1.1518304466,-0.306520495,0.4433220718
C,0,-0.2358180828,-1.5378742554,0.3131300121
O,0,-1.0121984263,-2.6966654854,0.462571508
C,0,-1.9948466433,-2.8952102561,-0.5589804429
O,0,0.4292313241,-1.5416832116,-0.9705324618
C,0,1.6938523881,-2.0759504669,-0.8539657456
N,0,1.986770767,-2.157332595,0.5141652504
C,0,0.9017426306,-1.605662944,1.3311664726
O,0,-0.4959355576,0.9456516209,0.6300328614
O,0,-1.5281858227,-0.1187430018,1.7163973376
C,0,3.1736032092,-2.6384893256,1.0564439328
O,0,4.118888369,-3.0707958018,0.4417896266
O,0,2.3711400342,-2.3742212336,-1.7957824333
C,0,-4.73211362,0.1516501026,1.6104991246
C,0,-5.6018772484,-0.1253178936,-0.7657782262
C,0,0.1959032745,2.025879175,-1.0210573703
C,0,-1.0001056981,2.9026028966,-1.2992983446
C,0,-1.2878790518,3.8940175242,-0.1675440246
C,0,0.0025815366,4.5820808514,0.2832299104
C,0,1.0423029785,3.5560394374,0.7621331218
C,0,1.2445135741,2.404558394,-0.1986536187
C,0,2.5236508811,1.6831210355,-0.1780298125
C,0,3.3289674824,1.6806974707,0.9814846152

C,0,4.5380110922,0.9915881199,1.0111635679
C,0,4.9828435555,0.3005506696,-0.1191546865
C,0,4.2093904582,0.3075972879,-1.2819894927
C,0,2.9980413655,0.9918338734,-1.3123826988
H,0,0.3548140269,1.1880392082,-1.6951231401
H,0,-5.0998862233,1.1826502856,1.622873584
H,0,-5.5068572572,-0.5009628842,2.0260326848
H,0,-3.8271758168,0.0853556728,2.2155888348
H,0,-5.895550418,0.9259502709,-0.8459393418
H,0,-5.3447918637,-0.4848565666,-1.7670189776
H,0,-6.4547400252,-0.7016821496,-0.3935355179
H,0,0.6334653273,-2.2693610448,2.1537730891
H,0,1.1449061716,-0.609457087,1.7072773673
H,0,-1.7919125851,-0.0054930024,-1.6032479017
H,0,-3.3559340016,-1.800906178,-1.7884755543
H,0,-1.495033616,-3.1417172035,-1.503155127
H,0,-2.582295619,-3.7570075145,-0.235314758
H,0,3.1446865412,-2.5792883301,2.1618535359
H,0,2.9923414804,2.1995384742,1.8732198005
H,0,5.1337990086,0.9902088889,1.9199140881
H,0,5.9198005386,-0.24727797,-0.092584617
H,0,4.5409794988,-0.234889336,-2.1610836202
H,0,2.4216274143,1.0029981368,-2.2316725204
H,0,0.7094802283,3.1257037396,1.7196815729
H,0,2.0001263449,4.049785719,0.9582867127
H,0,-1.8827944289,2.2859291845,-1.4913264547
H,0,-0.7945975022,3.4471148007,-2.2363085553
H,0,-0.1968513624,5.2951410679,1.0917307887
H,0,0.4238094383,5.1613734573,-0.5504940824
H,0,-2.0237704223,4.6351251136,-0.5009076661
H,0,-1.7321725199,3.345635392,0.6704363378

Transition Structure for reaction of oxazolidinone-derived dioxirane with 1-phenylcyclohexene, Isomer C

E(RB+HF-LYP) = -1549.11565119

Zero-point correction= 0.480241 (Hartree/Particle)
Thermal correction to Energy= 0.508718
Thermal correction to Enthalpy= 0.509662
Thermal correction to Gibbs Free Energy= 0.420921
Sum of electronic and zero-point Energies= -1548.635411
Sum of electronic and thermal Energies= -1548.606933

Sum of electronic and thermal Enthalpies= -1548.605989
Sum of electronic and thermal Free Energies= -1548.694730

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	319.226	111.304	186.772

C,0,1.8875340513,1.0762524642,3.6100993679
C,0,0.5629233216,1.7669359944,3.2688415559
C,0,0.315468532,1.8701058327,1.7852632116
C,0,1.3337792803,1.8936658422,0.842401404
C,0,2.7226687124,1.4287334537,1.2377212243
C,0,3.0186651894,1.6235116101,2.734966114
C,0,1.1107839084,2.4002643795,-0.5188753213
C,0,1.9581243212,2.0240681947,-1.5838782846
C,0,1.7603216879,2.5245837384,-2.8672541733
C,0,0.7256057851,3.4270334993,-3.1226885567
C,0,-0.1173862639,3.8227193403,-2.0807266781
C,0,0.0703797882,3.3164361937,-0.7987018771
O,0,-0.2173045375,-0.0666417876,1.6063397993
C,0,-0.9097639109,-0.7820119121,0.5987712495
C,0,-0.033176307,-1.7269100913,-0.2582778938
O,0,-0.8568399895,-2.5388646074,-1.0474767095
C,0,-1.6678091545,-1.8361777653,-1.9950710788
C,0,-2.5221354945,-0.7345888978,-1.3845259088
C,0,-1.8446700655,0.0805227313,-0.2749933858
C,0,0.8645555078,-2.6470145657,0.5759672329
N,0,2.1345910905,-2.5714273457,-0.150105184
C,0,2.127250477,-1.5406044854,-1.0972666174
O,0,0.8787155175,-0.9744460943,-1.0896099449
O,0,-2.9403160637,0.5937038804,0.4596551379
C,0,-4.1002311379,-0.2370300993,0.2010418398
O,0,-3.6573330628,-1.2539904797,-0.7041964986
O,0,-1.4150818889,-1.4734602163,1.6378099526
O,0,3.0248057875,-1.1504821462,-1.7931647246
C,0,3.2166836142,-3.404856402,0.1252882729
O,0,4.2974170841,-3.3726611888,-0.4106388514
C,0,-4.5779153296,-0.9038780541,1.4815962716
C,0,-5.1674718915,0.6427884392,-0.4522387816
H,0,-0.6624619976,2.2477873184,1.5059343775
H,0,-4.9183372497,-0.1445590629,2.1928623642
H,0,-5.4123256241,-1.5784094531,1.2634877066
H,0,-3.7536936333,-1.4648745427,1.9242106519
H,0,-5.4246735679,1.4747385188,0.2108675178

H,0,-4.8020106188,1.0588103316,-1.396347838
H,0,-6.0716974898,0.0589472649,-0.6513505599
H,0,0.4581340586,-3.6592386133,0.5800976601
H,0,0.9568044613,-2.2746522696,1.5975891131
H,0,-1.264702524,0.9142156914,-0.6827744193
H,0,-2.8387076283,-0.0631958392,-2.1994623335
H,0,-1.0279418336,-1.3991205525,-2.7712270564
H,0,-2.3062886945,-2.5958431422,-2.4510465445
H,0,2.9544793363,-4.1281275903,0.9216865021
H,0,2.7487011418,1.3002480692,-1.4251356665
H,0,2.4151914083,2.2006371782,-3.6708755323
H,0,0.5792256375,3.8231444413,-4.1238571184
H,0,-0.9158318273,4.5363493102,-2.2643405971
H,0,-0.574082429,3.6647932966,0.0017939458
H,0,2.8296635615,0.365473835,0.9803718982
H,0,3.4710451374,1.9568957503,0.6383621184
H,0,-0.2846891794,1.2497518846,3.7291219618
H,0,0.5609790151,2.7930854068,3.6707384382
H,0,3.9710482277,1.1386768258,2.9791261491
H,0,3.1513308364,2.6956129251,2.9374560903
H,0,2.1202745733,1.218923643,4.6719555066
H,0,1.7808187653,-0.002634731,3.4469915414

Transition Structure for reaction of oxazolidinone-derived dioxirane with 1-phenylcyclohexene, Isomer D

E(RB+HF-LYP) = -1549.11523420

Zero-point correction=	0.480155 (Hartree/Particle)
Thermal correction to Energy=	0.508626
Thermal correction to Enthalpy=	0.509570
Thermal correction to Gibbs Free Energy=	0.420934
Sum of electronic and zero-point Energies=	-1548.635079
Sum of electronic and thermal Energies=	-1548.606609
Sum of electronic and thermal Enthalpies=	-1548.605664
Sum of electronic and thermal Free Energies=	-1548.694300

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	319.167	111.314	186.551

C,0,1.4965971704,2.7360300312,-0.7385692745
C,0,0.6575441381,2.5775172623,0.386221277

C,0,-0.4867755589,3.4043773669,0.4743754068
C,0,-0.7821958282,4.3353006915,-0.5160708178
C,0,0.0570682376,4.4698018615,-1.624969652
C,0,1.1936293831,3.6653626006,-1.7298782925
C,0,0.986199906,1.6373033292,1.4695118501
C,0,0.0034576493,1.1377853505,2.316917308
O,0,-0.2007290894,-0.6624541281,1.4403620191
C,0,-0.7735426372,-1.081584914,0.2100437789
C,0,0.2577572656,-1.5441570428,-0.8504206533
O,0,-0.4047781265,-2.1110224758,-1.9430879662
C,0,-1.2830405937,-1.2249889721,-2.6451020364
C,0,-2.3169386316,-0.5457201835,-1.7602471437
C,0,-1.8067705861,-0.0979052582,-0.3842036102
O,0,1.0806282358,-0.4328872717,-1.278882556
C,0,2.4073099825,-0.7636848213,-1.2866539049
N,0,2.5336369849,-2.0580265895,-0.7744782337
C,0,1.2474027757,-2.5859667271,-0.3136902428
O,0,-2.9912673744,-0.0343161154,0.3887680874
C,0,-3.9963329036,-0.8721086969,-0.2355217435
O,0,-3.3746498838,-1.4246289636,-1.4011523343
O,0,3.2717703284,-0.0091556413,-1.6481420105
C,0,3.7329246644,-2.753022987,-0.6291932382
O,0,4.828769047,-2.3601665282,-0.9467795664
O,0,-1.1976461035,-2.1483461439,0.907657814
C,0,-4.3936572104,-2.0136736773,0.6874096598
C,0,-5.1744987908,0.0232648351,-0.6229694559
H,0,-1.0293524107,1.4132106884,2.1343951359
H,0,-4.8743307929,-1.6161069949,1.5870039146
H,0,-5.0994713926,-2.6776569578,0.1776767622
H,0,-3.5011845636,-2.5711458254,0.9748392502
H,0,-5.5754171042,0.5205399416,0.2658675234
H,0,-4.8590224397,0.7944558332,-1.3325927836
H,0,-5.9700034857,-0.572646657,-1.081506878
H,0,1.0292753332,-3.5614806162,-0.7510081066
H,0,1.1957431863,-2.6420129904,0.7745682217
H,0,-1.3555665721,0.8977414496,-0.4275100545
H,0,-2.7116983716,0.3237803604,-2.3115645589
H,0,-0.6925251721,-0.4539505345,-3.1550401558
H,0,-1.7796108016,-1.8430567775,-3.3961218292
C,0,2.4351702549,1.2925494228,1.7281152187
C,0,0.2908320159,0.5952339297,3.6964622833
H,0,3.5511714502,-3.7461828826,-0.1747120237
H,0,2.3649941787,2.1020617652,-0.8712307926
H,0,1.8484094951,3.7549424294,-2.5919705562

H,0,-0.1718417751,5.1979729743,-2.3983406997
H,0,-1.6615362868,4.9654466075,-0.4157455466
H,0,-1.1310991216,3.3435802886,1.3451895597
H,0,2.9493108196,2.2269039281,2.0062553319
C,0,2.6341847018,0.2431886559,2.8289927372
H,0,2.9236242386,0.9698746625,0.8018462469
H,0,-0.2729397283,1.2020133519,4.4186752432
H,0,-0.1325306702,-0.4141472407,3.7527500617
C,0,1.785672731,0.5896412387,4.0560965473
H,0,3.6971654319,0.1902310146,3.0896283513
H,0,2.3418046269,-0.7434437087,2.4503984625
H,0,1.9686322293,-0.1183576718,4.8720705553
H,0,2.0837757226,1.5801780589,4.4276430968

Transition structure for 5-chair + trans-2-butene, analog of structure 34

C---O distances 2.087, 2.061
E(RB+HF-LYP) = -1151.75762959

Zero-point correction= 0.413088 (Hartree/Particle)
Thermal correction to Energy= 0.436622
Thermal correction to Enthalpy= 0.437566
Thermal correction to Gibbs Free Energy= 0.362883
Sum of electronic and zero-point Energies= -1151.344541
Sum of electronic and thermal Energies= -1151.321008
Sum of electronic and thermal Enthalpies= -1151.320064
Sum of electronic and thermal Free Energies= -1151.394746

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	273.984	91.885	157.183

C,0,2.1403268978,-1.419843954,0.3956811187
C,0,1.2305870029,-0.1780398319,0.3589597042
O,0,0.8327678462,0.0097024442,1.7104807769
C,0,1.8117250473,-0.6570427093,2.5390597424
O,0,2.1929759855,-1.7945535063,1.7766951144
O,0,2.0149183873,0.9071982688,-0.125318886
C,0,1.3831035552,2.180908298,-0.0264359121
C,0,0.0034745105,2.2539548239,-0.6706604428
C,0,-0.8465127154,0.9811849622,-0.5370934768
C,0,0.0214801844,-0.2928959941,-0.604238713
O,0,0.077610733,2.4048723552,-2.0825321414

C,0,-1.1786737705,1.9788423156,-2.6167540427
O,0,-1.7463869537,1.0848942699,-1.6265046209
O,0,-0.7465627265,-1.5342002606,-0.5061412841
O,0,0.3955064207,-0.7584448226,-1.7869045966
C,0,-0.9255342277,1.2381643514,-3.9207360955
C,0,-2.1305571959,3.1663406046,-2.7739260675
C,0,1.1403901579,-1.1175677248,3.8232710201
C,0,3.0102423326,0.2590131061,2.8128040983
C,0,-2.5656833587,-2.0258900054,0.3912021046
C,0,-3.4897404924,-0.8553357471,0.4469380832
C,0,-1.5216026726,-2.2784014323,1.2522597753
C,0,-0.8087002598,-3.5886807819,1.367237795
H,0,1.8646525748,-1.6444903303,4.4515041012
H,0,0.7582301641,-0.2566750933,4.3799386736
H,0,0.3143020912,-1.7971126173,3.6028726626
H,0,3.7550755521,-0.2757007394,3.4109574544
H,0,3.4706561297,0.5834613119,1.8775594007
H,0,2.6889509238,1.1474356573,3.3668385824
H,0,-1.8753064591,0.9054469493,-4.3521635429
H,0,-0.4297987869,1.9017628004,-4.6369590958
H,0,-0.296570118,0.3701864001,-3.7193803864
H,0,-3.1195551032,2.8171519608,-3.0875676281
H,0,-2.2418846131,3.702538556,-1.8261632471
H,0,-1.7482055389,3.8616509517,-3.5280385069
H,0,3.1317320466,-1.1612790083,0.0099696591
H,0,1.7239699682,-2.2459559509,-0.1794712694
H,0,-1.4142068757,0.9791088079,0.3978978426
H,0,-0.5338742209,3.1087778201,-0.2265928829
H,0,1.2852548539,2.4634576204,1.0297956246
H,0,2.0567724126,2.887482053,-0.5175853715
H,0,-1.287305566,-1.5192326536,1.99442185
H,0,-2.8016982444,-2.7878304796,-0.349280976
H,0,-4.5206729513,-1.2112337502,0.5793290261
H,0,-3.2538818781,-0.1814121009,1.2760959076
H,0,-3.4558702028,-0.290461737,-0.4918802744
H,0,0.261782631,-3.4301268578,1.5273895618
H,0,-1.1914731422,-4.1484614182,2.2333514777
H,0,-0.9536631602,-4.2024998268,0.4735543098

Transition structure for 5-chair + 2-methyl-2-butene, analog of structure 34

C---O distances 2.192, 2.047
E(RB+HF-LYP) = -1191.07820111

Zero-point correction= 0.440994 (Hartree/Particle)
Thermal correction to Energy= 0.466259
Thermal correction to Enthalpy= 0.467204
Thermal correction to Gibbs Free Energy= 0.388365
Sum of electronic and zero-point Energies= -1190.637207
Sum of electronic and thermal Energies= -1190.611942
Sum of electronic and thermal Enthalpies= -1190.610997
Sum of electronic and thermal Free Energies= -1190.689836

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	292.582	97.577	165.930

O,0,-1.6119333286,1.2015885066,-1.5886601087
C,0,-0.7077611621,1.1060355584,-0.5010572021
C,0,0.1266568254,2.3887221122,-0.6321567837
O,0,0.1961362362,2.5441371591,-2.0440653501
C,0,-1.0568729513,2.1061567854,-2.5761309733
C,0,0.1732170009,-0.1585951408,-0.5721501384
C,0,1.3770668064,-0.0308369712,0.393418536
O,0,2.153149444,1.0619034662,-0.0870781679
C,0,1.5085869186,2.3293317049,0.0098434276
O,0,0.9673455627,0.1542715003,1.7417438175
C,0,1.9429814993,-0.5032091898,2.5799002199
O,0,2.3471326051,-1.6347319242,1.8202509264
C,0,2.298474643,-1.2631884777,0.4382014581
C,0,1.259337992,-0.9743948543,3.8537011339
C,0,3.1281835165,0.425010341,2.8701789992
O,0,-0.5745586543,-1.3974037706,-0.5007570726
O,0,0.561004003,-0.6090834464,-1.7624548918
C,0,-0.7988064664,1.3741378073,-3.884193178
C,0,-2.022037373,3.2840441972,-2.7255806075
C,0,-2.4920938751,-1.9536119825,0.4035158351
C,0,-1.3889684842,-2.1777583406,1.2075561815
C,0,-0.6181166809,-3.4549878314,1.3519410252
C,0,-3.3468013664,-0.7316515755,0.576251645
H,0,1.9768100839,-1.5089200733,4.4833572951
H,0,0.8736262568,-0.1181513479,4.4151325386
H,0,0.433272732,-1.648974888,3.6180470523
H,0,3.8705082105,-0.1021205324,3.4781175246
H,0,3.5979043699,0.753972854,1.9410454614
H,0,2.7901226696,1.3098754436,3.4197866341
H,0,-1.7459475226,1.0333111496,-4.3151756348

H,0,-0.3117142937,2.0460742711,-4.598573776
H,0,-0.1598111305,0.5123881252,-3.6876005626
H,0,-3.0080524482,2.9259978443,-3.0386999594
H,0,-2.1367136664,3.8137933131,-1.7746312678
H,0,-1.6488610526,3.9873591847,-3.4768672337
H,0,3.2896218472,-0.9960990071,0.057653898
H,0,1.893026771,-2.0949484631,-0.1370226849
H,0,-1.2741842575,1.0926600331,0.4344674324
H,0,-0.4187990452,3.2368912535,-0.185123925
H,0,1.4089261529,2.6124942192,1.0657346343
H,0,2.1746685116,3.0418063929,-0.4831377915
H,0,-1.1718286123,-1.4131074121,1.949021209
C,0,-2.9573102415,-2.9211209949,-0.6439826927
H,0,-4.3901350691,-1.032346221,0.744980202
H,0,-3.0290187345,-0.1183169219,1.4241466529
H,0,-3.329400602,-0.1173454974,-0.3322814934
H,0,0.4260937555,-3.2357314519,1.5914205217
H,0,-1.0304481627,-4.0492935172,2.1807580558
H,0,-0.6490180354,-4.0702459799,0.4501837022
H,0,-3.2124268777,-2.3814304154,-1.5623891766
H,0,-2.2098472973,-3.6769788597,-0.8872909972
H,0,-3.8690011035,-3.4325643108,-0.3024328484

Trans-β-methylstyreneoxide (27)

E(RB+HF-LYP) = -424.168478116

Zero-point correction= 0.167261 (Hartree/Particle)
Thermal correction to Energy= 0.175998
THERMAL CORRECTION TO ENTHALPY= 0.176942
Thermal correction to Gibbs Free Energy= 0.133131
Sum of electronic and zero-point Energies= -424.001217
Sum of electronic and thermal Energies= -423.992480
Sum of electronic and thermal Enthalpies= -423.991536
Sum of electronic and thermal Free Energies= -424.035347

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.440	33.514	92.208

C,0,1.3694610907,-0.2284562731,-0.1596944793
C,0,0.0796860486,-0.1654614341,0.3825380287
C,0,-0.0789653036,0.1949700745,1.7264767279

C,0,1.0311063878,0.505219027,2.5122225002
C,0,2.3139028638,0.4488878438,1.9639292366
C,0,2.4790352186,0.0778168378,0.6274220059
C,0,-1.1202896438,-0.4608515849,-0.4530707506
C,0,-1.391545975,0.2261960246,-1.7355766663
C,0,-2.7858747856,0.4381266906,-2.2678223513
H,0,-0.6409349213,0.9476505858,-2.0669683873
H,0,-1.989250775,-0.8251893773,0.1000326477
H,0,-2.7974201691,0.3515827648,-3.3606313709
H,0,-3.4748806179,-0.308360531,-1.8601497775
H,0,-3.1526265022,1.4371821007,-2.0038390264
H,0,-1.0767156403,0.232393583,2.1590553712
H,0,0.8943503779,0.7846628895,3.5536213171
H,0,3.1798926216,0.685456179,2.5763682433
H,0,3.4760885677,0.0206913767,0.1982834316
H,0,1.4896151931,-0.5394960997,-1.1930422323
O,0,-0.910901693,-1.1256570886,-1.7101594659

Acrolein-cis

B3LYP/6-31+G*
E(RB+HF-LYP) = -191.920479353

Zero-point correction= 0.061477 (Hartree/Particle)
Thermal correction to Energy= 0.065881
Thermal correction to Enthalpy= 0.066825
Thermal correction to Gibbs Free Energy= 0.034960
Sum of electronic and zero-point Energies= -191.859002
Sum of electronic and thermal Energies= -191.854598
Sum of electronic and thermal Enthalpies= -191.853654
Sum of electronic and thermal Free Energies= -191.885519

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.341	13.741	67.065

C,0,-0.094603166,-0.0335068748,-0.9305544994
O,0,0.9302027871,0.6144330323,-1.0546615958
C,0,-0.685841477,-0.4411399485,0.368819743
C,0,-0.1222892045,-0.1203677296,1.542335167
H,0,-0.6547485108,-0.3610046659,-1.8312392287
H,0,-1.6078640082,-1.0188050314,0.3232402997
H,0,-0.5611481533,-0.4225114488,2.4890947163

H,0,0.7985414601,0.4569442047,1.5725945161

Acrolein-trans (65)

B3LYP/6-31G*
E(RB+HF-LYP) = -191.911973566

Zero-point correction= 0.061650 (Hartree/Particle)
Thermal correction to Energy= 0.066006
Thermal correction to Enthalpy= 0.066950
Thermal correction to Gibbs Free Energy= 0.035371
Sum of electronic and zero-point Energies= -191.850323
Sum of electronic and thermal Energies= -191.845968
Sum of electronic and thermal Enthalpies= -191.845024
Sum of electronic and thermal Free Energies= -191.876602

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.419	13.706	66.463

C,0,-1.0191469533,0.4475923027,-1.3762667296
C,0,-0.4405206989,-0.3356727565,-0.4586905493
C,0,0.486167306,0.2214781787,0.54467616
O,0,1.0426239101,-0.4363848204,1.4018950643
H,0,-0.6231748628,-1.4066488836,-0.4084864956
H,0,-1.7047141563,0.0591087256,-2.1234559418
H,0,-0.821897764,1.517834573,-1.4064360817
H,0,0.6497975797,1.3203977989,0.4649047182

B3LYP/6-31+G*
E(RB+HF-LYP) = -191.911973566

Zero-point correction= 0.061521 (Hartree/Particle)
Thermal correction to Energy= 0.065881
Thermal correction to Enthalpy= 0.066825
Thermal correction to Gibbs Free Energy= 0.035228
Sum of electronic and zero-point Energies= -191.862395
Sum of electronic and thermal Energies= -191.858035
Sum of electronic and thermal Enthalpies= -191.857091
Sum of electronic and thermal Free Energies= -191.888688

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.341	13.729	66.501

C,0,-1.0191469533,0.4475923027,-1.3762667296
C,0,-0.4405206989,-0.3356727565,-0.4586905493
C,0,0.486167306,0.2214781787,0.54467616
O,0,1.0426239101,-0.4363848204,1.4018950643
H,0,-0.6231748628,-1.4066488836,-0.4084864956
H,0,-1.7047141563,0.0591087256,-2.1234559418

CCSD(T)/6-31G(d) single point energy
CCSD(T)=-191.3619094

mPW1K/6-31G*
E(RmPW+HF-PW91) = -191.84892629

Zero-point correction= 0.063605 (Hartree/Particle)
Thermal correction to Energy= 0.067915
Thermal correction to Enthalpy= 0.068859
Thermal correction to Gibbs Free Energy= 0.037357
Sum of electronic and zero-point Energies= -191.785321
Sum of electronic and thermal Energies= -191.781011
Sum of electronic and thermal Enthalpies= -191.780067
Sum of electronic and thermal Free Energies= -191.811570

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	42.617	13.413	66.303

O,0,-1.7807223148,-0.1172169639,0.
C,0,-0.6715616151,0.3496445433,0.
C,0,0.5576559648,-0.4496578116,0.
C,0,1.7501091673,0.1382892098,0.
H,0,-0.5225745639,1.4427148765,0.
H,0,0.4395852125,-1.5242443258,0.
H,0,2.6698364314,-0.427202314,0.
H,0,1.8417103363,1.2168118254,0.

MP2/6-31G*
E(RHF) = -190.75899694 2

Zero-point correction= 0.062257 (Hartree/Particle)
Thermal correction to Energy= 0.066624
Thermal correction to Enthalpy= 0.067568
Thermal correction to Gibbs Free Energy= 0.035934
Sum of electronic and zero-point Energies= -191.249368

Sum of electronic and thermal Energies= -191.245001
Sum of electronic and thermal Enthalpies= -191.244056
Sum of electronic and thermal Free Energies= -191.275691

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.807	13.681	66.580

C,0,-1.7646514181,0.1488821236,0.
C,0,-0.5634600038,-0.449482802,0.
C,0,0.6725903445,0.351543421,0.
O,0,1.8008104197,-0.130710814,0.
H,0,-0.4506216834,-1.5303504602,0.
H,0,-2.6916120052,-0.4141616446,0.
H,0,-1.8508243226,1.232802628,0.
H,0,0.5197011183,1.4517395329,0.

MVK-cis

B3LYP/6-31+G*
E(RB+HF-LYP) = -231.247287070

Zero-point correction= 0.061521 (Hartree/Particle)
Thermal correction to Energy= 0.065881
Thermal correction to Enthalpy= 0.066825
Thermal correction to Gibbs Free Energy= 0.035228
Sum of electronic and zero-point Energies= -191.862395
Sum of electronic and thermal Energies= -191.858035
Sum of electronic and thermal Enthalpies= -191.857091
Sum of electronic and thermal Free Energies= -191.888688

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.341	13.729	66.501

C,0,0.6102510509,1.729695009,0.2717633289
C,0,0.2845267841,0.248505942,0.2850095503
C,0,-0.6678391823,-0.2315365768,-0.7654121393
C,0,-1.031622041,-1.516730169,-0.8589606261
O,0,0.7744321976,-0.5102034154,1.1094780592
H,0,1.3103515175,1.9674860771,1.0752657878
H,0,1.0474281244,2.0150635996,-0.6944589108
H,0,-0.3062413459,2.3223331893,0.3942190629

H,0,-1.0594011328,0.5103250589,-1.4601716349
H,0,-0.6365241413,-2.2518877685,-0.1620503429

MVK-trans (66)

B3LYP/6-31G*
E(RB+HF-LYP) = -231.234878390

Zero-point correction= 0.089970 (Hartree/Particle)
Thermal correction to Energy= 0.095758
Thermal correction to Enthalpy= 0.096702
Thermal correction to Gibbs Free Energy= 0.061113
Sum of electronic and zero-point Energies= -231.144908
Sum of electronic and thermal Energies= -231.139120
Sum of electronic and thermal Enthalpies= -231.138176
Sum of electronic and thermal Free Energies= -231.173765

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	60.089	19.389	74.904

C,0,0.8606503016,1.2964775841,0.
C,0,0.5439876262,-0.1904547443,0.
O,0,1.4338966025,-1.0277277841,0.
C,0,-0.8776781468,-0.6335358855,0.
C,0,-1.9419099042,0.176387197,0.
H,0,1.9443560908,1.4246843624,0.
H,0,0.4371653642,1.7888891688,-0.8835844299
H,0,0.4371653642,1.7888891688,0.8835844299
H,0,-0.997259267,-1.7148586954,0.
H,0,-1.8486287899,1.2590866733,0.
H,0,-2.9542708428,-0.2181133129,0.

B3LYP/6-31+G*
E(RB+HF-LYP) = -231.247559203

Zero-point correction= 0.089797 (Hartree/Particle)
Thermal correction to Energy= 0.095577
Thermal correction to Enthalpy= 0.096521
Thermal correction to Gibbs Free Energy= 0.060944
Sum of electronic and zero-point Energies= -231.157762
Sum of electronic and thermal Energies= -231.151982
Sum of electronic and thermal Enthalpies= -231.151038

Sum of electronic and thermal Free Energies= -231.186615

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	59.976	19.385	74.879

C,0,0.6622768237,1.3338835003,0.4588978651
C,0,0.3328028991,-0.1488938804,0.4436831291
O,0,0.8358713911,-0.9162287841,1.2550793071
C,0,-0.6165462463,-0.6833482931,-0.5720456942
C,0,-1.2342268723,0.0437733066,-1.5132281581
H,0,1.3689654477,1.531267281,1.2674379683
H,0,1.10627582,1.6468753506,-0.4940024918
H,0,-0.2419683773,1.9350528494,0.614000311
H,0,-0.7834564363,-1.7560523692,-0.495637438
H,0,-1.0862262747,1.1161890231,-1.6126538979

CCSD(T)/6-31G(d) single point energy
CCSD(T)=-230.5526161

mPW1K/6-31G*
E(RmPW+HF-PW91) = -231.16483638

Zero-point correction= 0.092604 (Hartree/Particle)
Thermal correction to Energy= 0.098301
Thermal correction to Enthalpy= 0.099245
Thermal correction to Gibbs Free Energy= 0.063828
Sum of electronic and zero-point Energies= -231.072228
Sum of electronic and thermal Energies= -231.066531
Sum of electronic and thermal Enthalpies= -231.065586
Sum of electronic and thermal Free Energies= -231.101004

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	61.685	18.939	74.543

C,0,-1.0165251203,0.,-1.6412895916
C,0,-1.0310591288,0.,-0.3126884618
C,0,0.1754184704,0.,0.544851532
O,0,0.0478249156,0.,1.7477285715
C,0,1.5360181578,0.,-0.0958862967
H,0,-1.9627339071,0.,0.2366734197
H,0,-1.9339360339,0.,-2.2115696556
H,0,-0.0968193868,0.,-2.2090686327

H,0,1.6683883591,0.8792857501,-0.7255511351
H,0,2.2909990101,0.,0.6833154746
H,0,1.6683883591,-0.8792857501,-0.7255511351

MP2/6-31G*
E(RHF) = -229.802486549

Zero-point correction= 0.091295 (Hartree/Particle)
Thermal correction to Energy= 0.097034
Thermal correction to Enthalpy= 0.097979
Thermal correction to Gibbs Free Energy= 0.062510
Sum of electronic and zero-point Energies= -230.395074
Sum of electronic and thermal Energies= -230.389335
Sum of electronic and thermal Enthalpies= -230.388390
Sum of electronic and thermal Free Energies= -230.423859

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	60.890	19.238	74.650

C,0,0.8482396699,1.2944193627,0.
C,0,0.5414043193,-0.1877683238,0.
O,0,1.4426649883,-1.0290673744,0.
C,0,-0.8743756032,-0.6368440425,0.
C,0,-1.9371131142,0.1828253657,0.
H,0,1.9309369156,1.4210975524,0.
H,0,0.4231039114,1.7788318117,-0.8838536366
H,0,0.4231039114,1.7788318117,0.8838536366
H,0,-1.0013695374,-1.7169523225,0.
H,0,-1.8367863441,1.2632721189,0.
H,0,-2.9492403933,-0.2083361488,0.

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B3LYP/6-31G*
E(RB+HF-LYP) = -423.119431252

Zero-point correction= 0.155197 (Hartree/Particle)
Thermal correction to Energy= 0.164593
Thermal correction to Enthalpy= 0.165537
Thermal correction to Gibbs Free Energy= 0.120728
Sum of electronic and zero-point Energies= -422.964234
Sum of electronic and thermal Energies= -422.954839

Sum of electronic and thermal Enthalpies= -422.953894
Sum of electronic and thermal Free Energies= -422.998703

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.283	34.055	94.307

C,0,-0.6367061771,1.6733205189,-0.1476237647
C,0,0.490082034,1.0069108758,-0.6537797647
H,0,0.7354850245,1.0366609536,-1.7100407647
C,0,1.3736292586,0.2979041557,0.2749282353
O,0,1.0129593086,0.1398850415,1.4441792353
C,0,-2.1424308113,0.5185610419,-0.1213227647
C,0,-1.8404204398,-0.6542808624,0.5961082353
C,0,-0.8816941633,-1.5270695587,0.0262072353
O,0,-0.3172262571,-1.2308393799,-1.0549307647
C,0,2.6718094406,-0.276640433,-0.2532027647
H,0,-2.9013610213,1.1814198015,0.2905732353
H,0,-0.5598748819,-2.4152794568,0.5942472353
H,0,-1.0674214234,2.4506103824,-0.7761037647
H,0,-2.1609603945,-0.797251964,1.6238992353
H,0,-2.1884307736,0.3993640273,-1.2008907647
H,0,-0.5910342529,1.9124205334,0.9116672353
H,0,3.2659395645,-0.6677372448,0.5753142353
H,0,2.4464896973,-1.0870185044,-0.9558317647
H,0,3.2496892002,0.4822117501,-0.7947097647

B3LYP/6-31+G*
E(RB+HF-LYP) = -423.138660922

Zero-point correction= 0.154716 (Hartree/Particle)
Thermal correction to Energy= 0.164202
Thermal correction to Enthalpy= 0.165146
Thermal correction to Gibbs Free Energy= 0.119971
Sum of electronic and zero-point Energies= -422.983945
Sum of electronic and thermal Energies= -422.974459
Sum of electronic and thermal Enthalpies= -422.973515
Sum of electronic and thermal Free Energies= -423.018690

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.038	34.174	95.079

C,0,-0.6371929288,1.6567503147,-0.1478712623

C,0,0.4839815989,0.9744209967,-0.6520870592
H,0,0.717780751,0.9885117333,-1.7118037234
C,0,1.3983544416,0.2905944113,0.2714124059
O,0,1.0690015172,0.1471483584,1.4531160692
C,0,-2.1621445996,0.5325302528,-0.1346693356
C,0,-1.8855130376,-0.6481051868,0.5856382738
C,0,-0.920551459,-1.5302093377,0.0429885046
O,0,-0.3279464333,-1.2420530392,-1.0293538404
C,0,2.7031320307,-0.2501186287,-0.2729473005
H,0,-2.9116770651,1.2068241911,0.276785677
H,0,-0.6101324123,-2.4149488457,0.6198434201
H,0,-1.0542980877,2.4349921611,-0.7850310437
H,0,-2.2253843101,-0.7869297884,1.6084272919
H,0,-2.2084365052,0.4187358316,-1.2153594342
H,0,-0.5908324134,1.9078751496,0.909193701
H,0,3.2882760485,-0.6903614566,0.5376948377
H,0,2.500907726,-1.0108500843,-1.0360584292
H,0,3.2849593198,0.550211622,-0.748575487

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42188632730D+03

mPW1K/6-31G*
E(RmPW+HF-PW91) = -422.984153306

Zero-point correction= 0.159770 (Hartree/Particle)
Thermal correction to Energy= 0.168990
Thermal correction to Enthalpy= 0.169934
Thermal correction to Gibbs Free Energy= 0.125472
Sum of electronic and zero-point Energies= -422.824383
Sum of electronic and thermal Energies= -422.815163
Sum of electronic and thermal Enthalpies= -422.814219
Sum of electronic and thermal Free Energies= -422.858681

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	106.043	33.265	93.579

C,0,-1.6685006931,-0.5535221752,-0.2560620945
C,0,-0.8793661278,-0.310276161,0.8574204119
H,0,-1.2299463271,0.2992517633,1.6757588994
C,0,0.4254564869,-0.9596038543,0.9539922927
O,0,0.880397481,-1.5243863216,-0.0262526432
C,0,-1.3203205437,0.776834133,-1.5899280285

C,0,0.0400293147,0.7815541223,-1.8820701932
C,0,0.9004820335,1.2074463586,-0.8522397568
O,0,0.4350183147,1.5271914427,0.2540824924
C,0,1.1745783414,-0.8646622385,2.2482273533
H,0,-2.0088329784,0.4543668294,-2.3601236066
H,0,1.9826390108,1.1479983443,-0.9938915269
H,0,-2.7271275354,-0.3475566157,-0.1678339298
H,0,0.4416826976,0.2964709773,-2.7588787305
H,0,-1.6738846713,1.5890661416,-0.9707375661
H,0,-1.4076955061,-1.4260638684,-0.8382909974
H,0,2.1037955579,-1.4211560676,2.1780792465
H,0,1.3873935295,0.1802890481,2.4698810223
H,0,0.5744969853,-1.2617286307,3.0673584863

MP2/6-31G*

E(RHF) = -420.494772097

Zero-point correction= 0.157046 (Hartree/Particle)
Thermal correction to Energy= 0.166389
Thermal correction to Enthalpy= 0.167333
Thermal correction to Gibbs Free Energy= 0.122951
Sum of electronic and zero-point Energies= -421.627486
Sum of electronic and thermal Energies= -421.618143
Sum of electronic and thermal Enthalpies= -421.617199
Sum of electronic and thermal Free Energies= -421.661581

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.410	34.102	93.410

C,0,-1.7669669289,-0.6096960706,-0.2109781655
C,0,-0.9849873687,-0.4237600279,0.9248357749
H,0,-1.334255681,0.1620263698,1.7709376689
C,0,0.3648365079,-0.9505091044,0.9056064267
O,0,0.818738908,-1.3981993383,-0.1714545419
C,0,-1.247033511,0.743467646,-1.6003955269
C,0,0.1289255909,0.6615540767,-1.7860475617
C,0,0.9607041056,1.211506271,-0.7525981153
O,0,0.453517062,1.6615482429,0.2996578052
C,0,1.2213924352,-0.843907122,2.141821925
H,0,-1.9055844193,0.4186646119,-2.4023033577
H,0,2.0560399799,1.1543355776,-0.8671961854
H,0,-2.8240703209,-0.3601368945,-0.159993056
H,0,0.5738008577,0.0884553807,-2.5943446

H,0,-1.5979279247,1.5780817601,-1.0015262992
H,0,-1.5031468583,-1.4572243099,-0.835632673
H,0,2.1291645509,-1.434054824,2.0064084265
H,0,1.4871610518,0.2059243445,2.2991266469
H,0,0.679546018,-1.1947972669,3.0254287786

TS, Ac as diene, MVK-cis, exo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.117268113

Zero-point correction= 0.155089 (Hartree/Particle)
Thermal correction to Energy= 0.164483
Thermal correction to Enthalpy= 0.165427
Thermal correction to Gibbs Free Energy= 0.120641
Sum of electronic and zero-point Energies= -422.962179
Sum of electronic and thermal Energies= -422.952785
Sum of electronic and thermal Enthalpies= -422.951841
Sum of electronic and thermal Free Energies= -422.996627

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.215	34.113	94.260

H,0,-0.3456614275,-2.6245496685,1.7917670175
C,0,-0.6061548875,-1.7778100685,1.1325670213
O,0,0.1293023176,-1.5226299294,0.1431766542
C,0,-1.6655114614,-0.9261312375,1.503795631
H,0,-2.1527553883,-1.0667165178,2.465456836
C,0,-1.8349965516,0.2576372065,0.7626875125
H,0,-2.6141283504,0.9461264546,1.0858369275
H,0,-1.7188441772,0.1931766166,-0.3176104246
C,0,-0.2543966745,1.3466902422,0.9456173141
H,0,-0.2001154342,1.5297020216,2.0151266723
H,0,-0.6802508262,2.1589686287,0.3597830861
C,0,0.8114129398,0.675409573,0.3373188124
H,0,1.5983358965,0.2116203828,0.9202778051
C,0,0.9406042251,0.694050236,-1.1396883879
O,0,0.0758700791,1.2262482176,-1.8273094056
C,0,2.1384234719,-0.0052106275,-1.7425861453
H,0,2.0600009415,-1.0791388536,-1.5373719025
H,0,2.1640890676,0.1643448623,-2.8206690181
H,0,3.0716641536,0.3497078215,-1.2878055371

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42188234550D+03

TS, Ac as diene, MVK-trans, endo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.110288892

Zero-point correction=	0.155013 (Hartree/Particle)
Thermal correction to Energy=	0.164379
Thermal correction to Enthalpy=	0.165323
Thermal correction to Gibbs Free Energy=	0.120757
Sum of electronic and zero-point Energies=	-422.955276
Sum of electronic and thermal Energies=	-422.945910
Sum of electronic and thermal Enthalpies=	-422.944966
Sum of electronic and thermal Free Energies=	-422.989532

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.149	34.281	93.797

C,0,-0.6189109653,1.5337274049,-0.2271330998
C,0,0.4740213529,0.8172942643,-0.7246008314
C,0,1.6245223627,0.353776882,0.0902506177
C,0,1.4508096666,0.22532491,1.5953134317
O,0,2.7007848161,0.1414669719,-0.4481705801
C,0,-2.2435791986,0.4039104836,-0.3602652777
C,0,-2.0767354341,-0.7307872991,0.4458691785
C,0,-1.0090458104,-1.5958731405,0.1192247682
O,0,-0.2472030872,-1.3481469896,-0.8502437392
H,0,0.6535049671,0.7790564854,-1.7937890751
H,0,-3.0178832308,1.1210761139,-0.0955343735
H,0,-0.7752166609,-2.4398707874,0.7913101655
H,0,-1.0369945423,2.3002520876,-0.8762990509
H,0,-2.5788458884,-0.8269816805,1.4052216213
H,0,-2.1032488299,0.2630052166,-1.4277676429
H,0,-0.6293608746,1.7988852932,0.8267157189
H,0,2.2671292105,-0.3820557148,1.9912459486
H,0,1.4979690965,1.216381816,2.065029463
H,0,0.4878010787,-0.2205497203,1.8692290558

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42187537756D+03

TS, Ac as diene, MVK-trans, exo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.109903999

Zero-point correction=	0.154937 (Hartree/Particle)
Thermal correction to Energy=	0.164376
Thermal correction to Enthalpy=	0.165320
Thermal correction to Gibbs Free Energy=	0.120360
Sum of electronic and zero-point Energies=	-422.954967
Sum of electronic and thermal Energies=	-422.945528
Sum of electronic and thermal Enthalpies=	-422.944584
Sum of electronic and thermal Free Energies=	-422.989544

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.147	34.325	94.627

C,0,-1.8453895717,0.1560329903,1.0124908461
C,0,-1.5964833113,-1.1110528572,1.5614063811
C,0,-0.648174946,-1.9147544191,0.8966460404
O,0,-0.0666995157,-1.5078944454,-0.1440233812
C,0,-0.1839630065,1.2153571769,1.0221755003
C,0,0.8364161667,0.5219389551,0.3588395313
C,0,1.2214187481,0.7127265948,-1.0639983993
C,0,0.1518370064,1.0992723967,-2.0663955225
O,0,2.3829860584,0.5304876354,-1.3956134106
H,0,-0.3282933827,-2.8655349159,1.3565811023
H,0,-1.91825819,-1.3703574855,2.5666865994
H,0,-2.5218982048,0.8265173749,1.539106023
H,0,-1.9192376179,0.204256,-0.069771607
H,0,-0.0702742554,1.3482663281,2.0947242097
H,0,-0.6165569223,2.078497824,0.5201834093
H,0,1.5797425424,-0.0208807092,0.9323826747
H,0,-0.4186408823,1.9804826955,-1.7511112866
H,0,0.6203991416,1.2974387269,-3.0322736283
H,0,-0.5512410845,0.2634436158,-2.1663994265

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42187489319D+03

TS, MVK as diene, Ac-cis, exo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.114013965

Zero-point correction= 0.154875 (Hartree/Particle)
Thermal correction to Energy= 0.164447
Thermal correction to Enthalpy= 0.165391
Thermal correction to Gibbs Free Energy= 0.119980
Sum of electronic and zero-point Energies= -422.959139
Sum of electronic and thermal Energies= -422.949567
Sum of electronic and thermal Enthalpies= -422.948623
Sum of electronic and thermal Free Energies= -422.994034

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.192	34.245	95.577

C,0,-0.2260577471,1.5639156359,-0.5836189934
C,0,1.0549939596,1.1181125699,-0.9602574026
C,0,1.5916982577,-0.0000096836,-0.2756269661
O,0,0.9375638589,-0.5182127717,0.6722646084
C,0,2.8684460528,-0.6701601858,-0.7479027744
C,0,-1.494641026,0.1920846096,-0.9357231352
C,0,-1.2178479036,-0.8919992063,-0.0897133014
C,0,-1.6213082659,-0.8359281561,1.3202982665
O,0,-2.1631776123,0.1401493987,1.8187519914
H,0,1.5073204172,1.4497483171,-1.8916294183
H,0,-1.4139687682,0.0332264307,-2.0076771991
H,0,-1.378483983,-1.7272877152,1.9303102546
H,0,-0.6427125042,2.4027022785,-1.1395168139
H,0,-0.7719999157,-1.8101849097,-0.4542370763
H,0,-2.3439972358,0.8015950614,-0.6316456314
H,0,-0.4485781598,1.5851401963,0.4823179778
H,0,3.5062101165,-0.9011441452,0.1110976113
H,0,2.633016119,-1.6219034959,-1.2412227314
H,0,3.4264039768,-0.0434785352,-1.4506639315

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42187915121D+03

TS, MVK as diene, Ac-trans, endo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.110961698

Zero-point correction= 0.154384 (Hartree/Particle)
Thermal correction to Energy= 0.164039
Thermal correction to Enthalpy= 0.164983
Thermal correction to Gibbs Free Energy= 0.119458
Sum of electronic and zero-point Energies= -422.956577
Sum of electronic and thermal Energies= -422.946923
Sum of electronic and thermal Enthalpies= -422.945979
Sum of electronic and thermal Free Energies= -422.991504

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	102.936	34.620	95.816

C,0,-0.5300093501,2.0724816652,-0.2589620379
C,0,0.723166474,1.6337373143,-0.7105231004
C,0,1.3373823773,0.5691870287,-0.003652299
C,0,2.620357685,-0.0702965669,-0.4960559149
O,0,0.7389897154,0.0753934191,0.9940753357
C,0,-1.7941239085,0.584194704,-0.416753497
C,0,-1.4182232971,-0.428060178,0.4737078285
C,0,-0.9111910978,-1.7247807287,0.0040020325
O,0,-0.9647964733,-2.7578238929,0.6445950713
H,0,1.0923136042,1.9180675449,-1.692738406
H,0,-2.6517144778,1.1923132355,-0.136753972
H,0,-0.4980446583,-1.7068726404,-1.0313379747
H,0,-1.0354644512,2.8516179556,-0.8265966591
H,0,-1.6894010827,-0.3754278977,1.5231420077
H,0,-1.7459123517,0.3599090229,-1.4808665115
H,0,-0.6606496485,2.1432158845,0.8170803021
H,0,3.306066283,-0.215805497,0.3445876491
H,0,2.4103273027,-1.0622569317,-0.9148919149
H,0,3.1147802464,0.5359036824,-1.2615658484

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42187523669D+03

TS, MVK as diene, Ac-trans, exo

B3LYP/6-31G*
E(RB+HF-LYP) = -423.109587118

Zero-point correction= 0.154382 (Hartree/Particle)
Thermal correction to Energy= 0.164086
Thermal correction to Enthalpy= 0.165030
Thermal correction to Gibbs Free Energy= 0.119229
Sum of electronic and zero-point Energies= -422.955205
Sum of electronic and thermal Energies= -422.945502
Sum of electronic and thermal Enthalpies= -422.944557
Sum of electronic and thermal Free Energies= -422.990358

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	102.965	34.592	96.395

C,0,-0.2398046464,1.838698666,-0.6899790896
C,0,1.0144728608,1.3325528768,-1.0715115632
C,0,1.539125679,0.266217129,-0.3007781963
C,0,2.8021437406,-0.4629230706,-0.7142699909
O,0,0.8717263682,-0.1594594806,0.6846956759
C,0,-1.5649678929,0.4438557274,-0.8620886836
C,0,-1.2104683771,-0.6599835272,-0.0697401257
C,0,-1.7006138361,-0.7903291562,1.3086438479
O,0,-1.7156147136,-1.8318438976,1.9365105473
H,0,1.4389032681,1.5625896067,-2.0455358966
H,0,-1.5715659072,0.3047641748,-1.9395847278
H,0,-2.0859780239,0.1558072781,1.7526565259
H,0,-0.6774693566,2.6309858429,-1.2950773663
H,0,-0.7525734476,-1.5450218368,-0.4964798154
H,0,-2.3977534578,1.0465523089,-0.4979331508
H,0,-0.3980766091,1.9539586833,0.3787116395
H,0,3.4420918726,-0.6201137806,0.1596841682
H,0,2.5506291262,-1.454457405,-1.1115265705
H,0,3.363574131,0.0868302826,-1.4762217834

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42187385732D+03

Product 67, Ac as diene

B3LYP/6-31G*
E(RB+HF-LYP) = -423.203789817

Zero-point correction= 0.159678 (Hartree/Particle)
Thermal correction to Energy= 0.168427
Thermal correction to Enthalpy= 0.169372
Thermal correction to Gibbs Free Energy= 0.125483
Sum of electronic and zero-point Energies= -423.044112
Sum of electronic and thermal Energies= -423.035362
Sum of electronic and thermal Enthalpies= -423.034418
Sum of electronic and thermal Free Energies= -423.078307

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	105.690	32.365	92.372

C,0,2.5253480297,-0.568755751,0.5643736329
C,0,1.6532276139,0.5701928441,0.092332038
O,0,2.0433516671,1.7245471204,0.0485396555
C,0,0.2119224179,0.2752603868,-0.3326422325
C,0,-0.8026729153,0.8896800977,0.6461964466
C,0,-2.2317304063,0.6198875446,0.1490785587
C,0,-2.34518302,-0.7997142024,-0.3477785055
C,0,-1.2671685804,-1.5617850314,-0.5725764059
O,0,0.0338574561,-1.1447748392,-0.4503657333
H,0,0.0658836071,0.7207173079,-1.3279634351
H,0,-2.9451454476,0.7914448518,0.966237591
H,0,-1.3102457965,-2.6033100023,-0.8749196033
H,0,-0.5984520804,1.9604994012,0.7387812781
H,0,-3.3261321236,-1.2405911261,-0.5013842154
H,0,-2.5018327594,1.3340646965,-0.6432117983
H,0,-0.6584953895,0.4332594779,1.6344455981
H,0,3.4952832463,-0.1760186041,0.8767647535
H,0,2.0451953254,-1.104376035,1.3921268952
H,0,2.653809596,-1.3024635485,-0.2401696353

B3LYP/6-31+G*
E(RB+HF-LYP) = -423.203789817

Zero-point correction= 0.159678 (Hartree/Particle)
Thermal correction to Energy= 0.168427
Thermal correction to Enthalpy= 0.169371

Thermal correction to Gibbs Free Energy= 0.125483
Sum of electronic and zero-point Energies= -423.044112
Sum of electronic and thermal Energies= -423.035363
Sum of electronic and thermal Enthalpies= -423.034419
Sum of electronic and thermal Free Energies= -423.078307

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.690	32.365	92.371

C,0,-2.6181438492,-0.1191402018,0.3879591702
C,0,-1.4777566176,-0.9192171471,-0.1951494067
O,0,-1.5852790187,-2.0952569385,-0.4984924045
C,0,-0.1212507301,-0.23872816,-0.399545777
C,0,0.9463144385,-0.8108381383,0.5481005516
C,0,2.3012095904,-0.1418994758,0.267214209
C,0,2.1117105711,1.3405306711,0.0634980464
C,0,0.9019290019,1.882319055,-0.1270117599
O,0,-0.2714260883,1.1788296208,-0.226217229
H,0,0.1852390222,-0.4243013714,-1.4397618816
H,0,2.9833770557,-0.3226283125,1.1087165766
H,0,0.7200968525,2.9483007096,-0.2200817849
H,0,0.9914321569,-1.895647351,0.4136204664
H,0,2.9707642675,2.0044212927,0.1022789049
H,0,2.7781431176,-0.5995101303,-0.6124768425
H,0,0.6395146608,-0.6129283603,1.5836927028
H,0,-3.4874567885,-0.7679060793,0.5144591384
H,0,-2.3275021263,0.3222891267,1.3488328631
H,0,-2.8640417649,0.7211716399,-0.2719886962

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42195963304D+03

mPW1K/6-31G*
E(RmPW+HF-PW91) = -423.072002448

Zero-point correction= 0.165100 (Hartree/Particle)
Thermal correction to Energy= 0.173637
Thermal correction to Enthalpy= 0.174581
Thermal correction to Gibbs Free Energy= 0.130957
Sum of electronic and zero-point Energies= -422.906902
Sum of electronic and thermal Energies= -422.898366
Sum of electronic and thermal Enthalpies= -422.897421
Sum of electronic and thermal Free Energies= -422.941046

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	108.959	31.266	91.816

C,0,2.5189460935,-0.5705615404,0.5075975565
C,0,1.6310348456,0.564550852,0.1068253609
O,0,1.9935285628,1.7141513534,0.1172216389
C,0,0.2084764443,0.2604697658,-0.3215724703
C,0,-0.8028982951,0.8881739062,0.6253957334
C,0,-2.2091720873,0.6263926189,0.1091033588
C,0,-2.3156246444,-0.7886862046,-0.3634793311
C,0,-1.2432766632,-1.5503709428,-0.550087157
O,0,0.038025981,-1.1377695708,-0.4091542047
H,0,0.0735429236,0.6869525885,-1.3202530748
H,0,-2.9352383229,0.8109773014,0.9021141135
H,0,-1.2885989055,-2.5902492017,-0.8342970298
H,0,-0.5901686628,1.9509110789,0.7117618737
H,0,-3.2872137419,-1.2289847129,-0.5308708884
H,0,-2.4559761897,1.3231916209,-0.6959488653
H,0,-0.6797850945,0.4406460519,1.61317987
H,0,3.4835926209,-0.1799934052,0.8149847243
H,0,2.0640644423,-1.1409842574,1.316388372
H,0,2.6384304198,-1.2633320559,-0.324296875

MP2/6-31G*

E(RHF) = -420.598445892

Zero-point correction= 0.162898 (Hartree/Particle)
Thermal correction to Energy= 0.171530
Thermal correction to Enthalpy= 0.172474
Thermal correction to Gibbs Free Energy= 0.128558
Sum of electronic and zero-point Energies= -421.685741
Sum of electronic and thermal Energies= -421.677108
Sum of electronic and thermal Enthalpies= -421.676164
Sum of electronic and thermal Free Energies= -421.720081

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	107.637	31.774	92.430

C,0,2.5338395055,-0.5702447732,0.5001709908
C,0,1.6353122706,0.5709179736,0.104677371
O,0,1.9922883878,1.7460715024,0.1280368387

C,0,0.2081024955,0.259510971,-0.3241956963
C,0,-0.8062435592,0.8808639126,0.6317175115
C,0,-2.2169701061,0.6373046647,0.0980633714
C,0,-2.3294935278,-0.7844738512,-0.374522782
C,0,-1.2536353566,-1.5671125145,-0.5467690132
O,0,0.0525101073,-1.1651027869,-0.3952091149
H,0,0.0575036197,0.6776116902,-1.3318715725
H,0,-2.9542517265,0.8314435203,0.8863955808
H,0,-1.3041390597,-2.6152011517,-0.8250970037
H,0,-0.5800847068,1.9452658088,0.7412675069
H,0,-3.3073404695,-1.2219498084,-0.5516632025
H,0,-2.4431302522,1.3416740052,-0.7136509581
H,0,-0.687078926,0.4034757616,1.6116695556
H,0,3.5056147063,-0.1692103433,0.7903367945
H,0,2.0889602458,-1.130589302,1.3275240621
H,0,2.6400882763,-1.2708682021,-0.3323830716

Product 68, MVK as diene

B3LYP/6-31G*
E(RB+HF-LYP) = -423.200266945

Zero-point correction= 0.159094 (Hartree/Particle)
Thermal correction to Energy= 0.168016
Thermal correction to Enthalpy= 0.168960
Thermal correction to Gibbs Free Energy= 0.124929
Sum of electronic and zero-point Energies= -423.041173
Sum of electronic and thermal Energies= -423.032251
Sum of electronic and thermal Enthalpies= -423.031307
Sum of electronic and thermal Free Energies= -423.075338

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	105.431	32.669	92.670

C,0,2.6884538955,-0.1252036319,-1.2067930041
C,0,1.3094514745,0.2910662753,-0.794696627
O,0,0.7547809967,-0.6351697947,0.0670078499
C,0,0.6620809454,1.3981682299,-1.193269423
C,0,-0.7612793267,1.7069989229,-0.7995062172
C,0,-1.425913867,0.4635347482,-0.1917522769
C,0,-0.432054141,-0.2251708068,0.7540682347
C,0,-1.0120949844,-1.4742696111,1.3950987976

O,0,-1.9622130521,-1.4489788228,2.147488858
H,0,1.1835583505,2.0840694837,-1.8548321106
H,0,-2.3342878489,0.7132618091,0.3656869252
H,0,-0.5101648971,-2.4252823695,1.1191683223
H,0,-1.3314173171,2.0359273761,-1.6787456315
H,0,-0.1507693709,0.474674211,1.5569232805
H,0,-1.7022389934,-0.2423956126,-0.9855629819
H,0,-0.797282798,2.5443919107,-0.0860238381
H,0,3.3503648965,-0.2007608323,-0.3349546985
H,0,2.6643218849,-1.1134537987,-1.6833523939
H,0,3.1155085593,0.592012003,-1.9131774413

B3LYP/6-31+G*
E(RB+HF-LYP) = -423.200266945

Zero-point correction= 0.159094 (Hartree/Particle)
Thermal correction to Energy= 0.168016
Thermal correction to Enthalpy= 0.168960
Thermal correction to Gibbs Free Energy= 0.124929
Sum of electronic and zero-point Energies= -423.041173
Sum of electronic and thermal Energies= -423.032251
Sum of electronic and thermal Enthalpies= -423.031307
Sum of electronic and thermal Free Energies= -423.075338

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	105.431	32.669	92.670

C,0,2.6884538955,-0.1252036319,-1.2067930041
C,0,1.3094514745,0.2910662753,-0.794696627
O,0,0.7547809967,-0.6351697947,0.0670078499
C,0,0.6620809454,1.3981682299,-1.193269423
C,0,-0.7612793267,1.7069989229,-0.7995062172
C,0,-1.425913867,0.4635347482,-0.1917522769
C,0,-0.432054141,-0.2251708068,0.7540682347
C,0,-1.0120949844,-1.4742696111,1.3950987976
O,0,-1.9622130521,-1.4489788228,2.147488858
H,0,1.1835583505,2.0840694837,-1.8548321106
H,0,-2.3342878489,0.7132618091,0.3656869252
H,0,-0.5101648971,-2.4252823695,1.1191683223
H,0,-1.3314173171,2.0359273761,-1.6787456315
H,0,-0.1507693709,0.474674211,1.5569232805
H,0,-1.7022389934,-0.2423956126,-0.9855629819
H,0,-0.797282798,2.5443919107,-0.0860238381

H,0,3.3503648965,-0.2007608323,-0.3349546985
H,0,2.6643218849,-1.1134537987,-1.6833523939
H,0,3.1155085593,0.592012003,-1.9131774413

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42195600585D+03

mPW1K/6-31G*
E(RmPW+HF-PW91) = -423.068177390

Zero-point correction= 0.164563 (Hartree/Particle)
Thermal correction to Energy= 0.173254
Thermal correction to Enthalpy= 0.174198
Thermal correction to Gibbs Free Energy= 0.130674
Sum of electronic and zero-point Energies= -422.903614
Sum of electronic and thermal Energies= -422.894924
Sum of electronic and thermal Enthalpies= -422.893980
Sum of electronic and thermal Free Energies= -422.937503

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	108.718	31.615	91.604

C,0,2.6622605309,-0.1291065366,-1.1937297396
C,0,1.2963372573,0.2828540943,-0.7784182507
O,0,0.7455501694,-0.6345208695,0.0637320214
C,0,0.6611398682,1.3885964576,-1.164477979
C,0,-0.7501181247,1.6955726891,-0.7737824891
C,0,-1.4042815317,0.4565970068,-0.1860424296
C,0,-0.4164243751,-0.2236788241,0.744404194
C,0,-0.9905512819,-1.4538491874,1.3961608449
O,0,-1.9873408626,-1.4321773752,2.0614518071
H,0,1.1858735206,2.0721808514,-1.8152265798
H,0,-2.3107270268,0.6916720711,0.3674949488
H,0,-0.4301978121,-2.3856834704,1.2192509582
H,0,-1.3129327451,2.0317329396,-1.6458947805
H,0,-0.1312021946,0.4751147903,1.5386313717
H,0,-1.6700062279,-0.2409020842,-0.9816195503
H,0,-0.7841045919,2.5198350431,-0.056315566
H,0,3.3166702605,-0.2189714952,-0.3270302299
H,0,2.6306006278,-1.1041193417,-1.6798452271
H,0,3.090177677,0.5908124562,-1.8856008769

MP2/6-31G*
E(RHF) = -420.595295908

Zero-point correction= 0.162334 (Hartree/Particle)
Thermal correction to Energy= 0.171156
Thermal correction to Enthalpy= 0.172101
Thermal correction to Gibbs Free Energy= 0.128265
Sum of electronic and zero-point Energies= -421.683067
Sum of electronic and thermal Energies= -421.674245
Sum of electronic and thermal Enthalpies= -421.673300
Sum of electronic and thermal Free Energies= -421.717137

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	107.402	32.132	92.261

C,0,2.6812188684,-0.133227827,-1.2039124194
C,0,1.3117565784,0.2840230281,-0.7781191305
O,0,0.7586287347,-0.6642557823,0.0632500917
C,0,0.6737819335,1.4100548424,-1.1450504915
C,0,-0.7428941317,1.7172315877,-0.7485517425
C,0,-1.3966338881,0.4617891698,-0.1765278718
C,0,-0.4102949657,-0.2187336456,0.7602726059
C,0,-0.9845832788,-1.4500414336,1.4268191281
O,0,-2.0840412111,-1.4572056131,1.9624728579
H,0,1.2059866873,2.1052923345,-1.7878430268
H,0,-2.3191044766,0.6784839646,0.3701606251
H,0,-0.3357536928,-2.3471420801,1.4012155759
H,0,-1.3080500296,2.0690764795,-1.6202732403
H,0,-0.1032830058,0.4930499994,1.5454801174
H,0,-1.638294599,-0.2412355066,-0.9816747987
H,0,-0.7784192115,2.5325339195,-0.0129240131
H,0,3.3404287988,-0.2272490208,-0.3357583763
H,0,2.6393709853,-1.1107868129,-1.6941152924
H,0,3.1063116588,0.5930935552,-1.899631637

TS 72, [3,3]-rearrangement between products

B3LYP/6-31G*
E(RB+HF-LYP) = -423.137974685

Zero-point correction= 0.155799 (Hartree/Particle)
Thermal correction to Energy= 0.164642

Thermal correction to Enthalpy= 0.165586
Thermal correction to Gibbs Free Energy= 0.122127
Sum of electronic and zero-point Energies= -422.982176
Sum of electronic and thermal Energies= -422.973333
Sum of electronic and thermal Enthalpies= -422.972388
Sum of electronic and thermal Free Energies= -423.015847

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	103.315	33.026	91.467

C,0,2.5990298965,-0.34952107,-0.1170200596
C,0,1.2801225376,0.2841163506,0.2619438187
O,0,0.727042871,0.0065623278,1.3610952517
C,0,0.5489654874,1.1103226409,-0.6378298025
C,0,-0.6793543884,1.7030169963,-0.1553535528
C,0,-1.9503352476,0.6153729861,0.0141314835
C,0,-1.5716451112,-0.620631351,0.6625791181
C,0,-0.8089429187,-1.5477487434,-0.0990349785
O,0,-0.3859208558,-1.2156237563,-1.2298313452
H,0,0.8756614985,1.2363128747,-1.665075053
H,0,-2.7190444565,1.1723591904,0.5535168232
H,0,-0.4985885569,-2.4996548266,0.3596049858
H,0,-1.0700021877,2.4832753779,-0.8120745792
H,0,-1.8159279768,-0.8310982851,1.6986226994
H,0,-2.2417913517,0.4358604175,-1.0233649062
H,0,-0.5584352453,2.0671336855,0.8677152305
H,0,3.3219904555,-0.2052090566,0.6932693866
H,0,2.4639801217,-1.4281284455,-0.2570768608
H,0,3.0061400424,0.0720736385,-1.0417451397

B3LYP/6-31+G*
E(RB+HF-LYP) = -423.137974685

Zero-point correction= 0.155799 (Hartree/Particle)
Thermal correction to Energy= 0.164642
Thermal correction to Enthalpy= 0.165586
Thermal correction to Gibbs Free Energy= 0.122127
Sum of electronic and zero-point Energies= -422.982176
Sum of electronic and thermal Energies= -422.973333
Sum of electronic and thermal Enthalpies= -422.972388
Sum of electronic and thermal Free Energies= -423.015847

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	103.315	33.026	91.467

C,0,2.5990298965,-0.34952107,-0.1170200596
C,0,1.2801225376,0.2841163506,0.2619438187
O,0,0.727042871,0.0065623278,1.3610952517
C,0,0.5489654874,1.1103226409,-0.6378298025
C,0,-0.6793543884,1.7030169963,-0.1553535528
C,0,-1.9503352476,0.6153729861,0.0141314835
C,0,-1.5716451112,-0.620631351,0.6625791181
C,0,-0.8089429187,-1.5477487434,-0.0990349785
O,0,-0.3859208558,-1.2156237563,-1.2298313452
H,0,0.8756614985,1.2363128747,-1.665075053
H,0,-2.7190444565,1.1723591904,0.5535168232
H,0,-0.4985885569,-2.4996548266,0.3596049858
H,0,-1.0700021877,2.4832753779,-0.8120745792
H,0,-1.8159279768,-0.8310982851,1.6986226994
H,0,-2.2417913517,0.4358604175,-1.0233649062
H,0,-0.5584352453,2.0671336855,0.8677152305
H,0,3.3219904555,-0.2052090566,0.6932693866
H,0,2.4639801217,-1.4281284455,-0.2570768608
H,0,3.0061400424,0.0720736385,-1.0417451397

CCSD(T)/6-31G(d) single point energy
CCSD(T)= -.42188891695D+03

mPW1K/6-31G*
E(RmPW+HF-PW91) = -422.985557384

Zero-point correction= 0.161707 (Hartree/Particle)
Thermal correction to Energy= 0.169967
Thermal correction to Enthalpy= 0.170911
Thermal correction to Gibbs Free Energy= 0.128877
Sum of electronic and zero-point Energies= -422.823850
Sum of electronic and thermal Energies= -422.815590
Sum of electronic and thermal Enthalpies= -422.814646
Sum of electronic and thermal Free Energies= -422.856680

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	106.656	31.193	88.469

C,0,2.531538047,-0.4066609512,-0.0420828082
C,0,1.2299879962,0.2635222565,0.2656028323

O,0,0.62384767,0.0191455195,1.3344920705
C,0,0.5230739228,1.0276467303,-0.6767851951
C,0,-0.7070038788,1.6452986809,-0.2093830826
C,0,-1.8957938368,0.6110091058,0.1015313079
C,0,-1.4516265079,-0.6415434007,0.6892913329
C,0,-0.7314984268,-1.4909721234,-0.1617565998
O,0,-0.3536086049,-1.032789396,-1.2566146216
H,0,0.8970866879,1.1804367908,-1.6764484082
H,0,-2.6173440538,1.132075254,0.7238966686
H,0,-0.3630696956,-2.4539262419,0.1980945475
H,0,-1.0972126292,2.3771466301,-0.910917598
H,0,-1.7040605424,-0.9350349332,1.6953623425
H,0,-2.3272564,0.4060702096,-0.8762711063
H,0,-0.5189807446,2.1168016205,0.7532547401
H,0,3.2315902818,-0.2454314753,0.7754248125
H,0,2.3753951852,-1.4807929689,-0.1375619535
H,0,2.9698754947,-0.0379956626,-0.966360361

MP2/6-31G*

E(RHF) = -420.474984807

Zero-point correction= 0.159570 (Hartree/Particle)
Thermal correction to Energy= 0.167803
Thermal correction to Enthalpy= 0.168747
Thermal correction to Gibbs Free Energy= 0.127109
Sum of electronic and zero-point Energies= -421.632661
Sum of electronic and thermal Energies= -421.624428
Sum of electronic and thermal Enthalpies= -421.623484
Sum of electronic and thermal Free Energies= -421.665122

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	105.298	31.824	87.635

C,0,0.858174991,-1.5691279362,-0.3000825699
C,0,-0.4109132059,-1.0327008068,-0.7692343218
H,0,-0.7261131499,-1.1110547019,-1.8062622174
C,0,-1.2125176791,-0.3923635737,0.2102287018
O,0,-0.6744906816,-0.1986807143,1.3482823272
C,0,1.9774762892,-0.4240201963,0.0194791338
C,0,1.4492033045,0.7099737159,0.7633019588
C,0,0.5912373689,1.5639229475,0.0370334882
O,0,0.2327421451,1.2088614088,-1.1285829873
C,0,-2.5732955588,0.1660987294,-0.1164424906

H,0,2.7967393711,-0.9285311502,0.5362598173
H,0,0.1272479739,2.4341282779,0.524789214
H,0,1.3194752649,-2.2529320433,-1.0164509345
H,0,1.680613663,0.8905227277,1.8090221604
H,0,2.290826907,-0.0925618358,-0.9730343794
H,0,0.7133718035,-2.0578409058,0.6657203899
H,0,-2.8080124714,0.9630391364,0.5921197682
H,0,-2.6022762438,0.5588437539,-1.1354827333
H,0,-3.3340778854,-0.615756095,-0.019979206

VITA

Zhihong Wang received her Bachelor of Science in 1996 and Master of Science degrees in 2000, both in chemistry from Nankai University in People Republic of China. She entered the Ph.D. program in the Department of Chemistry at Texas A&M University in August 2000 and has studied under the supervision of Dr. Daniel A. Singleton. She received her Ph.D. degree in chemistry in December 2005.

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