OBSERVATION AND NATURE OF NON-STATISTICAL DYNAMIC EFFECTS IN ORDINARY ORGANIC REACTIONS

A Dissertation

by

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ABSTRACT

Statistical models like Transition State Theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) Theory have generally been successful in predicting the rates and selectivities of chemical reactions. However, these statistical models can fail to explain experimental results of ordinary organic reactions. For these reactions, consideration of nonstatistical dynamic effects or the detailed motion and momenta of the atoms is necessary to account for the experimental observations. Dynamic effects have been found to be important in a growing number of reactions and the nature of these effects can be varied.

One of the most interesting reactions investigated is the ozonolysis of vinyl ethers. Ozonolysis of a homologous series of vinyl ethers in solution exhibit experimental product ratios wherein the selectivity among cleavage pathways increases with the size of the alkyl group to an extent that is far less than RRKM theory would predict. Trajectory studies account for the observed selectivities and support a mechanism involving a competition between cleavage of the primary ozonide and intramolecular vibrational energy redistribution.

A recent theoretical study from our group predicted that a highly asynchronous organocatalytic Diels-Alder (DA) reaction, which is concerted in the potential energy surface, is stepwise in the free energy surface. Kinetic isotope effects (KIEs) were measured for three DA reactions. We envision that the entropic barrier may have several experimental consequences such as unusual isotope effects due to extensive recrossing.

Preliminary results for the organocatalytic reaction show an intramolecular KIE close to unity that cannot be reconciled with statistical theories. This is in contrast with Lewis-acid catalyzed and thermal DA reactions, which exhibit substantial “normal” intramolecular KIEs that are in accord with TST predictions.

Finally, the Baeyer-Villiger oxidation of cylohexanone in water was investigated. KIEs were measured for the oxidation of cyclohexanone with peracetic acid and trifluoroperacetic acid. When using peracetic acid as the oxidant, the alkyl migration was determined to be the rate-determining step based on significant intermolecular KIEs on the carbonyl and α-methylene carbons. A change in the rate-determining step is seen when trifluoroperacetic acid is used. Only the carbonyl carbon exhibits a significant isotope effect. Theoretical predictions provide an experimental picture of the transition states and qualitatively support these conclusions.

DEDICATION

To my husband, Jeremy Chris

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I would like to thank my advisor, Prof. Daniel Singleton, for his guidance and support. Thank you for helping your students become better chemists and stronger persons. I will forever be grateful for this experience.

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I. INTRODUCTION

Transition State Theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory are commonly used statistical models to understand the rates and selectivities of chemical reactions. A transition state is a hypersurface that separates the reactants and products. In TST, it is assumed that the rate of passage through the transition state is governed by the energies of reactants in thermal equilibrium. RRKM theory allows for molecular energies that are not in thermal equilibrium, as is common in gas phase reactions since collisional transfer of heat can be slow.[1-3] However, the internal excess energy within molecules is assumed to be statistically distributed. In effect, the intramolecular vibrational energy redistribution (IVR) is assumed to be faster than the timescale of the reaction; however, this is not always the case.[1-2]

1.1 Dynamic Effects

Although the statistical theories mentioned above have been broadly successful in predicting the rates and selectivities of chemical reactions, these are still models that can fail. Carpenter has discussed several cases where these models fail. One case is where a reactant passes over a low energy barrier in a highly exergonic reaction and subsequently overcomes a second barrier.[4] The intermediate formed in the first step possesses high potential energy. Any reactive intermediate initially possesses a non-statistical distribution of energy. Because of this, RRKM theory will fail in predicting the rates of subsequent steps when these steps are sufficiently fast.[4] Hase has also suggested the failure of TST and rapid IVR of RRKM theory in predicting product partitioning from an intermediate arising from an exergonic reaction.[3,5] Hase argued that this excess energy can be partitioned to product formation instead of being redistributed among the normal modes of the intermediate.[4] For two competing pathways, a major assumption that TST makes is that product distribution is controlled by the relative energies of the two competing transition states. However, if there is excess energy that is available in the system to overcome the barrier to the higher energy transition state, TST can fail. For the scenarios envisioned by Carpenter and Hase, a minimal assumption approximation of reality may be more appropriate. We fall back on considering the dynamics or the detailed positions and momenta of the atoms to give an accurate picture of the rates and selectivities of the reaction.[3-5] Dynamic effects is an experimental observation that cannot be rationalized with statistical models. A growing number of reactions that exhibit dynamic effects have been recognized.[2,4,6-11]

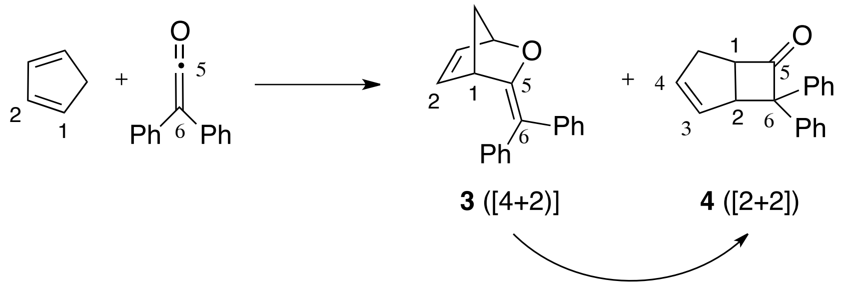
The Singleton Research group has investigated several common organic reactions exhibiting dynamic effects.[6-8] In the hydroboration of alkenes, Oyola and Singleton showed that TST incorrectly predicts the experimental product ratio of the Markovnikov vs. anti-Markovnikov products.[6] Classical trajectory studies were performed using direct dynamics simulation to account for the product ratios. Based on the calculations, the detailed mechanistic picture of this well-known reaction involves three distinct stages. Early in the reaction, the direct trajectories from the pre-complexation of borane and alkene, affords the products directly showing low selectivity between the Markovnikov and anti-Markovnikov products. The second stage is the RRKM stage where IVR has happened and medium selectivity is observed. Lastly, some of the trajectories reach a thermally equilibrated stage exhibiting high selectivity of the anti-Markovnikov product over the Markovnikov product. At this point, however, the selectivity has already been limited by low selectivity in the direct-trajectory stage.

Another assumption of conventional TST is that reactants passing through the transition state towards the direction of the products do not go back and reform reactants. The inclusion of transmission coefficient κ into TST recognizes that this "no-recrossing" is an approximation (eq 1).[12] When recrossing occurs, the rate is overestimated and a κ of less than unity corrects for this.

$$k = \kappa \, \frac{kT}{h} \, e^{-\Delta G^{\ddagger}/RT} \; = \kappa \, \frac{kT}{h} \, e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (1)$$

The hypersurface in conventional TST is placed perpendicular to the minimum-energy path at a potential energy saddle point. In variational transition state theory, the hypersurface is moved away from the potential energy saddle point and is adjusted to minimize recrossing. However, this correction is only applicable to the extent that recrossing is statistically predictable.[13] Nonstatistical recrossing is in a way a result of relatively slow IVR and it cannot be reconciled with the current statistical theories. Hase has extensively studied the effects of nonstatistical recrossing in the gas-phase S_N2 reactions.[2,14] One S_N2 reaction they studied was the $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$ reaction which has a central barrier higher than the reactants and according to TST, passage through the central barrier is rate-controlling. High-level quasiclassical direct dynamics performed to study the central barrier dynamics of the system found non-RRKM dynamics and extensive trajectory recrossings. The latter finding is important because it renders TST as an invalid model to predict the rate constant for the reaction.

The Singleton group has explored the experimental consequence of nonstatistical recrossing in the cycloaddition of diphenylketene with cyclopentadiene.[8] Previous work believed that the reaction afforded the [2+2] cyclobutanone product (**4)** only from the 3,3-sigmatropic rearrangement of the [4+2] cycloadduct (**3**); however, detailed kinetic studies by the Singleton group observed that **4** is formed concurrently with **3** early in the reaction. This is surprising given that the [2+2] transition state is so much higher in energy than the [4+2] pathway. The direct formation of **4** was reconciled by quasiclassical dynamics calculations. Trajectories from the low-energy "[4+2]" transition structure dynamically affords both [4+2] and [2+2] products.



3 ([4+2)] **4** ([2+2])

(2)

Another striking and important observation is the large number of nonstatistical recrossing trajectories. The "[4+2]" transition structure is highly asynchronous to start with and the recrossing trajectories form the C1-C5 bond completely before bouncing off a potential energy wall to go back to starting materials. The experimental rate of this particular reaction is not greatly affected by nonstatistical recrossing observed in the trajectories because of the exponential effect of the energy barrier but it has a substantial effect on the experimental kinetic isotope effects (KIE). An inverse intramolecular KIE at C1 for **4** was determined which means there was more C13 at C1 versus C4. This is inconsistent with a highly asynchronous rate-limiting step which involves bonding at C1 and C5 therefore a substantial normal (>1) isotope effect is expected. Prediction of the KIEs from the conventional transition structure does not agree with the experimental result but KIEs predicted from the 3,3-sigmatropic rearrangement transition structure is surprisingly close to the experimental value. Dynamic trajectories once again explained the KIEs. The nonstatistical recrossing effectively delays the decision on isotopic distinction towards the area where the C1-C5 is fully formed thus accounting for the KIEs.

1.2 Kinetic Isotope Effects

One of the most powerful and well-established methods for probing reaction mechanisms is the measurement of kinetic isotope effects. The theory behind this tool comes from the competitive reactivity of isotopically labeled substances in reactions. Isotopic substitution affects the zero-point energy (ZPE) of the vibrational modes of a molecule. Vibrational frequencies (ν), and thus vibrational zero point energies, are dependent on the reduced mass (μ) of the two connected atoms (eq 3).

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3}$$

To understand the physical origins of KIEs, the simplest case to consider is the homolytic cleavage of a C-H/D bond. The reaction progress below (Figure 1) shows the C-H/D bond stretch where it fully breaks at the transition state. At the transition state, the stretch becomes a translation therefore for this mechanism; the isotope effect only comes from the difference in energies of the ground state ZPE and this exhibits the “maximum” k_H/k_D of 7.[15]

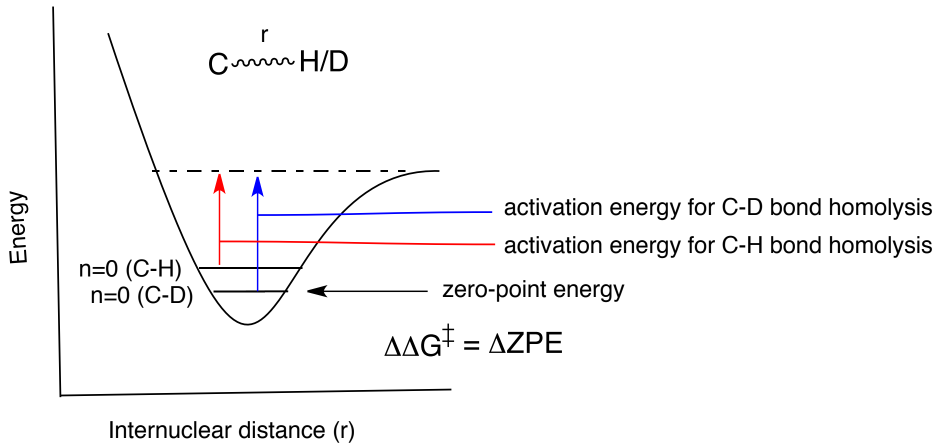


Figure 1. Primary kinetic isotope effect of a homolytic C-H/D bond cleavage.

However, in most reactions the bond of interest is not fully broken at the transition state thus the magnitude of the isotope effect will depend on the difference in energy between the ΔZPE in the transition state and the ground state. The example shown below is for the stretching of a C-H/D bond; however, KIEs for heavier isotopes like ^{13}C, ^{18}O and ^{15}N follow the same principle and are also useful probes for reaction mechanisms. Figure 2 shows the vibrational normal modes associated with the ground state and the transition state where the normal modes are looser at the transition state versus the starting material, as in most reactions. Because the transition state is more loosely bound than the starting material, the vibrational levels are more closely spaced and the ZPE is decreased causing the lighter isotope to react faster. This gives a normal isotope effect where $k_{light}/k_{heavy} > 1$.

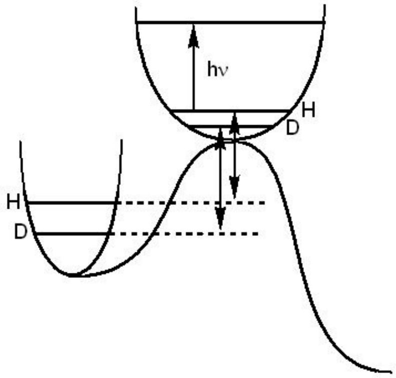


Figure 2. Origin of the kinetic isotope effect.

At times, the transition state is more tightly bound than the starting material causing the ZPE to increase at the transition state. The net effect for the heavier isotope is a lower barrier and thus a faster reaction rate than the lighter isotope. In such cases, an inverse isotope effect is expected and $k_{light}/k_{heavy} < 1$. As seen above, the KIEs are closely associated with the normal modes at the transition state. This is very useful because the KIEs can provide an accurate experimental picture of the transition state geometry, i.e. the extent of bond formation or bond breaking happening as the reaction goes through the transition state.

Competition reactions employing isotopically labeled materials have been the traditional way of measuring kinetic isotope effects. Although these experiments are useful mechanistic probes, syntheses of isotopically labeled materials are laborious and expensive. Because atoms exist as a mixture of isotopes, the use of materials at natural abundance is an ingenious alternative. High precision isotope ratio mass spectrometry has used labeled molecules at natural abundance although this approach has a disadvantage wherein it selectively degrades materials into smaller molecules, such as

CO_2, suitable for mass spectra analyses.[16] The Singleton group has developed a method for precise measurement of ^{13}C, ^{2}H and ^{17}O KIEs at natural abundance using high field magnetic NMR.[17-20] The use of NMR avoids degradation of the samples and provides both quantitative and position-specific data for KIEs. These experiments rely on the precise measurement of the isotopic composition of either the starting materials or products and so NMR conditions have been extensively optimized to obtain small kinetic isotope effects at natural abundance.

In a naturally occurring organic molecule, the carbons and hydrogens have a natural abundance of 1.1% ^{13}C and 0.015% ^{2}H, respectively. In the course of a reaction, the starting material is enriched in the heavier and slower isotopomer and the products with the lighter and faster isotopomer. The KIEs at each position in the molecule can then be determined by the measured isotopic compositions. When the starting material is taken to high conversion, typically ~80%, the recovered starting material's isotopic composition is compared to that of an unreacted starting material (R/R_o) through a comparison of the relative ^{13}C (or the isotope in question) integrations.[17] The KIEs are then calculated according to eq 4 where F_1 is the fractional conversion of the reaction.

$$KIE = \frac{\log(1 - F_1)}{\log(1 - F_1)(\frac{R}{R_o})} \quad (4)$$

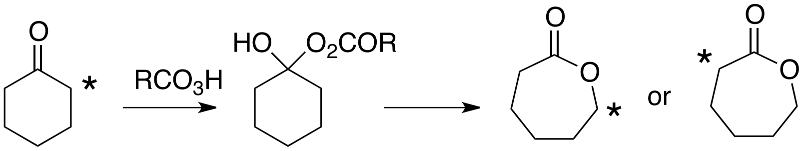
This is referred to as the starting material intermolecular KIE and this particular methodology is useful in understanding changes in bond organization in the rate-determining step. The isotopic enrichment measured here is for the first irreversible step in the reaction. Naturally, there are some limitations for this process namely a sufficient amount of starting material for the NMR measurements must be recovered, reaction must go to high levels of completion and the starting material should not undergo side reactions. The advantages, on the other hand, are that the precision of the KIEs obtained can exceed the precision of the analysis and it is insensitive to product side reactions or degradation.

An alternative method was also developed where the products are analyzed.[19] Reactions are taken to low conversion, typically ~20%, and the isotopic composition of the isolated product is compared to that of product isolated from a reaction taken to a 100% conversion. The KIEs can then be calculated from equation 5 and this is referred to as the product intermolecular KIE. The problems with this methodology are the inefficiency of the "100% conversion" and product side reactions can adversely affect the measurement and interpretation of the KIE.

$$KIE = \frac{\log(1-F_1)}{\log[1-\left(F_1\frac{R_p}{R_o}\right)]} \qquad (5)$$

The above intermolecular methods are certainly useful in understanding the rate-determining step of a reaction; however, they provide no clues about the rest of the mechanism of a reaction. Intramolecular KIEs can provide information on the product – determining step when a partially-labeled reactant, having passed through the rate-determining transition state, still has a stereochemical or regiochemical choice. Moreover, when used in combination with intermolecular KIEs, intramolecular KIEs can distinguish between single step and multi-step reactions. The method for measurement of intramolecular KIEs at natural abundance was rigorously optimized to obtain accurate and precise measurement of the relative integration of two different peaks in the same

NMR spectrum.[20] The efficacy of this methodology was shown in the Baeyer-Villiger oxidation of cyclohexanone using m-chloroperoxybenzoic acid (shown below). When partially labeled cyclohexanone (assuming * is a ^{13}C label) passes through the rate-limiting carbonyl addition, it still has a choice between the two enantiotopic α-methylene groups. The rate of the migration of the labeled versus unlabeled group reflects the KIE of the second step. The intramolecular KIE obtained in this case represents the first-desymmetrizing step in the reaction, which corresponds to the product determining step.



(6)

1.3 Theoretical Calculations

Computational studies can provide a detailed picture of the reaction mechanism and can help us understand the intricacies in a chemical reaction. However, the conclusions obtained from these studies are only as good as the proposed mechanism and the accuracy of the method used. Theoretical calculations employed in quantum chemistry are only approximate models of electronic structure in reality. Caution must always be exercised in the interpretation of computational results. The best way to gauge the accuracy of the calculations is by comparison with experimental results. Some calculational methods employed in the Singleton group include semi-empirical methods, density functional theory, ab-initio methods, RRKM theory and variational transition state theory among others. The theory or theories ultimately chosen will be dependent on the goals of the study, practicality of the method and which best fits experimental evidence.

The interpretation of experimental KIEs is aided by theoretical models to quantitatively predict the isotope effects. For most standard reactions, the prediction of the KIEs result from the theoretical structure of the ground state reactants and the transition state of the reaction. The predicted KIEs are then calculated from scaled theoretical vibrational frequencies using conventional TST by the Bigeleisen and Mayer method.[21] Tunneling corrections are also applied using a one-dimensional infinite parabolic barrier model.[22]

Various experimental and theoretical methods to investigate the specific details of ordinary organic reactions will be discussed in this dissertation. This includes the use of trajectory studies to understand the product selectivity and energy flow in the ozonolysis reaction of vinyl ethers. Seemingly concerted Diels-Alder cycloadditions are also probed using trajectory studies to check for hidden entropic barriers. In several cases, the measurement of KIEs at natural abundance together with theoretically predicted isotope effects provide a complete and detailed picture of the reaction mechanisms.

II. DYNAMIC EFFECTS ON PRODUCT SELECTIVITY IN OZONOLYSIS REACTIONS OF VINYL ETHERS*

2.1 Introduction

Motion along a reaction coordinate is faster than either loss of energy to the medium or intramolecular vibrational energy redistribution (IVR). As a result, mechanistic intermediates are formed with excess energy, and that excess energy is to varying degrees not initially statistically distributed.[2,23] The governing theory for understanding the rates and selectivities of further conversions of the intermediate then depends on the time scale o[1]f those conversions. If they are slow, thermal equilibration will occur, and the rate and selectivity are predictable from transition state theory (TST). Rice–Ramsperger–Kassel–Marcus (RRKM) theory governs well the realm in which the steps following formation of an intermediate are slower than IVR but faster than or competitive with thermal equilibration, as is common in gas-phase reactions. In the fastest realm, the kinetic energy acquired during the formation of the intermediate is strongly coupled into modes that bring about its subsequent reaction faster than IVR. In such cases, experimental results (e.g., product formation selectivity) can be demonstrably inconsistent with statistical expectations,[24] but the selectivity can often be understood (at least qualitatively) by the idea of “dynamic matching.” Such

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* Reprinted with permission from “Competition between Reaction and Intramolecular Energy Redistribution in Solution: Observation and Nature of Nonstatistical Dynamics in the Ozonolysis of Vinyl Ethers” by L.M. Quijano and D. A. Singleton. *Journal of American Chemical Society*, **2011**, *133*, 13824-13827. Copyright 2011 American Chemical Society.

nonstatistical dynamic effects have been proposed to be important in many reactions.[6,8,10,11,25-28]

A middle realm in which the reaction of a mechanistic intermediate competes with IVR of the excess energy in that intermediate has long been considered.[29] Classic experiments by Doering and Rabinovitch sought to probe this competition by generating a formally symmetrical intermediate with an unsymmetrical energy distribution and then looking for product distributions betraying a lack of symmetry.[30] Alternatively, a competition between reaction and IVR has been inferred from pressure effects on product selectivity.[31] These experiments did not exclude the direct coupling of an intermediate's excess energy into its decomposition pathways; unusual rates and selectivities were assumed to arise simply from uneven distributions of molecular vibrational energy. The applicability of such experimental probes is limited,[32] and little is known about the competition between IVR and reaction in ordinary solution reactions.

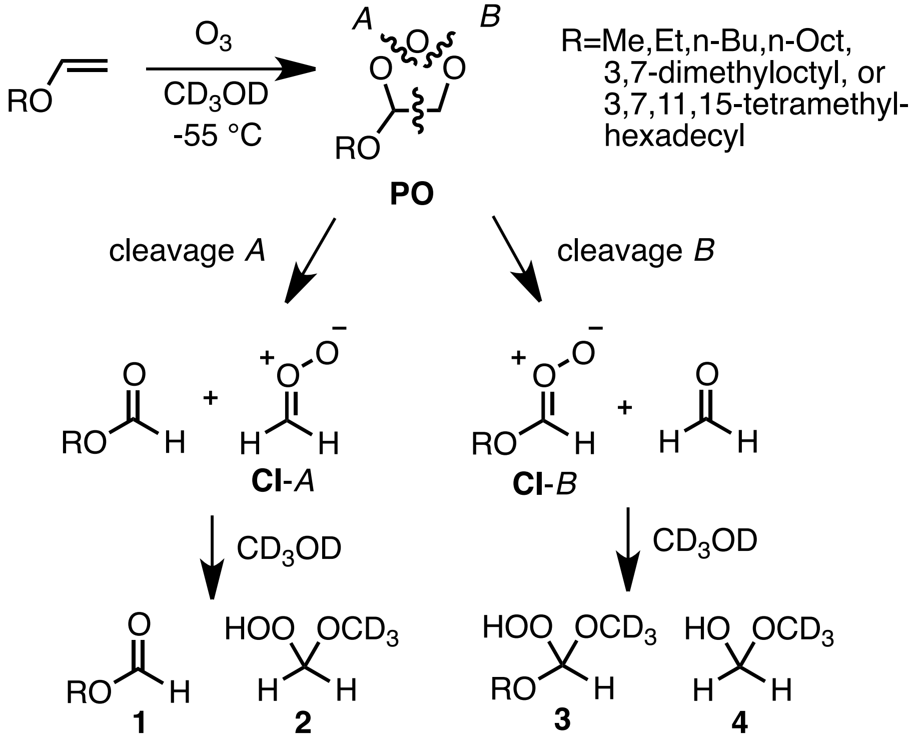
We describe here a different approach to probing the competition between reaction and IVR, the importance of this competition in an ozonolysis reaction in solution and the unusual observations that result, and a simple theoretical model for understanding those observations.

2.2 Design of Experiment and Experimental Results

The ozonolysis of alkenes is a fundamental organic reaction that is also of importance in atmospheric chemistry. The normal mechanism for these cycloadditions involves a 1,3-dipolar cycloaddition to afford a 1,2,3-trioxolane called the primary ozonide (**PO**), followed by cleavage of the **PO** to afford a carbonyl compound and a carbonyl oxide, known as the Criegee intermediate (**CI**). The combination of the high exothermicity of the cycloaddition step (>50 kcal/mol) and the low stability of the **PO**, initially saddled with that excess energy, would promote nonstatistical dynamics in the cleavage step. In fact, Hase and co-workers performed theoretical studies of the dynamics of the gas-phase ozonolysis of propene and predicted aspects of its post-transition-state dynamics to be nonstatistical.[33] We envisioned that in the right system we might be able to see substantial experimental consequences of nonstatistical dynamics on ozonolyses in solution and use the experimental observations to probe the dynamics.

We chose to study the ozonolysis of vinyl ethers because it is a well-behaved reaction that avoids some of the common complications in ozonolyses of alkenes and because the regiochemistry of the cleavage of the **PO** can be readily studied. The **PO** derived from a vinyl ether may cleave in two ways: cleavage *A*, which affords an alkyl formate (**1**) and formaldehyde oxide (**CI**-*A*), or cleavage *B*, which affords a formate oxide (**CI**-*B*) and formaldehyde. In methanol, the **CI**s are rapidly trapped, affording hydroperoxides **2** and **3**, and the formaldehyde is converted to its hemiacetal **4**. The pathways for conversion to the products are shown in Scheme 1.

Scheme 1. Ozonolysis Reaction of Vinyl Ethers in Methanol-d_4



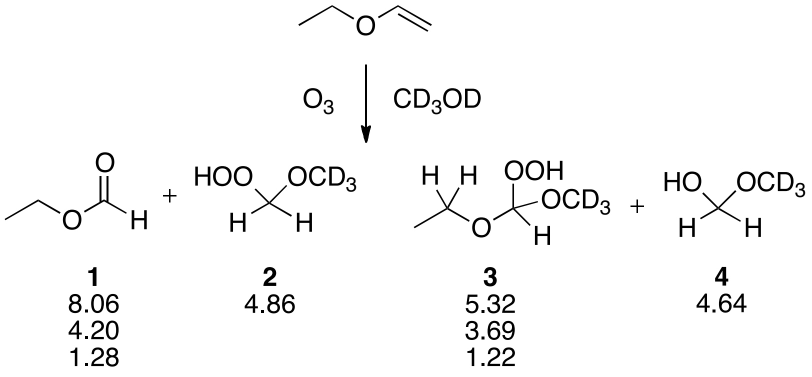
In ozonolysis of vinyl ethers in methanol-d_4, ^{1}H NMR peaks attributable to products **1**–**4** were readily identified. The NMR assignments were confirmed by independent syntheses (ozonolyses of ethylene and *trans*-1,2-diethoxyethylene) as well as a ^{2}H NMR study of a reaction employing 1-deutero-1-ethoxyethylene [see Section 2.3 below].

2.3 NMR Peak Assignments and Analyses

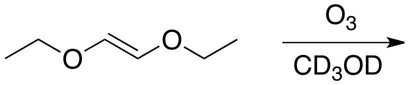
The ozonolysis of ethyl vinyl ether in methanol-d_4 affords a mixture that exhibits major ^{1}H NMR peaks at δ 8.06 (s), 5.32 (s), 4.86 (s), 4.64 (s), 4.20 (q), 3.69 (m), 1.28 (t), and 1.22 (t). Trace peaks were observed at δ 8.09 (≈0.4% versus 1 H in the major products), 6.13 (≈0.2%), 5.80 (<0.1%), 5.79 (<0.1%), 5.62 (<0.1%), 5.56 (<0.1%), 5.52

(<0.1%), 5.48 (≈0.2%), 5.28 (≈0.2%), 5.08 (≈0.1%), 5.07 (≈0.5%), 5.06 (≈0.2%), 5.01 (≈0.5%), 4.55 (≈0.1%), 4.44 (t, ≈0.2%), 3.59 (m, ≈0.2%), 3.49 (d of d, ≈0.4%), 3.39 (≈0.3%), 2.77 (<0.1%), 2.52 (<0.1%), 2.16 (<0.1%), 2.01 (<0.1%), and 1.99 (<0.1%). At 500 MHz, ^{13}C satellite peaks were observed at δ 8.29, 7.83, 5.02, 4.70, 4.35, 4.05, 3.45, 3.17, 1.40, and 1.15. The residual hydroxylic protons in the methanol were observed at δ 4.83. In some cases traces of ethanol were observed as an impurity in the starting ethyl vinyl ether.

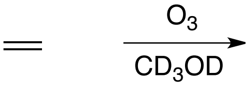
Scheme 2. ^{1}H-NMR Signals of the Observed Products



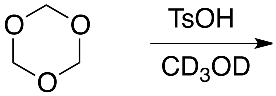
The peaks at δ 8.06 (s), 4.20 (q), and 1.28 (t) were assigned to ethyl formate (**1**). The peak at δ 4.86 was assigned to structure **2**, and this was supported by the formation of this peak as a major product in the ozonolysis of ethylene in methanol-d_4 (eq 8). The peak position also approximately matched its literature value at δ 4.89.[34] The peak at δ 4.64 was assigned to **4**, and this was supported by the formation of the same peak from 1,3,5-trioxolane in methanol-d_4 in the presence of *p*-TsOH (eq 9), as well as its formation as a major product in the ozonolysis of ethylene in methanol-d_4 (eq 8). The peak position also approximately matched its literature value at δ 4.67.[34] The peaks at δ 5.32, 3.69, and 1.22 were assigned to **3**. This was supported by the formation of these peaks in the ozonolysis of trans-1,2-diethoxyethylene in methanol-d_4 (eq 7).



1 + 3 (7)



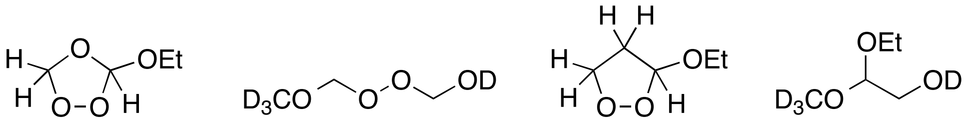
2 + 4 (8)



4 (9)

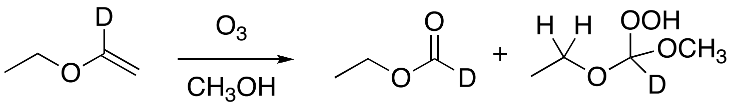
The trace peaks at δ 6.13 and 5.48 were assigned to structure **S1**. In the literature in $CDCl_3$, **S1** exhibits peaks at δ 6.08, 5.47, 4.93, 3.73, and 1.26.[35] The last three of these peaks were not observed but were assumed to be obscured by peaks for the major products. The trace peaks at δ 5.28 and 5.06 were assigned to structure **S2**. **S2** could be formed at equilibrium from **2** and **4**, and it was noted that the peaks δ 5.28 and 5.06 were larger in high-concentration reactions and negligible in low-concentration reactions. In the literature in $CDCl_3$, the unlabeled analog of **S2** exhibits peaks at δ 5.16 and 5.05.[36] These peaks are triplets in the literature, exhibiting an unusual small long-range coupling of 0.8 Hz, and with careful shimming we observed that the peaks for **S2** were triplets with J = 0.9 Hz. The equilibrium formation of **S2** diminishes the amount of **4**, so that cleavage *B* was most accurately judged by the amount of **3**. The trace peaks at δ 2.77 and 2.52 were assigned to **S3**. In the literature in $CDCl_3$, **S3** exhibits peaks at δ 5.32, 4.24, 3.94, 3.82, 3.50, 2.76, 2.59, 1.23.[37] There is so little **S3** present that its multiplets are only discernable in areas of the spectrum devoid of other peaks. The peaks at δ 4.44 and 3.49 were assigned to **S4**. These peaks exhibit an ABX pattern that was simulated with reasonable accuracy with J_{AX} and J_{BX} = 5.3 Hz, J_{AB} = 12 Hz and a separation of the diastereotopic A and B peaks of 8 Hz. (For the corresponding methyl vinyl ether, the pattern reduces to an apparent A_2X.) The shifts and coupling constants fit with that observed in similar compounds.[38] **S4** could reasonably arise by the epoxidation of ethyl vinyl ether followed by ring opening with the deuterated methanol.

Scheme 3. Possible Side Products



S1 **S2** **S3** **S4**

Aside from the independent syntheses discussed above, the assignment of peaks and the relative cleanliness of the reaction were supported by ^{2}H NMR analysis of the ozonolysis of 1-deutero-1-ethoxyethylene in CH_3OH. The ^{2}H NMR spectrum of the reaction mixture exhibited peaks at δ 8.07 and 5.33, assigned to deuterated analogs of **1** and **3**.



(10)

Closely analogous peak observations and assignments were made for the ozonolyses of other vinyl ethers.

The quantitation of the product ratios was determined from ^{1}H NMR integrations, using a variety of precautions to minimize systematic and random error. The ratio of the cleavage-*A* and -*B* products did not vary significantly with ozonolysis conversions from 20 to 100% conducted within a few minutes, though secondary reactions did occur with excess ozone or extended reaction times. The ratios of the cleavage products observed for a series of alkyl vinyl ethers are shown in Table 1.

Table 1. Experimental and Statistically Predicted A/B Ratios.

		Predicted A/B[d,e]	
Alkyl Group	**Exptl A/B[a,b,c] (n)**	**TST**	**RRKM**
methyl	25.9 ± 1.2 (12)	43 x 10^5	10.0
ethyl	36.3 ± 1.0 (33)	9.8 x 10^5	10.9
butyl	47.2 ± 2.0 (14)	8.5 x 10^5	18.5
octyl	54.8 ± 1.8 (16)	9.6 x 10^5	47.8
3,7-dimethyloctyl	63.2 ± 2.0 (7)	5.7 x 10^5	61
3,7,11,15-tetramethylhexadecyl	74.5 ± 1.9 (9)	9.6 x 10^5	343
ethyl (-31 °C)	33.7 ± 1.3 (10)	2.4 x 10^5	10.9
ethyl (8 °C)	24.7 ± 1.4 (10)	0.45 x 10^5	10.9
ethyl (23 °C)	23.6 ± 2.1 (14)	0.26 x 10^5	10.8
octyl (-31 °C)	51.5 ± 1.0 (5)	2.5 x 10^5	47.9
octyl (8 °C)	43.1 ± 0.6 (7)	0.44 x 10^5	48.0
octyl (23 °C)	40.0 ± 0.7 (8)	0.26 x 10^5	48.1

[a] The ratios given are based on the 1H NMR integration for the methine peak of 3 vs the formyl peak of 1.
[b] Uncertainties are 95% confidence ranges; the number of measurements is given in parentheses.
[c] The reactions were conducted at −55 °C unless otherwise noted. [d] Gaussian- 4 (G4) energetics were used for R = methyl, ethyl, and butyl. For the larger alkyl groups, the R = butyl G4 relative energies were used, and small correction factors for differences in the relative energies seen in B3LYP/GTBas3 calculations were included. The two lowest-energy cleavage-A TSs and the two lowest-energy cleavage-B TSs were used in all of the calculations.

2.4 Discussion of Results

The experimental selectivities are surprising in a number of ways. The selectivity increases consistently with the size of the alkyl group, and the selectivity changes in going from R = ethyl to R = butyl or from R = butyl to R = octyl are larger than normally attributable to electronic substituent effects. The selectivity with R = 3,7,11,15-tetramethylhexadecyl is greater than that with R = 3,7-dimethyloctyl, even though the first structural difference between the two is 10 bonds away from a reactive center. The effect of the alkyl groups is not attributable to a medium effect; addition of pentane to the reaction mixture had no effect on the selectivity.

Another observation is that the changes in selectivity with temperature are relatively small. The observed selectivities with R = ethyl and R = octyl from −55 to 23 °C correspond to $\Delta\Delta H^{\ddagger}$ values of 0.8 and 0.5 kcal/mol, with $\Delta\Delta S^{\ddagger}$ values of −4 and −6 e.u., respectively. If $\Delta\Delta S^{\ddagger}$ were ~0 e.u., as might be expected intuitively for the similar *A* and *B* cleavages (in the G4 calculations, it is +0.6 e.u. at −55 °C), then the selectivity would change by a factor of 2.6–2.9 instead of only 1.4–1.5 over the temperature range. The most striking observation is that the experimental selectivities are 4–5 orders of magnitude lower than expected on the basis of TST. The energy profile for the reaction of ozone with vinyl ethers is depicted in Figure 3. Cleavage *A* is thermodynamically favored over cleavage *B* by 13.0 kcal/mol, and the calculated free-energy barriers reflect the thermodynamics, favoring cleavage *A* by 5.9–6.6 kcal/mol in G4 calculations (see the Section 5.3 Computational Procedure and Supporting Computational Results for alternative computational methods, including solvent-model calculations). If TST were applicable in this reaction, cleavage *B* would be unobservable.

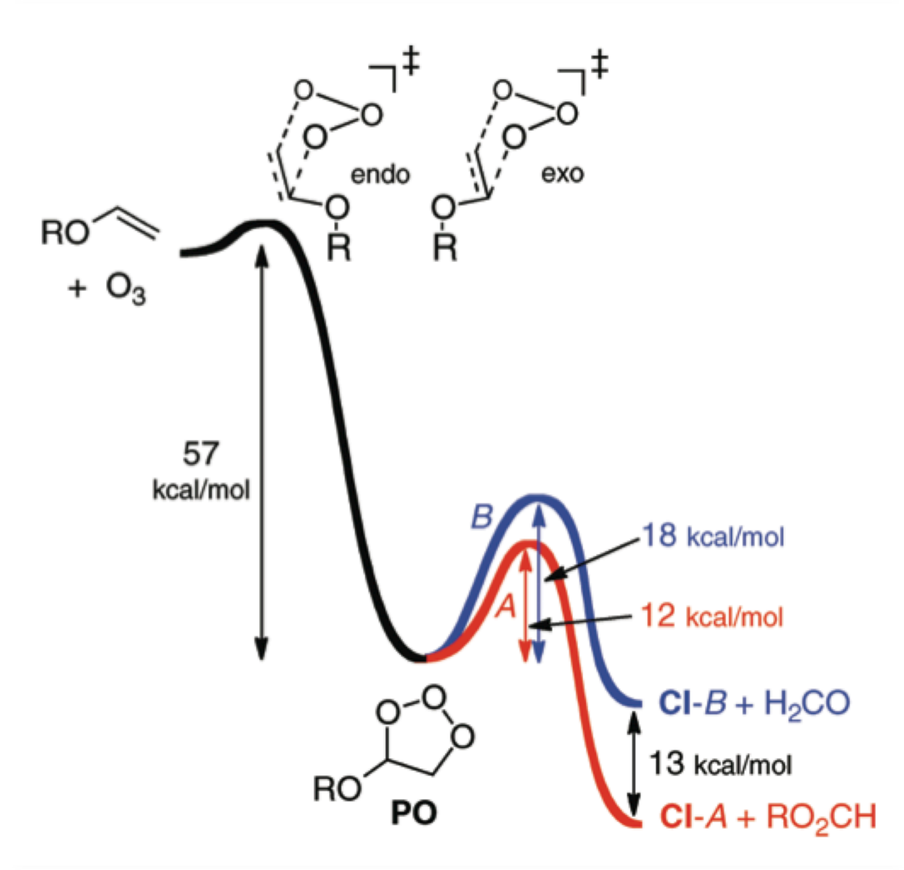


Figure 3. Approximate energy profile for the reaction of the various vinyl ethers with ozone based on G4 calculations.

RRKM theory comes closer to predicting the observed selectivity but fails in an important way. RRKM rate constants were calculated for the cleavage of the **PO**s, assuming that the ozone/vinyl ether cycloaddition transition states (TSs) have a canonical energy distribution and that no energy is lost in forming the **PO**s. With the resulting >57 kcal/mol of extra energy, the RRKM-predicted *A*/*B* selectivities are much lower than the TST-predicted selectivities and fall in a range similar to that for the experimental results. However, there is a substantial problem with the trend in the RRKM-predicted selectivities: the RRKM calculations predict that as the size of the alkyl group increases, the selectivity should increase greatly. This prediction is understandable because RRKM theory assumes that the distribution of molecular energy is equilibrated, allowing large alkyl groups to act as "heat sinks" for the reactions. Such a heat-sink effect would in essence cool the hot 1,2,3-trioxolane ring, causing the selectivity to rise dramatically. Experimentally, this does not happen; the increase in selectivity is much smaller than that predicted by RRKM theory.

The most economical explanation for this data is that the selectivities reflect a competition between cleavage of the **PO** ring and IVR. Larger alkyl groups can better accept the energy generated by **PO** formation, but the vibrational energy that is initially localized in the 1,2,3-trioxolane cannot be fully distributed throughout the molecule before substantial ring cleavage occurs.

2.5 Quasiclassical Direct-Dynamics Trajectory Calculations

To explore this idea, quasiclassical direct-dynamics trajectory calculation[39] were used to study these reactions. The trajectories were carried out on an ONIOM potential energy surface using density functional theory (DFT) for the **PO** ring and the PDDG/PM3 semiempirical method[40] for the various alkyl chains. The DFT part of the calculation employed a locally modified hybrid functional (see the Section 5.3 for details) that was parametrized to approximately reproduce a known barrier for a primary ozonide cleavage as well as G4 energetics for the initial cycloaddition barrier and exothermicity. The lowest-energy endo and exo TSs (Figure 1) for the various ozone/vinyl ether cycloadditions were used as the starting point for the trajectories. Each normal mode was given its zero-point energy (ZPE) plus a Boltzmann sampling of additional energy appropriate for a temperature of −55 °C and a random phase and sign for its initial velocity. The trajectories were integrated in 1 fs steps until either ring cleavage occurred or a 500 fs time limit (to minimize nonphysical IVR of the ZPE) was reached.

Table 2. Trajectory Results, Projected Cleavage-B Percentages after 1 ps (%B), and Projected A/B Ratios.

alkyl group	endo TS	exo TS	%B[a]	A/B[b]
methyl	A: 522 B: 38 (1.0%) no rxn: 3129	A: 1147 B: 129 (2.2%) no rxn: 4470	3.6	27
ethyl	A: 420 B: 36 (0.6%) no rxn: 5423	A: 1089 B: 131 (2.3%) no rxn: 4445	2.8	35
butyl	A: 395 B: 24 (0.4%) no rxn: 5731	A: 1075 B: 119 (2.1%) no rxn: 4564	2.2	45
octyl	A: 417 B: 27 (0.4%) no rxn: 7136	A: 560 B: 52 (1.6%) no rxn: 2655	1.8	55
3,7-dimethyloctyl	A: 258 B: 24 (0.4%) no rxn: 5278	A: 811 B: 61 (1.3%) no rxn: 3872	1.7	57
3,7,11,15-tetramethylhexadecyl	A: 265 B: 12 (0.3%) no rxn: 4163	A: 561 B: 51 (1.5%) no rxn: 2709	1.6	62

[a] Calculated by weighting the endo and exo results in a 74:26 ratio (based on G4 energetics) and assuming that the average rate of cleavage B observed between 200 and 500 fs continues for, on average, a total time of 1 ps (see the text). [b] Calculated as (100% − %B)/%B.

The trajectory results (Table 2) provide both qualitative and quantitative support for a competition between ring cleavage and IVR. Qualitatively, the trajectories show a substantial proportion of cleavage *B* that falls off moderately as the size of the alkyl group increases. With R = methyl and R = ethyl, the proportion of cleavage *B* observed in the trajectories is very close to that predicted by the RRKM calculations. With larger alkyl groups, the proportion of cleavage *B* decreases but by only a factor of 2–3 for the largest group as opposed to a factor of 34 in the RRKM predictions. All of this fits with the experimental observations.

The energy generated from formation of the **PO** should undergo both IVR and loss to solvent as time goes on, and a quantitative analysis of the trajectory results requires some allowance for this cooling. As the simplest possibility, we considered a two-state model. In this model, most **PO** molecules undergo thermal deactivation to give a “cold” state that affords only cleavage *A*, but the initially formed “hot” state affords either cleavage *A* or cleavage *B* at a rate that is assumed to match that given by the trajectory results in the time period between 200 and 500 fs after the cycloaddition TS. (Negligible cleavage *B* occurs before 200 fs into the trajectories.) From an average lifetime of the hot state, the *A*/*B* ratio can be calculated. This process is to some degree an exercise in numerology, but the lifetime of the hot state is the only adjustable parameter. When the average lifetime of the hot state is set at the seemingly reasonable value of 1 ps, the projected *A*/*B* ratios for the various vinyl ethers are in phenomenal agreement with experiment.

Recent work[41] has proposed a “canonical competitive nonstatistical model” (CCNM) to predict product branching ratios after dynamical bottlenecks of the type seen in the current reaction. The CCNM model divides the branching into “indirect” and “direct” components, the former being predicted using TST and the latter using phase-space theory. The large barriers for the reaction of the primary ozonide in the present work cause the CCNM model to allocate 100% of the reaction to the indirect component, so the CCNM model fails qualitatively to the extent that TST itself fails.

The flow of energy from the primary ozonide ring into the alkyl groups was examined by following the kinetic energy of the atoms in the alkyl groups in the 100–500 fs time frame. The average rates of increase in the alkyl group energy for R = ethyl, R = butyl, and R = octyl (based on ~400 trajectories in each case) were 17, 19, and 20 kcal mol^{-1} ps^{-1}, respectively. This observation suggests that the decrease in cleavage *B* as the alkyl group size is increased, experimentally and in the trajectories, is associated with the increasing rate at which the larger alkyl groups take up energy. However, the rate at which the octyl group absorbs energy in the trajectories within the first few hundred femtoseconds is only moderately greater than that for the ethyl group, and the selectivity change is lower than would be expected from the two groups’ total ability to take up energy.

2.6 Trajectory Results VS RRKM Prediction

Since the trajectory results appear to reflect the experimental observations well, it is of interest to compare some of the details of the trajectory results with RRKM predictions. For this comparison, we consider only the trajectories initiated from the exo cycloaddition TS, because the endo TS leads to a **PO** conformer that must undergo conformational interconversion to access the lowest-energy cleavage TSs (see the SI for a discussion of this conformational interconversion). For the small R = methyl system, RRKM theory appears to work quite well in predicting both the rate of cleavage *B* ($5 \times 10^{10}\ \mathrm{s}^{-1}$ vs ~6 × $10^{10}\ \mathrm{s}^{-1}$ in the trajectories) and the *A*/*B* ratio (10:1 vs 9:1 in the trajectories). On the other hand, for the R = tetramethylhexadecyl system, RRKM theory predictions are off by 3 orders of magnitude for the rate of cleavage *B* ($4 \times 10^{7}\ \mathrm{s}^{-1}$ vs ~4 × $10^{10}\ \mathrm{s}^{-1}$ in the trajectories) and a factor of 31 for the *A*/*B* ratio (343:1 vs 11:1 in the trajectories).

The success of RRKM theory for the R = methyl system suggests that cleavage *B* does not arise by a strong coupling of the **PO**'s initial excess energy into the cleavage pathway, as in the dynamic matching phenomenon. This idea is supported by the observation that in the trajectories there is a significant time lag between the formation of the **PO** (median time 71 fs) and the rise of cleavage-*B* events (>200 fs). This contrasts with the nonstatistical behavior seen in the cleavage of the acetone cation radical, where the reaction reaches a maximum rate within 50 fs and many trajectories bypass the area of the formal intermediate.[25d] The onset of cleavage within the **PO** appears to *require* some IVR within the ring, which takes some time, and the cleavage then proceeds nonstatistically simply by virtue of the localization of the energy within the area of the ring.

If RRKM theory may be viewed as applicable for each system within a "molecular subset" equal to the size of the R = methyl system (or, more precisely, a subset of the normal modes localized in that portion of the molecule), then an approximate statistical model can be developed to interpret our experimental observations. Following an extension of a process used previously by Rabinovitch,[31a] our model assumes that the ensemble of energies *Et* within the molecular subset decays exponentially from the initial ensemble of energies E^0 (eq 11) and that the rate constants *kA*(*Et*) for cleavage *A* and *kB*(*Et*) for cleavage *B* are those calculated from RRKM theory for the R = methyl system. The amount of cleavage *B* observed is then calculated using eq 12, in which PO*(*t*) is the amount of energetic **PO** that survives to time *t* [decreased by *kA*(*Et*) and *kB*(*Et*) processes]. The decay constant λ is then set for each reaction to the value that affords the experimental product ratio.

$$E^t = E^\circ e^{-\lambda t} \tag{11}$$

$$amount\ of\ cleavage\ B = \int_{E^\circ,t} k_B(E^t)PO^*(t)dt \tag{12}$$

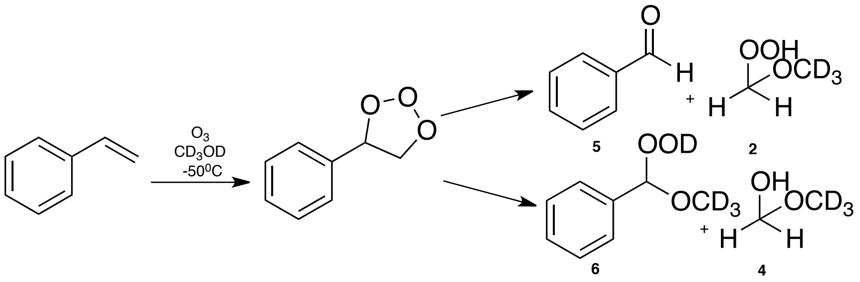
The λ values obtained in this way are 1.6×10^{11}, 2.5×10^{11}, 3.5×10^{11}, 4.2×10^{11}, 4.9×10^{11}, and 5.5×10^{11} s^{-1} for *R* = methyl, ethyl, butyl, octyl, dimethyloctyl, and tetramethylhexadecyl, respectively. These values are notably slower than IVR rate constants of 10^{12}–10^{13} s^{-1} inferred by Rabinovitch but quite consistent with directly measured IVR rate constants observed by Schwarzer.[42] These λ values also fit well with the rates of energy loss to the alkyl groups found in the trajectories studies ($\lambda = 4 \times 10^{11}$ s^{-1} corresponds to an energy loss of ∼20 kcal/mol in 1 ps). The particular values of λ depend on both the applicability of the model and the accuracy of the calculated barriers,[43] so there is some danger of overinterpretation, but it is interesting that λ values for the larger alkyl groups are more than a factor of 2 greater than that for the methyl system. This suggests that most of the **PO** cooling in the larger systems is intramolecular, as would be consistent with direct observations of vibrational relaxation by Crim.[44]

2.7 Extension of the Role of Dynamic Effects in Atmospheric Chemistry

Having established the role of dynamic effects in ozonolysis reactions of vinyl ethers, we wish to extend the scope of this study by employing several alkenes that have importance in atmospheric chemistry. We chose 2,3-dimethyl butadiene and isoprene. Isoprene has two unequal double bonds with very close reactivities, giving a mixture of products upon complete ozonolysis of the two double bonds. This makes analysis of the product ratios from the reaction of one double bond complicated. Therefore, we chose to study 2,3-dimethyl-1,3,-butadiene as our isoprene analogue to simplify the system.

Ozonolysis reactions in atmospheric chemistry have been the subject of many studies due to their environmental implications. Isoprene and monoterpenes make up 44% and 11%, respectively, of the annual global volatile organic compounds emissions.[45] One of the more important reactions these volatile organic compounds can undergo in the atmosphere is their reaction with ozone. Alkene ozonolysis produce significant amounts of hydroxyl radicals and secondary organic aerosol.[46-48] Organic compounds of this nature have been shown to be detrimental to our health and environment.[49] Styrene, on the other hand, has been classified by the US Environmental Protection Agency as a Hazardous Air Pollutant. Styrene is mainly used in polystyrene plastics and resins production. This pollutant is emitted from building materials and consumer products.

The experimental approach on the selected alkenes is the same as the one presented above for ethyl vinyl ether. Equation 13 presents the different products obtained from the decomposition of the styrene POZ. Product ratios from the ozonolysis of styrene at 0 °C did not vary over the course of the reaction. It is important to note that the aromatic ring is also susceptible to ozonolysis. However, this is not much of a concern because the terminal double bond of styrene is more reactive than the benzene ring. Complete ozonolysis of the terminal double bond was achieved without ozonolysis of the phenyl ring. All of the peaks corresponding to the 4 products below (**2,4,5,6)** were observed in the ^{1}H-NMR of the crude reaction mixture.



(13)

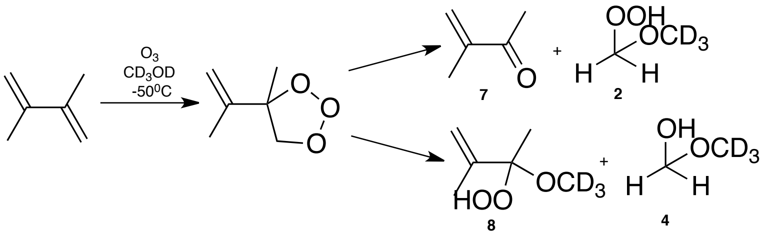
To confirm the presence of alkoxy hydroperoxide **6**, ozonolysis of trans-stilbene was accomplished. Proton peaks corresponding to **5** and **6** were observed verifying the assignment of the proton peaks for the products. After obtaining the experimental product ratio as shown in Table 3, computational studies were done to determine the TST prediction (second entry in Table 3).

Table 3. Styrene Ozonolysis Product Ratios.

	Product ratio (**5**:**6**)
Experimental	46.8 (0.3) : 53.2 (0.3)
B3LYP/6-31+G*	12:88

Analysis of the experimental product ratios versus the theoretical prediction clearly shows that TST once again has failed to explain the product distribution in this ozonolysis reaction.

The expected products from the ozonolysis of 2,3-dimethyl-1,3-butadiene are shown in the equation 14 below. Ozonolysis of one of the two equivalent double bonds in 2,3-dimethyl-1,3-butadiene will give rise to an alpha,beta-unsaturated ketone **7** or an alkoxy hydroperoxide **8**. The newly generated compounds are less activated for the attack of the ozone. This is crucial because we want to monitor the product ratios of the reaction of ozone with only one of the double bonds. Furthermore, ozonolysis of products **7** and **8** will compromise the accurate calculation of the product ratios from the POZ decomposition. To avoid these problems, aliquots were taken at low product conversions.



(14)

The experimental product ratios were obtained through the analysis of the crude ozonized 2,3-dimethyl-1,3-butadiene in MeOH-d4 at -50°C. No statistical trend between percent conversion and product ratios was observed. The product ratio was then compared to the theoretical prediction according to TST (Table 4).

Table 4. 2,3-Dimethyl-1,3-butadiene Ozonolysis Product Ratios.

	Product ratio (**7**:**8**)
Experimental	14.7 (1.9) : 85.3 (1.9)
modified B3LYP/6-31+G**	1:140

Based on the results shown above, TST cannot predict the product distribution in the ozonolysis reaction of 2,3-dimethyl-1,3-butadiene. Although both the styrene and 2,3-dimethyl-1,3-butadiene results are encouraging, dynamic trajectory studies were not pursued in both cases.

2.8 Conclusion

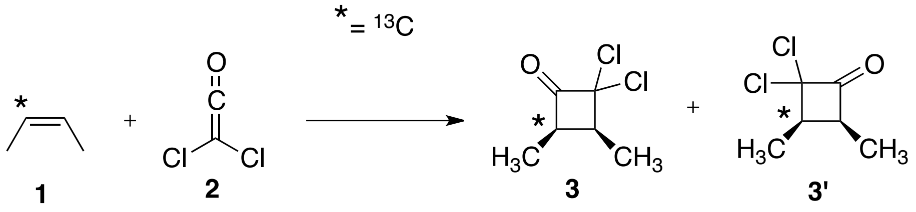
When an experimental product ratio does not fit with a calculated selectivity based on theoretically calculated barriers and statistical theory, it would normally be assumed that the calculated barriers are simply inaccurate, not that statistical theory is inapplicable to a reaction. In this way, outside of the special cases of formally symmetrical intermediates, any single selectivity observation may be shoehorned into statistical rate theories. This is normally perfectly correct, but the present results show that it need not be so, even for simple reactions in solution. Our process of examining the selectivity in a homologous series of reactions should be of broader value in recognizing reactions involving nonstatistical dynamics. The physical ideas here are not new; for example, the idea that large molecules might behave like smaller molecules was suggested by Rice in 1930.[50] However, the results herein support and provide considerable insight into the impact of a fundamental physical phenomenon, the redistribution of vibrational energy in molecules, on the experimentally observed products in an ordinary organic reaction in solution.

III. CONCERTED TO UNCONVENTIONAL “STEPWISE” MECHANISMS IN A DIELS-ALDER REACTION: OBSERVATION AND PREDICTION OF ISOTOPE EFFECTS

3.1 Introduction

The success of conventional transition state theory (TST) is reflected on the extensive use of one of its most valuable branch of applications, kinetic isotope effects (KIEs). The combination of experimental and high-level prediction of KIEs is a powerful tool that has helped elucidate details of reaction mechanisms. Even with the widespread use of TST, it has its limitations and when these arise, the validity of the basic assumptions in TST must be questioned. It has been recognized that certain corrections such as the transmission coefficient, κ, must be incorporated in TST to minimize the inaccuracies and this has led to an improvement of the theory.[12] The failure of conventional TST has been well documented in reactions that exhibit variational TS corrections, tunneling and dynamic effects. Some instances variational TS corrections are performed are in cases where there is no potential energy saddle point or the free energy maximum is not the same as the “generalized” saddle point.[51] Corrections such as the small curvature tunneling and least-action tunneling models have been applied to correct for tunneling effects.[51] Dynamic effects include dynamic matching, incomplete IVR and non-statistical recrossing among others. For these types of reactions, the detailed motions and momenta of the atoms in the reaction must be taken into consideration to account for the experimental selectivity.

A recent paper published from our group has shown experimental evidence for one of these dynamic effects – nonstatistical recrossing.[52] As mentioned in Section 1, recrossing occurs when reactants passing through a transition state runs into an "energy wall" and instead of forming products, it bounces back to reactants. Statistical recrossing can be accounted for by variational TST by adjusting the hypersurface to minimize recrossing. Nonstatistical recrossing, on the other hand, was accounted for by trajectory studies. The cycloaddition of dichloroketene **2** with cis-2-butene **1** exhibited unusual intramolecular KIE. The equivalent products **3** and **3'** are isotopomeric when one of the carbons in starting material **1** is labeled with ^{13}C.



KIE = 3' : 3 = 0.993 ± 0.001

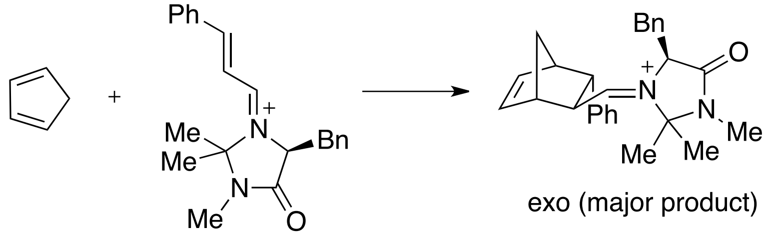
(15)

The intramolecular KIE of 0.993 for **3'/3** indicates that there is a preference for ^{13}C to be on the methine carbon next to the carbonyl carbon. This is unusual because if this reaction is viewed in a conventional way, that is an electrophilic attack of the carbonyl carbon of the ketene on one of the olefinic carbons, the methine carbon next to the carbonyl carbon should end up with more ^{12}C. Calculated KIEs from conventional TST using several methods predicted a "normal" isotope effect in the range of 1.01-1.02 inconsistent with experiment. Instead, the experimentally observed KIE was accurately predicted by quassiclassical trajectory studies. The origin of this isotope effect was further probed by looking at trajectory results in detail. One of the most striking observations is the large number of trajectories that recross. The inverse KIE arises from the observation that the heavier atom, ^{13}C, recrosses less; therefore, they end up in the product on the methine position adjacent to the carbonyl carbon. A statistical perspective was also explored in trying to understand the origin of the isotope effect. The cycloaddition was thought to be highly asynchronous from TS searches from high level calculational methods. As the second C-C bond is forming, the atoms forming the ring are now restricted in their motion causing the vibrational frequency to increase and causing the zero point energy to increase while the entropy decreases. The major consequence of this is seen in the free energy surface where a second barrier arises after the intial C-C bond formation. This second step is higher in energy than the first barrier by 1.2 kcal/mol and is attributed to an entropic effect. Prediction of the KIE from this statistical perspective using microcanonical variational RRKM procedure and taking into account this "hidden" rate-limting step, gives 0.992 that is in excellent agreement with experiment. This phenomenon was explored theoretically in another seemingly concerted cycloaddition – the organocatalytic Diels-Alder reaction.

The Diels-Alder (DA) reaction is one of the most popular pericyclic reactions in organic chemistry owing to its simplicity and usefulness. This cycloaddition reaction, depending on the reactants and conditions used, can exhibit a range of mechanisms from concerted (synchronous or asynchronous) to stepwise. The parent cycloaddition reaction is widely accepted to be concerted synchronous.[53] The reaction of isoprene with maleic anhydride was shown to be concerted and moderately asynchronous[54] while Lewis-acid catalyzed reactions of isoprene with acrolein, methyl vinyl ketone and ethyl acrylate have also demonstrated a concerted transition state but highly asynchronous.[55] On the other end of the spectrum, the Lewis-acid catalyzed reaction of 2-phenyl-2-cyclohexen-1-one and butadiene showed experimental evidence supporting a stepwise process.[56] With the purpose of seeking another reaction that exhibits an entropic intermediate and a "hidden" rate-limiting step, three different DA reactions of cyclopentadiene and trans-cinnamaldehyde will be presented here. The first is an organocatalytic DA reaction, second is a Lewis-acid catalyzed DA reaction and finally a thermal DA reaction.

3.2 Organocatalytic Diels-Alder Reaction

The novel idea of an entropic intermediate and "hidden" rate-limiting step was theoretically examined[52] for the organocatalytic DA reaction first reported by MacMillan in 2000.[57]



(16)

The B3LYP/6-31G* energy surface for this reaction exhibits a single potential energy saddle point corresponding to a highly asynchronous transition structure, **8**‡. The potential energy profile (red line) is shown in Figure 4 as well as the transition structure associated with the saddle point.

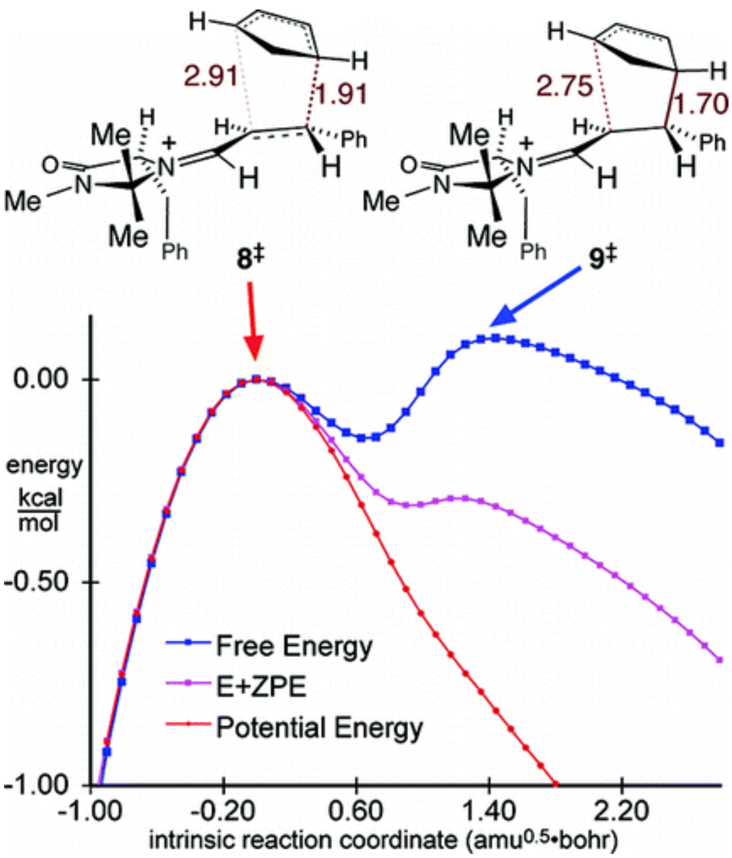


Figure 4*. Energy profiles along the IRC through TS 8‡, with the saddle point taken as the zero of energy. The free energy profile is based on generalized free energies of activation obtained from GAUSSRATE.[58]

When trajectory studies were initiated from **8**‡, a large number of trajectories (46%) completely form the first C-C bond and then reverted back to starting materials. For the trajectories that are started from the minor isomer, an even larger amount of recrossing (63%) was observed.

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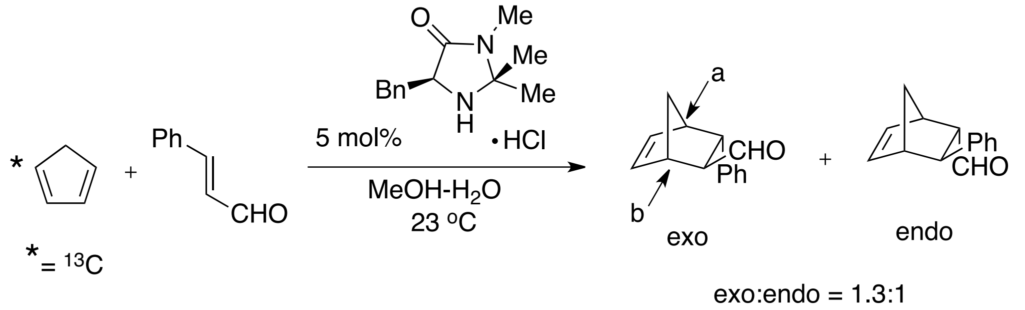
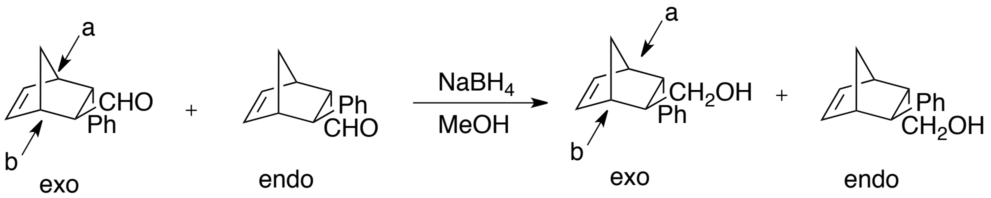
These are very interesting results because this resembles the findings from the cycloaddition of dichloroketene and cis-2-butene discussed earlier. The organocatalytic DA transition structure is highly asynchronous with the second C-C bond forming progressively later. In the time that it takes for the second bond to form, the motion of the atoms involved in the ring formation is now restricted and the entropy decreases. This effect is seen in the free energy profile where a second step corresponding to the second C-C bond formation (blue line) is observed. This second barrier is higher in energy than the first barrier by 1.2 kcal/mol which makes it the rate-limiting step. For the endo pathway, the second "hidden" rate-limiting step is 0.6 kcal/mol higher than the potential energy saddle point. All these theoretical findings are interesting but we seek to find experimental evidence for this phenomenon. Because our previous work[52] has shown that the unusual kinetic isotope effects observed were explained using a dynamical perspective by trajectory studies as well as a statistical perspective by allowing for the "hidden" rate-limiting step, the next logical step would be to measure the intramolecular KIE for the MacMillan system.



(17)

The above reaction is a suitable system because the bridgehead carbons (a and b) in the product are distinct from each other but are equivalent in the starting material, cyclopentadiene. However, if cyclopentadiene is labeled with ^{13}C as indicated above then the relative amount of ^{13}C on these two carbons constitutes an intramolecular KIE that can be measured and it will provide a mechanistic picture on the origin of the selectivity at these positions in the product-determining step. If the selectivity is decided on the potential energy saddle point, then based on conventional TST the expected intramolecular KIE for the bridgehead carbons should mirror **8‡.** Since this transition structure is highly asynchronous, the intramolecular KIE for a/b is expected to be a large "normal" isotope effect. This means that more ^{12}C in the position where C-C bond formation is more advanced in the product-determining step (position a) is expected, leaving the heavier isotope in the bridgehead carbon that forms the second bond in the cycloaddition (position b).



(18)

Ivonne Andujar of the Singleton group measured the intramolecular KIEs of the reduced aldehyde cycloadducts. The ^{13}C KIEs were measured at natural abundance using previous NMR methodology.[20] The KIE samples contained both the exo and endo cylocadducts. Extensive column chromatography could not separate the exo and endo products. The complication with having both products in the same sample is that the set of NMR peaks corresponding to carbon b in the exo and endo cycloadducts are close to each other and the integrations of the two peaks can affect the amount of the measured ^{13}C composition in those peaks thus compromising the accuracy and reliability of the numbers. Nevertheless, the measured KIEs proved to be very interesting. Preliminary intramolecular a/b KIE for the exo adduct exhibited a very small “normal” isotope effect of 1.004(3) and 1.016(2) for the endo and exo, respectively. This is intriguing because the highly asynchronous concerted transition state based on conventional TST does not account for this experimental observation. This KIE suggests a synchronous or very moderately asynchronous TS. Parallel to the dichloroketene and cis-2-butene cycloaddition, this unusual KIE can be explained from a dynamical perspective and statistical perspective. Trajectory studies show a considerable amount of recrossing. Since heavier atoms recross less, a substantial amount of ^{13}C may be present in the carbon that forms the first C-C bond (position a), however not to the extent where the KIE becomes inverse like in the dichloroketene case. From a statistical perspective, consideration of the second “hidden” rate-limting step that is due to entropic effects might give a more accurate prediction of the KIE. Future work involves prediction of the intramolecular KIE from the trajectory studies and from a canonical variation RRKM procedure for the statistical perspective to give a more quantitative interpretation of the experimentally observed KIE.

3.3 Lewis-acid Catalyzed Diels-Alder Reaction

Our interest in this novel idea of entropic intermediate and “hidden” rate limiting step prompted us to look at other highly asynchronous cycloadditions. Why highly asynchronous? The current hypothesis as mentioned earlier is that for a seemingly concerted cycloaddition, a delayed second bond formation would mean that the motions of the atoms associated with the ring closure are constrained causing the vibrational frequencies to increase, the zero point energy to increase and the entropy to decrease. This decrease in entropy will show up in the free energy profile of the reaction as a two-step process instead of a concerted cycloaddition. Theoretically, intial tests such as trajectory studies and POLYRATE[59] calculations can be performed to check the viability of the chosen highly asynchronous cycloadditions. Significant amount of recrossing or the appearance of a second barrier in the free energy profile are probable theoretical evidences for an entropic barrier. These can be performed before measuring experimental KIEs, which is sometimes lengthy and arduous.

3.3.1 Diels-Alder Reaction of Cyclopentadiene with Crotonalydehyde, Trans-3-penten-2-one and Methyl Crotonate

Several Lewis-acid catalyzed DA reactions were modeled to check for their propensity to recross. The BF_3-catalyzed reactions of cyclopentadiene with the dienophiles crotonaldehyde, trans-3-penten-2-one and methyl crotonate were investigated and all three transition structures were highly asynchronous as shown in Figure 5. The method used was B3LYP/6-31G* and only the endo pathways were considered in the calculations. An interesting feature of the endo transition structure is its bis-pericyclic nature; that is the same transition structure could potentially lead to the hetero-DA product. This feature was explored in the direct-dynamics calculations where the formation of hetero-DA products was also monitored.

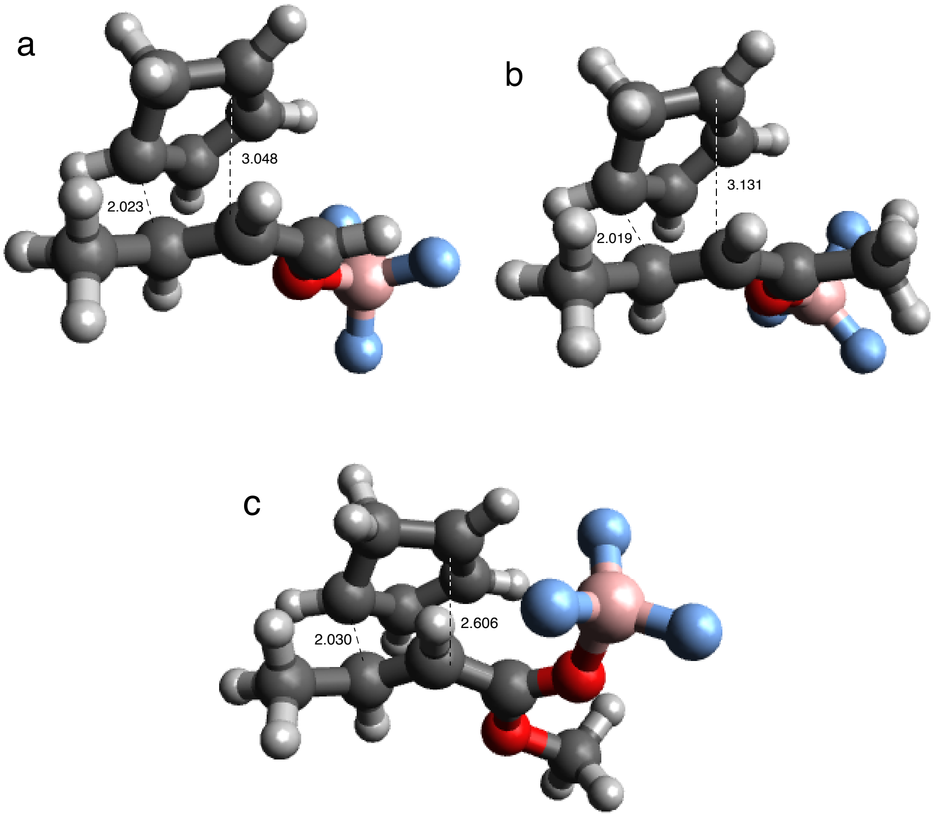
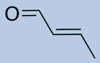
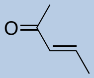
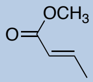


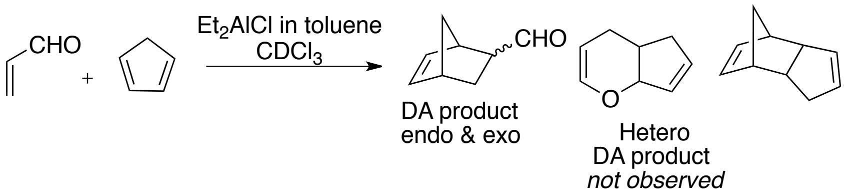
Figure 5. B3LYP/6-31G* Cycloaddition TS of cyclopentadiene with (a) crotonaldehyde, (b) trans-3-penten-2-one and (c) methyl crotonate. Bond lengths are in Å.

Preliminary quasiclassical trajectory studies on the B3LYP/6-31G* surface were initiated from the three different transition structures a,b and c in Figure 5. Each normal mode in the TS was given its zero-point energy plus a Boltzmann sampling of additional energy appropriate for 25 °C, with a random phase. The transition vector was given a Bolzmann sampling of energy 'forward' from the col. The trajectories were integrated in 1-fs steps until either the product was formed or separate starting materials were reformed. The results are summarized in Table 5.

Table 5. Trajectory Results for the Cycloaddition of Cyclopentadiene with Different Dienophiles.

			
Reformed Starting Material	22 (17%)	8 (11%)	29 (32%)
Diels Alder Product	61	27	57
Hetero Diels Alder Product	49 (37%)	35 (50%)	4 (4%)
TOTAL	132	70	90

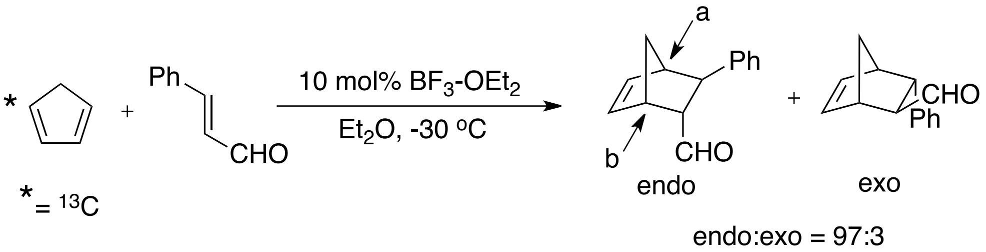
The results looked promising with methyl crotonate giving the highest amount of recrossing. A more striking observation is the substantial amount of hetero-DA products that formed from crotonaldehyde and trans-3-penten-2-one. Even though the total number of trajectories are limited, the significant formation of the hetero-DA product deserves further investigation. Low-temperature NMR studies on the reaction of acrolein with cyclopentadiene were performed with the hope of detecting the presence of the hetero-DA cycloadduct. However, even at -78 °C, no signs of this product was observed. This is not surprising because of the facile conversion of this cycloadduct via a 3,3-sigmatropic rearrangement to the thermodynamically more favorable DA cycloadduct. Only the regular endo and exo DA adducts and dicyclopentadiene were detected by ^{1}H NMR. The search for the hetero-DA product was not further explored.



(19)

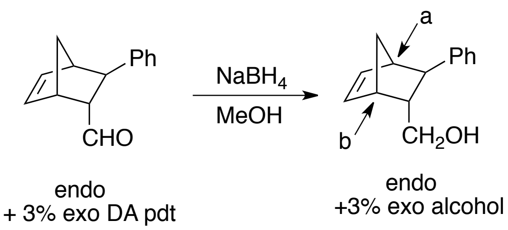
3.3.2 Diels Alder Reaction of Cylopentadiene with Trans-cinnamaldehyde

The trajectory results for the BF_3-catalyzed DA reaction between cyclopentadiene and crotonaldehyde gave modest recrossing trajectories. We postulated that switching to a bulkier substituent on the dienophile (methyl to phenyl) might give a better candidate for a reaction that exhibits a “hidden” rate-limting step as the transition structure would be more asynchronous. Moreover, the use of trans-cinnamaldehyde will give a good comparison with the organocatalytic DA reaction. Thus, the BF_3-catalyzed DA reaction of cyclopentadiene and trans-cinnamaldehyde was carried out.



(20)

The reaction was ran for 24h (≈50% conversion) and the products were isolated after an extractive work-up and column chromatography. After several chromatography attempts to purify the major endo product, the isolated mixture still contained 3% of the minor exo product. The mixture also contained minor polymeric products that could possibly be caused by side reactions of trans-cinnamaldehyde with the Lewis-acid. The mixture was reduced with sodium borohydride in methanol. The resulting solution contained only a mixture of the endo and exo (97:3) reduced cycloadducts.



(21)

An intramolecular KIE was measured for the a and b positions in the endo product at natural abundance using previous NMR methodology.[20] The NMR peaks at 45.09 (b) and 49.76 (a) ppm were integrated and the resulting relative composition and the corresponding intramolecular KIE for two independent samples are summarized in Figure 6.

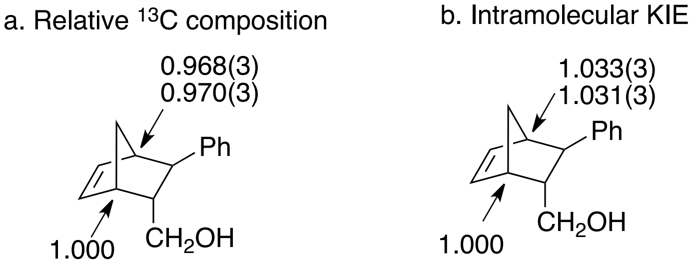


Figure 6. Relative isotopic composition (a) and experimental intramolecular KIE (b) for the endo DA product from two independent measurements. Standard deviations are shown in parenthesis.

The results are in qualitative agreement with expectations from conventional TST! A highly asynchronous transition structure is expected to give an isotope effect of greater than 1.00 as discussed earlier. The relative depletion of ^{13}C in position a is consistent with the idea that the lighter atom ends up preferentially in the more advanced C-C bond. Predicted KIEs form the lowest energy endo TS were determined to quantitatively interpret the experimental KIEs. Figure 7 shows the B3LYP/6-31+G* transition structure. The imaginary frequency corresponds to a highly asynchronous cycloaddition with a very advanced C-C bond formation proximal to the phenyl and slight movement at the other forming C-C bond.

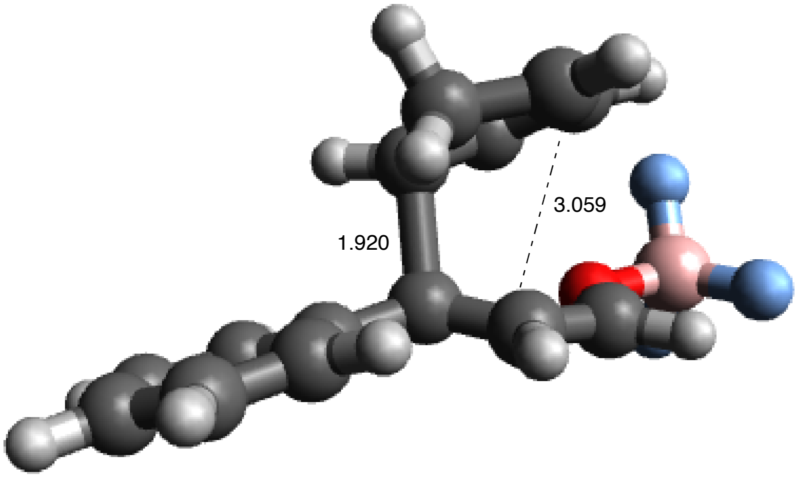


Figure 7. B3LYP/6-31G* TS for the Lewis-acid catalyzed endo-DA cycloaddition of cyclopentadiene and trans-cinnamaldehyde. Bond lengths are shown in Å.

It is generally accepted that B3LYP overestimates the strength of sigma bonds leading to an underestimation of the barrier for cycloaddition reactions. A recently developed popular method, M06-2X, was developed to overcome these errors associated with B3LYP.[60] M06-2X/6-31G* and B3LYP/6-31G* with PCM model using diethyl ether as solvent were also used to calculate the TS and predict the KIE to compare the values obtained from gas-phase B3LYP calculation. The predicted KIEs were calculated at -30 °C by the method of Bigeleisen and Mayer[21] from the scaled theoretical vibrational frequencies[61], and tunneling corrections were applied using the one-dimensional infinite parabolic barrier model.[22] The results are summarized in Figure 8.

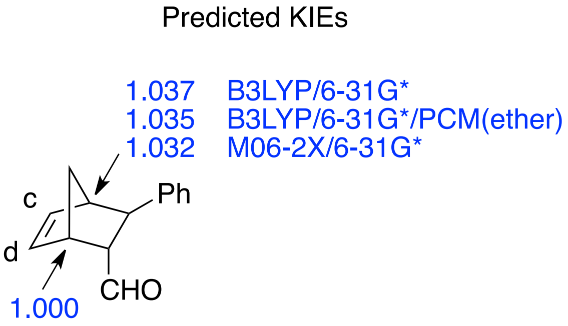


Figure 8. Predicted KIEs based on the lowest-energy endo TS for the Lewis-acid catalyzed DA reaction of cyclopentadiene and trans-cinnamaldehyde.

The predicted KIEs are in excellent agreement with the experimentally observed KIEs with the M06-2X predictions giving the best match. The intramolecular KIEs were also calculated for positions c and d. Negligible KIEs (0.999-1.005) using the three methods were calculated for c/d as expected because no selectivity should be observed at these positions at the transition state.

The excellent quantitative match between theory and experiment for the BF_3-catalyzed DA reaction is evidence that conventional TST is able to explain the observed KIEs and that the TS modeled for this reaction is an accurate experimental picture of the real TS of the cycloaddition. However, a crucial conclusion is that even though the Lewis-acid catalyzed DA reaction of cyclopentadiene and trans-cinnamaldehyde is highly asynchronous, this reaction does not possess a “hidden” rate-limiting step or an entropic intermediate, but rather the said reaction is simply a highly asynchronous concerted DA reaction.

3.4 Thermal Diels-Alder Reaction

The success of conventional TST on the Lewis-acid catalyzed DA reaction but not on the organocatalytic reaction prompted us to study the thermal reaction of cyclopentadiene and trans-cinnamaldehyde. The TS should be fairly synchronous and this reaction is expected to follow TST. Thus, the KIEs obtained for this reaction should be a good "standard" for the organocatalytic reaction, as the thermal reaction is expected to give an intramolecular KIE of close to unity. Low-energy transition structures for both the exo and the endo were calculated using B3LYP/6-31G* and M06-2X/6-31G*. The structures using the latter method are shown in Figure 9.

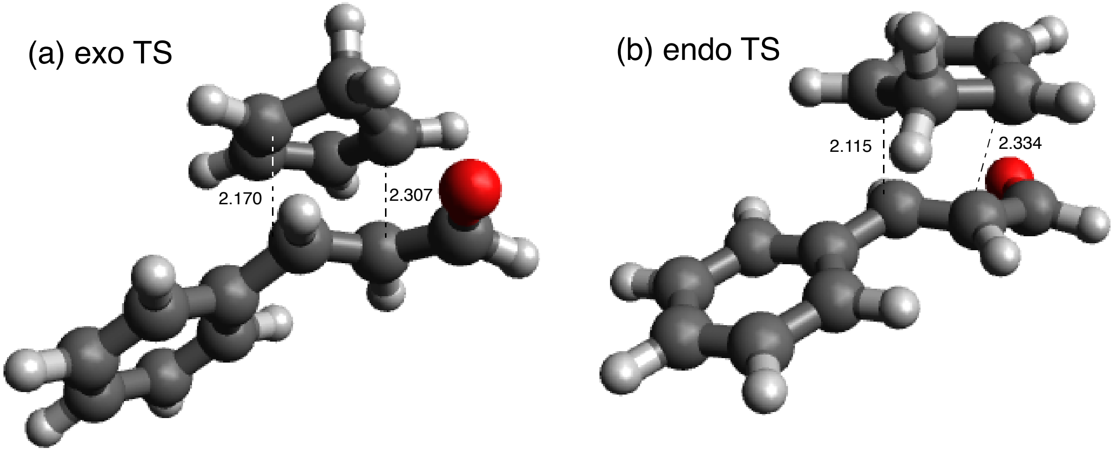


Figure 9. M06-2X/6-31G* Thermal DA exo TS (a) and endo TS (b). Bond lengths are shown in Å.

The M06-2X structures for both the exo and endo TSs as shown in Figure 9 are moderately asynchronous. The B3LYP structures are slightly more asynchronous (for the exo TS, the bond lengths are 2.098 and 2.379). Figure 10 shows the predited KIES from both methods for the thermal process using the methodology described earlier.

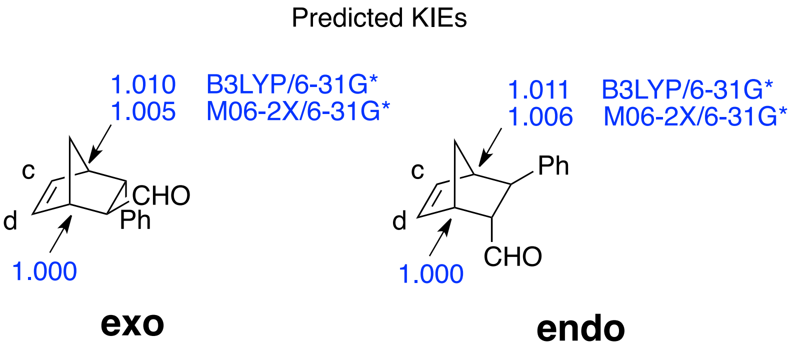


Figure 10. Predicted KIES for the thermal DA reaction of cyclopentadiene and trans-cinnamaldehyde. M06-2X/6-31G* exo TS (a) and endo TS (b).

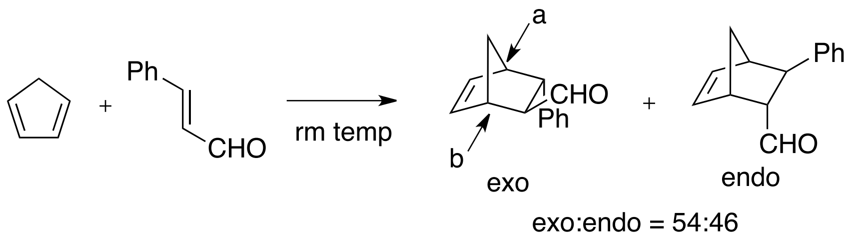
The predicted KIEs are in accord with what is expected from the calculated transition structures. The B3LYP structures were slightly more asynchronous and this is seen in a larger intramolecular KIE of 1.010 compared to moderately asynchronous M06-2X structures which gave a modest predicted KIE of 1.004 for the exo TS and 1.005 for the endo TS. The intramolecular c/d KIE (0.999-1.001) was also determined and provides as an internal check on the accuracy of both methods. Because the M06-2X KIE prediction performed fairly well in the BF_3-catalyzed DA reaction and B3LYP underestimates the energies of dative bonds, M06-2X is seen as more reliable than B3LYP.

Table 6. M06-2X/6-31G* Energies Relative to SM for the Thermal Cycloaddition of Cylopentadiene and Trans-cinnamaldehyde.

	Free Energies (kcal/mol)	
	Exo	Endo
Separate Starting Materials	0	
Cycloaddition TS	25.7	26.3
3,3-Sigmatropic TS	30.8	
Product	-8.8	-7.3

Table 6 shows the relative free energies of the cycloaddition transition structures, 3,3-sigmatropic transition structures and products relative to the starting materials for both the endo and exo pathways.

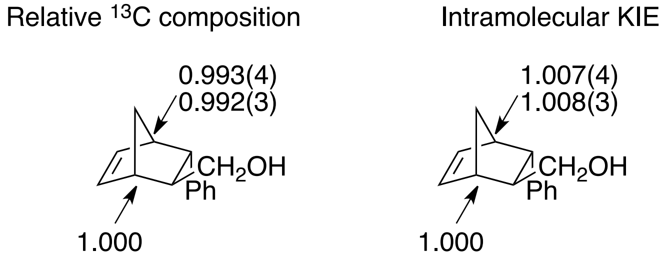
The thermal DA reaction was accomplished by mixing cyclopentadiene and trans-cinnamaldehyde for 2 weeks. The percent conversion was ≈45% and the products obtained were almost an equal mixture of the exo and endo cycloadduct. In a way, this is favorable; as it will give a good comparison with the organocatalytic DA reaction because of the same composition of exo and endo products in the KIE sample, assuming that the experimental KIEs for this reaction is accurate. The aldehyde cycloadducts were further reduced to their alcohol counterparts for the KIE measurements.



(22)

Intramolecular KIEs were measured for the a and b positions in the exo and endo products at natural abundance using previous NMR methodology.[20] The NMR peaks at 45.76 (b) and 49.55 (a) in the exo cycloadduct and 45.09 (b) and 49.76 (a) ppm in the endo cycloadduct were integrated and the resulting relative composition and the corresponding intramolecular KIE are summarized in Figure 11.

(a) exo



(b) endo

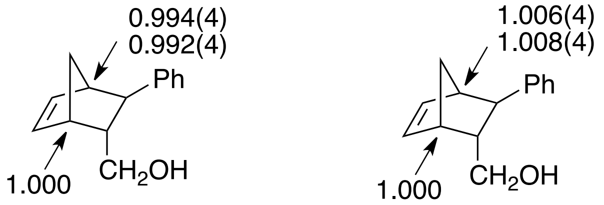


Figure 11. Relative isotopic composition (left) and experimental intramolecular KIEs (right) for the exo (a) and endo (b) DA products from two independent measurements. Standard deviations are shown in parenthesis.

The results are in excellent agreement with the theoretical predictions! The experimental KIEs show a slight preference for ^{13}C to be in the second C-C bond formation (position b) as expected from conventional TST. This is consistent with moderately asynchronous transition structures such as the ones shown in Figure 9. An important realization comes with these results; that is, conventional TST accurately predicts the intramolecular KIEs for the Lewis-acid catalyzed and thermal DA reactions but not for the organocatalytic reaction. This suggests that the transition structure for the organocatalytic reaction is unlikely to be inaccurate but instead TST may not be applicable to explain the experimental observations for this reaction. Intramolecular KIE predictions from trajectories and statistical perspectives such as “hidden” rate-limiting steps are underway to determine the nature of the unusual KIEs from the organocatalytic reaction.

3.5 Conclusions

The organocatalytic DA reaction between cyclopentadiene and trans-cinnamaldehyde showed a high propensity for recrossing based on preliminary quasi-classical direct-dynamics trajectory studies.[52] When trajectories were initiated at the endo and exo TSs, a substantial amount of recrossing was observed. Intramolecular KIEs of the product were measured as it was thought to show the experimental consequence of this phenomenon as successfully showed in the reaction of dichloroketene and cis-2-butene.[52] Initial results showed a very small ‘normal’ intramolecular KIE that cannot be reconciled with a highly asynchronous TS calculated for this reaction using conventional TST. The Lewis-acid catalyzed DA reaction was explored and the experimentally observed intramolecular KIE and predicted KIEs are in excellent agreement. For this particular reaction, conventional TST accounts for the highly asynchronous TS. This indicates that reactions with a “hidden” rate-limiting step must possess other characteristics other than a highly asynchronous transition state. Lastly, the thermal reaction is explored to serve as a “standard” for the organocatalytic reaction wherein both reactions produce almost an equal mixture of exo and endo products. The experimental observation for the thermal reaction is a modest “normal” isotope effect because of a moderately asynchronous TS which is consistent with predictions from conventional TST. This is in contrast with the preliminary KIEs from the organocatalytic reaction.

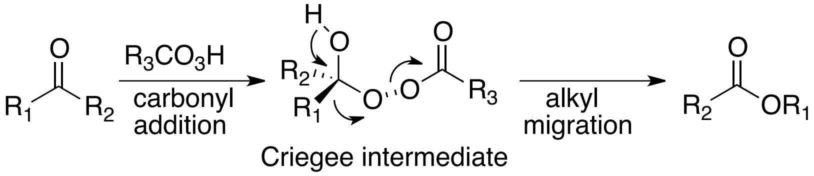
IV. EXPERIMENTAL AND PREDICTED KINETIC ISOTOPE EFFECTS ON THE BAEYER-VILLIGER REACTION IN WATER

4.1 Introduction

Water is scientifically the most interesting solvent for reactions. An array of water molecules that can interact via hydrogen bonding and influence chemical steps makes reaction mechanisms in water complex and intriguing. With the increasing awareness for green chemistry, water is also the preferred choice because it is the ultimate green solvent. We are intrigued by Baeyer-Villiger oxidations, particularly in changes in mechanism when this reaction is performed in water. Using peracids (RCO_3H) or peroxides (ROOH), this valuable organic reaction oxidizes ketones into esters or lactones with largely predictable regiochemistry[62] and retention of configuration of the migrating group[63]. This reaction is of importance in organic syntheses and in the chemical and pharmaceutical industries. An abundance of experimental[20, 62-64] and theoretical[65-66] studies have been reported on this oxidation reaction using a wide range of oxidants and these are predominantly done in organic solvents. The Baeyer-Villiger oxidation in water has been accomplished in a variety of ways[67] yet a complete mechanistic investigation is limited to a theoretical study.[65]

A two-step mechanism is generally accepted for the Baeyer-Villiger reaction (Scheme 4). The first step is the attack of the peroxyacid on the carbonyl carbon of the ketone to produce a hemiperacetal intermediate, also known as the Criegee intermediate. The second step involves the migration of one of the alkyl groups to the nearest oxygen of the peracid and the simultaneous cleavage of the peroxidic O-O bond. The rate-determining step is dependent on many factors, including but not limited to the substrate, solvent, acidity of the system and catalyst used.[62c] For various systems that have been studied, experimental evidence has established the alkyl migration as the rate-determining step.[64] In certain cases, however, the carbonyl addition is considered to be rate-determining.[20, 64b, 64d]

Scheme 4. Generic two-step mechanism for the Baeyer-Villiger Reaction.

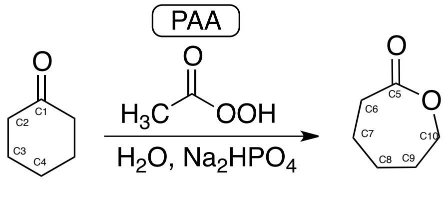


We chose to study the oxidation of cyclohexanone to ε-caprolactone using peracetic acid (PAA) and trifluoroperacetic acid (TFPAA) in water. A previous study[20] by Singleton and Szymanski on the oxidation of cyclohexanone with mCPBA provides convincing evidence with the use of intermolecular kinetic isotope effects (KIEs) that the rate-determining step is the carbonyl addition. They also probed the nature of the alkyl migration step with the use of intramolecular isotope effects. Alvarez-Idaboy and Reyes modeled the acid-catalyzed oxidation of cyclohexanone with performic acid.[66b] Their calculations support a rate-determining carbonyl addition, consistent with the conclusions obtained by Singleton and Szymanski. These experimental and theoretical studies both used dichloromethane as the solvent. Alvarez-Idaboy and co-workers performed a computational study on the oxidation of propanone with performic acid in water and concluded that this acid-catalyzed reaction involved a rate-limiting alkyl migration.[65] Considering that the mechanism is dependent on the exact conditions of the reaction, we decided to employ intermolecular and intramolecular KIEs in combination with theoretical calculations for our chosen system to understand the details of the mechanism in water fully.

4.2 Results and Discussion

4.2.1 Experimental Isotope Effects: Cyclohexanone and Peracetic Acid

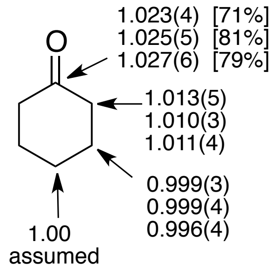
The ^{13}C starting material intermolecular KIEs for the oxidation of cyclohexanone with PAA were determined combinatorially by NMR methodology at natural abundance.[17] Three reactions of cyclohexanone on a 0.20 mol scale were taken to ≈80% conversion, and the unreacted cyclohexanone was recovered by an extractive workup followed by distillation. The samples of recovered cyclohexanone were analyzed by ^{13}C NMR, along with a standard sample that had not been subjected to the reaction conditions. The change in isotopic composition in each unique position was determined relative to the C4 methylene in the ring, with the assumption that the isotopic fractionation of this position was negligible. From the percentage conversions and the changes in isotopic composition, the KIEs were calculated as previously described.[17]



(23)

The results are summarized in Figure 12a. The independent sets of ^{13}C KIEs agree within the standard deviation of the measurements. For cyclohexanone, the substantial KIEs on the carbonyl and α-methylene carbons indicate that these two carbons are undergoing significant changes in bonding at the rate-limiting step. This is consistent with a rate-limiting alkyl migration. The average experimental value of 1.011 for the α-methylene is quite small considering that this is a primary isotope effect but it should be recognized that this is an average of a migrating and non-migrating carbon. The non-migrating carbon would be expected to have a negligible isotope effect and averaging this with the migrating carbon will lower the over-all isotope effect.

(a) Intermolecular KIEs



(b) ^{13}C Relative Composition

(c) Intramolecular KIEs

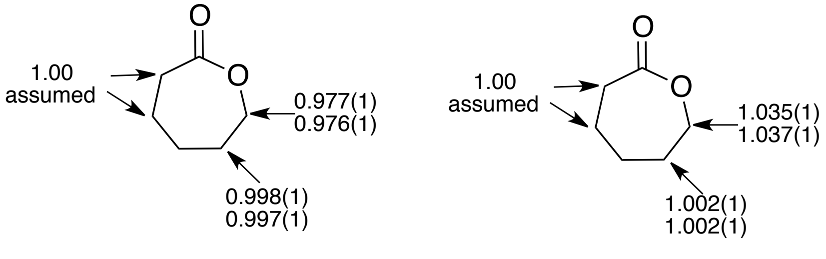
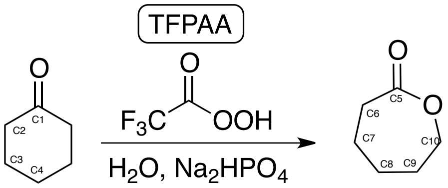


Figure 12. Starting material intermolecular KIEs (a), ^{13}C relative integrations (b) and intramolecular KIEs (c) for the peracetic acid system. Standard deviations are shown in parentheses. Reaction conversions are shown in brackets.

The ^{13}C intramolecular KIEs of the product can be obtained from the same reaction. The product, ε-caprolactone, was obtained pure as the residue from the distillation of cyclohexanone in the above reaction. ^{13}C NMR analysis of caprolactone was then carried out using the developed methodology for the accurate and precise measurement of the relative integrations of C6 vs C10 and C7 vs C9, assigning 1.00 for the non-migrating side of the lactone. Figure 12b shows the relative ^{13}C composition of the carbons of interest and the relative depletion at the migrating carbon is the degree to which a ^{13}C nucleus migrates slower than ^{12}C. This large intramolecular ^{13}C KIE is consistent with a concerted migration and departure of the leaving group. The β-methylene ^{13}C KIEs of 1.002 is negligible, providing an internal check of the accuracy of the NMR measurements.

4.2.2 Experimental Isotope Effects: Cyclohexanone and Trifluoroperacetic Acid

Isotope effects for the oxidation of cyclohexanone with TFPAA were determined by natural abundance ^{13}C NMR analysis of isolated product taken to low conversion.[19] This particular methodology was used because taking the reaction to high conversion proved to be challenging. The reaction of cyclohexanone with TFPAA was taken to ≈15% conversion on a 0.050 mol scale and caprolactone was isolated after an extractive workup followed by distillation. This sample was used for both the intramolecular and intermolecular product KIEs. For the intermolecular KIE, an NMR standard sample of caprolactone from a reaction taken to 100% conversion was used.



(24)

The KIEs are summarized in Figure 13. The results are distinct from the PAA reaction. The only significant isotope effect for the intermolecular KIEs is at the carbonyl carbon, indicating a rate-limiting carbonyl addition. An interesting result is the large intramolecular and negligible intermolecular KIEs for the α-methylene carbon (Figure 13c). The differing KIEs indicate that the alkyl migration step occurs after the rate-limiting step. As with the PAA results, the large intramolecular KIE provides strong evidence that the alkyl migration is concerted with the departure of the leaving group.

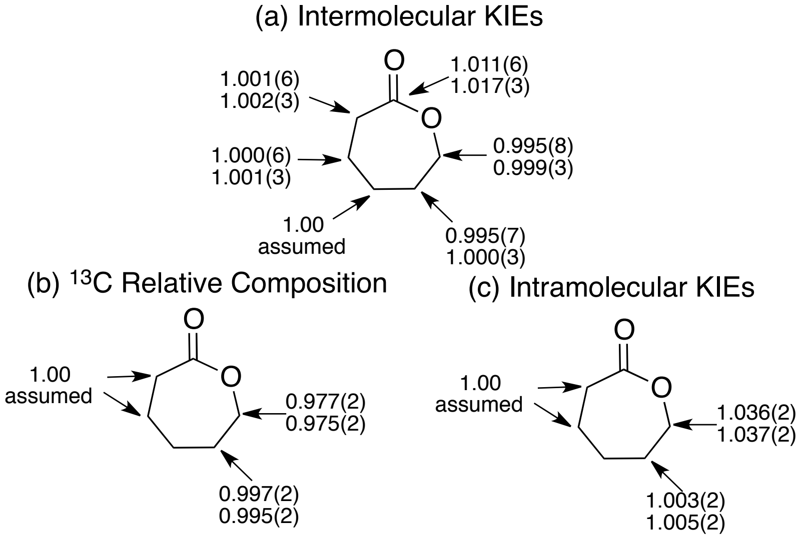


Figure 13. Product intermolecular KIEs and intramolecular KIEs for the trifluoroperacetic acid system. Standard deviations are shown in parentheses.

4.2.3 Theoretical Calculations

The complete mechanistic pathways for the reaction of cyclohexanone with peracetic acid and trifluoroperacetic acid were studied using the CBS-QB3//M06-2X/6-311++g(d,p) level of theory, and to include solvent effects, the IEF-PCM continuum model with water as solvent was utilized. This is the highest level of theory that is practical for the system of this size.

Figure 14 shows the relevant calculated transition structures in the reaction. Although water is a possible catalyst for this reaction, Alvarez-Idaboy, et. al. showed that the water-catalyzed reaction has a higher energy barrier compared to an acid-catalyzed reaction.[65] For the present study, hydronium ion was used as the catalyst along with three explicit solvent molecules. The choice on the number of explicit solvent molecules was also justified in the same study[65] because of the overall favorable energetics in an ionic mechanism. The ground state structures used as reference to calculate the absolute energies are the separate starting materials: cyclohexanone, PAA or TFPA, and solvated hydronium ion. The first transition structure involves the attack of the neutral peracid on the carbonyl carbon of the protonated ketone. This step involves two water molecules, where one is hydrogen bonded to the protonated ketone and the other is assisting in the deprotonation of the peracid. The deprotonation is believed to be concerted with the addition step based on IRC calculations of the propanone-formic acid system.[65] This addition and deprotonation step gives the Criegee intermediate. The second transition state involves the Criegee intermediate undergoing a unimolecular and concerted migration of one of the α-methylene carbons to the peracid oxygen and cleavage of the O-O bond. The final products are lactone and acetic acid or trifluoroacetic acid.

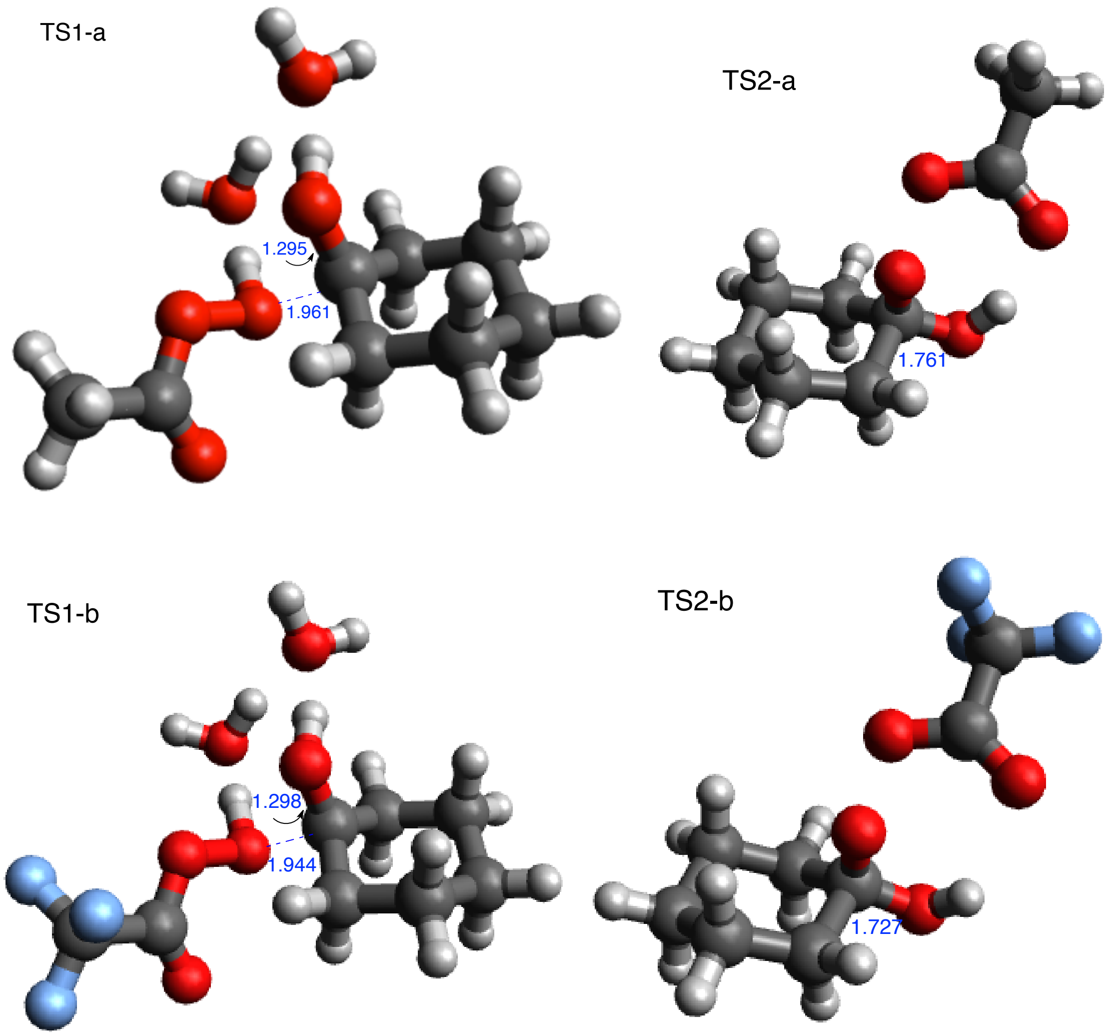


Figure 14. Calculated transition structures with relevant bond lengths for the oxidation of cyclohexanone with peracetic acid (TS1-a, TS2-a) and trifluoroperacetic acid (TS1-b, TS2-b).

The free energy profiles for both systems are shown in Figure 15. In highly polar conditions, the carbonyl addition step becomes favorable as the solvent stabilizes the ionic transition state. The migration step does not benefit as much from the polarity of the solution, and this is demonstrated in free energies such that in both cases the second step appears to be rate-limiting. However, the absolute energies should be taken with caution and viewed as rough estimates of the real energy barriers. The structures modeled for these reactions, especially the inclusion and participation of the explicit solvent molecules, were generated to represent minimal expectations for the acid-catalyzed water solvated reactions. Addition of water molecules or extensive searches of different involvement of water molecules in significant structures were not explored due to numerous possibilities. Other crucial assumptions that may impact the energies are the use of the hydronium ion as the catalyst instead of an organic acid, and the uncatalyzed migration step. With this in mind, we can use the experimental results as a guide on the reliability of the calculational results.

From the PAA energy diagram (blue line), the alkyl migration is 7.1 kcal/mol higher than the addition step. It is highly unlikely that the calculations would be off by this much and the experimental results indicate that the rate-limiting step is the alkyl migration. Therefore, qualitatively at least, the energy diagram for the PAA reaction is consistent with the experimental results. The alkyl migration step for the TFPAA system (red line) is lower in energy than that for the PAA reaction. This difference may be due to the electron-withdrawing ability of a trifluoromethyl group, making trifluoroacetate a better leaving group and thus facilitating the concerted migration and departure of the leaving group. This decrease in energy puts the migration step only 1.1 kcal/mol higher in energy than the addition step. In this case, it is not as convincing that the migration step is rate-limiting, especially since the experimental results indicate otherwise. Thus for the TFPAA energy diagram, it appears from the calculations that the two steps are similar in energy.

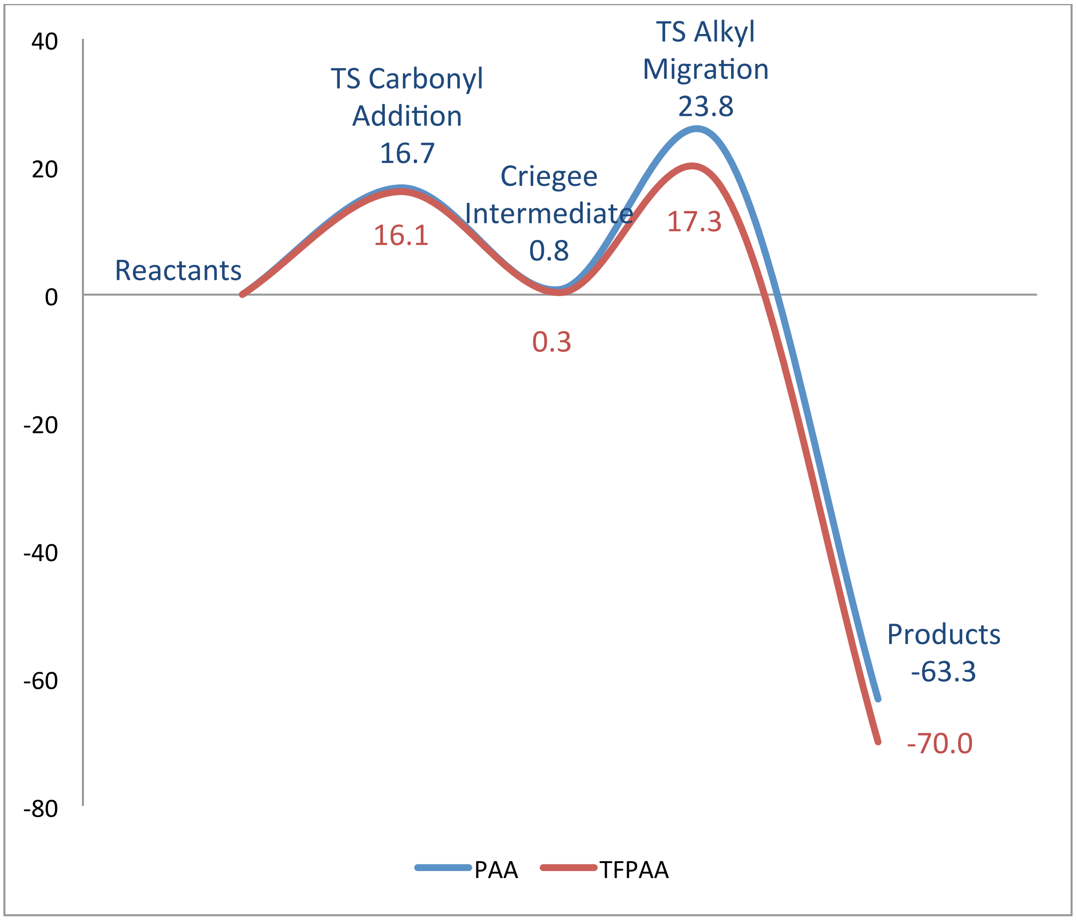
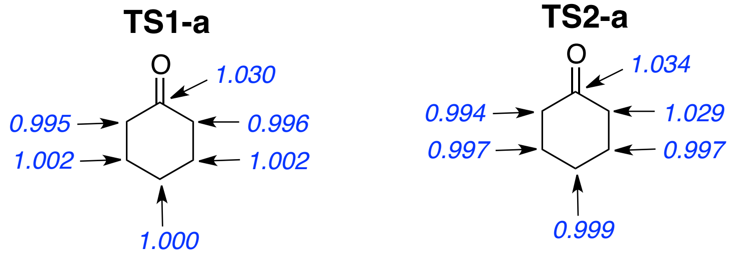


Figure 15. Relative free energies in kcal/mol along the reaction path of cyclohexanone with peracetic and trifluoroperacetic acids in water using CBS-QB3//M06-2X/6-311++g(d,p) level of theory.

Theoretical prediction of the isotope effects can aid in distinguishing the rate-determining step, thus ^{13}C KIEs were calculated for each of the transition structures (TS1-a, TS1-b, TS2-a and TS2-b) in Figure 14. These predictions used the scaled theoretical vibrational frequencies[61] in conventional transition state theory by the method of Bigeleisen and Meyer.[21] Tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[22] The predicted KIEs are summarized in Figure 16.

(a) Peracetic Acid System



(b) Trifluoroperacetic Acid System

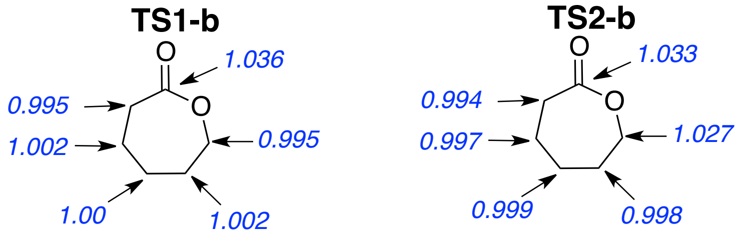


Figure 16. Predicted isotope effects based on the lowest energy TS1 and TS2 for the oxidation of cyclohexanone with peracetic acid (a) and trifluoroperacetic acid (b).

The KIEs in both systems are qualitatively consistent with expectations for both TSs. For TS1-a and TS1-b, a carbonyl addition rate-limiting step would exhibit a large isotope effect on the carbonyl carbon. A significant isotope effect on the carbonyl carbon and migrating α-methylene carbon is expected as shown in TS2-a and TS2-b. Even with the concerns raised earlier regarding the theoretical calculations, comparison of the predicted KIEs with the experimentally observed values should give us insight into which transition structure best represents the rate-limiting steps.

For the PAA reaction, the KIEs calculated from the alkyl migration transition structure (TS2-a) qualitatively match the experimental KIEs. On the other hand, for the TFPAA reaction, the experimental KIEs qualitatively match the values predicted from the carbonyl addition transition structure (TS1-b). Although the quantitative agreement is not as good as compared to our previous studies, given the limitation in our calculations, the concurrence between the predicted and experimental KIEs is reasonable.

4.3 Conclusions

A complete mechanistic investigation of the Baeyer-Villieger oxidation of cyclohexanone using peracetic and trifluoroperacetic acid in water using a combination of kinetic isotope effects and theoretical calculations was presented. High-level theoretical calculations have been successful in numerous cases in interpreting experimental results and understanding mechanisms of both simple and complicated reactions. However, for some reactions, most importantly complicated reactions where the solvent can be so involved in the mechanism, an extensive theoretical investigation is challenging. The results from the calculations, though taken cautiously, can still be used as a guide in understanding the mechanistic details in a reaction. For the oxidation of cyclohexanone using peracetic acid in water, the rate-limiting step was determined to be the alkyl migration based on the experimental KIEs. Calculations of the free energies of the TSs and prediction of the isotope effects support this conclusion. On the other hand, when trifluoroperacetic acid is used, the experimentally observed KIEs indicate a rate-determining carbonyl addition. The free energy diagram was not consistent with this result, but predicted isotope effects from the carbonyl addition TS qualitatively match with experiment. For complex reactions such as using water as a solvent, where calculations are challenging, the experimental KIEs proved to be a powerful tool in giving a detailed mechanistic picture on the reaction presented here.

V. EXPERIMENTAL AND CALCULATIONAL PROCEDURES

5.1 Experimental Procedure for the Ozonolysis of Vinyl Ethers*

Ethyl vinyl ether and butyl vinyl ether were obtained commercially and distilled prior to use. Methyl vinyl ether was obtained by the mercuric acetate-mediated [2]exchange reaction of butyl vinyl ether with a 20-fold excess of methanol followed by direct distillation of the reaction mixture. Ozone was generated by passing dry oxygen through an Ozone Solutions Inc. SR-8 ozone generator at a flow rate of approximately 200 mL/min and it was bubbled into solutions using a fine-fritted-glass dispersion tube. All solutions resulting from ozonolyses were treated with triphenylphosphine before waste disposal. ^1H NMR chemical shifts in methanol-d_4 are referenced versus the residual protons in the methyl group of the methanol-d_4 at δ 3.31.

5.1.1 Octyl Vinyl Ether

Adapting a literature procedure[68], a mixture of 0.8 g (2.5 mmol) of mercuric acetate, 17 mL (108 mmol) of 1-octanol and 50 mL of ethyl vinyl ether was heated to reflux with constant stirring for 48 h. The resulting mixture was then allowed to cool to room temperature and 5 mL of 10% aqueous NaOH was stirred into the solution. The solution was extracted with two 10-mL portions of hexanes and the combined organic layers were dried (K_2CO_3) and concentrated on a rotary evaporator. The residue was

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* Reprinted with permission from "Competition between Reaction and Intramolecular Energy Redistribution in Solution: Observation and Nature of Nonstatistical Dynamics in the Ozonolysis of Vinyl Ethers" by L.M. Quijano and D. A. Singleton. *Journal of American Chemical Society*, **2011**, *133*, 13824-13827. Copyright 2011 American Chemical Society.

chromatographed on basic alumina, eluting with hexanes to afford 5.2 g (31%) of octyl vinyl ether. A closely analogous procedure was employed to synthesize 3,7-dimethyloctyl vinyl ether from 3,7-dimethyl octanol. Both of these known compounds[69, 70] did not exhibit any detectable impurities by NMR analysis.

5.1.2 3,7,11,15-Tetramethylhexadecyl Vinyl Ether

Adapting a literature procedure[71], a solution of 20 g (67 mmol) of commercial phytol (3,7,11,15-tetramethyl-hexadec-2-en-1-ol, 97% mixture of isomers) in 100 mL of ethanol was stirred under a nitrogen atmosphere over 4 g Raney nickel (50% slurry in water) for 50 hours. The catalyst was removed by filtration through a regular filter paper and the filtrate was concentrated under reduced pressure. The residue was chromatographed on basic alumina, eluting with hexanes to afford 12.4 g (62% yield) of 3,7,11,15-tetramethyl-hexadecanol. The purified alcohol was used in the synthesis of the corresponding vinyl ether using analogous amounts and procedures as described above for octyl vinyl ether.

5.1.3 Ozonolysis of Vinyl Ethers: Example Procedure

A mixture of 0.24 mL (0.18 g, 2.5 mmol) of ethyl vinyl ether in 4.76 mL of methanol-d_4 under N_2 was cooled in a dry-ice / acetone bath to an internal temperature of -65 °C. A slow stream of ozone was then passed through the solution until a light blue color persisted (~5 min). During the course of the reaction the internal temperature rose with the reaction conversion to -45 °C. (Due to the exothermicity of the reaction, it was not possible to hold the temperature constant at concentrations practical for NMR analysis, and the temperatures in the main text refer to average reaction temperatures.)

At 1-min intervals, aliquots were removed from the reaction and analyzed directly using ^{1}H NMR spectroscopy (see the discussion of the NMR analyses below). These analyses were conducted immediately after collecting the aliquot, usually within 10 -30 min and in every case within 40 min. In control experiments, the composition determined by NMR did not change significantly over the course of 24 h.

Closely analogous procedures were employed for the ozonolysis of methyl, butyl, octyl, 3,7-dimethyloctyl, 3,7,11,15-tetramethylhexadecyl vinyl ethers, styrene and 2,3-dimethyl-1,3-butadiene and for the ozonolysis of ethyl and octyl vinyl ethers at higher temperatures.

5.1.4 Ozonolysis of Ethylene

A saturated solution of ethylene in 5 mL of methanol-d_4 at -78 °C was prepared by bubbling ethylene through the methanol-d_4 for 10 min. Ozone was then bubbled into the solution until a light blue color persisted. The resulting solution was analyzed directly using ^{1}H-NMR spectroscopy.

5.1.5 Trans-1,2-diethoxyethylene

Adapting a literature procedure[72], a 15 x 2.5 cm basic alumina column was wrapped with heat tape and the temperature was adjusted to 190 °C, and a 3-necked round bottom flask equipped with a stopper, a septum, and an outlet needle was attached at the end of the column. The top of the column was equipped with a pressure-equalizing addition funnel and an N_2 inlet, and 15 g (0.09 mol) of 1,1,2-triethoxyethane was added dropwise to the column over 30 min while maintaining a slow flow of N_2. The liquid that accumulated in the 3-necked collecting flask contained a complex mixture of materials by NMR analysis, and this mixture was chromatographed on an 8 in x 3.5 cm neutral alumina column using 9:1 pentane:diethyl ether as eluent. A fraction containing pure 1,2-diethoxyethylene by NMR analysis was concentrated and distilled to afford 0.16 g (1.5%) of *trans*-1,2-diethoxyethylene (bp 132-135 °C). The 1,2-diethoxyethylene was then ozonized in methanol-d_4 by the procedure described above for ethyl vinyl ether.

5.1.6 1-Deutero-1-ethoxyethylene (CH_2=CDOEt)

Adapting a literature procedure[73], 5.0 g (71 mmol) of ethoxyacetylene (40% wt in hexanes) was added dropwise over 1 h to a mixture of 1.78 g (42 mmol) of lithium aluminum deuteride in 45 mL of diglyme at 25 °C. After an additional 1 h, 40 mL of water was added dropwise while the reaction was maintained at <30 °C. The complete reaction mixture was then directly distilled under vacuum (37.5 mm) into a trap at -196 °C. A second distillation at atmospheric pressure and drying with calcium hydride afforded 2.5 g of the labeled vinyl ether (15% wt), ethoxyacetylene and hexanes. Based on ^{2}H-NMR, the labeled vinyl ether contained traces of cis and trans CHD=CHOEt. The mixture was used without further purification. A solution of 0.47 mL of this mixture in 4.53 mL of methanol under N_2 was cooled to -65 °C. A slow stream of ozone was then passed through the solution until a light blue color persisted (~5min). The resulting solution was analyzed directly using ^{2}H NMR spectroscopy.

5.1.7 Ozonolysis of Ethyl Vinyl Ether with Added Pentane

A mixture of 0.24 mL (0.18 g, 2.5 mmol) of ethyl vinyl ether and 0.40 mL (3.5 mmol) of pentane in 4.36 mL of methanol-d_4 under N_2 was cooled to -55 °C . A slow stream of ozone was then passed through the solution until a light blue color persisted (~5 min). To monitor the progress of the reaction, aliquots were taken during regular intervals and analyzed directly using ^{1}H NMR spectroscopy.

The quantitation of the product ratios was determined from ^{1}H NMR integrations, using a variety of precautions to minimize systematic and random error. A total delay of 6.9 s was used between 30° pulses, collecting 22784 points. The product ratios were determined from the ratio of the methine peak of **3** versus the formyl hydrogen of **1**, taking great care to phase and level the baseline carefully and identically for all samples. The s/n ratio for the methine peak was typically around 800 : 1.

5.2 Observed Individual Experimental Ratios

Table 7. Individual Experimental Ratios.

alkyl group	temperature	A/B ratio
Methyl	**-55 °C**	26.3, 23.9, 22.1, 26.9, 25.7, 24.1, 28.4, 26.9, 26.0, 25.1
Ethyl	**-55 °C**	30.8, 28.4, 35.5, 32.2, 30.8, 36.6, 37.2, 35.5, 34.9, 36.0, 37.6, 35.5, 34.3, 34.2, 34.6, 40.2, 37.9, 35.9, 33.5, 37.8, 38.4, 40.3, 41.9, 37.6, 41.0, 39.6, 36.7, 37.2, 39.0, 37.2
	-31 °C	33.6, 34.7, 33.6, 33.1, 31.6, 31.4, 38.1, 33.7, 33.6, 33.4
	8 °C	27.0, 23.4, 21.7, 27.1, 26.0, 23.4, 27.1, 25.6, 23.7, 23.1
	23 °C	25.6, 20.7, 26.4, 18.4, 22.3, 24.1, 21.0, 26.3, 25.1, 22.6, 36.5, 24.8, 23.4, 20.6

Table 7 Continued

alkyl group	temperature	A/B ratio
Butyl	**-55 °C**	49.5, 46.6, 46.6, 47.3, 47.8, 50.5, 49.2, 42.4, 44.3, 42.3, 41.4, 51.6, 49.2, 51.6
Octyl	**-55 °C**	55.5, 56.5, 52.8, 55.8, 57.5, 55.2, 55.8, 58.5, 53.3, 52.8, 45.9, 49.0, 55.5, 56.8, 58.5, 57.8
	-31 °C	52.0, 50.7, 50.8, 51.3, 52.7
	8 °C	43.1, 42.9, 42.3, 43.0, 44.2, 42.7, 43.8
	23 °C	41.0, 41.4, 40.8, 39.6, 39.2, 39.3, 39.5, 39.5
3,7-Dimethyloctyl	**-55 °C**	58.5, 64.8, 63.5, 63.1, 63.5, 65.3, 63.9
3,7,11,15-Tetramethylhexadecyl	**-55 °C**	75.3, 73.1, 75.3, 74.2, 75.9, 75.4, 75.5, 68.5, 77.1

Table 7 lists the individual experimental ratios for the different vinyl ethers. The 95% confidence ranges for the experimental data in Table 1 were calculated in a standard way using a t-distribution function, as defined by IUPAC. See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf

The observed ratio of major to minor products of the ethyl vinyl ether ozonolysis reaction with added pentane was 37.6±2.7.

5.3 Computational Procedures and Supporting Computational Results for the Ozonolysis of Vinyl Ethers

5.3.1 General

Calculations of structures, energies, and frequencies employed standard procedures in Gaussian09[74] unless otherwise noted. The GTBas3 basis set referred to below is the basis set used in the geometry optimization for G4 calculations[75]. Complete structures and energetics are provided in Appendix B.

The program suite PROGDYN used for dynamics is listed at the end of Appendix B as a series of component programs as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories.

RRKM calculations were carried out using an available program[76] and employing the Beyer-Swinehart direct count algorithm[77]. See below for further details.

5.3.2 Detailed Description of RRKM Calculations

For the RRKM calculations in Table 1 in Section 2.2 Design of Experiment and Experimental Results, rate constants were calculated based on the most stable conformation of the primary ozonide and two lowest-energy cleavage-A* and two lowest-energy cleavage-B* transition structures. For the systems involving large alkyl chains, this analysis necessarily involves a large error in the calculated entropy due to the presence of a large number of conformations as well as the inaccuracy of the harmonic approximation in dealing with torsional modes. An assumption in our analysis is that the error is similar in the **PO** and in the cleavage transition states.

An example input file for the RRKM calculations is given in a later section. In each calculation, the rate constant was calculated at a series of energies that ranged from, at minimum, the zero-point energy difference between the most-stable endo cycloaddition transition state (TS1) and the most-stable primary ozonide, up to 15 kcal/mol above this energy in 0.5 kcal/mole increments. The threshold energy barriers in each calculation were then the difference between the zero-point level energies for the cleavage TS versus the primary ozonide. The actual energies used in the calculation are tabulated in Table 8 below.

Table 8. Energies Used in the RRKM Calculations.

Vinyl Ether	Minimum applied energy (kcal/mol)	Threshold barriers (kcal/mol)	
		Cleavage A*	Cleavage B*
Methyl	57.09	12.64	19.27
Ethyl	56.78	12.87; 13.44	18.97; 19.44
Butyl	56.73	12.87; 13.20	18.88; 19.13
Octyl	56.72	12.87; 13.19	18.86; 19.10
3,7-Dimethyloctyl	56.71	12.84; 13.17	18.79; 18.93
3,7,11,15-Tetramethylhexadecyl	56.67	12.85; 13.18	18.88; 18.97

For the R = methyl, ethyl, and butyl systems, the energies employed were based on G4 relative energies. For the larger alkyl groups, the R=butyl G4 relative energies were corrected based on the difference in relative energies seen in the B3LYP/GTBas3 calculations. For example, the threshold energy barrier for R = octyl would be calculated by the equation below:

$$\Delta E^{\ddagger}_{\text{octyl}} = \Delta E^{\ddagger}_{\text{butyl}}\ (\text{G4}) + [\Delta E^{\ddagger}_{\text{octyl}}\ (\text{B3LYP/GTBas3}) - \Delta E^{\ddagger}_{\text{butyl}}\ (\text{B3LYP/GTBas3})] \qquad (25)$$

The series of rate constants obtained in this way were then weighted by the distribution of energies that would be present assuming that the cycloaddition transition states (TSs) have a canonical energy distribution and that no energy is lost in forming the **PO**s. The distribution of energies in the cycloaddition TSs was calculated using the program proggenHP, a module of PROGDYN that is listed at the end of Appendix B.

This program reads the output from a Gaussian09 frequency calculation and uses a random-number generator to Boltzmann-sample the energies for each normal mode. By calling this program repeatedly, we generated a list of total energies that would be present in molecules at random at the temperature of interest. A histogram analysis of this list generated the distribution of energies used to weight the rate constants.

As an example, the distribution of energies used for the R = methyl calculations is shown in Table 9 below along with the RRKM rate constant at each energy for cleavage A (via one of the two possible transition states). The 'Count' column gives the number of molecules at that energy out of 1650 Boltzmann samples generated by proggenHP. The rate constants at each energy are then weighted by the count/1650, and the summation over rate constant * weighting is the weighted rate constant.

Table 9. RRKM Distribution of Energies for the Methyl Vinyl Ether System.

energy level	rate constant for cleavage A	Count	Weighting (= count / total count)	rate contribution	
57.59	4.670E+11	25	0.0152	7.08E+09	
58.09	4.814E+11	155	0.0939	4.52E+10	
58.59	4.961E+11	231	0.1400	6.95E+10	
59.09	5.110E+11	302	0.1830	9.35E+10	
59.59	5.261E+11	274	0.1661	8.74E+10	
60.09	5.415E+11	233	0.1412	7.65E+10	
60.59	5.571E+11	148	0.0897	5.00E+10	
61.09	5.729E+11	106	0.0642	3.68E+10	weighted
61.59	5.890E+11	71	0.0430	2.53E+10	rate constant

Table 9 Continued

energy level	rate constant for cleavage A	Count	Weighting (= count / total count)	rate contribution	
62.09	6.052E+11	42	0.0255	1.54E+10	5.31E+11
62.59	6.217E+11	30	0.0182	1.13E+10	
63.09	6.385E+11	14	0.0085	5.42E+09	
63.59	6.554E+11	9	0.0055	3.57E+09	
64.09	6.726E+11	2	0.0012	8.15E+08	
64.59	6.900E+11	4	0.0024	1.67E+09	
65.09	7.076E+11	1	0.0006	4.29E+08	
65.59	7.255E+11	0	0.0000	0.00E+00	
66.09	7.435E+11	2	0.0012	9.01E+08	
66.59	7.618E+11	1	0.0006	4.62E+08	

For the calculations of eq 11 in the Section 2, the list of energies above was allowed to evolve with time by taking time steps Δt of 20 fs, with the new energy being calculated from eq 1 in Section 2, i.e.:

$$\text{new energy} = \text{old energy times } e^{-\lambda\Delta t} \tag{26}$$

The Count evolved with time by the equation:

$$\text{newcount} = \text{oldcount} - \text{oldcount times } \Delta t \text{ times } [k_A(E^t) + k_B(E^t)] \tag{27}$$

The $k_A(E^t)$ and $k_B(E^t)$ values were based on a RRKM-calculated rate constants at energies from 12 to 70 kcal/mol, fit to a sixth-order polynomial. (Because the fit polynomials pass below 0 at energies below 20 kcal/mol, the low rate constants at these energies were taken as 0.)

The amount of cleavage B evolved with time (from 0) by the equation:

$$\text{cleavage B} = \text{cleavage B} + \text{oldcount times } \Delta \text{t times } k_B(E^t) \tag{28}$$

The time steps Δt of 20 fs were then taken repeatedly until the amount of cleavage B occurring was negligible. After assuming an initial λ, λ was varied and the calculation repeated until the experimental product ratio was obtained.

5.3.3 Validation of the G4 Calculations, and Consideration of the Effect of Potential Error

In a detailed study of the ozonolysis of ethylene and acetylene, Wheeler, Ess, and Houk had found that G4 calculations has performed well[78]. For the current study it is most important that the calculational method accurately predict the barriers for cleavage A and cleavage B of the primary ozonide, and particularly their relative values, and this cleavage step was not covered directly by the previous work. We therefore explored the accuracy of G4 calculations versus a relevant experimental observation and via a focal-point extrapolation process based on other high-level calculations.

Experimentally, Donahue had found[79] that the barrier for cleavage of the primary ozonide derived from tetramethylethylene is 13.8 ± 1.0 kcal/mol. Table 10 below lists the absolute energies from the G4 calculations. The G4 calculations predict a barrier of 13.8 kcal/mol, in excellent agreement with experiment.

Table 10. G4 Calculated Energies for the Cleavage of Tetramethylethylene Primary Ozonide.

	0 K	enthalpy	free energy	zpe corr	0 K - zpe
primary ozonide	-461.105375	-461.094271	-461.140003	0.174206	-461.279581
TS for cleavage	-461.083656	-461.072328	-461.117794	0.171622	-461.255278
Energy difference (kcal/mole)	13.6	13.8	13.9		15.3

Computationally, we employed a focal-point extrapolation process of the type in the Wheeler, Ess, and Houk paper. The calculations employed were limited by the size of our system – it was not practical to carry out full CCSDT calculations on these systems or carry out CCSD(T) calculations with an aug-cc-pvqz basis set – but the previous work suggests that the effect of these limitations will be small. The focal-point study employed the geometries from the G4 calculations for the R=methyl system for the single-point energies, with the calculations carried out on the primary ozonide, the TS for cleavage A, and the TS for cleavage B.

The absolute energies obtained are listed in Table 11. In this table, DZ, ADZ, TZ, etc. refers to the basis sets (DZ = cc-pvdz, ADZ = aug-cc-pvdz, TZ = cc-pvtz, etc.).

Table 11. Focal Point Extrapolation Study: Absolute Energies.

Primary ozonide				
	HF	MP2	CCSD	CCSD(T)
DZ	-416.347178	-417.507472	-417.554867	-417.594078
ADZ	-416.381099	-417.610118	-417.653512	-417.702349
TZ	-416.476900	-417.934337	-417.961029	-418.026333
ATZ	-416.482946	-417.970395	-417.994705	-418.063718
QZ	-416.506471	-418.070164		
AQZ	-416.508163	-418.085965		
5Z	-416.514156	-418.120920		
A5z	-416.514357	-418.128192		
TS cleavage A				
	HF	MP2	CCSD	CCSD(T)
DZ	-416.268971	-417.505549	-417.518843	-417.571967
ADZ	-416.300064	-417.610600	-417.616034	-417.679465
TZ	-416.393638	-417.930151	-417.918344	-417.999069
ATZ	-416.399599	-417.967833	-417.952503	-418.037283
QZ	-416.423612	-418.067247		
AQZ	-416.425282	-418.083527		
5Z	-416.431169	-418.117981		
a5z	-416.431379	-418.125467		
TS cleavage B				
	HF	MP2	CCSD	CCSD(T)
DZ	-416.265286	-417.489718	-417.507691	-417.559896
ADZ	-416.296422	-417.595460	-417.605273	-417.667735
TZ	-416.390727	-417.915683	-417.908330	-417.987981
ATZ	-416.397084	-417.953899	-417.942817	-418.026514
QZ	-416.421030	-418.053249		
AQZ	-416.422815	-418.069715		
5Z	-416.428689	-418.104109		
A5z	-416.428916	-418.111621		

The barriers and the difference in cleavage A versus cleavage B barriers are listed in Table 12 below.

Table 12. Focal Point Extrapolation Study: Cleavage A and Cleavage B Barriers.

barrier cleavage A				
	HF	MP2	CCSD	CCSD(T)
DZ	49.1	1.2	22.6	13.9
ADZ	50.9	-0.3	23.5	14.4
TZ	52.2	2.6	26.8	17.1
ATZ	52.3	1.6	26.5	16.6
QZ	52.0	1.8		
AQZ	52.0	1.5		
5Z	52.1	1.8		
A5z	52.1			
barrier cleavage B				
	HF	MP2	CCSD	CCSD(T)
DZ	51.4	11.1	29.6	21.4
ADZ	53.1	9.2	30.3	21.7
TZ	54.1	11.7	33.1	24.1
ATZ	53.9	10.4	32.6	23.3
QZ	53.6	10.6		
AQZ	53.6	10.2		
5Z	53.6	10.5		
A5z	53.6			
difference in barriers				
	HF	MP2	CCSD	CCSD(T)
DZ	2.3	9.9	7.0	7.6
ADZ	2.3	9.5	6.8	7.4
TZ	1.8	9.1	6.3	7.0
ATZ	1.6	8.7	6.1	6.8
	HF	MP2	CCSD	CCSD(T)
QZ	1.6	8.8		
AQZ	1.5	8.7		
5Z	1.6	8.7		
A5z	1.5	8.7		

The incremental corrections are listed in Table 13 below. The rows marked CBS show the extrapolated values. The HF extrapolation was performed based on the ATZ, AQZ, and A5Z energies by fitting the calculated values to the equation $E(X) = E_{CBS} + Be^{-(X-1)} + Ce^{-(X-1)^{\wedge}2}$ (S20) (X = 2 for ADZ, 3 for ATZ, 4 for AQZ, 5 for A5Z). The MP2 extrapolation was based on the AQZ and A5Z incremental corrections by fitting to the equation $E^{corr} = a + bX^{-3}$ as done in the Wheeler, Ess, and Houk paper. The remaining extrapolations were based on the ADZ and AQZ incremental corrections by fitting to the same equation $E^{corr} = a + bX^{-3}$. The final CBS values were calculated as the sum of the extrapolated HF value and the extrapolated incremental corrections.

Table 13. Focal Point Results: Cleavage A and Cleavage B Barriers.

barrier cleavage A					
	HF	delta MP2	delta CCSD	delta CCSD(T)	sum
DZ	49.076	-47.869	21.399	-8.730	13.9
ADZ	50.850	-51.153	23.820	-9.158	14.4
TZ	52.248	-49.621	24.158	-9.677	17.1
ATZ	52.301	-50.693	24.874	-9.893	16.6
QZ	51.995	-50.165			
AQZ	52.008	-50.478			
5Z	52.075	-50.230			
A5z	52.070	-50.359			
CBS	52.1070	-50.2341	25.3179	-10.2032	**17.0**
barrier cleavage B					
	HF	delta MP2	delta CCSD	delta CCSD(T)	
DZ	51.39	-40.248	18.5	-8.2	21.4
ADZ	53.14	-43.938	21.1	-8.5	21.7
TZ	54.07	-42.368	21.4	-9.0	24.1
ATZ	53.88	-43.527	22.2	-9.2	23.3
QZ	53.62	-43.001			
AQZ	53.56	-43.359			
5Z	53.63	-43.082			

Table 13 Continued

barrier cleavage B					
	HF	delta MP2	delta CCSD	delta CCSD(T)	
A5z	53.61	-43.216			
CBS	53.6504	-43.0661	22.687	-9.494	**23.8**
difference in barriers					
	HF	delta MP2	delta CCSD	delta CCSD(T)	
DZ	2.312	7.621	-2.9	0.58	7.6
ADZ	2.285	7.215	-2.7	0.61	7.4
TZ	1.826	7.253	-2.8	0.67	7.0
ATZ	1.578	7.166	-2.7	0.68	6.8
QZ	1.620	7.164			
AQZ	1.548	7.119			
5Z	1.557	7.148			
A5z	1.545	7.143			
CBS	1.5433	7.1680	-2.631	0.710	**6.8**

The critical calculation of the difference in barriers for cleavage A versus cleavage B has reasonably converged, since the "delta CCSD(T)" values are small. From this, the focal-point result from this process, 6.8 kcal/mol, is likely to be correct within a few tenths of a kcal/mol. The G4 potential energy difference in barriers is 6.9 kcal/mol, in excellent agreement with the focal point result.

The accuracy of the absolute barriers is less important (see the discussion below), but there is a significant issue with their calculated values. Because the "delta CCSD(T)" values for the absolute barriers in the table above are still substantial, the extrapolation has not converged in correlation energy. Because of this, the absolute barriers obtained by this process (17.0 kcal/mol for cleavage A and 23.8 kcal/mol for cleavage B) are still subject to significant uncertainty. In analogy with the Wheeler, Ess, and Houk work, this uncertainty would be at least 2 kcal/mol. The G4 potential energy barriers for comparison are 14.4 and 21.3 kcal/mol, so the focal point extrapolation suggests that the G4 barriers are low by 2.5 kcal/mol. However, considering that the G4 calculation accurately predicts the experimental barrier for cleavage of the primary ozonide derived from tetramethylethylene (see above) and considering the uncertainty in the focal-point extrapolation, we have opted to present the G4 results in the main text.

It is of interest to consider the potential impact of errors in the calculated barriers on the results and conclusions in the main text. As might be expected intuitively, it makes little difference if the cycloaddition provides to the primary ozonide 54 kcal/mol versus 57 kcal/mol versus 60 kcal/mol. For a 3 kcal/mol error, the rate constant for cleavage A changes by only 20% and the A/B ratio changes by only 12%. It is perhaps less intuitively obvious that the absolute barriers for cleavage make little difference. If the calculated barriers for cleavage are both low by 2 kcal/mol, then that would affect the RRKM rate constants by about a factor of only 2, and it would affect the RRKM A/B ratio by only a factor of 8%. The former would lead to a change in our calculated decay constants by about a factor of 2, as discussed already in footnote 17 of the main text. The latter would have no effect on the manuscript. The worst conceivable error would be if the critical relative barrier for cleavage A versus cleavage B was off drastically, e.g. if it were only 2 kcal/mol instead of 6.9. That would compromise the conclusions of the manuscript, but considering the convergence of the focal point extrapolation it is not plausible. A remotely plausible error of 2 kcal/mol in the relative barrier would change numbers in the main text but not affect its central conclusions.

5.3.4 Exploration of Potential Calculational Methods for Trajectories

For trajectory calculations on these reactions, we sought a calculational method that would accurately depict the exothermicity of the cycloaddition step and the barrier for the PO cleavage processes. A substantial practical limitation on the applicable methodology was that tens of thousands of trajectories would be required, ultimately requiring approximately 20 million force calculations.

To explore the applicability of methods and basis sets, energies corresponding to the first transition state (cycloaddition TS), exothermicity of the first step (formation of PO) and the second transition state (cleavage of the PO) were determined. A series of combinations of methods and basis sets were evaluated using G4 energetics of the methyl vinyl ether-ozone system and a known experimental barrier[79] for the cleavage of tetramethylethylene PO as standards. The following methods were evaluated and a basis set of 6-31G* was used unless otherwise indicated: B3LYP, B1B95, B1LYP, B3PW91, BB1K, BHandHLYP, BLYP, BP86, MPW1B95, MPW3LYP, MPWB1K, MPWLYP1M, MPWLYP1W, M05, M05/6-31+G**, M052x, M052x/6-31+G**, O3LYP, PBE1W, PBELYP1W, TPSS1KCIS, TPSSLYP1W, MP4, CCSD(T), UBD(T), UBD(T)/ccpvdz, UBD(T)/aug-ccpvdz and UBD(T)/ccpvtz. (Clearly the highest-level calculations would not be practical for trajectories but they served to gauge the reliability of the G4 and experimental results.) In general, the DFT methods underestimate the barrier of the cycloaddition TS because they overestimate the stabilization of the system as the ozone approaches the alkene. For our purposes, it was not necessary that the cycloaddition barrier be highly accurate (since our interest was in the process after the initial barrier), but none of the DFT calculations were judged to be sufficiently accurate.

A more satisfactory DFT method was obtained by reparameterizing B3LYP to better fit with the test energetics described in the previous paragraph. The functional obtained as a result of this fitting was:

$$P_2E_X^{HF} + P_1(P_4E_X^{Slater} + P_3\Delta E_x^{non\text{-}local}) + P_6E_C^{local} + P_5\Delta E_C^{non\text{-}local}$$

where ΔE_C is the LYP correlation functional, $\Delta E_x^{non\text{-}local}$ is Becke's 1988 exchange functional, P_2 is 0.1970, P_1 is 1, P_3 is 0.8, P_4 is 0.8, P_5 is 0.7 , and P_6 is 1. For comparison, B3LYP has P_2 is 0.2, P_1 is 1, P_3 is 0.72, P_4 is 0.8, P_5 is 0.81 , and P_6 is 1.

For the trajectories, a two-layer ONIOM calculation was performed for each force calculation, use the DFT method above for the PO ring and the PDDG/PM3 method for the alkyl chain. Listed below is an example force calculation for the trajectories. By this method, each force calculation could be performed in less than 40 processor-seconds, and a total of approximately 25 processor-years was used for the trajectories in Table 2 of Section 2.5 Quasiclassical Direct-Dynamics Trajectory Calculations.

```
# ONIOM(BLYP/6-31G*:PDDG) force scf=(tight,nosym)
iop(2/9=2000)
IOp(3/76=1000001970)IOp(3/77=0800008000)IOp(3/78=0700010000)

MVE ozonolysis oniom 218dis2
runpoint 1
runisomer  1

0 1
C -0.4396817 1.6530086 0.2240750
```

C	0.5607332	0.7301999	0.4336312		
O	1.4937786	0.3858805	-0.5455084		
O	-2.1787222	0.0844517	-0.3585275		
O	-1.3830679	-0.9236458	-0.4166167		
O	-0.6781152	-1.1090375	0.6651703		
H	0.7968537	0.4803651	1.5288116		
H	-1.1455555	1.8666788	1.1990271		
H	-0.6350660	2.1260657	-0.7282562		
C	2.3792852	-0.5929510	-0.0899968	M	H
H	3.3352863	-0.5955343	-0.7575330	M	
H	2.7670298	-0.4280944	1.0813129	M	
H	1.8912268	-1.7108838	-0.0589319	M	

5.3.5 Initialization of Trajectories

The trajectories employed in Section 2 are quasiclassical, i. e. including zero-point energy. (Exploratory classical trajectories were carried out but the number of cleavage events was decreased, making the classical trajectories less practical.) For trajectories starting at the endo- and exo-cyloaddition TS, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. Because of the anharmonicity of the lowest-energy modes, the choice of a random phase for these modes led to a problem for the trajectories using the larger alkyl groups, as the energy of the starting point structure for trajectories would inevitably be far from its desired value. To avoid this problem, the mode displacements were turned off for frequencies less than 100 cm^{-1}. (In other words, the mode phases for the lowest-energy modes were initialized only 0 or 180°. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy. (This is a variation of the conventional practice of scaling energies.[80])

5.3.6 Kinetic Energy Analysis

The flow of energy from the PO ring to the alkyl chain mentioned in the main text (17,19 and 20 kcal/mol/ps for ethyl, butyl and octyl vinyl ethers , respectively) was determined by kinetic energy analysis of the trajectories. This analysis was not built into PROGDYN at the time the trajectories were carried out, and so it had to be done based on the saved trajectories later. The awk program progKE, listed at the end of Appendix B, was used to calculate the kinetic energies in the alkyl chains by simply adding up the kinetic energy for each atom at each point in the trajectory.

The energies for points 100-500 in the trajectories were plotted against time and linear regression was used to determine the slope of the energy versus time. The rates of energy flow reported in the main text were determined from the average of the slopes.

5.3.7 Interconversion of Primary Ozonide Conformers

As mentioned briefly earlier, the endo and exo transition structures for ozonolyses of vinyl ethers lead to separate conformers of the primary ozonide. (The full structures are given below.) The trajectory study of the ozonolysis of propene by Hase and coworkers (ref 33) had observed that the rate of interconversion of the analogous isomers from propene did not fit with RRKM expectations. We have briefly examined whether the same is true for the reactions studied here. Interestingly, our observations for the vinyl ether ozonolyses differ from those found by Hase for propene.

In analogy with Hase, we will describe here the primary ozonide obtained from the endo transition structure as the "syn" conformer and the primary ozonide obtained from the exo transition structure as the "anti" conformer. (In our "Key to Structure Titles" below, the full structures retain our original designations as "endo" or "exo" structures.) In the R = methyl system, the threshold barrier for the conversion of the syn conformer to the anti conformer is 4.2 kcal/mol. This is somewhat higher than the barrier that Hase found for the propene case. Using the process described above for RRKM calculations, the weighted predicted RRKM rate constant for the conversion of the syn conformer to the anti conformer is 1.9×10^{12} s^{-1}. This would lead to an RRKM lifetime of 0.5 ps, which may be compared with Hase's calculated lifetime for the lower-barrier propene system of 0.3 ps.

To determine the trajectory rate of conformational interconversion, we examined a sample of 44 500-fs non-reactive trajectories starting from the endo transition structure in the R = methyl system. In these trajectories, 20 did not undergo conformational interconversion and 24 did. That corresponds roughly to a rate constant of 1.6×10^{12} s^{-1} if we count all 500 fs as being possible for the conformational interconversion, or 2.0×10^{12} s^{-1} if we only count the last 400 fs (no significant conformational interconversion can occur in the first 100 fs because the primary ozonide is in the process of forming during that time).

Clearly, the trajectory rates that we observe are reasonably consistent with RRKM expectations, and this is another observation that supports the idea that RRKM theory can be approximately applied to the "molecular subset" of the primary ozonide.

5.3.8 G4 and PCM Free Energies

The G4 free energies tabulated below are relative to the most stable primary ozonides. The following formula was used for the calculation of the free energies for octyl, 3,7-dimethyl octyl and 3,7,11,15-tetramethylhexadecyl vinyl ethers:

$$\Delta G^{\ddagger}_{\text{octyl}} = \Delta G^{\ddagger}_{\text{butyl}}\ (\text{G4}) + [\Delta G^{\ddagger}_{\text{octyl}}\ (\text{B3LYP/GTBas3}) - \Delta G^{\ddagger}_{\text{butyl}}\ (\text{B3LYP/GTBas3})] \quad (29)$$

The PCM calculations for the methyl vinyl ether systems are also tabulated below. The free energies are relative to the most stable primary ozonide.

The structure titles in the table and in Appendix B have retained the original file names for the computational output files. This allows consistency in naming structures, single point energies in tables and our records. We will give here some general explanation of the titles along with some structural drawings.

Structures with “G4-ufg” in the title indicate that the calculation was done using the Gaussian-4 (G4) method and a pruned (99,590) grid (Integral(Grid=UltraFineGrid)). For the larger alkyl groups, “b3lypGTBas3-ufg” in the title refers to the B3LYP method with a GTBas3 basis set. For titles with “pcm”, B3LYP/GTBas3 calculations with a Polarizable Continuum Model with methanol as the solvent was used.

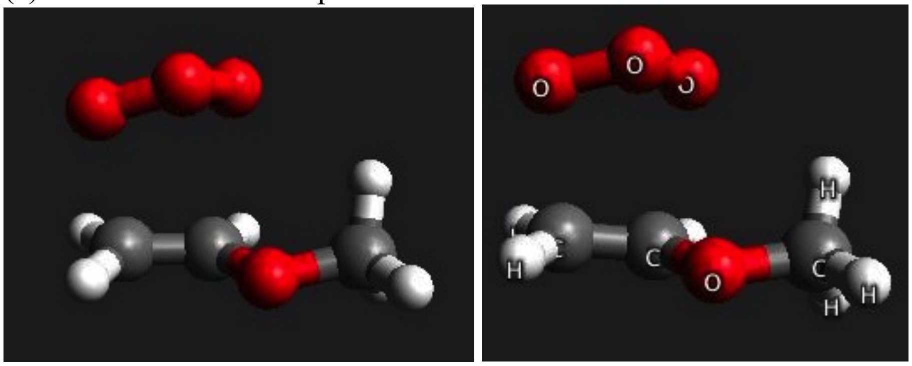
The vinyl ethers involved are identified in most of the titles; i.e. “MVE”, “EVE”, “BVE”, “OVE”, “GVE” and “PVE” refer to methyl, ethyl, butyl, octyl, 3,7-dimethyloctyl and 3,7,11,15-tetramethylhexadecyl vinyl ethers, respectively. The titles “ozone-G4-ufg”, “carbonyloxide-G4-ufg”, “methylformate-G4-ufg”, and “formaldehyde-G4-ufg” are self-explanatory. “MinorpdtfromMVE-G4-ufg” refers to structure CI-B in the main text.

Structures with TS in the title are transition structures and in every case had one imaginary frequency. “TS1” refers to the cycloaddition transition structure while “TS2” refers to the primary ozonide cleavage transition structures. For TS2 structures, “2carb” and “2form” indicate cleavage-A and cleavage-B, respectively. Different conformations of the alkyl chain are designated by a number after the vinyl ether name; for example “EVE3TS2-2carb-G4-ufg” and “EVE2TS2-2carb-G4-ufg”. This is the same in the other cases.

The use of “POZ” in titles means primary ozonide. Conformations of the primary ozonide and cycloaddition structures (TS1) are designated as “endotrans” or “exotrans” in the titles and are represented by Figure 17 below. “MVEPOZTSinterc-G4-ufg” refers to the methyl vinyl ether endo to exo primary ozonide transition structure.

Table 14 lists all the relevant free energies of the transition structures relative to the primary ozonides for the different vinyl ethers.

(a) MVETS1-endotrans-pcm



(b) MVETS1-exotrans-pcm

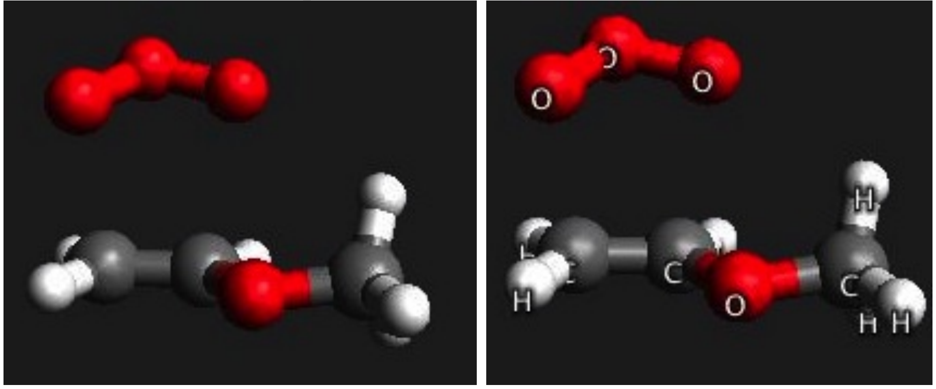


Figure 17. Methyl vinyl ether cycloaddition endo TS (a) and exo TS (b).

Table 14. Ozonolysis G4 and PCM Free Energies.

	Free Energy	**$\Delta G^{\ddagger}$ at 218.15K (kcal/mol)**
ozone-G4-ufg + MVE-G4-ufg	-418.388265	47.2
MVETS1-endotrans-G4-ufg	-418.373344	56.6
MVEPOZ-endotrans-G4-ufg	-418.463477	
MVEPOZTSinterc-G4-ufg	-418.456748	4.2
MVETS2-2carb-G4-ufg	-418.443469	12.6
MVETS2-2form-G4-ufg	-418.432916	19.2

Table 14 Continued

	Free Energy	$\Delta G^{\ddagger}$ at 218.15K (kcal/mol)
carbonyloxide-G4-ufg + methylformate-G4-ufg	-418.500994	-23.5
minorpdtfromMVE-G4-ufg + formaldehyde-G4-ufg	-418.480465	-10.7
MVETS1-endotrans-pcm	-418.500033	54.0
MVETS1-exotrans-pcm	-418.498774	54.7
MVEPOZ-endotrans-pcm	-418.586102	
MVETS2-carb-pcm	-418.566749	12.1
MVETS2-form-pcm	-418.560169	16.3
EVETS1-endotrans-G4-ufg	-457.658634	56.2
EVEPOZ-endotrans-G4-ufg	-457.748242	
EVE3TS2-2carb-G4-ufg	-457.727844	12.8
EVE2TS2-2carb-G4-ufg	-457.726729	13.5
EVE3TS2-2form-G4-ufg	-457.718141	18.9
EVE2TS2-2form-G4-ufg	-457.717236	19.5
BVETS1-endotrans-G4-ufg	-536.217613	56.2
BVEPOZ-endotrans-G4-ufg	-536.307148	
BVE3TS2-2carb-G4-ufg	-536.286705	12.8
BVE2TS2-2carb-G4-ufg	-536.285997	13.3
BVE3TS2-2form-G4-ufg	-536.277194	18.8
BVE2TS2-2form-G4-ufg	-536.276593	19.2
OVETS1-endotrans-b3lypGTBas3-ufg	-693.377169	56.2
OVEPOZ-endotrans-b3lypGTBas3-ufg	-693.466691	

Table 14 Continued

	Free Energy	**ΔG[‡] at 218.15K (kcal/mol)**
OVE3TS2-2carb-b3lypGTBas3-ufg	-693.446301	12.8
OVE2TS2-2carb-b3lypGTBas3-ufg	-693.445586	13.2
OVE3TS2-2form-b3lypGTBas3-ufg	-693.436752	18.8
OVE2TS2-2form-b3lypGTBas3-ufg	-693.436079	19.2
GVETS1-endotrans-b3lypGTBas3-ufg	-771.954266	56.2
GVEPOZ-endotrans-b3lypGTBas3-ufg	-772.043829	
GVE3TS2-2carb-b3lypGTBas3-ufg	-772.023371	12.8
GVE2TS2-2carb-b3lypGTBas3-ufg	-772.022653	13.3
GVE3TS2-2form-b3lypGTBas3-ufg	-772.013879	18.8
GVE2TS2-2form-b3lypGTBas3-ufg	-772.013672	18.9
PVETS1-endotrans-b3lypGTBas3-ufg	-1164.848689	56.1
PVEPOZ-endotrans-b3lypGTBas3-ufg	-1164.938024	
PVE3TS2-2carb-b3lypGTBas3-ufg	-1164.917553	12.8
PVE2TS2-2carb-b3lypGTBas3-ufg	-1164.917211	13.1
PVE3TS2-2form-b3lypGTBas3-ufg	-1164.907886	18.9
PVE2TS2-2form-b3lypGTBas3-ufg	-1164.907809	19.0

5.4 Experimental Procedure for the Diels-Alder Reactions

Trans-cinnamaldehyde, acrolein, boron trifluoride diethyl etherate and sodium borohydride were obtained commercially from Sigma Aldrich and used withour further purification. Cyclopentadiene was freshly prepared from distillation of diyclopentadiene. Freshly distilled diethyl ether was used in the reactions.

5.4.1 Lewis-acid Catalyzed DA Reaction

A mixture of 1.50 g (0.01 mol) of trans-cinnamaldehyde and freshly prepared 5.0 g (0.06 mol) of cyclopentadiene in 10 mL of freshly distilled diethyl ether under N_2 was cooled in a dry ice/acetonritrile bath to an internal temperature of -30 °C. With constant stirring, 0.12 mL (0.14 g, 0.001 mol) of boron trifluoride diethyl etherate was added into the mixture. The solution was stirred for 24h and maintained at a temperature of -30 °C. After 24h, the reaction was quenched with 3 mL of triethylamine and 20 mL of saturated sodium bicarbonate was also added into the solution. The reaction mixture was extracted with 3-20mL portions of diethyl ether. The organic layers were combined and dried with sodium sulfate and concentrated in vacuo to yield 1.0 g of crude material. The crude mixture was then subjected to column chromatography using 10% ethyl acetate/hexanes as the eluent. After chromatography, 750 mg of a mixture of the endo-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde cycloadduct along with a small amount of exo cycloadduct and polymeric residue was recovered. This crude material was dissolved in 20 mL of methanol and 0.7 g of sodium borohydride (≈5eq) was added into the mixture. After 1h of stirring, the reaction was quenched with saturated sodium bicarbonate and extracted with 3-20mL portions of diethyl ether. The organic layers were combined and dried with sodium sulfate and concentrated in vacuo. This material was then directly subjected to column chromatography using 20% ethyl acetate/hexanes. The recovered material, after concentration in vacuo, was contained a mixture of 500 mg of mainly endo alcohol cycloadduct with ~3% of the exo isomer. This sample was used for the intramolecular KIE measurements.^{1}H and ^{13}C NMR chemical shifts in C_6D_6 are referenced at δ 7.14 and δ 128.62, respectively.

Endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol. ^{1}H NMR (500 MHz, C_6D_6) : δ 6.98-7.18 (5H), 6.12 (dd, J= 5.6, 3.1 Hz, 1H), 6.07 (dd, J= 5.6, 2.9 Hz, 1H), 3.50 (dd, J= 10.5, 5.8 Hz, 1H), 3.19 (dd, J= 10.7, 9.9 Hz, 1H), 2.98 (m, 1H), 2.68 (m, 1H), 2.25 (m, 1H), 1.94 (dd, J= 4.8, 1.2 Hz, 1H), 1.59 (m, 1H), 1.46 (m, 1H). ^{13}C NMR (125.81 MHz, C_6D_6) : δ 145.99, 139.15, 135.37, 129.25, 128.41, 126.62, 66.71, 51.24, 49.76, 48.58, 47.84, 45.09.

The KIE sample was prepared using 300 mg of the purified endo cycloadduct (with a small amount of exo isomer) in a 5-mm NMR tube filled to a height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 10 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 312 500 points. Integrations were numerically determined using a constant integration region for the same peak of each spectra (i.e. sample and standard). A zero-order baseline correction was applied, but to avoid any qualitative manipulation, no first-order or higher order baseline correction is ever applied. Two independent samples were prepared and six spectra were recorded for each sample.

5.4.2 Low-temperature Lewis-acid Catalyzed DA Reaction

A mixture of 1.50 g (0.027 mol) of acrolein and freshly prepared 5.0 g (0.06 mol) of cyclopentadiene in 10 mL of deuterated chloroform under N_2 was cooled in a dry ice/acetone bath to an internal temperature of -78 °C. With constant stirring, 0.35 mL (0.37 g, 0.001 mol) of diethyl aluminum chloride in toluene was added into the mixture. An aliquot was then transferred to an NMR tube that was also pre-cooled to -78 °C. ^{1}H-NMR spectra was collected over 6h starting at 78 °C (2h), then at -50 °C (2h) and finally at -20 °C (2h). No reaction was observed for the first 4h and only dicyclopentadiene and trace amounts of the endo and exo cycloadduct was observed after 6h. No evidence of the presence of the hetero-DA product was seen.

5.4.3 Thermal DA Reaction

A mixture of 1.50 g (0.01 mol) of trans-cinnamaldehyde and freshly prepared 5.0 g (0.06 mol) of cyclopentadiene under N_2 was stirred for 2 weeks at room temperature. Fresh cyclopentadiene was continuously added over the course of the reaction. After 2 weeks, the percent conversion of the reaction was ≈50% and the reaction was stopped. The crude reaction mixture was directly subjected to column chromatography using 10% ethyl acetate/hexanes as eluent. After chromatography, 1 g of exo and endo aldehyde cycloadducts was recovered and was directly subjected to the same reduction conditions as above (20 mL methanol and 1 g of sodium borohydride was used). The reaction mixture was quenched with saturated sodium bicarbonate and extracted with 3-20mL portions of diethyl ether. The organic layers were combined and dried with sodium sulfate and after concentration in vacuo yielded 700 mg of a pure mixture of the exo and endo alcohol cycloadducts. This was used as the sample for the KIE measurements.

Exo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol (mixture with the endo cyloadduct). ^{1}H NMR (500 MHz, C_6D_6) : δ 6.96-7.18 (m, overlap with aromatic protons for endo product), 6.14 (dd, J= 5.8, 3.3 Hz, 1H), 5.8 (dd, J= 5.6, 2.9 Hz, 1H), 3.68 (dd, J= 10.6, 5.8 Hz, 1H), 3.39 (dd, J=10.6, 8.8 Hz, 1H), 2.81 (m, 1H), 2.80 (m, 1H), 2.60 (dd, J= 5.3, 3.4 Hz), 1.86 (m, 1H), 1.42 (m, 2H). ^{13}C NMR (125.81 MHz, C_6D_6) : δ 145.04, 138.38, 135.33, 128.92, 128.81, 126.78, 66.98, 50.61, 49.55, 49.05, 47.83, 45.76.

The KIE sample was prepared using 300 mg of the purified mixture of endo and exo cycloadducts in a 5-mm NMR tube filled to a height of 5 cm with benzene-d_6. The following parameters were used for this experiment: 10 s delays between calibrated π/2 pulses, and a 5 s acquisition time to collect 312 500 points. Six spectra were recorded for each sample.

5.5 NMR Peak Assignments for the Endo and Exo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

^{1}H and ^{13}C NMR peaks were assigned using COSY, APT and HMQC. Figure 18 shows the proton and carbon assignments of the endo and exo products.

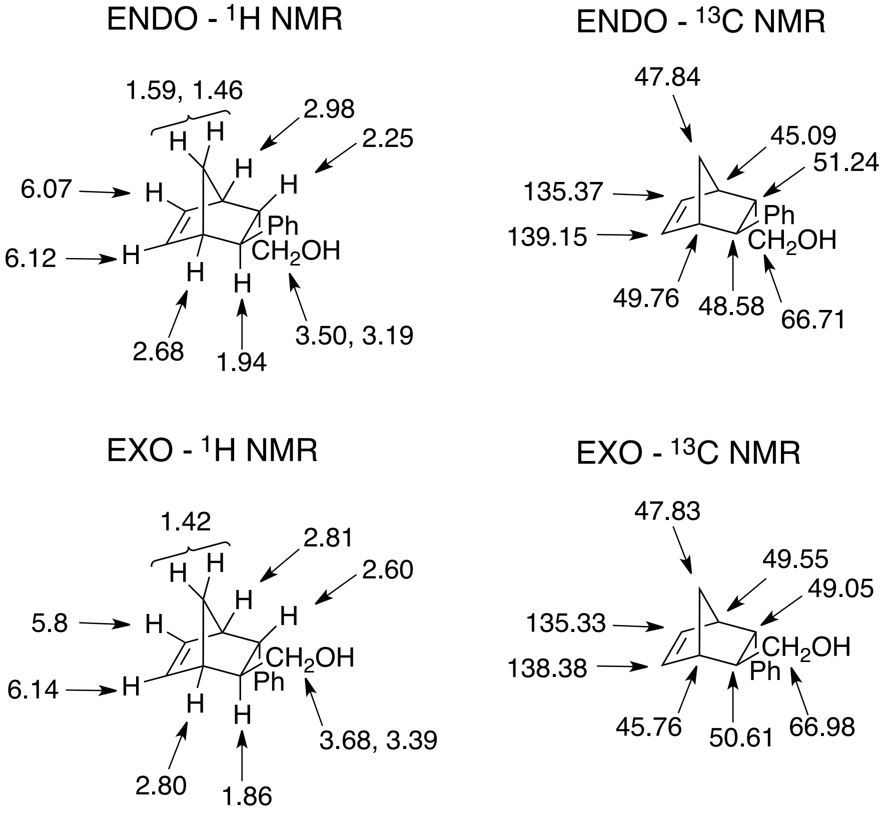


Figure 18. NMR peak assignments for the endo and exo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol.

5.6 Initialization of the Exploratory Trajectory Studies for the DA Reactions

The trajectories employed in Table 5 are quasiclassical, i. e. including zero-point energy. For trajectories starting at the endo-cyloaddition TS, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy.

5.7 Experimental Procedure for the BV Oxidation of Cyclohexanone in Water

Cyclohexanone and 32% wt. peracetic acid, trifluoroacetic anhydride and 30% wt. hydrogen peroxide were obtained commercially and used without further purification.

5.7.1 Oxidation of Cyclohexanone with Peracetic Acid

A mixture of 20.8 mL (0.2 mol) of cyclohexanone and 30 g of sodium hydrogen phosphate dibasic was dissolved in 380 mL of H_2O at 35-40^{0}C in a flask equipped with a reflux condenser; then 20.0 mL of 32% wt. peracetic acid was added dropwise and was left to stir for 2hrs. Aliquots were taken every 2 h checked by ^{1}H-NMR, and an additional 30 g of sodium phosphate dibasic (to maintain solution pH=6) and 20.0 mL of

32% wt. peracetic acid was added into the mixture until the reaction reached ≈80% conversion of the cyclohexanone. Sodium bicarbonate (5 g) was then stirred into the mixture and the solution was extracted three times with 25-mL portions of dichloromethane. The organic layers were combined, dried (Na_2SO_4) and concentrated on a rotary evaporator. Cyclohexanone was distilled off (65^0C, 37.5 mmHg) affording 180 mg of pure recovered starting material and giving pure caprolactone (3.09 g) in the residue.

Note: The buffer, sodium hydrogen phosphate dibasic, was added to the reaction to minimize hydrolysis of caprolactone into the hydroxy acid (less than 5% of the hydroxy acid in the mixture was observed based on proton NMR). Figure 19 shows the carbon-13 assignments for cyclohexanone and caprolactone.

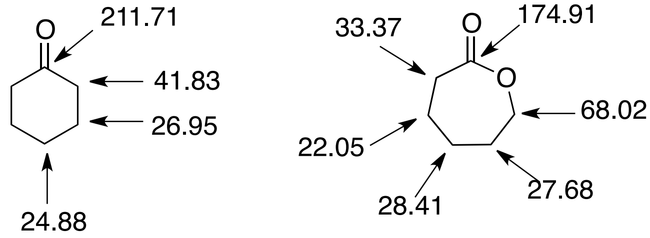


Figure 19. ^{13}C NMR peak assignments for cyclohexanone (left) and caprolactone (right).

The NMR sample for starting material KIE was prepared using 180 mg of recovered cyclohexanone in a 5-mm NMR tube filled to a height of 5 cm with $CDCl_3$. For starting molecular KIE standard, an identical NMR sample was prepared using 180 mg of cyclohexanone from the original reagent bottle used in the reaction.

The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 85 s delays between calibrated $\pi/2$ pulses, and a 10 s acquisition time to collect 675 676 points. Integrations were numerically determined using a constant integration region for the same peak of each spectra (i.e. sample and standard). A zero-order baseline correction was applied, but to avoid any qualitative manipulation, no first-order or higher order baseline correction is ever applied. Six spectra were recorded for each sample and standard. The NMR sample for intramolecular KIE was prepared using 400 mg of caprolactone in a 5-mm NMR tube filled to a 5 cm height with $CDCl_3$. The same procedure for NMR measurement was followed with the following parameters appropriate for the sample: 20 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 378 788 points. A total of 24 spectra were collected.

5.7.2 Oxidation of Cyclohexanone with Trifluoroperacetic Acid

Trifluoroperacetic acid was prepared by the dropwise addition of 13 g of trifluoroacetic anhydride to 2.5 g of 30% wt. hydrogen peroxide at 0^0C. This freshly prepared solution was added dropwise to a mixture of 5.2 mL (0.05 mol) of cyclohexanone and 30 g of sodium hydrogen phosphate dibasic dissolved in 380 mL of H_2O at 35-40^0C in a flask equipped with a reflux condenser. The solution was left to stir for 1 h. Aliquots were taken every hour and checked by ^1H-NMR, and an additional 30 g of sodium phosphate dibasic and a fresh batch of trifluoroperacetic acid was added into the mixture until the reaction reached 15% conversion of the cyclohexanone. Sodium bicarbonate (5-10 g) was then stirred into the mixture and the solution was extracted three times with 25-mL portions of dichloromethane. The organic layers were combined, dried (Na_2SO_4) and concentrated on a rotary evaporator. Cyclohexanone was distilled off (65^{0}C, 37.5 mmHg) to yield pure caprolactone (1.2 g) in the residue.

The NMR sample was prepared using 160 mg of caprolactone in a 5-mm NMR tube filled to a height of 5 cm with $CDCl_3$. This served as the sample for both product intramolecular and product intermolecular (low conversion) KIE studies.

A mixture of 3 g (0.03 mol) of cyclohexanone in 100 mL of dichloromethane was stirred at room temperature then 7.5 g (0.04 mol) meta-chloroperoxybenzoic acid (MCPBA) was stirred into the mixture. The solution was left to stir for 3 h or until 100% conversion of cyclohexanone was achieved. Sodium thiosulfate, sodium bicarbonate and water was stirred into the mixture and the solution was extracted three times with 25-mL portions of dicholoromethane. The organic layers were combined, dried (Na_2SO_4) and concentrated on a rotary evaporator to yield 3.5 g caprolactone.

The NMR sample was prepared using 160 mg of caprolactone in a 5-mm NMR tube filled to a height of 5 cm with $CDCl_3$.The following NMR parameters were used for the product intermolecular KIEs: 160 s delays between calibrated $\pi/2$ pulses, and an 8 s acquisition time to collect 476 192 points. Six spectra were recorded for each sample and standard. For the intramolecular KIEs: 30 s delays between calibrated between calibrated $\pi/2$ pulses, and a 6 s acquisition time to collect 454 544 points. A total of 24 spectra were collected.

VI. CONCLUSIONS

The emphasis on experimental results has been apparent through this dissertation. The mechanisms of ordinary and simple organic reactions have been thoroughly investigated and at the core of these investigations are the experimental findings. Understanding the different reactions studied necessitated exploring beyond the conventional theories used in chemistry and this has allowed us to generate the best possible explanation for the unusual observations we encountered.

Quasiclassical direct-dynamics trajectories were successful in explaining the product selectivity in the ozonolysis of vinyl ethers where conventional TST and RRKM predictions were found to be inaccurate models for this reaction. The trajectory results uncovered another form of dynamic effect, incomplete intramolecular vibrational energy redistribution, at play in this reaction. It seems that the excess energy in the primary ozonide is not statistical distributed within the molecule and that some of the energy promotes product formation. The experimental consequence of this “competition” is seen in the observation of the minor product and in the increase in the product selectivity as the length of the alkyl chain on the vinyl ether is increased. This form of dynamic effect may also be happening in other reactions having a barrier following a highly exergonic step.

The Lewis-acid catalyzed DA reaction revealed a ‘normal’ intramolecular KIE that is in excellent agreement with predictions from conventional TST. This in contrast with the results obtained from the organocatalytic DA reaction, which showed a small ‘normal’ intramolecular KIE that cannot be reconciled with the conventional transition structure. Dynamic trajectory studies demonstrated a substantial amount of recrossing in this reaction. The unusual KIE may be explained by a novel idea where a “hidden” rate-limiting step corresponding to the second C-C bond formation is present in the free energy surface. The thermal DA reaction was also explored to serve as a comparison for the organocatalytic DA reaction.

Finally, the complex mechanism of the BV reaction of cyclohexanone with PAA and TFPAA in water was investigated using a combination of experimental and theoretical techniques. A complete set of intermolecular and intramolecular KIEs for the PAA reaction points to a rate-limiting alkyl migration. The theoretical predictions are in accord with the experimental findings and support the conclusion. On the other hand, the TFPAA reaction displayed a modest but significant intermolecular KIE only on the carbonyl carbon indicating a rate-limiting peracid addition. The modest agreement with the predicted KIE from the carbonyl addition TS shows that the reaction in water is difficult to model due to the complexity arising from the large ensemble of possibilities wherein water can facilitate the steps in the reaction.

The complete understanding of a reaction starts from gathering accurate experimental data and searching for existing theories that can explain the results. Occasionally, ordinary organic reactions can exhibit intriguing and unusual outcomes that can only be explained by unconventional theories. This allows for novel ideas to be developed and to challenge the applicability of existing theories.

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APPENDIX A

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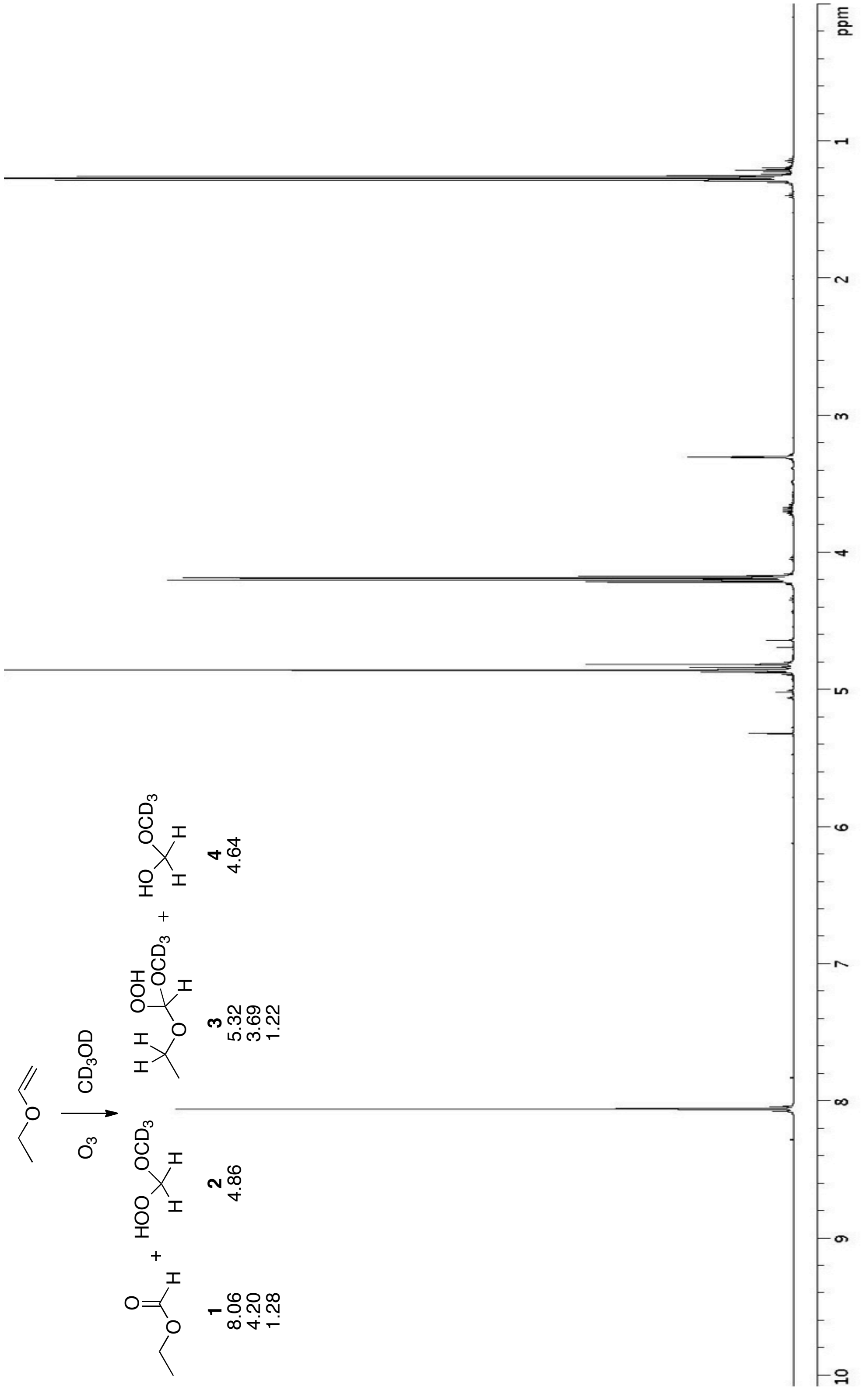
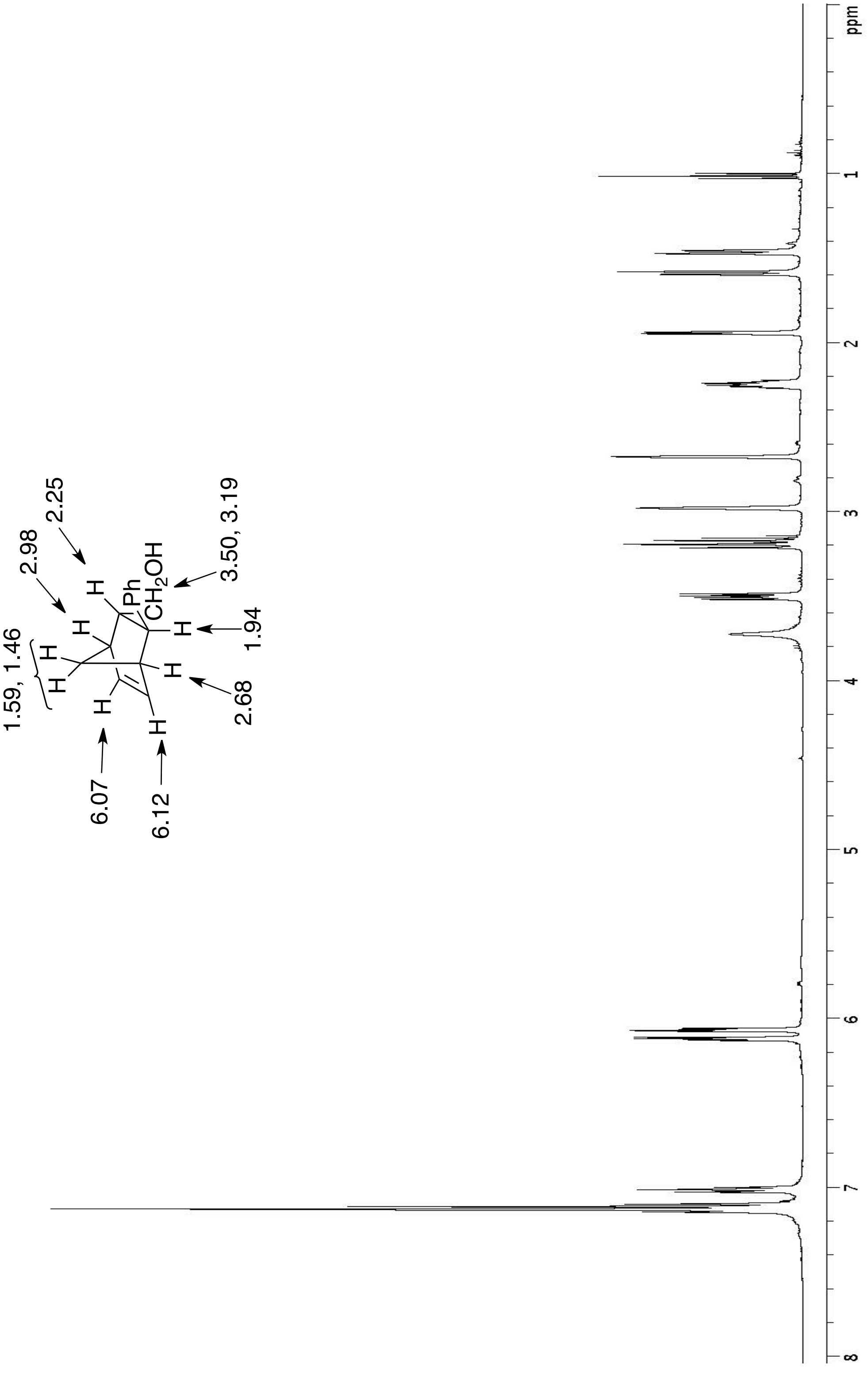
Crude ^{1}H NMR spectrum of Ethyl Vinyl Ether Ozonololysis in Methanol-d4



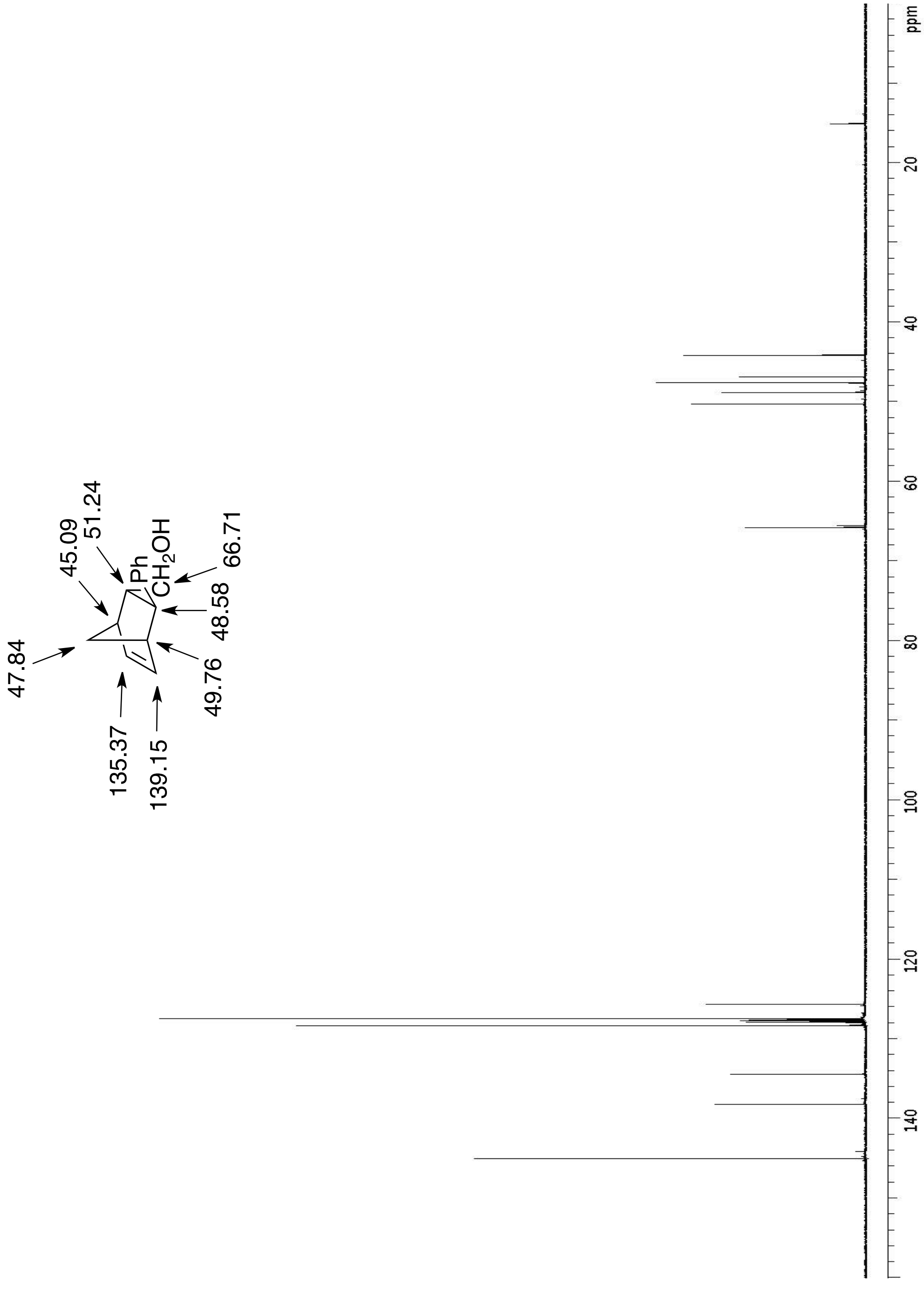
^{1}H-NMR spectrum of endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(BF$_3$-catalyzed Diels-Alder reaction of cyclopentadiene and trans-cinnamaldehyde)



^{13}C NMR spectrum for the intramolecular KIE of endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(BF_3-catalyzed Diels-Alder reaction of cyclopentadiene and trans-cinnamaldehyde)

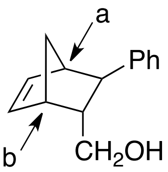


Intramolecular ^{13}C NMR KIE Sample Integration Results for

endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(BF_3-catalyzed Diels-Alder reaction of cyclopentadiene and trans-cinnamaldehyde)

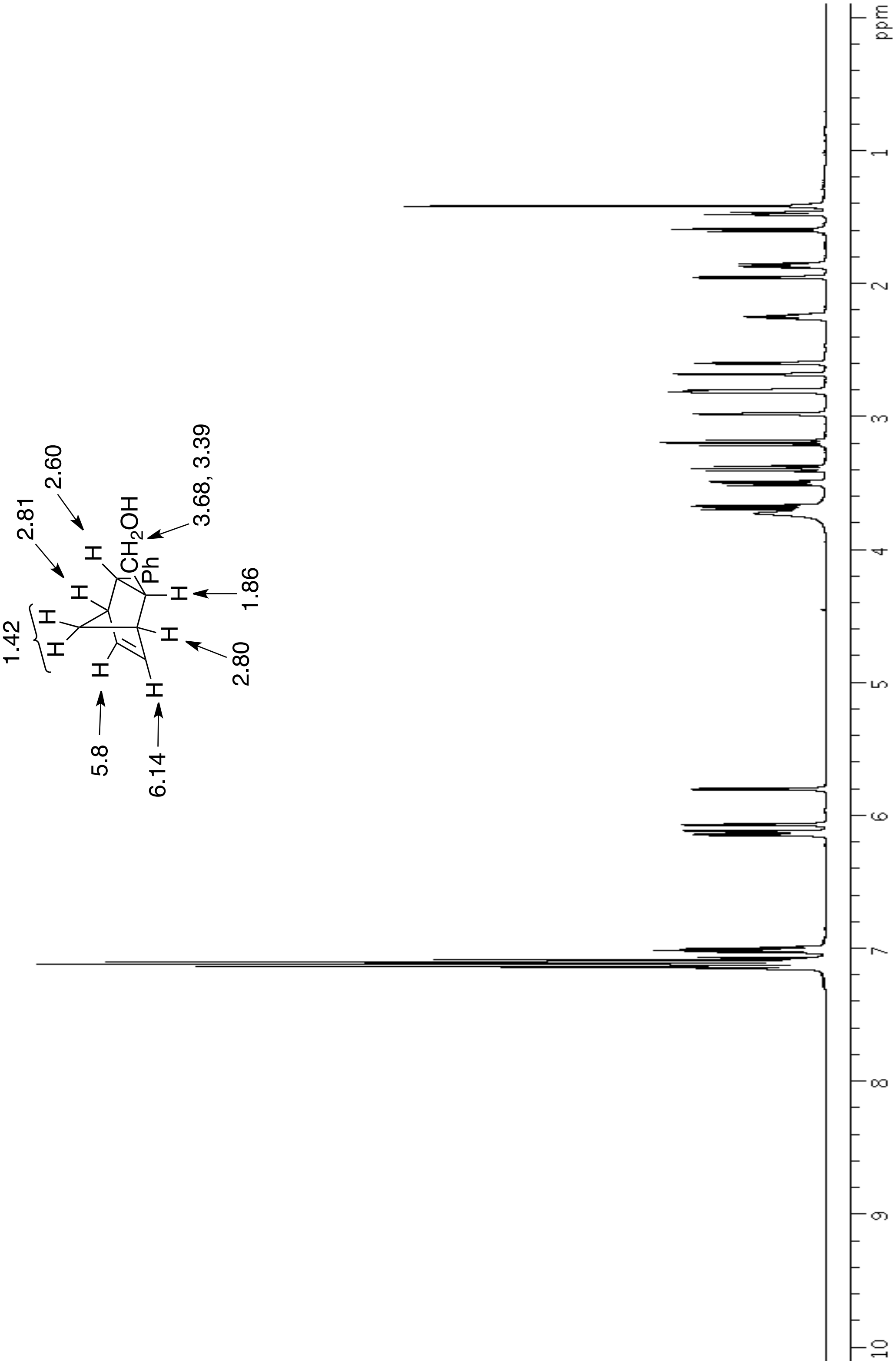
The integrations below are relative to position b (45.09) set as 1000.



a (49.76ppm)	AVE	Intramolecular KIE (b/a)
972.96		
967.35		
967.04		
970.44		
964.66		
966.53	968.16	1.033(3)

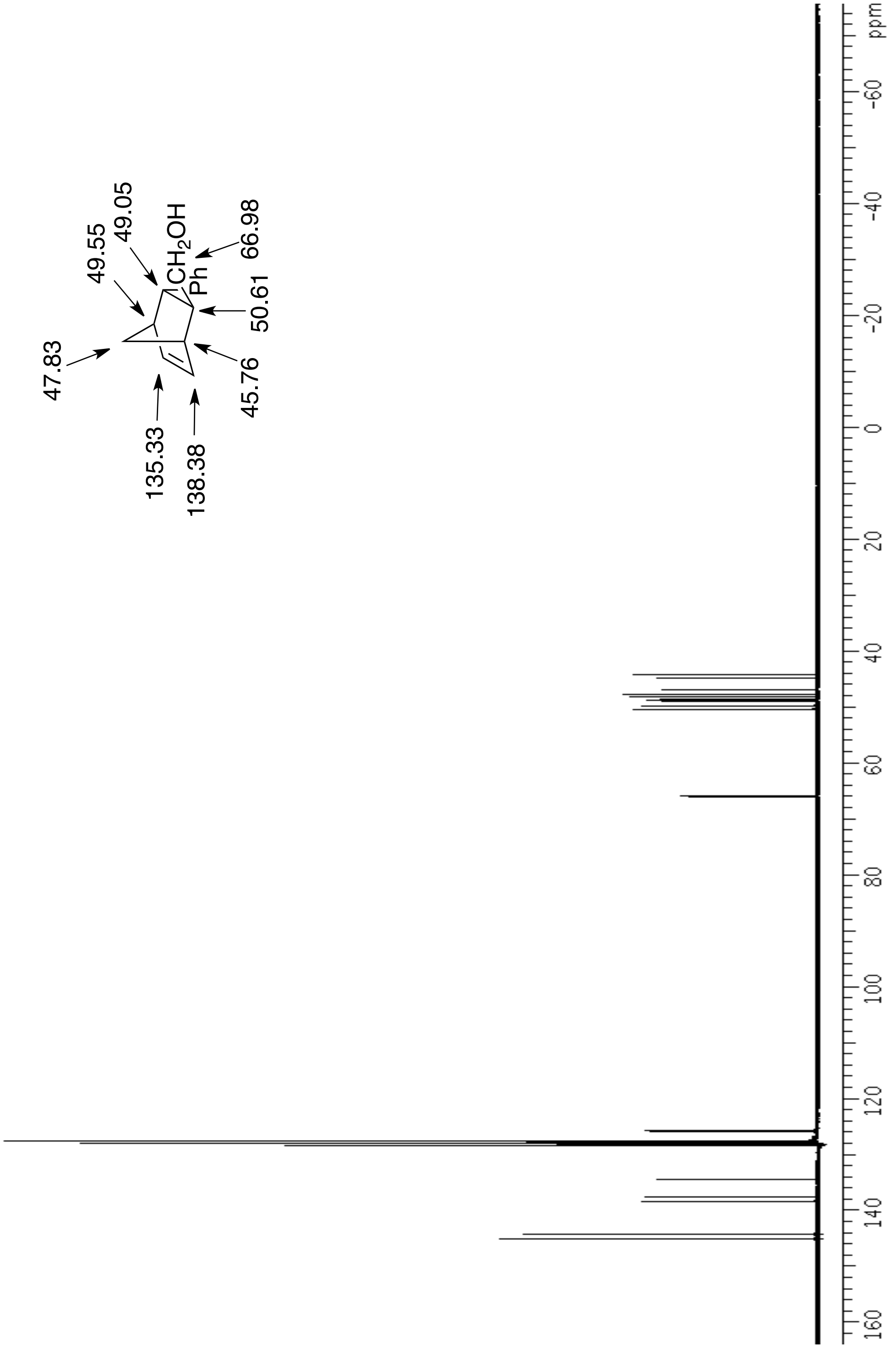
^{1}H-NMR spectrum of exo and endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(Thermal Diels-Alder Reaction at 25 °C) Structure shown is for exo cycloadduct.



^{13}C-NMR spectrum for the intramolecular KIE of exo and endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(Thermal Diels-Alder Reaction at 25 °C) Structure shown is for exo cycloadduct.

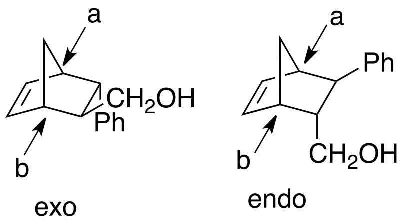


Intramolecular ^{13}C NMR KIE Sample Integration Results for

exo and endo-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

(Thermal Diels-Alder reaction of cyclopentadiene and trans-cinnamaldehyde)

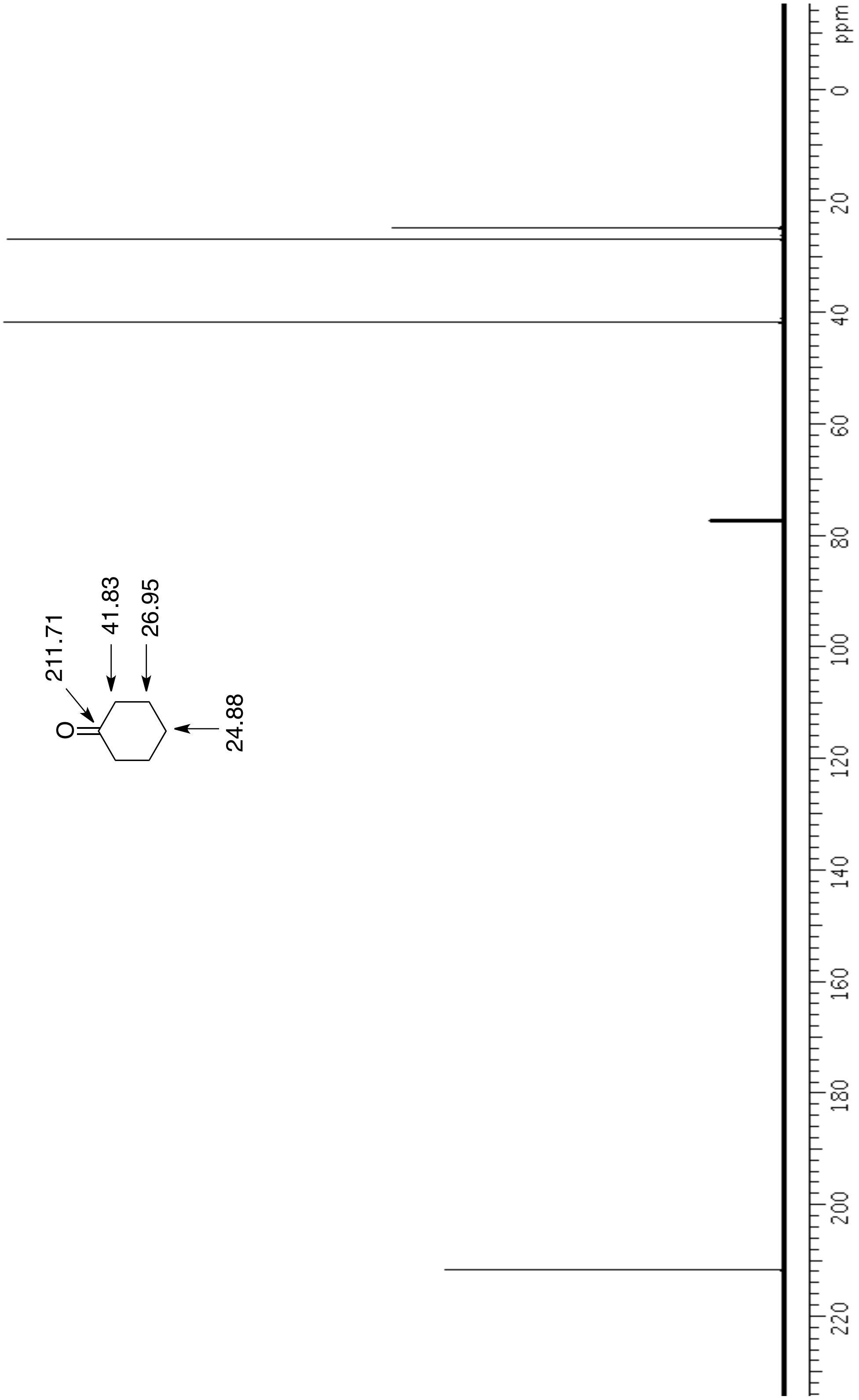
The integrations below are relative to position b (45.09ppm) in endo and (45.76ppm) set as 1000.



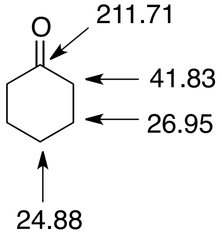
ENDO		
a (49.76ppm)	AVE	Intramolecular KIE (b/a)
1001.26		
996.19		
991.84		
993.44		
992.32		
988.17	993.87	1.006(4)

EXO		
a (49.55ppm)	AVE	Intramolecular KIE (b/a)
993.91		
992.62		
995.77		
991.91		
992.39		
990.53	992.85	1.007(4)

^{13}C-NMR spectrum for the intermolecular KIE of recovered cyclohexanone

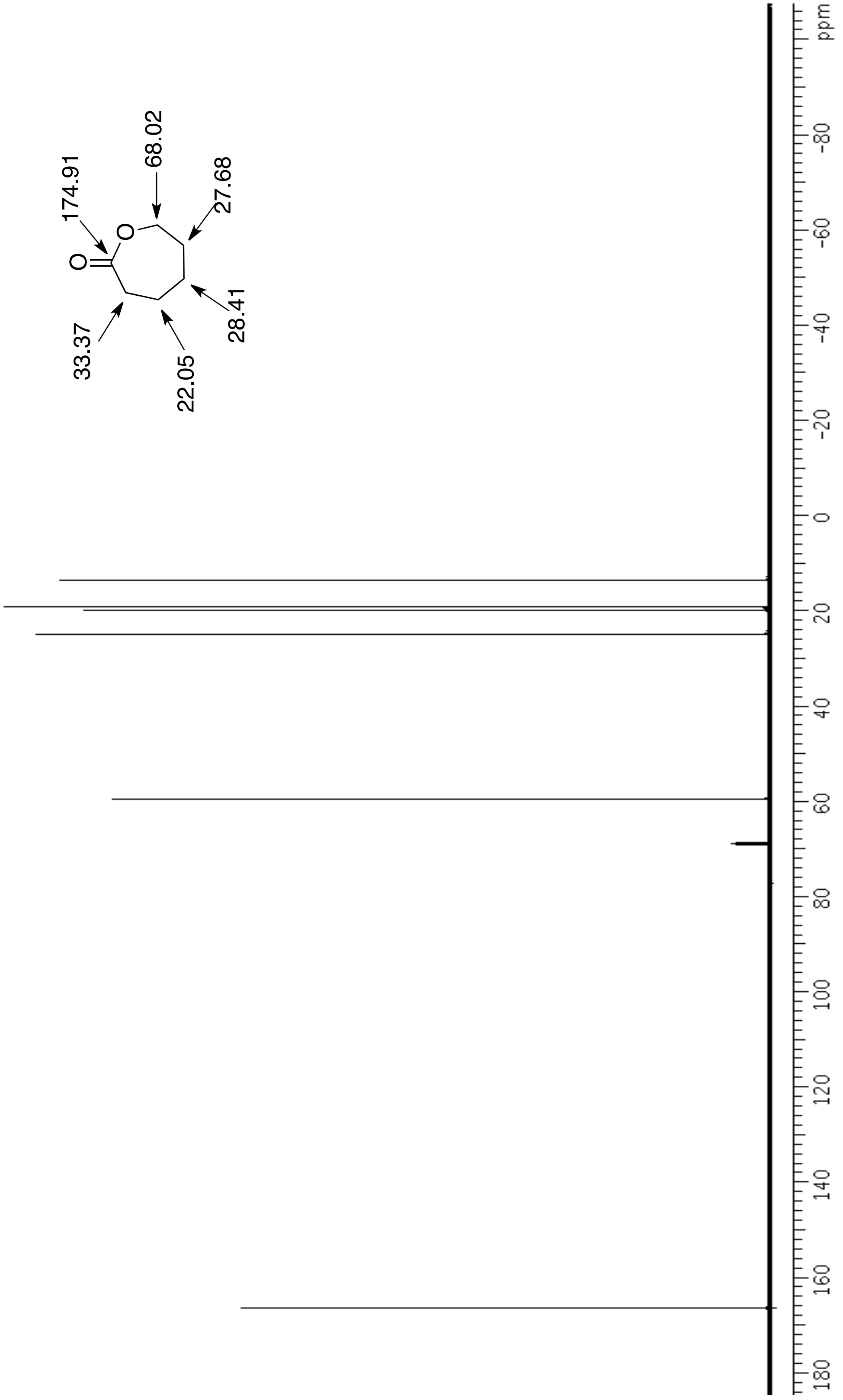


Starting material Intermolecular ^{13}C NMR KIE Sample Integration Results for Oxidation of Cyclohexanone with Peracetic Acid

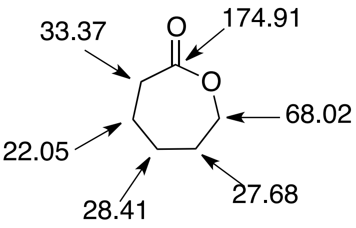


STD 1									
	FID1	**FID2**	**FID3**	**FID4**	**FID5**	**FID6**	**average**	**std. dev.**	
211.7	972.7	976.40	972.55	977.06	972.63	975.17	974.43	2.04	
41.83	2000.3	2000.6	1991.1	2009.0	2014.2	1995.6	2001.87	8.51	
26.95	2001.6	2001.3	2000.3	2002.9	1999.2	1986.3	1998.64	6.15	
24.88	1000	1000	1000	1000	1000	1000	1000	0	
RCV RD SM1									
	FID1	**FID2**	**FID3**	**FID4**	**FID5**	**FID6**	**average**	**std. dev.**	**KIE**
210	1003.1	1002.2	1004	1003.3	1003.1	993.71	1001.59	3.90	**1.023**
42	2029.3	2031.0	2044.4	2035.7	2035.7	2027.1	2033.89	6.18	**1.013**
26	1996.0	1996.8	1996.0	1998.3	2000.1	1994.8	1997.05	1.88	**0.999**
24	1000	1000	1000	1000	1000	1000	1000	0	**1.000**

^{13}C-NMR spectrum for the intramolecular KIE of caprolactone



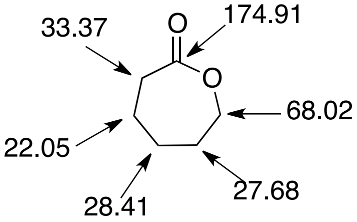
Product Intermolecular ^{13}C NMR KIE Sample Integration Results for Oxidation of Cyclohexanone with Trifluoroperacetic Acid



STD1									
	FID1	**FID2**	**FID3**	FID7	FID8	FID9	**average**	**std. dev.**	
174.91	1018.1	1020.16	1018.96	1019.84	1020.75	1015.21	1018.83	2.00	
68.02	987.02	990.68	990.44	991.59	994.64	987.30	990.28	2.84	
33.37	1016.44	1020.22	1022.07	1018.5	1021.32	1019.92	1019.74	2.03	
28.41	1000	1000	1000	1000	1000	1000	1000	0	
27.68	1004.27	1004.32	1006.17	1006.14	1007.39	1004.27	1005.42	1.32	
22.05	999.028	1001.68	1001.7	1004.14	1002.75	998.241	1001.25	2.23	
rec pdt									
	FID1	**FID2**	**FID3**	FID 7	FID 8	FID 9	**average**	**std. dev.**	**KIE**
174.91	1004.42	1002.92	1000.1	1004.94	1004.11	1003.46	1003.32	1.73	**1.017**
68.02	991.33	990.46	992.20	991.77	989.61	990.13	990.92	1.01	**0.999**
33.37	1017.19	1018.47	1019.16	1019.53	1018.86	1013.24	1017.74	2.34	**1.002**
28.41	1000	1000	1000	1000	1000	1000	1000	0	**1.000**
27.68	1006.03	1008.26	1007.2	1006.45	1003.01	1001.17	1005.35	2.70	**1.000**
22.05	998.951	1001.48	1003.74	1001.01	999.527	997.37	1000.34	2.22	**1.001**

Intramolecular ^{13}C NMR KIE Sample Integration Results for Caprolactone

The integrations for the migrating side of the lactone (a, 68.02 ppm and c, 27.68 ppm) are relative to the non-migrating side (b, 33.37 ppm and d, 22.05 ppm) which were assigned 1000. For the 68.02 ppm carbon, an adjustment of 0.0121 had to made because of an extra pair of carbon-13 satellites for 33.37 ppm, which is attached to two carbons, wheras the 68.02 ppm carbon is only attached to one carbon.



	a	b	c	d	KIE b/a	KIE d/c
FID	68.02 ppm	33.37 ppm	27.68 ppm	22.05 ppm		
1	973.358	1000	991.18	1000	1.037 (2)	1.004 (2)
2	972.702	1000	991.14	1000		
3	979.464	1000	995.00	1000		
4	976.654	1000	995.46	1000		
5	981.273	1000	996.99	1000		
6	969.85	1000	997.67	1000		

APPENDIX B

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Calculated Structures and Energies

ozone-G4-ufg

```
O,0,0.0201440711,0.,0.1482686392
O,0,0.1129301031,0.,1.4001460956
O,0,1.2622826927,0.,1.9049183594
```

```
E(ZPE)=                0.007359 E(Thermal)=              0.009460
E(CCSD(T))=          -224.874425 E(Empiric)=              -0.062523
DE(Plus)=             -0.018289 DE(2DF)=                -0.148726
E(Delta-G3XP)=        -0.238126 DE(HF)=                 -0.028217
G4(0 K)=            -225.362947 G4 Energy=            -225.360846
G4 Enthalpy=        -225.360156 G4 Free Energy=       -225.378977
```

MVE-G4-ufg

```
C,0,-0.0205023277,0.,0.0969129117
C,0,0.1484510073,0.,1.4186679423
H,0,0.8213167338,0.,-0.5893409514
H,0,1.1541942574,0.,1.8176588347
H,0,-0.6675245319,0.,2.1284961692
O,0,-1.1758662259,0.,-0.6059026069
C,0,-2.3762063373,0.,0.1453888914
H,0,-3.1940651733,0.,-0.5767181171
H,0,-2.4465237012,-0.8923787086,0.780524963
H,0,-2.4465237012,0.8923787086,0.780524963
```

```
E(ZPE)=                0.083951 E(Thermal)=              0.086916
 E(CCSD(T))=         -192.532456 E(Empiric)=              -0.083364
 DE(Plus)=            -0.014295 DE(2DF)=                -0.168358
 E(Delta-G3XP)=       -0.256674 DE(HF)=                 -0.019757
 G4(0 K)=           -192.990953 G4 Energy=            -192.987987
 G4 Enthalpy=       -192.987296 G4 Free Energy=       -193.009287
```

MVETS1-endotrans-G4-ufg

```
O,0,0.7304899682,-2.0125237568,1.2642603287
O,0,1.5640087255,-1.0326821638,1.4086004472
O,0,1.8965975688,-0.4827743074,0.3006480003
C,0,-0.1110571411,0.258111805,-0.4240930882
C,0,-0.9283652944,-0.3573587485,0.472639387
```

```
O,0,-1.1644621073,0.2130737445,1.6586289939
C,0,-1.7865355078,-0.627232927,2.6278749998
H,0,-1.4631071501,-1.2748559822,0.2471812772
H,0,-1.9451549104,-0.0153290088,3.5160593626
H,0,-2.7510783193,-0.9995338533,2.2616427723
H,0,-1.1263103273,-1.47144936,2.8545461324
H,0,0.0153502009,-0.1627760265,-1.4102602989
H,0,0.2609712944,1.2551905848,-0.2319933144
```

```
 E(ZPE)=                0.092980 E(Thermal)=              0.097782
 E(CCSD(T))=           -417.407195 E(Empiric)=               -0.145887
 DE(Plus)=             -0.034584 DE(2DF)=                -0.318990
 E(Delta-G3XP)=           -0.492313 DE(HF)=                  -0.045430
 G4(0 K)=             -418.351418 G4 Energy=              -418.346616
 G4 Enthalpy=           -418.345925 G4 Free Energy=           -418.373344
```

MVETS1-endotrans-pcm

E(RB3LYP) = -418.572196635

```
Zero-point correction=                           0.094212 (Hartree/Particle)
 Thermal correction to Energy=                   0.099033
 Thermal correction to Enthalpy=                 0.099724
 Thermal correction to Gibbs Free Energy=        0.072163
 Sum of electronic and zero-point Energies=          -418.477984
 Sum of electronic and thermal Energies=             -418.473163
 Sum of electronic and thermal Enthalpies=           -418.472472
 Sum of electronic and thermal Free Energies=        -418.500033
```

```
                 E (Thermal)            CV                S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total               62.144            21.162            79.279
```

O	-0.73665	-1.21791	0.72745
O	-1.29617	-0.94197	-0.40723
O	-2.01038	0.12132	-0.37413
C	-0.45462	1.66247	0.15889
C	0.59201	0.84963	0.46837
O	1.39826	0.40504	-0.50103
C	2.27185	-0.65847	-0.12928
H	0.85337	0.59104	1.48981
H	2.88243	-0.88171	-1.00438
H	2.91977	-0.35973	0.70385

H	1.67757	-1.53222	0.15933
H	-1.05457	2.0873	0.94964
H	-0.57454	2.04184	-0.84666

MVETS1-exotrans-pcm

E(RB3LYP) = -418.570444490

```
 Zero-point correction=                           0.093955 (Hartree/Particle)
 Thermal correction to Energy=                    0.098929
 Thermal correction to Enthalpy=                  0.099620
 Thermal correction to Gibbs Free Energy=         0.071671
 Sum of electronic and zero-point Energies=           -418.476490
 Sum of electronic and thermal Energies=              -418.471515
 Sum of electronic and thermal Enthalpies=            -418.470824
 Sum of electronic and thermal Free Energies=         -418.498774

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  62.079             21.508             80.397
```

C	-0.32636	1.61993	0.24791
C	0.64398	0.69926	0.49906
O	-1.89002	0.24633	-0.67426
O	-0.7541	-1.33952	0.24145
O	-1.87666	-0.7031	0.18301
H	0.76629	0.24012	1.47646
O	1.5645	0.40894	-0.42198
C	2.40342	-0.70398	-0.12608
H	3.12992	-0.76947	-0.9364
H	2.93031	-0.55636	0.82478
H	1.80935	-1.62165	-0.08064
H	-0.98488	1.93713	1.04314
H	-0.32695	2.17784	-0.67844

MVEPOZ-endotrans-G4-ufg

O,0,2.0097136322,-0.6399560834,0.6418421332
O,0,1.3245230393,-0.0909439588,-0.4854827908
C,0,0.006724791,0.0580906683,0.0196090274
C,0,-0.1456001313,-1.1068855745,1.0303279755
O,0,1.1278200991,-1.7308418813,1.0051128151

```
O,0,-0.4997154713,-0.5625619386,2.2543937807
C,0,-0.7177466805,-1.5276054674,3.273311359
H,0,-0.8449511659,-1.8979758332,0.7238974111
H,0,-1.0373414013,-0.9808574378,4.1619223513
H,0,-1.5058517032,-2.2385828523,2.9846104412
H,0,0.1992190659,-2.0838762785,3.4968084844
H,0,-0.6735008164,-0.0095020274,-0.8313276688
H,0,-0.1249902578,1.000779665,0.5599886806
```

```
E(ZPE)=                 0.097501 E(Thermal)=              0.101603
E(CCSD(T))=           -417.508666 E(Empiric)=               -0.145887
DE(Plus)=              -0.030517 DE(2DF)=                 -0.316413
E(Delta-G3XP)=         -0.493554 DE(HF)=                  -0.044861
G4(0 K)=             -418.442396 G4 Energy=              -418.438294
G4 Enthalpy=         -418.437603 G4 Free Energy=         -418.463477
```

MVEPOZ-endotrans-pcm

E(RB3LYP) = -418.663706476

```
 Zero-point correction=                           0.098849 (Hartree/Particle)
 Thermal correction to Energy=                    0.102946
 Thermal correction to Enthalpy=                  0.103637
 Thermal correction to Gibbs Free Energy=         0.077754
 Sum of electronic and zero-point Energies=           -418.565006
 Sum of electronic and thermal Energies=              -418.560910
 Sum of electronic and thermal Enthalpies=            -418.560219
 Sum of electronic and thermal Free Energies=         -418.586102

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  64.599             18.286            74.451
```

```
O,0,2.0230361456,-0.6226310004,0.6231256005
 O,0,1.3194280181,-0.074374328,-0.4955556666
 C,0,-0.0022506676,0.0535754649,0.0194821563
 C,0,-0.1290048638,-1.1051703037,1.0388730043
 O,0,1.1566913402,-1.721636861,0.9930114724
 O,0,-0.4528358613,-0.5620355037,2.26896672
 C,0,-0.7283241283,-1.5316532041,3.2770296896
 H,0,-0.8246061101,-1.901874772,0.7470114293
 H,0,-1.0295170009,-0.9808473393,4.1690889659
```

H,0,-1.544587943,-2.1979608342,2.9682603607
H,0,0.1593317723,-2.1324620442,3.5028068682
H,0,-0.6860799971,-0.0343656179,-0.8252190069
H,0,-0.1429777044,1.0007173436,0.5481324064

MVEPOZTSinterc-G4-ufg

O,0,1.3340991989,0.4256753395,-0.3430398816
C,0,0.0189237949,0.000014607,-0.0534877792
C,0,-0.0096743108,-0.0138477289,1.4708945773
O,0,1.2530356536,-0.5730097773,1.7639090583
O,0,2.1620782858,-0.0271678444,0.777647389
H,0,-0.1907089189,-1.0020094783,-0.4494253829
H,0,-0.7228691068,-0.7317047884,1.9034794881
O,0,-0.2064407411,1.2713683884,1.9428727388
H,0,-0.6600441664,0.7429570616,-0.4764064584
C,0,-0.1757073944,1.3768851322,3.3589584693
H,0,-0.3773847469,2.4216472665,3.5998789986
H,0,-0.9487727678,0.7445480408,3.8205990366
H,0,0.8032282199,1.0911317813,3.7582377461

```
E(ZPE)=              0.096761 E(Thermal)=              0.100635
E(CCSD(T))=        -417.502173 E(Empiric)=            -0.145887
DE(Plus)=           -0.029780 DE(2DF)=               -0.315428
E(Delta-G3XP)=      -0.494283 DE(HF)=                -0.045066
G4(0 K)=          -418.435855 G4 Energy=            -418.431981
G4 Enthalpy=      -418.431290 G4 Free Energy=       -418.456748
```

MVETS2-2carb-G4-ufg

C,0,0.1681642016,-0.2210179665,-0.1390615322
O,0,-0.1852244038,-0.1053155675,1.1603359445
O,0,0.893385297,0.127405066,1.8799974401
C,0,0.8045191928,1.4060090858,-0.3764514526
O,0,-0.2891243507,2.2435864593,-0.5937201893
C,0,-0.6915891982,3.0235877709,0.5275521836
O,0,1.5776086321,1.5759022001,0.6224658442
H,0,1.2863318124,1.2364733479,-1.3552764482
H,0,-0.703663968,-0.390893494,-0.7662473308
H,0,1.0416660087,-0.8499291799,-0.3056228907
H,0,-1.4977659855,3.6663430492,0.1699228755
H,0,-1.0619300555,2.3909057675,1.3428501363

```
H,0,0.1347858171,3.6315804613,0.9078154197
```

```
E(ZPE)=                 0.094625 E(Thermal)=              0.098864
E(CCSD(T))=           -417.483308 E(Empiric)=               -0.145887
DE(Plus)=             -0.032559 DE(2DF)=                -0.318587
E(Delta-G3XP)=            -0.493161 DE(HF)=                 -0.043383
G4(0 K)=             -418.422260 G4 Energy=             -418.418021
G4 Enthalpy=           -418.417330 G4 Free Energy=           -418.443469
```

MVETS2-2form-G4-ufg

```
C,0,0.0740268867,0.1184267663,-0.0608402636
O,0,0.0409385086,0.112101848,1.2081560489
C,0,1.9212392605,0.0227369856,-0.4790774078
O,0,2.2224357995,0.4148085682,-1.7195112001
C,0,2.3122293521,1.8268980502,-1.9607522917
O,0,2.347279208,0.8139779076,0.5194381118
O,0,1.99167872,0.2956373389,1.6921333954
H,0,2.0660698221,-1.0428756288,-0.3179083064
H,0,-0.1995124066,1.0433191086,-0.6005335346
H,0,-0.1944859451,-0.8050946607,-0.603595264
H,0,2.3599979412,1.9386064481,-3.0434901345
H,0,1.435557013,2.3482257501,-1.5652950997
H,0,3.2149498403,2.2364535178,-1.4994110538
```

```
E(ZPE)=                 0.094251 E(Thermal)=              0.098593
E(CCSD(T))=           -417.470676 E(Empiric)=               -0.145887
DE(Plus)=             -0.032900 DE(2DF)=                -0.318605
E(Delta-G3XP)=            -0.494122 DE(HF)=                 -0.043741
G4(0 K)=             -418.411679 G4 Energy=             -418.407338
G4 Enthalpy=           -418.406647 G4 Free Energy=           -418.432916
```

MVETS2-carb-pcm

```
E(RB3LYP) =  -418.641819281
```

```
Zero-point correction=                       0.096077 (Hartree/Particle)
 Thermal correction to Energy=                  0.100253
 Thermal correction to Enthalpy=                0.100944
 Thermal correction to Gibbs Free Energy=        0.074880
 Sum of electronic and zero-point Energies=          -418.545552
 Sum of electronic and thermal Energies=             -418.541376
```

```
 Sum of electronic and thermal Enthalpies=           -418.540685
 Sum of electronic and thermal Free Energies=        -418.566749

                  E (Thermal)           CV               S
                   KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total               62.910            18.642            74.973
```

```
C,0,0.1688684395,-0.2010376345,-0.1442354755
 O,0,-0.176434704,-0.0899508123,1.1694979966
 O,0,0.9146656579,0.1522086566,1.8702114428
 C,0,0.8005589198,1.3816855353,-0.3756264225
 O,0,-0.2759914687,2.2467944259,-0.5963700316
 C,0,-0.6947254909,3.0157859979,0.5267820881
 O,0,1.5846986157,1.566184791,0.6278697376
 H,0,1.2996373819,1.2269269105,-1.3470778348
 H,0,-0.7120567631,-0.3694088004,-0.7580273933
 H,0,1.0205767361,-0.8569245366,-0.3183388985
 H,0,-1.4982101363,3.6603371703,0.1669912724
 H,0,-1.0769481267,2.3752813344,1.3304382379
 H,0,0.1225239389,3.6267539619,0.9224452809
```

MVETS2-form-pcm

```
E(RB3LYP) =  -418.635207925
```

```
 Zero-point correction=                          0.095920 (Hartree/Particle)
 Thermal correction to Energy=                   0.100195
 Thermal correction to Enthalpy=                 0.100886
 Thermal correction to Gibbs Free Energy=        0.074733
 Sum of electronic and zero-point Energies=          -418.538983
 Sum of electronic and thermal Energies=             -418.534707
 Sum of electronic and thermal Enthalpies=           -418.534017
 Sum of electronic and thermal Free Energies=        -418.560169

                  E (Thermal)           CV               S
                   KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total               62.873            19.385            75.227
```

```
C,0,0.1168980811,0.1299677314,-0.0786318315
 O,0,0.0533809419,0.1087257738,1.2051184932
 C,0,1.9008312888,0.0154670277,-0.4750156516
 O,0,2.2188216629,0.4105776005,-1.7063066348
 C,0,2.29940818,1.826401164,-1.9615694966
```

```
O,0,2.3490945808,0.8057939787,0.5381434173
O,0,1.9675655125,0.2861029553,1.7009768242
H,0,2.0687342142,-1.0482941729,-0.3176367901
H,0,-0.166822142,1.0608329365,-0.5958549284
H,0,-0.1817505705,-0.783548083,-0.6172246076
H,0,2.3488142914,1.9264552516,-3.0444776683
H,0,1.417387643,2.3436837326,-1.5755527675
H,0,3.2000403163,2.2410561038,-1.5026553584
```

carbonyloxide-G4-ufg

```
C,0,-0.0282668216,0.,-0.0547487766
O,0,-0.0995434838,0.,1.2037710722
H,0,0.9739117878,0.,-0.4648152533
H,0,-0.946316756,0.,-0.634152936
O,0,-1.2951417263,0.,1.7942788937
```

```
E(ZPE)=                  0.030745 E(Thermal)=                 0.032954
E(CCSD(T))=            -189.082937 E(Empiric)=                -0.062523
DE(Plus)=               -0.019017 DE(2DF)=                   -0.135644
E(Delta-G3XP)=           -0.218832 DE(HF)=                    -0.021191
G4(0 K)=              -189.509400 G4 Energy=                -189.507191
G4 Enthalpy=            -189.506500 G4 Free Energy=            -189.526078
```

methylformate-G4-ufg

```
C,0,0.030844045,0.,0.0567202968
O,0,0.1657628916,0.,1.2491495013
H,0,0.8512053453,0.,-0.6774734942
O,0,-1.1348062503,0.,-0.602422082
C,0,-2.3075371433,0.,0.2274424695
H,0,-3.1549314881,0.,-0.457352174
H,0,-2.3268937,-0.888594505,0.8630737414
H,0,-2.3268937,0.888594505,0.8630737414
```

```
E(ZPE)=                  0.061040 E(Thermal)=                 0.064030
E(CCSD(T))=            -228.438336 E(Empiric)=                -0.083364
DE(Plus)=               -0.016799 DE(2DF)=                   -0.176994
E(Delta-G3XP)=           -0.278716 DE(HF)=                    -0.023254
G4(0 K)=              -228.956424 G4 Energy=                -228.953433
G4 Enthalpy=            -228.952742 G4 Free Energy=            -228.974916
```

minorpdtfromMVE-G4-ufg

C,0,0.069929,0.118677,-0.071641
O,0,0.031973,0.155732,1.370447
C,0,1.14331,-0.131326,2.00314
O,0,2.195917,-0.426706,1.391829
O,0,3.313371,-0.712936,2.187547
H,0,1.12467,-0.104838,3.087901
H,0,0.802407,0.837933,-0.445375
H,0,0.336222,-0.884239,-0.413381
H,0,-0.935107,0.384768,-0.393597

```
E(ZPE)=                0.063777 E(Thermal)=               0.067291
E(CCSD(T))=          -303.309171 E(Empiric)=                -0.104205
DE(Plus)=             -0.028516 DE(2DF)=                 -0.224888
E(Delta-G3XP)=          -0.357785 DE(HF)=                   -0.032488
G4(0 K)=           -303.993277 G4 Energy=              -303.989763
G4 Enthalpy=          -303.989073 G4 Free Energy=           -304.012773
```

formaldehyde-G4-ufg

C,0,0.,0.,0.031028
O,0,0.,0.,1.231002
H,0,0.937094,0.,-0.565515
H,0,-0.937094,0.,-0.565515

```
E(ZPE)=                0.026215 E(Thermal)=               0.028291
E(CCSD(T))=          -114.189969 E(Empiric)=                -0.041682
DE(Plus)=             -0.009370 DE(2DF)=                 -0.086551
E(Delta-G3XP)=          -0.139977 DE(HF)=                   -0.011858
G4(0 K)=           -114.453193 G4 Energy=              -114.451117
G4 Enthalpy=          -114.450426 G4 Free Energy=           -114.467692
```

EVETS1-endotrans-G4-ufg

C,0,2.5431337579,-0.3698970261,-0.2136616241
C,0,1.3382169426,0.2415010363,-0.370659696
O,0,0.217766341,-0.4849954199,-0.3813500712
C,0,-1.007249209,0.255833781,-0.2723443284
C,0,-2.1620247178,-0.7236175732,-0.3348101686
O,0,2.6140095377,-0.5132170318,2.0497032317
O,0,1.423280913,-0.1501678092,2.3502018409
O,0,1.1421909495,1.054608632,1.9703230338

```
H,0,1.2416137818,1.3078022427,-0.5507359831
H,0,3.4511763496,0.2108586006,-0.2763492885
H,0,2.6145165536,-1.4489334124,-0.2110761276
H,0,-0.9822674409,0.8027381297,0.6781725007
H,0,-1.058190796,0.9866141654,-1.0910786365
H,0,-3.1094859556,-0.1848596478,-0.2436237888
H,0,-2.1624581407,-1.268206458,-1.2830133519
H,0,-2.0960888666,-1.4479322091,0.4813184576
```

```
E(ZPE)=             0.120723 E(Thermal)=             0.126341
E(CCSD(T))=      -456.594867 E(Empiric)=            -0.166728
DE(Plus)=          -0.036412 DE(2DF)=               -0.358078
E(Delta-G3XP)=     -0.550605 DE(HF)=                -0.049266
G4(0 K)=         -457.635232 G4 Energy=           -457.629614
G4 Enthalpy=     -457.628924 G4 Free Energy=      -457.658634
```

EVEPOZ-endotrans-G4-ufg

```
O,0,1.1512887984,-1.7195707943,0.9965787627
O,0,2.0199223172,-0.61982737,0.6310884583
O,0,1.3329408822,-0.0862467164,-0.5032319903
C,0,0.0112781678,0.0486754354,-0.0048096271
C,0,-0.1319809427,-1.1122282575,1.0125486609
O,0,-0.5001506073,-0.5679150562,2.2305429312
C,0,-0.7345453942,-1.5296885325,3.2597664491
H,0,-0.8175895381,-1.9143882925,0.7041830088
C,0,-1.1833586499,-0.789448597,4.5062009653
H,0,-1.5056172198,-2.2423955614,2.9258168965
H,0,0.1848995813,-2.0978905521,3.4479108155
H,0,-0.6641865938,-0.0323606563,-0.858424617
H,0,-0.1347886663,0.9928227479,0.529311638
H,0,-1.3730556399,-1.4984229077,5.3173361697
H,0,-0.4118390228,-0.0869896826,4.8329764024
H,0,-2.1014944722,-0.2273282066,4.313643076
```

```
E(ZPE)=             0.125314 E(Thermal)=             0.130210
E(CCSD(T))=      -456.695980 E(Empiric)=            -0.166728
DE(Plus)=          -0.032295 DE(2DF)=               -0.355486
E(Delta-G3XP)=     -0.551817 DE(HF)=                -0.048727
G4(0 K)=         -457.725719 G4 Energy=           -457.720822
G4 Enthalpy=     -457.720131 G4 Free Energy=      -457.748242
```

EVE3TS2-2carb-G4-ufg

```
C,0,-0.6907612757,3.0170991003,0.5225806071
O,0,-0.2786860473,2.218433228,-0.5915458697
C,0,0.8163901011,1.3862916264,-0.3703485134
O,0,1.5867780409,1.5574156959,0.6315540301
C,0,0.1879935732,-0.2434141925,-0.1366879301
O,0,-0.1726250417,-0.1304918205,1.1610189578
O,0,0.9019518504,0.1067258867,1.8860620763
H,0,1.3046568183,1.2175726411,-1.3465031027
H,0,-0.6798047129,-0.4176028365,-0.7683127775
H,0,1.0651739677,-0.8683208841,-0.2989946328
C,0,-1.8335099241,3.9000203423,0.0549764221
H,0,-1.0055928417,2.365947781,1.3483578071
H,0,0.1566747812,3.6107244399,0.8834181485
H,0,-2.1808726462,4.5301668575,0.8791379256
H,0,-1.5113458503,4.5486899352,-0.7646349811
H,0,-2.6752257929,3.2964111994,-0.2968371673
```

```
E(ZPE)=             0.122432 E(Thermal)=             0.127433
E(CCSD(T))=        -456.670414 E(Empiric)=             -0.166728
DE(Plus)=          -0.034219 DE(2DF)=               -0.357651
E(Delta-G3XP)=        -0.551436 DE(HF)=                -0.047194
G4(0 K)=          -457.705211 G4 Energy=            -457.700210
G4 Enthalpy=        -457.699519 G4 Free Energy=          -457.727844
```

EVE2TS2-2carb-G4-ufg

```
C,0,-0.5235218544,2.9888651518,0.6616294188
O,0,-0.1033625067,2.2315565182,-0.4828520037
C,0,0.8819927344,1.2719427171,-0.2642465006
O,0,1.5734530868,1.2601527781,0.8084736338
C,0,0.0823083194,-0.2980163289,-0.2519886031
O,0,-0.3858506944,-0.2670258998,1.0154877698
O,0,0.6344533645,-0.2094344546,1.8485029787
H,0,1.439078812,1.1429631841,-1.2090947534
H,0,-0.7355322885,-0.3209608863,-0.9681568756
H,0,0.9064579312,-0.9940190552,-0.4029966745
H,0,-1.553211135,3.2843519702,0.4395803387
H,0,-0.5306744766,2.3496739602,1.5492422807
C,0,0.3555463533,4.2128363385,0.8886942456
H,0,-0.0462859107,4.8143511931,1.7109653646
H,0,1.3738100362,3.913252393,1.1469596194
```

```
H,0,0.3876342287,4.8355054204,-0.0103132391
```

```
E(ZPE)=              0.122626 E(Thermal)=             0.127538
E(CCSD(T))=        -456.670302 E(Empiric)=              -0.166728
DE(Plus)=           -0.033573 DE(2DF)=                -0.357789
E(Delta-G3XP)=        -0.551370 DE(HF)=                  -0.047166
G4(0 K)=          -457.704302 G4 Energy=            -457.699390
G4 Enthalpy=        -457.698700 G4 Free Energy=           -457.726729
```

EVE3TS2-2form-G4-ufg

```
C,0,0.0725669257,0.1077651275,-0.0475084552
O,0,0.0289234191,0.1088580317,1.2217657522
C,0,1.919451527,0.0151022124,-0.4522622409
O,0,2.3366470468,0.8148755146,0.545528971
O,0,1.9732121633,0.3018327572,1.7180036503
O,0,2.2290327065,0.3974602093,-1.6920934449
C,0,2.3143645813,1.8166740552,-1.9581999892
H,0,2.0669033572,-1.0484807511,-0.2785179702
H,0,-0.2013092814,1.02841784,-0.5943088915
H,0,-0.1910926859,-0.8197176898,-0.5859927045
C,0,2.3648110071,1.9971123716,-3.4617835969
H,0,1.447213587,2.31770411,-1.5142211641
H,0,3.2143575462,2.2076864019,-1.4721792909
H,0,2.45500632,3.0604200674,-3.7012031659
H,0,3.2254934281,1.473190493,-3.8858741766
H,0,1.456619352,1.6108702492,-3.931973283
```

```
E(ZPE)=              0.122038 E(Thermal)=             0.127149
E(CCSD(T))=        -456.658528 E(Empiric)=              -0.166728
DE(Plus)=           -0.034650 DE(2DF)=                -0.357712
E(Delta-G3XP)=        -0.552338 DE(HF)=                  -0.047563
G4(0 K)=          -457.695480 G4 Energy=            -457.690369
G4 Enthalpy=        -457.689678 G4 Free Energy=           -457.718141
```

EVE2TS2-2form-G4-ufg

```
C,0,0.0073001471,0.0405875016,-0.14509089
O,0,-0.1645624481,-0.0064201565,1.1114036618
C,0,1.8918340919,0.006701414,-0.3643957036
O,0,2.1824254518,0.7824973261,0.6965481085
O,0,1.715245506,0.2240457494,1.8103935903
```

O,0,2.309291951,0.4329559581,-1.5562146872
C,0,2.3289124273,1.8591379827,-1.8138495247
H,0,2.0510634207,-1.0576915168,-0.2071991505
H,0,-0.2329387647,0.9736285482,-0.6865026133
H,0,-0.1703638252,-0.8729738368,-0.7398495764
H,0,2.062069116,1.9513817522,-2.8693389997
H,0,1.5572802662,2.3459574562,-1.2106644539
C,0,3.7034541568,2.4492427566,-1.5398518737
H,0,3.7101290963,3.5043331908,-1.8310609161
H,0,3.9571618725,2.3834603039,-0.4796018676
H,0,4.4688575345,1.9271745702,-2.1203131041

```
E(ZPE)=                0.122153 E(Thermal)=               0.127213
E(CCSD(T))=          -456.657988 E(Empiric)=              -0.166728
DE(Plus)=             -0.034928 DE(2DF)=                  -0.357930
E(Delta-G3XP)=         -0.551788 DE(HF)=                   -0.047524
G4(0 K)=             -457.694734 G4 Energy=              -457.689673
G4 Enthalpy=          -457.688982 G4 Free Energy=          -457.717236
```

BVETS1-endotrans-G4-ufg

C,0,2.5926571438,-0.363080922,-0.2101078329
C,0,1.3887955088,0.2507976348,-0.3649730268
O,0,0.2673981467,-0.4736924239,-0.3803020334
C,0,-0.9571463365,0.2671881074,-0.2738385019
C,0,-2.1182782594,-0.7097449505,-0.3359906436
O,0,2.6580746398,-0.5220462191,2.0546827053
O,0,1.4680341733,-0.156450219,2.3546346661
O,0,1.1922529942,1.0518698196,1.9825468674
H,0,1.2937094762,1.3183318842,-0.5383499677
H,0,3.5015342785,0.216943654,-0.2672504818
H,0,2.6626381873,-1.4422055505,-0.2133738395
H,0,-0.9351658588,0.8162064482,0.6763176906
H,0,-1.0088215278,0.9976521409,-1.0937971326
C,0,-3.4750361617,-0.005636034,-0.2215465408
H,0,-2.0632474199,-1.2705604589,-1.2770320016
H,0,-2.0047293444,-1.4409752206,0.4731495971
C,0,-4.653742168,-0.9810678202,-0.2752153856
H,0,-3.5119749655,0.5632021822,0.7164907555
H,0,-3.5732434332,0.7321072227,-1.0288741343
H,0,-5.6089534883,-0.4541238912,-0.1918955739
H,0,-4.6618359562,-1.5405886845,-1.2169793875
H,0,-4.6015046292,-1.7090846996,0.5415102018

E(ZPE)= 0.176702 E(Thermal)= 0.183971
E(CCSD(T))= -534.958243 E(Empiric)= -0.208410
DE(Plus)= -0.040053 DE(2DF)= -0.437114
E(Delta-G3XP)= -0.667281 DE(HF)= -0.056989
G4(0 K)= -536.191388 G4 Energy= -536.184119
G4 Enthalpy= -536.183428 G4 Free Energy= -536.217613

BVEPOZ-endotrans-G4-ufg

C,0,-0.1154588406,-1.1077407898,0.9645169572
O,0,1.1690475919,-1.7128139394,0.9484428938
O,0,2.0361145143,-0.6107489372,0.5866258527
O,0,1.3495178205,-0.0755381729,-0.5473035819
C,0,0.0269369244,0.055539108,-0.050239209
O,0,-0.4857545301,-0.5667323502,2.1830931639
C,0,-0.7210246664,-1.5297329167,3.2102888199
C,0,-1.1716666418,-0.7948412778,4.4630270953
H,0,-0.7991819313,-1.9105781464,0.6537983721
H,0,-1.4928268788,-2.2427144224,2.8761910525
H,0,0.1980041995,-2.099626765,3.3995934173
H,0,-0.647255608,-0.0250872344,-0.9049153833
H,0,-0.1218042754,0.9982568513,0.4856848718
C,0,-1.4517387758,-1.7435404542,5.633331767
H,0,-0.3951826896,-0.0723792426,4.7420768579
H,0,-2.0704971001,-0.2119082108,4.2269331224
C,0,-1.9003975502,-1.007971377,6.8988806313
H,0,-2.2217181268,-2.4692469209,5.3395890849
H,0,-0.5494510589,-2.3298187535,5.8510329013
H,0,-2.0934941291,-1.7071453131,7.7181317231
H,0,-1.1353135302,-0.3006156733,7.236907571
H,0,-2.8199947176,-0.4396850617,6.7211870188

E(ZPE)= 0.181261 E(Thermal)= 0.187816
E(CCSD(T))= -535.059312 E(Empiric)= -0.208410
DE(Plus)= -0.035917 DE(2DF)= -0.434495
E(Delta-G3XP)= -0.668459 DE(HF)= -0.056464
G4(0 K)= -536.281796 G4 Energy= -536.275242
G4 Enthalpy= -536.274551 G4 Free Energy= -536.307148

BVE3TS2-2carb-G4-ufg

C,0,-1.8140617177,3.8580389435,0.0495251362
C,0,-0.6624304005,2.9783235019,0.511322011
O,0,-0.252542545,2.1766388152,-0.6005529977
C,0,0.8460875462,1.3487969303,-0.3818251374
C,0,0.2242094953,-0.2817442097,-0.1407287142
O,0,-0.1303535128,-0.1668865183,1.1585543739
O,0,0.9471003235,0.0759292403,1.8775254328
O,0,1.6206625913,1.5254170655,0.6160130863
H,0,1.3308805956,1.1791022043,-1.3595802255
H,0,-0.6462135057,-0.4602457355,-0.7675213867
H,0,1.102348295,-0.9046000229,-0.3058178611
H,0,-0.9711198808,2.330658672,1.3431491614
H,0,0.183607324,3.5789152739,0.8663140913
C,0,-2.3363638432,4.7704375161,1.1644843231
H,0,-1.4781014283,4.4615388922,-0.8028622104
H,0,-2.6249116067,3.2191413429,-0.3224345412
C,0,-3.495850282,5.6606521668,0.7095696078
H,0,-2.6575506669,4.1575107902,2.0168473702
H,0,-1.5158767998,5.3984188594,1.5354510886
H,0,-3.8493990723,6.3012781684,1.523272423
H,0,-3.1941255697,6.3102555375,-0.1194609528
H,0,-4.3447653395,5.0596025663,0.3653449214

```
E(ZPE)=                 0.178396 E(Thermal)=                0.185037
E(CCSD(T))=           -535.033792 E(Empiric)=                 -0.208410
DE(Plus)=              -0.037780 DE(2DF)=                  -0.436684
E(Delta-G3XP)=            -0.668085 DE(HF)=                    -0.054923
G4(0 K)=              -536.261278 G4 Energy=               -536.254637
G4 Enthalpy=            -536.253946 G4 Free Energy=            -536.286705
```

BVE2TS2-2carb-G4-ufg

C,0,0.3413661592,4.184878733,0.8589070839
C,0,-0.5210330052,2.9451033904,0.6334910374
O,0,-0.0903166436,2.1881229444,-0.5061799515
C,0,0.8868201701,1.2223689304,-0.2777611455
C,0,0.0783065182,-0.3421036333,-0.271400241
O,0,-0.4009122791,-0.3080959655,0.992029471
O,0,0.612476115,-0.2558143595,1.8338348906
O,0,1.5692609919,1.2075179293,0.80084112
H,0,1.4516919792,1.0899879626,-1.2174810001

```
H,0,-0.7334403966,-0.3609878306,-0.9946011165
H,0,0.8994145213,-1.0433213696,-0.4148125046
H,0,-1.5549946097,3.2295213025,0.4121980745
H,0,-0.5207256769,2.311589136,1.5259417438
C,0,-0.1788141968,5.0519432323,2.0107184056
H,0,1.3689137763,3.8667099174,1.0669391577
H,0,0.3672652182,4.7688574758,-0.0698368278
C,0,0.6721470041,6.3031013993,2.2448912391
H,0,-1.2165527029,5.3482968873,1.8061283544
H,0,-0.2094097704,4.4534004369,2.9304823844
H,0,0.2809247012,6.9026797714,3.0727176371
H,0,1.7070448015,6.0365804099,2.4855096075
H,0,0.6939523251,6.9393322997,1.35314558
```

```
E(ZPE)=               0.178632 E(Thermal)=               0.185181
E(CCSD(T))=           -535.033898 E(Empiric)=             -0.208410
DE(Plus)=             -0.037348 DE(2DF)=                 -0.436908
E(Delta-G3XP)=           -0.667938 DE(HF)=                  -0.054894
G4(0 K)=              -536.260764 G4 Energy=              -536.254215
G4 Enthalpy=          -536.253524 G4 Free Energy=            -536.285997
```

BVE3TS2-2form-G4-ufg

```
C,0,0.063261456,0.0844237169,-0.0184160536
O,0,0.0111131577,0.0860636001,1.2507273296
C,0,1.9111976218,-0.0136153781,-0.4116511257
O,0,2.2295196763,0.367262917,-1.6492978209
C,0,2.3183812155,1.7853561732,-1.9178241265
C,0,2.3639562684,1.9702847311,-3.4244649717
O,0,2.3249127338,0.7850820715,0.5889295473
O,0,1.9522560859,0.2732384036,1.7590705807
H,0,2.0550463565,-1.0775114429,-0.2364407446
H,0,-0.2045958353,1.0056216139,-0.5671588514
H,0,-0.2001862007,-0.8424173832,-0.5581220203
H,0,1.4548677814,2.2920505736,-1.4715765712
H,0,3.2221591646,2.1753759373,-1.4363112269
C,0,2.5007519168,3.4449052874,-3.8212260176
H,0,3.2057916262,1.393278863,-3.8256353501
H,0,1.4534216395,1.544524151,-3.8629290195
C,0,2.549125007,3.6449244213,-5.3382390464
H,0,1.6614712688,4.0153944452,-3.4026185255
H,0,3.4087956484,3.8619268235,-3.3668281212
H,0,2.6473569789,4.7038157439,-5.5945712189
```

```
H,0,3.3989313829,3.1137752918,-5.7803601621
H,0,1.6382670498,3.2685854391,-5.8162264837
```

```
E(ZPE)=                0.178026 E(Thermal)=               0.184787
E(CCSD(T))=         -535.022031 E(Empiric)=              -0.208410
DE(Plus)=             -0.038336 DE(2DF)=                 -0.436761
E(Delta-G3XP)=        -0.668910 DE(HF)=                  -0.055290
G4(0 K)=            -536.251712 G4 Energy=             -536.244951
G4 Enthalpy=        -536.244260 G4 Free Energy=        -536.277194
```

BVE2TS2-2form-G4-ufg

```
C,0,-0.0666810887,0.0395193799,-0.1346060078
O,0,-0.2666847868,0.0128003569,1.1183702919
C,0,1.821522502,-0.0165728645,-0.3112621827
O,0,2.2690750878,0.3852774255,-1.500432229
C,0,2.3042347645,1.8077122462,-1.7849847223
C,0,3.683315774,2.4013794265,-1.5206945762
O,0,2.0967154654,0.7729609369,0.7438619943
O,0,1.5997168605,0.2358867195,1.8553024222
H,0,1.9661153248,-1.0797838739,-0.1329139605
H,0,-0.2854018635,0.9667257534,-0.6947181908
H,0,-0.2404915725,-0.8810326489,-0.7196861263
H,0,2.0421624228,1.8812599216,-2.8443167044
H,0,1.5357441429,2.3118923338,-1.1924598289
H,0,3.6147664592,3.4767462127,-1.7335748938
H,0,3.9153425586,2.3121023328,-0.4534604262
C,0,4.7993307532,1.7731986558,-2.3630434619
C,0,6.1707658803,2.3916395131,-2.0814618523
H,0,4.8315145463,0.6950751688,-2.1697854474
H,0,4.5546705398,1.8857150566,-3.4277505971
H,0,6.9487528906,1.9268651835,-2.6944000751
H,0,6.1743497593,3.4660225938,-2.296468709
H,0,6.4540335795,2.2644731698,-1.0309247167
```

```
E(ZPE)=                0.178166 E(Thermal)=               0.184811
E(CCSD(T))=         -535.022141 E(Empiric)=              -0.208410
DE(Plus)=             -0.038583 DE(2DF)=                 -0.437146
E(Delta-G3XP)=        -0.668014 DE(HF)=                  -0.055182
G4(0 K)=            -536.251310 G4 Energy=             -536.244665
G4 Enthalpy=        -536.243974 G4 Free Energy=        -536.276593
```

OVETS1-endotrans-b3lypGTBas3-ufg

E(RB3LYP) = -693.790495877

```
Zero-point correction=                           0.292738 (Hartree/Particle)
Thermal correction to Energy=                    0.303233
Thermal correction to Enthalpy=                  0.303924
Thermal correction to Gibbs Free Energy=         0.261165
Sum of electronic and zero-point Energies=          -693.497758
Sum of electronic and thermal Energies=             -693.487263
Sum of electronic and thermal Enthalpies=           -693.486572
Sum of electronic and thermal Free Energies=        -693.529330
                 E (Thermal)             CV                S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               190.281             47.529            122.994
```

```
C,0,2.7410330278,-0.3557531555,-0.2062811383
C,0,1.5396593714,0.2634073719,-0.3593184065
O,0,0.4156506212,-0.4566877563,-0.3787372877
C,0,-0.8066937514,0.2881601934,-0.270982089
C,0,-1.9709873875,-0.6849957391,-0.3353621048
O,0,2.8006718788,-0.5284401758,2.0585287958
O,0,1.6119768372,-0.1580496653,2.3579277416
O,0,1.3436506832,1.0539294878,1.9924444883
H,0,1.448737647,1.332175937,-0.5272794897
H,0,3.652182449,0.221125902,-0.25912811
H,0,2.8069869447,-1.4351012061,-0.2149496012
H,0,-0.7830347108,0.8350147341,0.6803372372
H,0,-0.8555685705,1.0203919595,-1.0894790604
C,0,-3.3250395691,0.0239280516,-0.2201439986
H,0,-1.9166179244,-1.24400954,-1.2773953953
H,0,-1.8593238608,-1.4176891055,0.4725840125
C,0,-4.5140146465,-0.9416951021,-0.2736466665
H,0,-3.3612099831,0.592954219,0.7188529693
H,0,-3.4222061299,0.7635834718,-1.0270615495
C,0,-5.8720381851,-0.2411930164,-0.1598186021
H,0,-4.4756885326,-1.5121925167,-1.2119571525
H,0,-4.4163814035,-1.6807192349,0.5334150699
C,0,-7.0621112865,-1.2049032743,-0.2125178774
H,0,-5.908263206,0.3299176331,0.7784296846
H,0,-5.9677850154,0.4987893599,-0.9668295068
C,0,-8.4212271049,-0.5059854157,-0.0988921299
H,0,-7.0259589083,-1.7767164706,-1.1505655873
```

```
H,0,-6.9666885706,-1.9450554774,0.594417232
C,0,-9.6046731201,-1.4758644734,-0.1524945391
H,0,-8.4568214459,0.064544995,0.8387551254
H,0,-8.5159934476,0.2332598129,-0.9054734692
H,0,-10.5597297185,-0.9477854796,-0.0688814671
H,0,-9.6154121808,-2.0358079745,-1.0943744087
H,0,-9.5555618007,-2.2057863497,0.663310281
```

OVEPOZ-endotrans-b3lypGTBas3-ufg

```
E(RB3LYP) =  -693.881046375

Zero-point correction=                           0.297371 (Hartree/Particle)
Thermal correction to Energy=                    0.307158
Thermal correction to Enthalpy=                  0.307849
Thermal correction to Gibbs Free Energy=         0.266654
Sum of electronic and zero-point Energies=           -693.583676
Sum of electronic and thermal Energies=              -693.573888
Sum of electronic and thermal Enthalpies=            -693.573197
Sum of electronic and thermal Free Energies=         -693.614392
                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             192.745             44.551            118.496
```

```
C,0,-0.0685246277,-1.0889595972,0.821831538
O,0,1.2176522022,-1.6907313687,0.8058692232
O,0,2.0822962505,-0.5855036287,0.4482861225
O,0,1.3959794031,-0.0490613629,-0.6853169644
C,0,0.0722614984,0.0770931721,-0.1899725992
O,0,-0.4417473644,-0.5519116247,2.0411384213
C,0,-0.6766219406,-1.518024162,3.0657683593
C,0,-1.1298392527,-0.7870583501,4.3200088895
H,0,-0.7496878299,-1.8928534912,0.5082165766
H,0,-1.4468525212,-2.231316386,2.7288344445
H,0,0.2431693113,-2.0868088327,3.2545072566
H,0,-0.6003742692,-0.0034385339,-1.0458900519
H,0,-0.0800068256,1.018136429,0.3479003069
C,0,-1.4095442971,-1.7400708664,5.4867764718
H,0,-0.354435374,-0.0644085719,4.6011727656
H,0,-2.0290511457,-0.2049956647,4.0837216832
C,0,-1.8604068137,-1.0162786469,6.7602898977
H,0,-2.1793901705,-2.4665751792,5.1913066319
H,0,-0.5067525748,-2.3274197071,5.7040271445
```

C,0,-2.1419921364,-1.9630368121,7.9317374293
H,0,-1.0904719145,-0.2902326043,7.055705599
H,0,-2.7624708069,-0.4277267089,6.5426970674
C,0,-2.5919581019,-1.2411255155,9.2061550843
H,0,-2.9116066084,-2.6893807713,7.6347788471
H,0,-1.2394753089,-2.5519852452,8.1473593294
C,0,-2.8739081812,-2.1868423981,10.3786308697
H,0,-1.8225380198,-0.5147050109,9.5035485799
H,0,-3.4944331802,-0.6516242296,8.9910488051
C,0,-3.3225975811,-1.4574820356,11.6478137059
H,0,-3.6430484615,-2.9120679716,10.0810768071
H,0,-1.9717996849,-2.7751524604,10.5932812657
H,0,-3.5159369605,-2.1584528796,12.4659207485
H,0,-2.558277547,-0.7503532518,11.9892024081
H,0,-4.2424591653,-0.8881467318,11.4731003358

OVE3TS2-2carb-b3lypGTBas3-ufg

E(RB3LYP) = -693.856664258

```
Zero-point correction=                     0.294439 (Hartree/Particle)
Thermal correction to Energy=                 0.304315
Thermal correction to Enthalpy=                0.305006
Thermal correction to Gibbs Free Energy=         0.263601
Sum of electronic and zero-point Energies=          -693.562225
Sum of electronic and thermal Energies=             -693.552349
Sum of electronic and thermal Enthalpies=           -693.551658
Sum of electronic and thermal Free Energies=         -693.593064
                E (Thermal)           CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              190.961            45.168          119.102
```

C,0,-3.4148921467,5.5388687574,0.6965117432
C,0,-2.2452714398,4.6524444762,1.138048753
C,0,-1.725920694,3.7400347963,0.0218298549
C,0,-0.5669023596,2.8672452197,0.4787015503
O,0,-0.1579647712,2.067122182,-0.6348440911
C,0,0.9453897401,1.2444682811,-0.4210421512
O,0,1.7228845504,1.4237710164,0.5741249743
C,0,0.3324128508,-0.3891967507,-0.1794907532
O,0,-0.0179743164,-0.2775111998,1.12121874
O,0,1.0609658385,-0.0302062234,1.8364734187
H,0,1.4275371547,1.0781344951,-1.4007093215

```
H,0,-0.5393951613,-0.5712955577,-0.8033249982
H,0,1.2129157021,-1.0076739868,-0.34844193
H,0,-0.8676287556,2.2183507958,1.3124322101
H,0,0.2775276983,3.4728637882,0.8289224171
H,0,-1.3976052541,4.3424770201,-0.834131659
H,0,-2.5352374824,3.0955483952,-0.3434346191
H,0,-2.5572499082,4.0408215426,1.9959077047
H,0,-1.4259549178,5.2874553298,1.5022203015
C,0,-3.938273824,6.4557963205,1.8070649724
H,0,-3.103032524,6.1491541768,-0.1624701238
H,0,-4.2343924574,4.9033244347,0.3329683233
C,0,-5.1083122271,7.3420638272,1.3673964753
H,0,-4.248349759,5.8447280106,2.6663563437
H,0,-3.1179762786,7.0908432841,2.1699922065
C,0,-5.6322203529,8.2601991428,2.4769559962
H,0,-4.7988743162,7.953095653,0.5076472659
H,0,-5.9292605872,6.7073830649,1.0047005973
C,0,-6.8012071328,9.1418375698,2.0293575153
H,0,-5.9414391181,7.6492936012,3.3355510926
H,0,-4.8119116969,8.8946008289,2.8383603759
H,0,-7.1525467054,9.7851881145,2.8422370284
H,0,-6.5115923893,9.7893727136,1.1940903284
H,0,-7.6499459592,8.5344758798,1.695261458
```

OVE2TS2-2carb-b3lypGTBas3-ufg

E(RB3LYP) = -693.856181080

```
Zero-point correction=                           0.294706 (Hartree/Particle)
Thermal correction to Energy=                    0.304478
Thermal correction to Enthalpy=                  0.305169
Thermal correction to Gibbs Free Energy=         0.264065
Sum of electronic and zero-point Energies=          -693.561475
Sum of electronic and thermal Energies=             -693.551703
Sum of electronic and thermal Enthalpies=           -693.551012
Sum of electronic and thermal Free Energies=        -693.592116
                 E (Thermal)             CV                S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               191.063             44.972           118.236
```

```
C,0,0.6513318131,6.1778954912,2.178541611
C,0,-0.194832886,4.9236077731,1.9339095965
C,0,0.3293436078,4.0569601166,0.7837040926
```

```
C,0,-0.5328386395,2.8173412307,0.5557977837
O,0,-0.0976498977,2.0590966826,-0.5814994832
C,0,0.8767551322,1.091884874,-0.3479910965
O,0,1.5548040965,1.0769141027,0.7334485817
C,0,0.0655479153,-0.4710616993,-0.3434174384
O,0,-0.418535266,-0.4353229886,0.9181314675
O,0,0.5917115229,-0.3840110565,1.7637866089
H,0,1.4453742741,0.9576350019,-1.2851901164
H,0,-0.743439218,-0.4890578496,-1.0697263139
H,0,0.8859057322,-1.1739077528,-0.4831208742
H,0,-1.5657396871,3.1019673046,0.3299755768
H,0,-0.5364153186,2.1845645595,1.4487262717
H,0,1.3558224326,3.7376672032,0.9947719761
H,0,0.3581131454,4.6401650014,-0.1453039025
H,0,-1.2325271594,5.2215473453,1.7265618641
H,0,-0.2295918457,4.3252475474,2.8547092323
C,0,0.1338345563,7.0484277158,3.3285270018
H,0,1.6881726119,5.8794700323,2.3858812863
H,0,0.687836259,6.7760338057,1.2573439338
C,0,0.9792047888,8.3025283208,3.5742173787
H,0,-0.9040032164,7.3451236603,3.1209849356
H,0,0.0972040106,6.4491590155,4.2490697457
C,0,0.4626150629,9.1743617607,4.7238342035
H,0,2.0170648146,8.0064216374,3.7823755082
H,0,1.0168868935,8.9021205005,2.6536543883
C,0,1.312964119,10.4250295174,4.9624720963
H,0,-0.574238208,9.4702864499,4.5152984901
H,0,0.4258419589,8.5751112702,5.6433674726
H,0,0.9194362513,11.0262703099,5.7882079789
H,0,2.3474096015,10.1594360767,5.2078529217
H,0,1.3399237421,11.0615200395,4.0708162208
```

OVE3TS2-2form-b3lypGTBas3-ufg

```
E(RB3LYP) =  -693.849034499

Zero-point correction=                           0.294104 (Hartree/Particle)
Thermal correction to Energy=                    0.304090
Thermal correction to Enthalpy=                  0.304781
Thermal correction to Gibbs Free Energy=         0.263266
Sum of electronic and zero-point Energies=          -693.554930
Sum of electronic and thermal Energies=             -693.544944
Sum of electronic and thermal Enthalpies=           -693.544253
```

```
Sum of electronic and thermal Free Energies=         -693.585769
                 E (Thermal)            CV              S
                  KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              190.820             45.876           119.419
```

C,0,0.0434847907,-0.0098917763,0.0933471333
O,0,-0.0070218441,-0.0132395624,1.362638316
C,0,1.8901211711,-0.1120959751,-0.3028896713
O,0,2.3077350126,0.6815612677,0.7002786635
O,0,1.935087,0.1662328148,1.8688998237
O,0,2.2079776747,0.2722845182,-1.539439042
C,0,2.3000619312,1.6912954335,-1.8036575497
C,0,2.3459623272,1.8808770893,-3.3097747062
C,0,2.485276367,3.3566155148,-3.7009663653
C,0,2.5364928091,3.5708663211,-5.2177774826
H,0,2.0311620464,-1.1770476119,-0.1317002763
H,0,-0.222438299,0.9143054691,-0.4512430669
H,0,-0.2237521487,-0.9337238244,-0.4496478081
H,0,1.4376895694,2.1983545736,-1.355653643
H,0,3.2047528061,2.0775511532,-1.3209160525
H,0,3.1868262954,1.3033796368,-3.7120210326
H,0,1.434645463,1.4577265358,-3.7488925159
H,0,1.6461591675,3.9284650218,-3.2815571018
H,0,3.3938994397,3.7723173627,-3.2443669687
C,0,2.6761111821,5.0431867385,-5.618600121
H,0,3.3753207702,2.9977726518,-5.6361900508
H,0,1.6280257107,3.1534828634,-5.6734406223
C,0,2.7278204306,5.2600319562,-7.1345458379
H,0,1.8371673475,5.6150452912,-5.1980008622
H,0,3.5842616029,5.4594827581,-5.160650253
C,0,2.8674600187,6.7320480799,-7.537354794
H,0,3.5666434721,4.6878931948,-7.5554393732
H,0,1.8197809567,4.8434014388,-7.5928033759
C,0,2.9185543758,6.9400820039,-9.0533017432
H,0,2.0288646945,7.3028447453,-7.1167978317
H,0,3.7749340757,7.1474571793,-7.07925702
H,0,3.0183661869,7.9995832082,-9.3089249862
H,0,3.7680231231,6.409191457,-9.4974705839
H,0,2.008404473,6.5658524716,-9.5352821985

OVE2TS2-2form-b3lypGTBas3-ufg

E(RB3LYP) = -693.848387377

```
Zero-point correction=                           0.294288 (Hartree/Particle)
Thermal correction to Energy=                    0.304127
Thermal correction to Enthalpy=                  0.304818
Thermal correction to Gibbs Free Energy=         0.263668
Sum of electronic and zero-point Energies=          -693.554100
Sum of electronic and thermal Energies=             -693.544260
Sum of electronic and thermal Enthalpies=           -693.543569
Sum of electronic and thermal Free Energies=        -693.584719
                  E (Thermal)            CV                S
                   KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               190.843            45.574           118.368
```

```
C,0,-0.2597428591,0.0769588883,-0.0949685985
O,0,-0.4727160023,0.07077311,1.1562205723
C,0,1.628348224,-0.0162650759,-0.2518626109
O,0,1.9078015536,0.7820727025,0.7956745882
O,0,1.3898583743,0.2689796822,1.9088807047
O,0,2.0950224985,0.3610539819,-1.4415931666
C,0,2.1594980872,1.7786253862,-1.7451308275
C,0,3.5465617458,2.3507074381,-1.4745370328
C,0,4.6592699105,1.6918389091,-2.2972250253
C,0,6.0436643132,2.284915218,-2.0155868888
H,0,1.7515050615,-1.0794507732,-0.0578604355
H,0,-0.45583873,1.000383753,-0.6694989795
H,0,-0.4450474563,-0.8480163634,-0.6694525076
H,0,1.9093867928,1.8423528862,-2.8079371995
H,0,1.3946974742,2.304811362,-1.1670726709
H,0,3.4986448519,3.4241817983,-1.7017970199
H,0,3.7652842117,2.2711542956,-0.4038292553
H,0,4.671844336,0.6149348736,-2.0902185215
H,0,4.4282689375,1.7938358447,-3.3669597363
C,0,7.1624531599,1.6310967146,-2.833565615
H,0,6.0263129806,3.3646050454,-2.2203680757
H,0,6.2696845276,2.1850164351,-0.9449466985
C,0,8.5485890437,2.2200917928,-2.5519386079
H,0,7.1775021222,0.5515122996,-2.6286875245
H,0,6.9355913163,1.7313342967,-3.9042888992
C,0,9.6685570602,1.5671103282,-3.3691729995
H,0,8.5334225721,3.3000495333,-2.7561091207
H,0,8.7755688575,2.1198849497,-1.4812033879
C,0,11.0499996839,2.161276558,-3.0817559359
H,0,9.6834160187,0.4883410304,-3.1642538467
H,0,9.4412584928,1.6677796631,-4.4388709365
H,0,11.8274993753,1.674999076,-3.6792283954
```

H,0,11.0757508014,3.2325897383,-3.3106727404
H,0,11.319514663,2.0441006217,-2.0261406049

GVETS1-endotrans-b3lypGTBas3-ufg

E(RB3LYP) = -772.421181027

```
Zero-point correction=                           0.348629 (Hartree/Particle)
Thermal correction to Energy=                    0.360618
Thermal correction to Enthalpy=                  0.361309
Thermal correction to Gibbs Free Energy=         0.314754
Sum of electronic and zero-point Energies=          -772.072552
Sum of electronic and thermal Energies=             -772.060563
Sum of electronic and thermal Enthalpies=           -772.059872
Sum of electronic and thermal Free Energies=        -772.106427
                 E (Thermal)             CV                S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               226.291             55.973           133.914
```

C,0,2.682672975,-0.6781593772,0.1968444252
C,0,1.5908159108,0.0661081308,-0.1252110547
O,0,0.4069746699,-0.5258065753,-0.2988706517
C,0,-0.7281568489,0.3522128189,-0.3651496734
C,0,-1.9644750711,-0.4985980701,-0.6096242979
C,0,-3.2898646632,0.2851172499,-0.5547610695
H,0,-3.3328967132,0.7991745744,0.4173534857
C,0,-4.4735958211,-0.7008381447,-0.6111111619
C,0,-5.8521738462,-0.0878414531,-0.3333267194
C,0,-6.9683565935,-1.1400168501,-0.3051348653
C,0,-8.3663391441,-0.6060676148,0.0584601949
H,0,-8.2794439956,-0.074401595,1.0176784185
C,0,-9.3494822361,-1.7683597996,0.2547077727
O,0,2.4103557538,-0.810576194,2.4502457262
O,0,1.2396622629,-0.3084688853,2.5798919735
O,0,1.1581626539,0.9181784341,2.1763262451
H,0,1.6440039479,1.135070316,-0.3077417375
H,0,3.650992442,-0.2061005666,0.2694658904
H,0,2.6282165078,-1.7581637306,0.2028020804
H,0,-0.7882313692,0.8928920193,0.5885441779
H,0,-0.5630241069,1.082209975,-1.1674991062
H,0,-1.8685266036,-1.0012043598,-1.5807687967
H,0,-1.9773962301,-1.2872034937,0.1514228136
C,0,-3.3730668672,1.350020462,-1.6599871288

```
H,0,-4.4838583488,-1.1910697928,-1.5955501371
H,0,-4.2942906647,-1.5000450112,0.1204774093
H,0,-5.8260188948,0.4375962471,0.632064728
H,0,-6.0813413131,0.6710937298,-1.0891143285
H,0,-7.0212520379,-1.641095462,-1.2830164313
H,0,-6.6951662711,-1.9211295204,0.4175188616
C,0,-8.9079557256,0.3849392158,-0.9818742838
H,0,-10.3391328064,-1.4063652184,0.5526637075
H,0,-9.4717955763,-2.3383576782,-0.6743732576
H,0,-8.999328015,-2.4626158061,1.0259096643
H,0,-4.3123967498,1.9069526048,-1.6110806047
H,0,-2.5641527961,2.0830112127,-1.5849996179
H,0,-3.3118355761,0.8857548673,-2.6519702662
H,0,-9.9072234596,0.7361763526,-0.7038001337
H,0,-8.2679082176,1.2657634963,-1.0865754155
H,0,-8.9871165613,-0.0899935077,-1.9676438351
```

GVEPOZ-endotrans-b3lypGTBas3-ufg

```
E(RB3LYP) =  -772.511714375

Zero-point correction=                    0.353255 (Hartree/Particle)
Thermal correction to Energy=                0.364542
Thermal correction to Enthalpy=              0.365233
Thermal correction to Gibbs Free Energy=        0.320184
Sum of electronic and zero-point Energies=          -772.158459
Sum of electronic and thermal Energies=            -772.147172
Sum of electronic and thermal Enthalpies=           -772.146482
Sum of electronic and thermal Free Energies=        -772.191530
                E (Thermal)            CV              S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              228.754            52.991           129.583

C,0,-0.3391958118,0.3157802649,-0.1679104344
C,0,-0.320828038,-0.9316745124,0.7522786787
O,0,0.9481084263,-1.5121596617,0.4881739343
O,0,1.7460352577,-0.3691286662,0.0957908236
O,0,0.8923190486,0.2493991647,-0.8697747627
O,0,-0.501814107,-0.5020954291,2.0549733608
C,0,-0.5700890607,-1.5543126116,3.0194809177
C,0,-0.8005184977,-0.9209308689,4.3846474625
C,0,-1.0241303482,-1.9295262984,5.5272506263
C,0,-1.457870559,-1.1783261837,6.8017010368
```

```
C,0,-1.9268212456,-2.0667959629,7.9610764631
C,0,-2.4435877332,-1.2527800513,9.1543889093
C,0,-3.0117697644,-2.0829876614,10.3204517677
C,0,-3.6800882579,-1.1669168742,11.3549790027
H,0,-1.0414063397,-1.7163558621,0.4808784402
H,0,-1.3987273619,-2.2348675988,2.7615221561
H,0,0.3599276253,-2.1329523865,2.9892109626
H,0,-1.1358367075,0.2969625605,-0.9139161236
H,0,-0.407406295,1.2069062459,0.4639757159
H,0,0.0543473827,-0.2743525239,4.6205099577
H,0,-1.6744200473,-0.2637297908,4.3026681964
H,0,-1.8557310982,-2.588943682,5.234095282
C,0,0.2148598785,-2.806404804,5.7687450332
H,0,-0.6268964,-0.5434824742,7.1420773868
H,0,-2.272650114,-0.4902786694,6.5385945439
H,0,-2.7254183076,-2.733848521,7.605546535
H,0,-1.1074499269,-2.7167225526,8.2864255019
H,0,-1.6353008501,-0.6107167054,9.5345311172
H,0,-3.2271210747,-0.5693137436,8.799292382
H,0,-3.7871543578,-2.7462277955,9.9089249128
C,0,-1.9471972574,-2.9627842679,10.9914807895
H,0,-4.1238475061,-1.7460369461,12.1716624455
H,0,-2.9499241717,-0.4780043137,11.7968903845
H,0,-4.47323177,-0.5630070032,10.9014886847
H,0,0.0439314907,-3.5331543376,6.5673812515
H,0,0.4964314397,-3.371977953,4.8757751479
H,0,1.0754049394,-2.1901839179,6.0564073679
H,0,-2.3768848209,-3.5300174851,11.8238886688
H,0,-1.5074161711,-3.6831651084,10.2957648439
H,0,-1.1330224874,-2.3485510114,11.3956176292
```

GVE3TS2-2carb-b3lypGTBas3-ufg

```
E(RB3LYP) =  -772.487441016

Zero-point correction=                          0.350376 (Hartree/Particle)
Thermal correction to Energy=                   0.361732
Thermal correction to Enthalpy=                 0.362423
Thermal correction to Gibbs Free Energy=        0.317307
Sum of electronic and zero-point Energies=          -772.137065
Sum of electronic and thermal Energies=             -772.125709
Sum of electronic and thermal Enthalpies=           -772.125018
Sum of electronic and thermal Free Energies=        -772.170134
```

```
                E (Thermal)           CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              226.990          53.584          129.776
```

```
C,0,-6.92768362,8.9126041414,1.8250651947
C,0,-5.7769269304,8.1228602771,2.4638357918
C,0,-5.1191216458,7.1948976064,1.4258396066
C,0,-3.8363598348,6.4944200649,1.8922768654
C,0,-3.1801552223,5.6677538948,0.7788247338
C,0,-1.9477069549,4.8460107266,1.2050091971
C,0,-1.5314902908,3.9041088858,0.0592770442
C,0,-0.4551211259,2.8952882339,0.4372810189
O,0,-0.2715033763,2.0286512339,-0.6877058519
C,0,0.7604543283,1.0993925688,-0.5797615041
C,0,0.0206650863,-0.4517430081,-0.1951087728
O,0,-0.1456483039,-0.2662344078,1.1336145107
O,0,1.0360925951,-0.1146775638,1.6967324389
O,0,1.675062224,1.2223431318,0.3010060251
H,0,1.0921891414,0.855507779,-1.6045993231
H,0,-0.9384727024,-0.5578511179,-0.6962884605
H,0,0.8040931059,-1.165321407,-0.4469167963
H,0,-0.7624383131,2.3054795026,1.3124204856
H,0,0.4975377744,3.3730747711,0.685423608
H,0,-1.1803683304,4.4937821329,-0.7976938185
H,0,-2.4095719437,3.3461267593,-0.2877595472
H,0,-2.2472192118,4.2200641059,2.0596302278
C,0,-0.7862305774,5.7441088902,1.6594415628
H,0,-2.8975690089,6.3325229246,-0.0505355187
H,0,-3.9314816181,4.9792896118,0.3685756104
H,0,-4.0553191764,5.8351679463,2.7420234049
H,0,-3.135017048,7.2517223036,2.264743202
H,0,-4.8883802788,7.7851508313,0.5282551821
H,0,-5.8523218499,6.4391584182,1.1073449902
C,0,-6.2702472062,7.3630919525,3.7035792112
H,0,-5.0155999431,8.845968977,2.7923294252
H,0,-7.3800159327,9.606658476,2.5413300002
H,0,-6.5834107867,9.4952184255,0.9639543443
H,0,-7.7180675457,8.2376861992,1.4745175579
H,0,0.0719821702,5.159019382,2.0018042147
H,0,-0.4459815495,6.3836027868,0.8355620662
H,0,-1.0811029633,6.3958036571,2.4863374297
H,0,-6.7435785144,8.0452291089,4.4177096929
H,0,-7.0148248389,6.606796755,3.4256636348
H,0,-5.4561527812,6.8528220425,4.2262753151
```

GVE2TS2-2carb-b3lypGTBas3-ufg

```
E(RB3LYP) =  -772.486849246

Zero-point correction=                           0.350554 (Hartree/Particle)
Thermal correction to Energy=                    0.361830
Thermal correction to Enthalpy=                  0.362520
Thermal correction to Gibbs Free Energy=         0.317667
Sum of electronic and zero-point Energies=          -772.136295
Sum of electronic and thermal Energies=             -772.125020
Sum of electronic and thermal Enthalpies=           -772.124329
Sum of electronic and thermal Free Energies=        -772.169183
                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              227.051             53.417            129.022

C,0,1.4091127265,10.4956622703,4.6889992022
C,0,0.4070197346,9.3389238745,4.5717595912
C,0,0.8816580182,8.3193498806,3.5198707928
C,0,0.062867997,7.0240324387,3.4458741635
C,0,0.6500359176,6.0136263725,2.4517939586
C,0,-0.1817995037,4.7329720233,2.2417882334
C,0,0.4016692128,3.9215711147,1.06919421
C,0,-0.4663531317,2.7427037992,0.6289189931
O,0,0.0168464536,2.1642321716,-0.5930034089
C,0,0.9528497309,1.1406251561,-0.4687732803
C,0,0.106872689,-0.3753996348,-0.7587606334
O,0,-0.4472240229,-0.5265205328,0.4650326654
O,0,0.5145597042,-0.6432093215,1.3595279586
O,0,1.5687041614,0.9311918758,0.6296696768
H,0,1.57031852,1.1402821012,-1.3844450073
H,0,-0.6598787076,-0.2513035686,-1.519711104
H,0,0.9169487376,-1.0731929758,-0.9670624386
H,0,-1.4840354548,3.0786113156,0.4027687545
H,0,-0.5180915157,1.9741660549,1.4036511352
H,0,1.3969141883,3.5465191322,1.3363527817
H,0,0.5307414588,4.5794212465,0.2010392978
H,0,-1.2001443741,5.0438608721,1.9598405543
C,0,-0.2798657872,3.8929627577,3.5252003581
H,0,1.6634416193,5.7324820121,2.7730652259
H,0,0.7707234716,6.5121873268,1.4803841584
H,0,-0.9712992866,7.2489080958,3.1547585982
H,0,0.0096549991,6.5813538358,4.4485531178
H,0,1.9275337332,8.0597171203,3.734217772
```

```
H,0,0.8893377055,8.8031514431,2.5319145442
C,0,-1.0009831487,9.8760952371,4.2774428548
H,0,0.3748523176,8.8231907131,5.5430386151
H,0,1.1050125916,11.2092570606,5.4621265981
H,0,2.4110196817,10.1327558985,4.9418301467
H,0,1.4843012213,11.0454295258,3.742839717
H,0,-0.906383773,3.0071632058,3.3864659628
H,0,0.712736872,3.5488527751,3.8394289842
H,0,-0.7122225904,4.4663582713,4.349851098
H,0,-1.3069434752,10.6068657072,5.0335998889
H,0,-1.0300122929,10.3777649419,3.3021831647
H,0,-1.7519713988,9.0809624058,4.2655120987
```

GVE3TS2-2form-b3lypGTBas3-ufg

```
E(RB3LYP) =  -772.479816912

Zero-point correction=                           0.349989 (Hartree/Particle)
Thermal correction to Energy=                    0.361467
Thermal correction to Enthalpy=                  0.362158
Thermal correction to Gibbs Free Energy=         0.316921
Sum of electronic and zero-point Energies=          -772.129828
Sum of electronic and thermal Energies=             -772.118350
Sum of electronic and thermal Enthalpies=           -772.117659
Sum of electronic and thermal Free Energies=        -772.162896
                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  226.824             54.304           130.123
```

```
C,0,0.3391057245,-0.4216431918,0.1292109797
O,0,0.4071999742,-0.5525476915,1.3909375512
C,0,2.1409150852,-0.2665038954,-0.4245248371
O,0,2.2990745524,0.2698667845,-1.6348090686
C,0,2.2073181669,1.7095703578,-1.7530361186
C,0,2.0718318707,2.0333838396,-3.232373895
C,0,2.1368511819,3.5393245587,-3.5525185445
C,0,2.1851658304,3.7377244018,-5.0805455491
C,0,2.4815470077,5.1690119403,-5.5462892823
C,0,2.6189515798,5.2742223807,-7.0706767099
C,0,3.0038528887,6.6679829481,-7.6008164499
C,0,3.3117999312,6.6031762297,-9.1031311591
O,0,2.5610457773,0.4705933481,0.6201220182
O,0,2.3566981788,-0.1949697239,1.7538410808
```

```
H,0,2.4127470051,-1.3188437818,-0.3794352987
H,0,-0.0758622759,0.512445545,-0.2911929309
H,0,0.1251719631,-1.3142633845,-0.484953393
H,0,1.3544258259,2.0594150784,-1.1636417662
H,0,3.1159235143,2.1510135167,-1.3273622457
H,0,2.8784766795,1.5138139716,-3.7624061862
H,0,1.1293013927,1.6127104471,-3.605303393
C,0,0.9777514945,4.3133414919,-2.9047466772
H,0,3.079736932,3.9277935152,-3.1383327372
H,0,2.9541707265,3.0709226553,-5.4932957583
H,0,1.2319522381,3.4026004277,-5.5145982594
H,0,1.6911703699,5.8438954225,-5.2007691052
H,0,3.4114893207,5.5173795243,-5.0744364817
H,0,3.3771878709,4.552750032,-7.4047489675
H,0,1.6767807182,4.9603705503,-7.5437855345
C,0,1.925634954,7.724284423,-7.3190847083
H,0,3.9235832987,6.9778528243,-7.0827213768
H,0,3.6253962376,7.5795143303,-9.4871945723
H,0,4.1107524411,5.885403242,-9.3172824198
H,0,2.4260728896,6.2934100896,-9.6710274932
H,0,1.0336485822,5.3811870591,-3.130694564
H,0,0.0118512388,3.9450704051,-3.2714729984
H,0,0.9783505252,4.2187596836,-1.8146269369
H,0,2.2208350389,8.6999579164,-7.7190979681
H,0,0.9757007794,7.4468468477,-7.792514856
H,0,1.7401504896,7.8513708804,-6.2485923874
```

GVE2TS2-2form-b3lypGTBas3-ufg

```
E(RB3LYP) =  -772.479403863

Zero-point correction=                           0.350173 (Hartree/Particle)
Thermal correction to Energy=                    0.361513
Thermal correction to Enthalpy=                  0.362204
Thermal correction to Gibbs Free Energy=         0.317091
Sum of electronic and zero-point Energies=           -772.129231
Sum of electronic and thermal Energies=              -772.117890
Sum of electronic and thermal Enthalpies=            -772.117200
Sum of electronic and thermal Free Energies=         -772.162312
                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  226.853             53.977            129.767
```

```
C,0,-0.0061397744,-0.0117238834,0.3001686093
O,0,0.0039171393,-0.0526886137,1.5686909854
C,0,1.8266658435,-0.0437802995,-0.1867473415
O,0,2.0670810416,0.3733277764,-1.4291027422
C,0,2.0380561237,1.798426363,-1.7040591246
C,0,3.4352761973,2.4090418323,-1.6584310046
C,0,4.4658674039,1.78769335,-2.6223509507
C,0,5.8660987831,2.3484900007,-2.3059682587
C,0,7.0267449556,1.6640238695,-3.039407603
C,0,8.3964952668,2.1959685269,-2.5985214521
C,0,9.6103706741,1.4896786741,-3.2304420555
C,0,10.9108292471,1.9629769662,-2.5665313626
O,0,2.2645108046,0.7396380448,0.8170140868
O,0,1.963676279,0.1865509068,1.9893476636
H,0,2.0100028686,-1.1066366942,-0.0455930733
H,0,-0.3241843296,0.9179660646,-0.2055368896
H,0,-0.2651185623,-0.9287681137,-0.2583388522
H,0,1.5914638606,1.8761572135,-2.6975530526
H,0,1.3785531888,2.2901176055,-0.9834542805
H,0,3.3222469458,3.4799418685,-1.8787529614
H,0,3.8074549567,2.3431847311,-0.6304483762
H,0,4.4876057259,0.7065192556,-2.4286464693
C,0,4.0752216884,2.0020120133,-4.0921872127
H,0,5.879797755,3.4259157738,-2.5274216518
H,0,6.0387044047,2.2625605838,-1.2246259922
H,0,6.9822265888,0.581228707,-2.8540929674
H,0,6.9116979579,1.7947537873,-4.1208030126
H,0,8.4566721391,3.2724141876,-2.817056227
H,0,8.4716187565,2.1071595367,-1.5061024896
H,0,9.5064052618,0.412104186,-3.0346050363
C,0,9.6816710658,1.6872423924,-4.7515179536
H,0,11.7806940827,1.4404147514,-2.9781635258
H,0,11.0636811566,3.0371183654,-2.7273883875
H,0,10.8945568657,1.7886661832,-1.4854846223
H,0,4.7915152002,1.5300679071,-4.7695435657
H,0,3.0940475488,1.5757564814,-4.3226473921
H,0,4.0412658987,3.0712230748,-4.3355005675
H,0,10.5609267577,1.1860667114,-5.1697569729
H,0,8.8015173978,1.2864694397,-5.2626312198
H,0,9.7580158336,2.7524674728,-5.0025616977
```

PVETS1-endotrans-b3lypGTBas3-ufg

E(RB3LYP) = -1165.58515082

```
Zero-point correction=                          0.631312 (Hartree/Particle)
Thermal correction to Energy=                   0.651492
Thermal correction to Enthalpy=                 0.652183
Thermal correction to Gibbs Free Energy=        0.584301
Sum of electronic and zero-point Energies=         -1164.953838
Sum of electronic and thermal Energies=            -1164.933658
Sum of electronic and thermal Enthalpies=          -1164.932968
Sum of electronic and thermal Free Energies=       -1165.000850
                 E (Thermal)             CV                S
                  KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              408.818             94.633           195.263
```

```
C,0,-10.1246948355,-0.5375959363,-1.4129250697
C,0,-9.1492667348,0.158843902,-0.7708055543
O,0,-9.4031811896,-0.986018584,1.4313339016
O,0,-9.3344994067,-2.1056621632,0.786837336
O,0,-10.3303266682,-2.3077955642,0.0084454975
O,0,-7.8662454968,-0.1549337916,-0.9649410131
C,0,-6.9310280067,0.4396802679,-0.0508627304
C,0,-5.5346700471,-0.0100460744,-0.4509563375
C,0,-4.4046482305,0.6426062347,0.368134226
C,0,-3.0414985301,0.2787062016,-0.2527969577
C,0,-1.8354004886,1.0301256577,0.3257494236
C,0,-0.5323752608,0.7047751711,-0.4166673816
C,0,0.7433123162,1.3342981302,0.176882354
C,0,1.9884529253,0.7564261561,-0.5246221853
H,0,-9.3614714072,1.0134573325,-0.1356313934
H,0,-7.0231325437,1.5341766585,-0.1040198426
H,0,-7.208336753,0.1167681685,0.9588728507
H,0,-11.1566135855,-0.2385152033,-1.3057425893
H,0,-9.8706215891,-1.2709469088,-2.165977481
H,0,-5.4769985527,-1.1021657398,-0.3614372528
H,0,-5.3970043461,0.2250392509,-1.5129494457
H,0,-4.5220245326,1.7345350681,0.2892989292
C,0,-4.48095073,0.2620044088,1.8552552642
H,0,-2.8802976611,-0.8042871953,-0.1513242752
H,0,-3.0881002862,0.4754245023,-1.3324665868
H,0,-2.0360719648,2.1081673108,0.2831180996
H,0,-1.7091577635,0.7830471421,1.3874022933
H,0,-0.4057990686,-0.3863637534,-0.4330445726
```

H,0,-0.6271939114,1.0114104579,-1.4687378637
C,0,0.7079710533,2.8687036948,0.111436176
H,0,0.7946819259,1.0411894846,1.2370043286
C,0,3.3355109623,1.1275245919,0.10962137
H,0,1.9012523832,-0.3386130879,-0.5399156979
H,0,1.9839392546,1.0720101689,-1.578390916
C,0,4.519889644,0.4338111007,-0.5764085931
H,0,3.4732536822,2.2134944438,0.0771134805
H,0,3.3221527577,0.8513824367,1.1739033954
C,0,5.8977446198,0.6806380205,0.0693000825
H,0,4.3302708241,-0.6482606897,-0.5870269036
H,0,4.5591596018,0.7414192846,-1.6318232936
C,0,6.950432493,-0.2476979748,-0.5679690426
C,0,6.313089376,2.1574033402,-0.0121313542
H,0,5.8179774284,0.4091110557,1.1334367495
C,0,8.3220437571,-0.2611789078,0.1196615354
H,0,6.5536123203,-1.2721960498,-0.5700366636
H,0,7.0765593765,0.0267296379,-1.6256961097
C,0,9.2788998311,-1.2905899569,-0.4955073346
H,0,8.7850172822,0.7320106858,0.0599798443
H,0,8.1814814778,-0.46985601,1.1880437666
C,0,10.7075179876,-1.2877620825,0.0792974224
H,0,8.8514991245,-2.2981316042,-0.384284082
H,0,9.3390587425,-1.1088041933,-1.5774905535
C,0,11.6182049473,-2.21244141,-0.7402108985
H,0,11.0998665063,-0.2639112515,-0.0116357451
C,0,10.745070318,-1.6757439968,1.5644420021
H,0,12.6476274218,-2.1905625648,-0.3670719493
H,0,11.2696899407,-3.2511476234,-0.6880503828
H,0,11.6370971098,-1.9219941704,-1.7960395239
H,0,1.5991029301,3.3137138464,0.5626147133
H,0,0.6553991834,3.2111596231,-0.9296669447
H,0,-0.1580750223,3.2773775667,0.6397107158
H,0,7.2753799033,2.3347023279,0.4761785966
H,0,6.4064635814,2.4765111604,-1.0577982577
H,0,5.5817668525,2.8116651171,0.4706633977
H,0,11.7728519449,-1.6771881798,1.9426994469
H,0,10.1666283992,-0.9861544918,2.1859159711
H,0,10.3365191324,-2.6829101406,1.7137915122
H,0,-3.6862479337,0.7414094041,2.4328770194
H,0,-5.431169078,0.5608492421,2.3073556163
H,0,-4.3796106934,-0.8224939553,1.9832304609

PVEPOZ-endotrans-b3lypGTBas3-ufg

E(RB3LYP) = -1165.67564545

```
Zero-point correction=                      0.635961 (Hartree/Particle)
Thermal correction to Energy=                    0.655422
Thermal correction to Enthalpy=                  0.656113
Thermal correction to Gibbs Free Energy=         0.589921
Sum of electronic and zero-point Energies=         -1165.039684
Sum of electronic and thermal Energies=           -1165.020224
Sum of electronic and thermal Enthalpies=          -1165.019533
Sum of electronic and thermal Free Energies=        -1165.085725
                E (Thermal)           CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total                411.283           91.636          190.402
```

C,0,0.0990875045,1.0812771116,0.1509201634
C,0,0.1485967886,-0.269547016,0.909888568
O,0,1.4972009671,-0.6843816023,0.748161676
O,0,2.2021323946,0.5723550472,0.6037842366
O,0,1.4047449774,1.2280186853,-0.3851658781
O,0,-0.2329321719,-0.0361743658,2.2191746425
C,0,-0.2959682039,-1.2087440692,3.0335728717
C,0,-0.7571364967,-0.7878631892,4.422132252
C,0,-0.9971319955,-1.9564399807,5.39659507
C,0,-1.6646173697,-1.4289757275,6.6821018112
C,0,-2.1556576334,-2.50672179,7.6575251418
C,0,-2.9110363108,-1.913107968,8.8541572803
C,0,-3.3373377806,-2.9244325825,9.9365220855
C,0,-3.8825202042,-2.1756905676,11.1688064063
H,0,-0.4416098716,-1.0772835672,0.4539942414
H,0,-1.0057492029,-1.9262124671,2.5888565334
H,0,0.6904737016,-1.6852218984,3.057609879
H,0,-0.5962055001,1.0846461452,-0.6905499102
H,0,-0.1435588385,1.869878131,0.8701334663
H,0,-0.0157885318,-0.0972519075,4.8439348038
H,0,-1.6847163785,-0.2149802633,4.3048052501
H,0,-1.7051739087,-2.6511348472,4.9186705638
C,0,0.2973050721,-2.7291829722,5.6959405289
H,0,-0.9627904634,-0.7596934338,7.200562165
H,0,-2.5207006123,-0.80275372,6.3965197646
H,0,-2.8000923731,-3.2092769758,7.1139795898
H,0,-1.3073563653,-3.094280206,8.0307623765
H,0,-2.2736835756,-1.1509057586,9.3229145502

```
H,0,-3.8016693342,-1.3781929655,8.4928559482
C,0,-4.3453171816,-3.9499311362,9.3958994319
H,0,-2.4350209435,-3.4702589278,10.2532570447
C,0,-4.1394446796,-3.0430503963,12.4082690957
H,0,-3.1682245505,-1.3859920804,11.4391766776
H,0,-4.8114252281,-1.6566783464,10.8898559567
C,0,-4.5792573362,-2.2163409282,13.6238911386
H,0,-4.8984542397,-3.7989365695,12.1803150268
H,0,-3.2221751476,-3.594979924,12.6595297744
C,0,-4.760057895,-3.0079673537,14.9342419697
H,0,-3.8346123666,-1.4269322476,13.7950429019
H,0,-5.5190690091,-1.6955515849,13.3880828459
C,0,-4.9700843215,-2.0347832882,16.1110141124
C,0,-5.8975949532,-4.0352692485,14.8313379914
H,0,-3.8238039133,-3.5564713429,15.1214548754
C,0,-4.9552501011,-2.6723268973,17.5065939332
H,0,-4.1839178223,-1.2683187536,16.0717006102
H,0,-5.9192437031,-1.4978645151,15.9667047374
C,0,-5.0522412857,-1.6318323386,18.6298378766
H,0,-5.7871979018,-3.3808268877,17.6078468206
H,0,-4.0359005486,-3.2615007567,17.6180985446
C,0,-5.1484313427,-2.2076416602,20.0547751065
H,0,-4.1866405934,-0.9550709207,18.5759739241
H,0,-5.9351388644,-1.0033448415,18.4485637819
C,0,-5.4363200728,-1.0905529366,21.0673076991
H,0,-5.998966972,-2.9052734874,20.0740726584
C,0,-3.8902014839,-2.9886780201,20.4603422222
H,0,-5.5467515086,-1.4903525846,22.0809092101
H,0,-4.618048388,-0.3603966382,21.0872774658
H,0,-6.3558062508,-0.5508647978,20.8167630458
H,0,-4.6208111584,-4.6864099536,10.155802471
H,0,-5.2655590347,-3.4517771716,9.0658229545
H,0,-3.9427509921,-4.5032379097,8.5427288179
H,0,-6.0009235604,-4.6182276169,15.7507909816
H,0,-6.8560485458,-3.5346600879,14.6449697752
H,0,-5.7301496133,-4.7456492955,14.0168974755
H,0,-3.9817102699,-3.3754622076,21.4808525887
H,0,-3.7030880629,-3.841005407,19.8008945112
H,0,-3.0043775073,-2.3421414723,20.4301540094
H,0,0.1168331229,-3.5689874602,6.3722406139
H,0,0.7483924508,-3.139758014,4.7879141461
H,0,1.0392834924,-2.0736832722,6.1679980974
```

PVE3TS2-2carb-b3lypGTBas3-ufg

```
E(RB3LYP) =  -1165.65133622

Zero-point correction=                          0.633071 (Hartree/Particle)
Thermal correction to Energy=                   0.652614
Thermal correction to Enthalpy=                 0.653305
Thermal correction to Gibbs Free Energy=        0.587021
Sum of electronic and zero-point Energies=         -1165.018265
Sum of electronic and thermal Energies=            -1164.998722
Sum of electronic and thermal Enthalpies=          -1164.998032
Sum of electronic and thermal Free Energies=       -1165.064316
                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              409.521             92.242           190.666
```

```
 C,0,-6.8656025134,8.483056142,2.8275669466
 C,0,-5.6149759882,7.6897034981,3.2552421631
 C,0,-5.0575741292,6.9014473163,2.0535904534
 C,0,-3.6969508396,6.2285652152,2.2788509606
 C,0,-3.1547247334,5.5637664064,1.0067203671
 C,0,-1.8469106582,4.767308813,1.1833067782
 C,0,-1.5420095377,3.979754586,-0.1051098761
 C,0,-0.3900476361,2.9918732949,0.0221323031
 O,0,-0.3138107467,2.2676855783,-1.2108119913
 C,0,0.7546682274,1.3825866727,-1.333140106
 C,0,0.1194195983,-0.2356629976,-1.0524274487
 O,0,0.107260559,-0.2105133932,0.2991703025
 O,0,1.3421335115,-0.0676952881,0.7365801185
 O,0,1.7634741526,1.4482166357,-0.5550395325
 H,0,0.9694578373,1.2728075829,-2.4109389261
 H,0,-0.8886845125,-0.3296990917,-1.4489948085
 H,0,0.8907893589,-0.8778666147,-1.4754237666
 H,0,-0.5648563892,2.2925323741,0.8518742652
 H,0,0.5672512153,3.4873542918,0.2107105976
 H,0,-1.3227425933,4.6773920293,-0.9240277346
 H,0,-2.4350589592,3.4191396658,-0.406721442
 H,0,-2.0113381958,4.0367172143,1.9902088262
 C,0,-0.6735693931,5.6709753012,1.5939911247
 H,0,-3.00589114,6.3285949517,0.2305267473
 H,0,-3.9242426189,4.8847512959,0.6148587452
 H,0,-3.775846913,5.4704986734,3.0683560346
 H,0,-2.9865293981,6.9803254477,2.645348605
 H,0,-4.9681984703,7.5874168459,1.2000687044
```

```
H,0,-5.7932990547,6.1415731293,1.7514464684
C,0,-5.8985206903,6.7758501072,4.457091481
H,0,-4.8474014324,8.4190239808,3.5574838788
C,0,-7.3971296716,9.4858801634,3.8602086264
H,0,-6.6317185056,9.0277371594,1.9025678007
H,0,-7.6652492725,7.7750514089,2.5641643175
C,0,-8.5780899164,10.3082242477,3.3275767036
H,0,-7.6958466886,8.9561865812,4.7710361994
H,0,-6.5853771628,10.1671646657,4.1535126021
C,0,-9.1033971552,11.4056605296,4.2741783186
H,0,-8.2749981343,10.7803326597,2.3829885178
H,0,-9.4060315759,9.6306696513,3.0715713
C,0,-10.1212453163,12.2950387229,3.5332095195
C,0,-9.6919422595,10.8160977503,5.5649184464
H,0,-8.2480672882,12.0414413407,4.551059751
C,0,-10.57083737,13.5537646176,4.2866988817
H,0,-9.6799476453,12.6033126985,2.5754484743
H,0,-11.0037343044,11.6909537151,3.2756672223
C,0,-11.4919914673,14.4461815598,3.4447950237
H,0,-11.0952178658,13.2751740832,5.2096045698
H,0,-9.6821444989,14.1178723695,4.5977799989
C,0,-12.0661444841,15.6745271999,4.1747142384
H,0,-10.9525115773,14.7840338849,2.5475747075
H,0,-12.3295733447,13.8365491863,3.0784923747
C,0,-13.1175324775,16.3748239122,3.3028520539
H,0,-12.5702438042,15.3145892284,5.0840062676
C,0,-10.9760333473,16.6674221448,4.6029703974
H,0,-13.5636576338,17.2280545326,3.8247798236
H,0,-12.668542195,16.7522355079,2.3759921136
H,0,-13.9262693833,15.6907289255,3.0245430829
H,0,-11.4134725683,17.5348700811,5.1085524803
H,0,-10.2535191583,16.2162777005,5.2891113057
H,0,-10.422601405,17.0374942961,3.73097146
H,0,0.243368388,5.0985762807,1.7603235829
H,0,-0.4655720561,6.413806609,0.8139762645
H,0,-0.8871409526,6.2117948329,2.5198962879
H,0,-6.2639056118,7.3413891717,5.3187831816
H,0,-6.6592402989,6.02688733,4.2034243267
H,0,-5.0009423332,6.2411847433,4.7803056772
H,0,-10.033036904,11.5984559854,6.2486643314
H,0,-10.5515976234,10.1723600067,5.3399994183
H,0,-8.9581130477,10.2127558507,6.1065691111
```

PVE2TS2-2carb-b3lypGTBas3-ufg

E(RB3LYP) = -1165.65073975

```
Zero-point correction=                           0.633230 (Hartree/Particle)
Thermal correction to Energy=                    0.652706
Thermal correction to Enthalpy=                  0.653396
Thermal correction to Gibbs Free Energy=         0.586999
Sum of electronic and zero-point Energies=         -1165.017510
Sum of electronic and thermal Energies=            -1164.998034
Sum of electronic and thermal Enthalpies=          -1164.997343
Sum of electronic and thermal Free Energies=       -1165.063741
                E (Thermal)         CV               S
                 KCal/Mol     Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              409.579          92.082           190.993
```

```
C,0,0.4247462581,10.4787694328,4.6921940689
C,0,-0.4436725044,9.2254533397,4.4653618149
C,0,0.2636896191,8.2660588789,3.4880159529
C,0,-0.3870919225,6.8851821777,3.3313363657
C,0,0.4356678298,5.9475199589,2.4378832569
C,0,-0.2123695524,4.5809118836,2.1403161229
C,0,0.6098000843,3.8386824944,1.0693605963
C,0,-0.0550747422,2.5694659931,0.5364010507
O,0,0.6506308878,2.0460487686,-0.5990526613
C,0,1.6668118148,1.1319799592,-0.3323637828
C,0,1.0387034968,-0.4683902695,-0.7096923139
O,0,0.3422679762,-0.6779923936,0.4298590907
O,0,1.1796480674,-0.6868060556,1.4484442615
O,0,2.1460136678,0.9929930636,0.8426933842
H,0,2.3999095578,1.1985112437,-1.1556887407
H,0,0.374282554,-0.4305234071,-1.5696128261
H,0,1.9408126911,-1.0729666691,-0.7946422074
H,0,-1.0633707835,2.7892278179,0.1693849644
H,0,-0.1264807649,1.801668876,1.3102688404
H,0,1.5953917525,3.5776660614,1.4731564439
H,0,0.7808983658,4.5058517388,0.2157111992
H,0,-1.2120320862,4.7746020326,1.720405822
C,0,-0.3872443446,3.7370908439,3.413041283
H,0,1.4230636593,5.7830011587,2.8931000231
H,0,0.6264650401,6.4562635843,1.4831252939
H,0,-1.3934022474,6.9873857937,2.905555188
H,0,-0.5185352145,6.4409326809,4.3260926016
H,0,1.2986031004,8.1248904761,3.8285624578
```

H,0,0.3358623449,8.7481079983,2.5019094552
C,0,-1.8588158049,9.5866714192,3.9890631256
H,0,-0.5336858193,8.7058587129,5.4319764573
C,0,-0.0483763991,11.4160489556,5.8112450322
H,0,1.4492774617,10.1544398391,4.9204244669
H,0,0.4919552754,11.04274201,3.7501158841
C,0,0.9178037263,12.5842597907,6.0487601561
H,0,-1.0451806536,11.8025648629,5.5737402727
H,0,-0.1558599407,10.8412089197,6.7424584883
C,0,0.5613038434,13.5103970899,7.228389975
H,0,1.9227155692,12.1748145934,6.2203973275
H,0,0.9923584884,13.1862999862,5.131109813
C,0,1.7205861105,14.4903281366,7.4965103385
C,0,-0.7677018769,14.2459545333,6.9987756362
H,0,0.4487348114,12.8782953465,8.1229521967
C,0,1.5955432546,15.3265673743,8.7768990712
H,0,2.6556945501,13.9158740281,7.5477332232
H,0,1.8287987712,15.1622041765,6.6322814601
C,0,2.833951113,16.1938466285,9.0373122572
H,0,0.7137714478,15.9773535529,8.7193744841
H,0,1.4235362841,14.652200579,9.6256530403
C,0,2.7360818112,17.1333436564,10.2535355356
H,0,3.7147604588,15.5457505172,9.1570259168
H,0,3.0290912824,16.8017822103,8.1430566212
C,0,3.9406831949,18.0836352831,10.2967947266
H,0,1.830378037,17.7452961677,10.1282236921
C,0,2.6075312036,16.3688241479,11.5788922644
H,0,3.8652434243,18.7846549316,11.1348513385
H,0,4.8762508953,17.5238923536,10.4172240272
H,0,4.0213954943,18.669281581,9.3748379543
H,0,2.5514976951,17.0607322865,12.4259900243
H,0,1.7128881342,15.7402359804,11.6076145292
H,0,3.4772119468,15.7196004742,11.7394404688
H,0,-0.8862319996,2.7858167154,3.2068883028
H,0,0.5864186734,3.50809777,3.8624292927
H,0,-0.9879127827,4.2591619304,4.1629792141
H,0,-2.3710623856,10.2408802936,4.7000702186
H,0,-1.8216490447,10.1077192496,3.024108171
H,0,-2.4828487494,8.6975355073,3.8624834729
H,0,-1.0337166865,14.8771628772,7.8512918421
H,0,-0.7054175645,14.8910666767,6.1133677933
H,0,-1.5956258559,13.548492393,6.8437988814

PVE3TS2-2form-b3lypGTBas3-ufg

```
E(RB3LYP) =  -1165.64364116

Zero-point correction=                           0.632723 (Hartree/Particle)
Thermal correction to Energy=                    0.652369
Thermal correction to Enthalpy=                  0.653060
Thermal correction to Gibbs Free Energy=         0.586815
Sum of electronic and zero-point Energies=          -1165.010918
Sum of electronic and thermal Energies=             -1164.991272
Sum of electronic and thermal Enthalpies=           -1164.990581
Sum of electronic and thermal Free Energies=        -1165.056826
                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  409.368             92.958            190.554
```

```
C,0,0.2507685314,-0.6434055453,-0.4263386921
O,0,0.2073843015,-0.9486229382,0.8061840847
C,0,2.0823544536,-0.7713520666,-0.877051965
O,0,2.4191395466,-0.1243571002,-1.9930702821
C,0,2.6133584393,1.3077815813,-1.9117272398
C,0,2.6837412784,1.8347666341,-3.3360140119
C,0,2.8101555214,3.367887342,-3.4325865229
C,0,2.6534406425,3.8033691807,-4.9031255452
C,0,2.5429425943,5.3166132083,-5.1307876614
C,0,2.2751039759,5.6682219855,-6.6003623975
C,0,2.2622720887,7.17418911,-6.9287826962
C,0,2.2071110644,7.37730772,-8.4559003341
O,0,2.5608660394,-0.2715672801,0.2772881136
O,0,2.1594064894,-1.0265992961,1.2966712815
H,0,2.1490558584,-1.85332521,-0.9681628451
H,0,0.047274413,0.400335614,-0.7272990234
H,0,-0.0847092971,-1.3893938942,-1.1683996741
H,0,1.7787043931,1.7527382416,-1.3569951139
H,0,3.5317138844,1.4965985234,-1.3485925729
H,0,3.5290907248,1.3585647577,-3.8487310433
H,0,1.7768135662,1.5101445488,-3.8591468155
H,0,1.975554657,3.8090789422,-2.8665281722
C,0,4.1239489927,3.8758037012,-2.8175964675
H,0,3.4978791771,3.4066786007,-5.4851957804
H,0,1.7543730614,3.3239176534,-5.3133016265
H,0,1.7416820735,5.7130222776,-4.4944798243
H,0,3.4656606642,5.8162604687,-4.8099300205
H,0,3.0439065596,5.1844099857,-7.2182426318
```

```
H,0,1.3175872779,5.2253269589,-6.9114377582
C,0,1.1186867581,7.9065210426,-6.210598044
H,0,3.2137365934,7.5987677191,-6.572618769
C,0,2.4099011645,8.8200535116,-8.9374519823
H,0,2.9775323735,6.7450778704,-8.9182059637
H,0,1.2446940822,7.0004717713,-8.832403197
C,0,2.450106993,8.9291979019,-10.4675210729
H,0,1.6127277958,9.4581388441,-8.5414819893
H,0,3.3504260381,9.2105185083,-8.5226259636
C,0,2.7503947332,10.3349648242,-11.0243012299
H,0,3.2137293278,8.2356064308,-10.845404448
H,0,1.4939904217,8.5769018604,-10.8819756134
C,0,2.9936342681,10.2568480136,-12.5444136734
C,0,1.6426601024,11.3396117481,-10.6728365788
H,0,3.6847375911,10.6833216489,-10.5572487383
C,0,3.5072924617,11.5463556353,-13.1983501158
H,0,3.7206023033,9.4562684148,-12.738551342
H,0,2.0632567607,9.9432820399,-13.0404719465
C,0,3.83859156,11.3606634747,-14.6847851187
H,0,2.7603889631,12.3442484757,-13.0993067015
H,0,4.3967445185,11.8901920806,-12.6548239139
C,0,4.2605677895,12.6400513183,-15.4306143913
H,0,4.6335680617,10.6076044679,-14.7900326394
H,0,2.9581055567,10.9387713479,-15.1888681621
C,0,4.3741858815,12.3707437676,-16.937449045
H,0,3.4671375576,13.3876747863,-15.2823475132
C,0,5.5707557252,13.2312391017,-14.8906224723
H,0,4.6350310657,13.2818132429,-17.4863635857
H,0,5.1525426214,11.6260515342,-17.1440883098
H,0,3.4331755217,11.9889672581,-17.3476002439
H,0,4.199807942,4.9642811867,-2.8803698652
H,0,4.2132727887,3.6108799343,-1.7598704061
H,0,4.9879604655,3.4503126804,-3.3424185629
H,0,1.1315484222,8.9797697872,-6.4192901534
H,0,0.1454005709,7.5161883942,-6.5334039555
H,0,1.1800856469,7.7895584154,-5.1249038239
H,0,1.875331443,12.3432936444,-11.0393437423
H,0,0.6876695139,11.0351965773,-11.1192068397
H,0,1.4940813417,11.41810568,-9.5922070061
H,0,5.8519842174,14.1319957765,-15.4464434623
H,0,5.4950924785,13.5063377669,-13.8347133754
H,0,6.3926336051,12.511360811,-14.9902688045
```

PVE2TS2-2form-b3lypGTBas3-ufg

E(RB3LYP) = -1165.64333382

```
Zero-point correction=                          0.632936 (Hartree/Particle)
Thermal correction to Energy=                   0.652434
Thermal correction to Enthalpy=                 0.653125
Thermal correction to Gibbs Free Energy=        0.586808
Sum of electronic and zero-point Energies=         -1165.010397
Sum of electronic and thermal Energies=            -1164.990900
Sum of electronic and thermal Enthalpies=          -1164.990209
Sum of electronic and thermal Free Energies=       -1165.056526
               E (Thermal)           CV               S
                KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total            409.409            92.598          190.762
```

C,0,-0.2773545169,0.97443899,0.4119204367
O,0,-0.2614656917,0.9439437529,1.6806983947
C,0,1.5080272775,0.5789553552,-0.0913137629
O,0,1.8117629215,0.9297594539,-1.3402907883
C,0,2.0598389253,2.3304138421,-1.6302663737
C,0,3.5497156029,2.656701805,-1.6002102314
C,0,4.4306427698,1.8381343439,-2.565145774
C,0,5.9160924748,2.1131656774,-2.2609904228
C,0,6.9142453596,1.2148397426,-3.0032355018
C,0,8.3630585845,1.4611312339,-2.5615900908
C,0,9.4361711224,0.6783467595,-3.3435914312
C,0,10.8403899623,1.1770657396,-2.9488017675
O,0,2.1021336823,1.2700920449,0.8998337666
O,0,1.7115780889,0.7972539488,2.0807842217
H,0,1.4809130027,-0.4979221616,0.0597007606
H,0,-0.4124360542,1.9438078817,-0.1012026904
H,0,-0.7174508519,0.1210071797,-0.1339171178
H,0,1.6287763931,2.4846898952,-2.6216803677
H,0,1.5150643537,2.9481518268,-0.9107931026
H,0,3.6459849102,3.7272122677,-1.8301801727
H,0,3.9107998709,2.527975733,-0.5742336134
H,0,4.2397702562,0.7751578115,-2.3636404975
C,0,4.0805133948,2.1162493072,-4.0344792655
H,0,6.1392206581,3.1673005213,-2.4823495129
H,0,6.077443758,1.9931366068,-1.1811091959
H,0,6.639821117,0.1660265431,-2.8338331494
H,0,6.8404300798,1.3807636161,-4.0855101822
H,0,8.5773658253,2.5343827363,-2.657497979

```
H,0,8.460400101,1.2303980737,-1.4906454529
C,0,9.2909180595,-0.838906328,-3.1517206139
H,0,9.2944947309,0.9001708248,-4.412824651
C,0,11.9960820565,0.6409787314,-3.8040803828
H,0,10.8471211031,2.2743253927,-3.003448521
H,0,11.0242542176,0.9285982233,-1.8931572935
C,0,13.3469978919,1.260809281,-3.4226652045
H,0,12.0499081162,-0.4489728471,-3.7120959819
H,0,11.7889448923,0.8499061045,-4.863622044
C,0,14.5411027254,0.841704997,-4.3029992978
H,0,13.2518268649,2.3545105778,-3.4641978561
H,0,13.5738943779,1.0194691975,-2.3737189708
C,0,15.7724815706,1.7043409403,-3.9630090541
C,0,14.8434267003,-0.6595934778,-4.1822887585
H,0,14.2698921726,1.0499314872,-5.3497130652
C,0,16.9733614692,1.5416968598,-4.9041603245
H,0,15.4684696859,2.7601077701,-3.9682491886
H,0,16.087170471,1.488478937,-2.931335483
C,0,18.1147110173,2.5126604468,-4.5751269595
H,0,17.3570545481,0.5147619482,-4.8540706073
H,0,16.6372186942,1.6929593746,-5.9380334169
C,0,19.3926466816,2.3362630907,-5.415979454
H,0,17.7563292171,3.5470901622,-4.6833118118
H,0,18.377471907,2.3963902026,-3.51457888
C,0,20.5219039032,3.2203616454,-4.8690209045
H,0,19.7111507685,1.2875656034,-5.3198347685
C,0,19.1607067502,2.6226687109,-6.9065487792
H,0,21.4494711252,3.0761912694,-5.4331587652
H,0,20.2552344145,4.2821337526,-4.9370948936
H,0,20.7301896431,2.9979062117,-3.8170711781
H,0,4.6845205272,1.5069625571,-4.7116940369
H,0,3.0326324699,1.8922633135,-4.2566028427
H,0,4.2582839667,3.1692702819,-4.2857521502
H,0,10.0329524076,-1.3931408834,-3.7329973365
H,0,9.4233030633,-1.1107116748,-2.097000176
H,0,8.3055236896,-1.1950547124,-3.4652719673
H,0,15.6694088752,-0.9596559864,-4.8331388447
H,0,15.1204147559,-0.9173766205,-3.1523624884
H,0,13.9791021718,-1.2708785223,-4.4565867228
H,0,20.0875459167,2.5012582885,-7.4772018712
H,0,18.4146766858,1.9532036544,-7.3442943545
H,0,18.8135273164,3.6526936861,-7.0553622351
```

DACPcrotonaldehyde endocis TS

Zero-point correction= 0.201787 (Hartree/Particle)
Thermal correction to Energy= 0.215349
Thermal correction to Enthalpy= 0.216293
Thermal correction to Gibbs Free Energy= 0.160683
Sum of electronic and ZPE= -749.696042
Sum of electronic and thermal Energies= -749.682480
Sum of electronic and thermal Enthalpies= -749.681536
Sum of electronic and thermal Free Energies= -749.737146

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 135.133 50.796 117.040
```

```
C,0,-0.4398798578,0.0160780588,-0.2802430112
 C,0,-0.0181573151,0.2635430071,1.0403623347
 H,0,0.1103497646,0.2692385518,-1.178603354
 H,0,1.0379070624,0.3358108097,1.2850609351
 C,0,-0.9888457991,-0.4892401189,1.9425121863
 C,0,-1.7481474269,-0.5376116683,-0.2796568092
 C,0,-2.1425643199,-0.7307777012,1.0175040337
 H,0,-2.3423310294,-0.6800733221,-1.1726704772
 H,0,-3.1118447313,-1.0936855509,1.3417726517
 C,0,-0.4863370122,2.1957031819,1.4136702383
 C,0,-1.8975355252,2.2878212731,1.3623439037
 H,0,0.0208544782,2.5749941092,0.5304848758
 C,0,-2.5526415523,2.3525875847,0.1311386067
 H,0,-2.493889481,2.2738216478,2.2695126069
 C,0,0.2289507465,2.4825830586,2.7173358748
 O,0,-1.8880140815,2.3264884514,-0.962885775
 H,0,-3.6407869528,2.401506715,0.0651106811
 B,0,-2.6078669504,2.221186472,-2.3832812586
 F,0,-2.0991966298,3.2546797734,-3.116175502
 F,0,-2.2300769273,0.9721460406,-2.8498914615
 F,0,-3.965006244,2.3129288398,-2.1449685265
 H,0,-1.2540000027,0.0053230261,2.8799587381
 H,0,-0.5353685836,-1.4570004343,2.2132680091
 H,0,1.2788463999,2.1756469029,2.6927007171
 H,0,0.2085588546,3.5645577598,2.9000661085
 H,0,-0.2551658839,1.9976955321,3.5716606737
```

DACP3penten2oneBF3 endocis TS

Zero-point correction= 0.229724 (Hartree/Particle)
Thermal correction to Energy= 0.244770
Thermal correction to Enthalpy= 0.245715
Thermal correction to Gibbs Free Energy= 0.187888
Sum of electronic and ZPE= -788.991670
Sum of electronic and thermal Energies= -788.976623
Sum of electronic and thermal Enthalpies= -788.975679
Sum of electronic and thermal Free Energies= -789.033505

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	153.596	56.608	121.706

C,0,-0.4786222819,0.1641808845,-0.3640343304
C,0,0.0232457975,0.3438460775,0.9394757301
H,0,-0.0351209075,0.5493576705,-1.2746423935
H,0,1.0851540382,0.4974812614,1.110195731
C,0,-0.7951795663,-0.5711437615,1.843131385
C,0,-1.7218865971,-0.5298353138,-0.3144597422
C,0,-1.9837314174,-0.8726253963,0.9824886549
H,0,-2.3799334207,-0.6564712042,-1.1643353915
H,0,-2.8821100562,-1.3617146196,1.3435260415
C,0,-0.5659245498,2.1887459655,1.5085054127
C,0,-1.9807155201,2.2131544002,1.5108056337
H,0,-0.1107886214,2.6679903758,0.645949937
C,0,-2.6844512558,2.3295760612,0.3024398295
H,0,-2.5364118754,2.122265155,2.4389217324
C,0,0.175583872,2.4107581845,2.8108732107
O,0,-1.9793103191,2.3468785352,-0.7778499986
C,0,-4.1818536143,2.4212702271,0.2416721129
B,0,-2.5222107956,2.2748893242,-2.2610549827
F,0,-1.3724048268,2.1285656974,-2.9978789887
F,0,-3.343350378,1.1507994517,-2.3269766151
F,0,-3.2075602503,3.442693542,-2.4949348465
H,0,-1.0452534004,-0.1686254837,2.8280928427
H,0,-0.2257891874,-1.4987486022,2.0172782192
H,0,-4.5779109027,1.6016763403,-0.3637665552
H,0,-4.6251289264,2.4046616222,1.2400418238
H,0,-4.460251333,3.3455626812,-0.2752115522
H,0,1.2372618655,2.1578997441,2.7330481252
H,0,0.110882445,3.4732680983,3.0780604112
H,0,-0.2575440145,1.8390830813,3.6384015632

DACPmecrotonate endocis TS

Zero-point correction= 0.234809 (Hartree/Particle)
Thermal correction to Energy= 0.250911
Thermal correction to Enthalpy= 0.251855
Thermal correction to Gibbs Free Energy= 0.191226
Sum of electronic and ZPE= -864.195843
Sum of electronic and thermal Energies= -864.179741
Sum of electronic and thermal Enthalpies= -864.178797
Sum of electronic and thermal Free Energies= -864.239427

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 157.449 59.718 127.605

C,0,-0.4018208448,0.024864478,-0.3106277272
C,0,0.0652813867,0.3202556327,0.9932682181
H,0,0.0587261695,0.34331636,-1.2383431947
H,0,1.1289033555,0.4624170744,1.170229369
C,0,-0.7685508696,-0.5424614934,1.9370684159
C,0,-1.6546434107,-0.633642995,-0.2369946762
C,0,-1.9573112688,-0.856968742,1.0826756483
H,0,-2.3009600888,-0.8112720555,-1.0868311421
H,0,-2.8734215103,-1.3005222568,1.4582890001
C,0,-0.5503023228,2.1224136423,1.4038716916
C,0,-1.9707058115,2.1330026426,1.3973801473
H,0,-0.1014432419,2.5862427219,0.5293577945
C,0,-2.6400954191,2.2145652149,0.1557526535
H,0,-2.5267288373,2.0842325181,2.3248359987
C,0,0.1576066638,2.4696922657,2.7029821144
O,0,-1.9462698262,2.2148954215,-0.9123826594
O,0,-3.9660296515,2.2759473638,0.0157701146
B,0,-2.4338070857,1.932898053,-2.426945693
F,0,-1.240369935,1.616858007,-3.0386056905
F,0,-3.2961490485,0.8544655331,-2.3573127668
F,0,-3.012261852,3.0820285754,-2.8782413501
H,0,-1.009123456,-0.097586452,2.9053369121
H,0,-0.2148970196,-1.4732066574,2.1423990281
C,0,-4.8012265458,2.2290589487,1.1722532708
H,0,-5.8225369851,2.2836971662,0.7953633298
H,0,-4.6574411799,1.2898467447,1.7181063262
H,0,-4.6065365781,3.0792524067,1.834959849
H,0,1.2258344541,2.235283078,2.6656561324
H,0,0.0633052923,3.547225881,2.8847859495

```
H,0,-0.2779025327,1.9528349223,3.5648239361
```

Cyclopentadiene SM b3lyp/6-31G*

```
E(RB3LYP) = -194.101058763
```

```
Zero-point correction= 0.092894 (Hartree/Particle)
Thermal correction to Energy= 0.097038
Thermal correction to Enthalpy= 0.097982
Thermal correction to Gibbs Free Energy= 0.066295
Sum of electronic and ZPE= -194.008165
Sum of electronic and thermal Energies= -194.004021
Sum of electronic and thermal Enthalpies= -194.003077
Sum of electronic and thermal Free Energies= -194.034763
```

```
     E       CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 60.892 15.536 66.690
```

```
C,0,0.2096518322,-0.2348717547,0.0803865263
C,0,0.2585317487,-0.4516269451,1.4107424654
C,0,1.2502940978,0.4500545247,2.0141934607
C,0,1.8036239514,1.2143160987,1.0502862523
C,0,1.1919570576,0.85024599,-0.2781461719
H,0,-0.3321793732,-1.1725564352,1.9669020669
H,0,1.4858541384,0.4803292264,3.0731959603
H,0,2.5657076905,1.9747378732,1.1775865612
H,0,1.9478928309,0.5007837374,-0.9983234352
H,0,0.6991657891,1.711534986,-0.7551745243
H,0,-0.4221062306,-0.7417498181,-0.6401192656
```

Cyclopentadiene SM M06-2X/6-31G*

```
E(RM062X) = -194.004692007
```

```
Zero-point correction= 0.094043 (Hartree/Particle)
Thermal correction to Energy= 0.098160
Thermal correction to Enthalpy= 0.099104
Thermal correction to Gibbs Free Energy= 0.068110
Sum of electronic and ZPE= -193.910649
Sum of electronic and thermal Energies= -193.906532
Sum of electronic and thermal Enthalpies= -193.905588
Sum of electronic and thermal Free Energies= -193.936582
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 61.596 15.323 65.231
```

```
 C,0,0.0496102052,-0.0159357673,0.0437586446
 C,0,0.0776098148,0.1748278844,1.5341128882
 C,0,1.2478705257,-0.2760409492,2.0161923453
 C,0,2.0637742756,-0.7877241312,0.9048411167
 C,0,1.3838190276,-0.6442674106,-0.2450608224
 H,0,-0.7829838348,-0.6598421679,-0.2712682277
 H,0,-0.7358089144,0.6084520045,2.1028872599
 H,0,1.5583143543,-0.2730741745,3.054774004
 H,0,3.05630266,-1.2092310653,1.0155449785
 H,0,1.7177330955,-0.923865255,-1.2367818685
 H,0,-0.0784925471,0.9365652331,-0.4885962629
```

Transcinnamaldehyde SM B3LYP/6-31G*

```
E(RB3LYP) = -422.975950467
```

```
Zero-point correction= 0.143728 (Hartree/Particle)
Thermal correction to Energy= 0.152312
Thermal correction to Enthalpy= 0.153256
Thermal correction to Gibbs Free Energy= 0.109401
Sum of electronic and ZPE= -422.832222
Sum of electronic and thermal Energies= -422.823638
Sum of electronic and thermal Enthalpies= -422.822694
Sum of electronic and thermal Free Energies= -422.866550
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.577 32.002 92.302
```

```
 C,0,0.0576684061,0.,-0.11748167
 C,0,-0.1005081419,0.,1.2228320095
 C,0,1.3966039763,0.,-0.712166794
 H,0,0.8083702749,0.,1.8277920798
 C,0,-1.3459147913,0.,1.9884924102
 C,0,-1.2776354956,0.,3.3939614803
 C,0,-2.4345629087,0.,4.1699021494
 C,0,-3.6863803467,0.,3.55312342
 C,0,-3.7724000397,0.,2.1567655824
 C,0,-2.6176293377,0.,1.3823265636
 H,0,-0.3030313447,0.,3.8764999932
```

H,0,-2.3592408063,0.,5.2537177632
H,0,-4.5913341227,0.,4.1544002507
H,0,-4.7450111903,0.,1.672503055
H,0,-2.7000722258,0.,0.299735442
H,0,-0.7768162783,0.,-0.8140226711
O,0,1.620494675,0.,-1.9097995705
H,0,2.2322796974,0.,0.0254185065

Transcinnamaldehyde SM M06-2X/6-31G*

E(RM062X) = -422.784357511

Zero-point correction= 0.145193 (Hartree/Particle)
Thermal correction to Energy= 0.153790
Thermal correction to Enthalpy= 0.154734
Thermal correction to Gibbs Free Energy= 0.110623
Sum of electronic and ZPE= -422.639165
Sum of electronic and thermal Energies= -422.630568
Sum of electronic and thermal Enthalpies= -422.629623
Sum of electronic and thermal Free Energies= -422.673735

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 96.505 31.822 92.841
```

C,0,0.0431275525,0.,-0.1102083985
C,0,-0.0984480292,0.,1.2234016364
C,0,1.3879545187,0.,-0.7052381784
H,0,0.8136860974,0.,1.8236843223
C,0,-1.346460574,0.,1.9929007862
C,0,-1.2766062164,0.,3.3912039244
C,0,-2.432747454,0.,4.1637504813
C,0,-3.6795235792,0.,3.5455362828
C,0,-3.7636239242,0.,2.1528051367
C,0,-2.6090745632,0.,1.382850435
H,0,-0.3022913137,0.,3.8734424602
H,0,-2.3602647145,0.,5.2467728155
H,0,-4.5845826763,0.,4.1448322901
H,0,-4.734354851,0.,1.6670237622
H,0,-2.6865255818,0.,0.2999279402
H,0,-0.7931151205,0.,-0.8037569128
O,0,1.6057011967,0.,-1.8949056352
H,0,2.2220312327,0.,0.0299748515

DACPtranscinnaBF3 endocis TS B3LYP/6-31G*

E(RB3LYP) = -941.635803546

Zero-point correction= 0.255239 (Hartree/Particle)
Thermal correction to Energy= 0.271711
Thermal correction to Enthalpy= 0.272655
Thermal correction to Gibbs Free Energy= 0.209838
Sum of electronic and ZPE= -941.380564
Sum of electronic and thermal Energies= -941.364092
Sum of electronic and thermal Enthalpies= -941.363148
Sum of electronic and thermal Free Energies= -941.425966

```
     E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 170.501 63.787 132.211
```

```
C,0,-0.6033822118,-0.0253473482,-0.2287783457
C,0,-0.1822882505,0.2689956141,1.1001898017
H,0,-0.031886789,0.1601351369,-1.1294674023
H,0,0.8780288929,0.2435816565,1.3386484187
C,0,-1.1830914875,-0.4437960552,2.0083542668
C,0,-1.9225402118,-0.5358674722,-0.2214332057
C,0,-2.3374687611,-0.6594107092,1.0803802323
H,0,-2.5110253023,-0.6958188826,-1.1152484849
H,0,-3.327243506,-0.9628086765,1.4048104378
C,0,-0.5059408152,2.1335874813,1.4216579212
C,0,-1.9163100587,2.3631770626,1.2988428847
H,0,0.0512306399,2.4868197679,0.5564547
C,0,-2.485267897,2.4190022226,0.0352156073
H,0,-2.5562446782,2.4923358014,2.1634603124
C,0,0.203380206,2.4264695027,2.7060705142
O,0,-1.7532203992,2.2475933893,-1.0105413565
H,0,-3.5549688985,2.5704268231,-0.1117255924
B,0,-2.3793969208,2.1331570038,-2.4683611533
F,0,-1.7810273968,3.1210686861,-3.1983012015
F,0,-2.0257338321,0.8553393461,-2.8782912874
F,0,-3.7452530796,2.2867111275,-2.3281780365
H,0,-1.4279489896,0.0720679664,2.938560654
H,0,-0.7629325197,-1.4226352722,2.2914620397
C,0,1.5680222564,2.7562670204,2.6613364091
C,0,2.277809418,3.0462340197,3.8250243286
C,0,1.6346861824,3.0078314067,5.0635649518
C,0,0.2785399693,2.682344006,5.1251308155
```

C,0,-0.4298056692,2.3947040744,3.9587717446
H,0,2.0734770125,2.7952637285,1.6987888803
H,0,3.3308120644,3.306733793,3.7637273721
H,0,2.184178905,3.2342338084,5.9729583149
H,0,-0.2327037359,2.657169814,6.0836051324
H,0,-1.4874551364,2.1581641568,4.0311563262

DACPtranscinnaBF3 endocis TS B3LYP/6-31G*/PCMether

E(RB3LYP) = -941.650513191

Zero-point correction= 0.254992 (Hartree/Particle)
Thermal correction to Energy= 0.271614
Thermal correction to Enthalpy= 0.272558
Thermal correction to Gibbs Free Energy= 0.208812
Sum of electronic and ZPE= -941.395521
Sum of electronic and thermal Energies= -941.378899
Sum of electronic and thermal Enthalpies= -941.377955
Sum of electronic and thermal Free Energies= -941.441701

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	170.440	63.879	134.165

C,0,-0.4751156729,-0.124414086,-0.1560431814
C,0,-0.1525071506,0.1696661805,1.1948780023
H,0,0.184733005,0.0370779814,-1.0006907621
H,0,0.8822288945,0.1411027017,1.5232075374
C,0,-1.2505541164,-0.4843493534,2.0259932266
C,0,-1.8108341732,-0.5697585952,-0.255411118
C,0,-2.3357554925,-0.6612443245,1.0129848799
H,0,-2.340997475,-0.7103333201,-1.1877298236
H,0,-3.3588448944,-0.9229067457,1.2594817916
C,0,-0.4848335347,2.0784586103,1.4189720508
C,0,-1.8986696398,2.2766799424,1.2892239111
H,0,0.0758005401,2.4009905105,0.5454216278
C,0,-2.4913883499,2.3712782065,0.0431724045
H,0,-2.5403906787,2.3665890706,2.1574913134
C,0,0.2180281015,2.412802079,2.6945549644
O,0,-1.7954846653,2.2794732505,-1.0456060124
H,0,-3.5658988146,2.5220247387,-0.0574028034
B,0,-2.4626798712,2.2565884715,-2.440662271
F,0,-1.7461322757,3.146280281,-3.2146566375
F,0,-2.3444744871,0.9500552573,-2.9069386676

```
F,0,-3.7932905478,2.6292311144,-2.2983436064
H,0,-1.5459369376,0.041881341,2.9348833573
H,0,-0.895874522,-1.4797195649,2.3397365103
C,0,1.5750434448,2.773869094,2.6385191514
C,0,2.2784179299,3.1073303152,3.7948431762
C,0,1.6371391758,3.0807519272,5.0352891769
C,0,0.2888354228,2.7231070234,5.1068169671
C,0,-0.4143653481,2.3925341857,3.9486503368
H,0,2.0792719445,2.8010152054,1.6752917824
H,0,3.3247615628,3.3912728204,3.7262608537
H,0,2.1819154128,3.3402772025,5.9385525293
H,0,-0.2201838023,2.705572253,6.0664511098
H,0,-1.4649349846,2.1305472258,4.0306552223
```

DACPtranscinnaBF3 endocis TS M06-2X/6-31G*

E(RM062X) = -941.269061713

```
Zero-point correction= 0.258038 (Hartree/Particle)
Thermal correction to Energy= 0.274196
Thermal correction to Enthalpy= 0.275140
Thermal correction to Gibbs Free Energy= 0.213661
Sum of electronic and ZPE= -941.011024
Sum of electronic and thermal Energies= -940.994866
Sum of electronic and thermal Enthalpies= -940.993922
Sum of electronic and thermal Free Energies= -941.055400
```

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 172.060 63.037 129.392
```

```
C,0,-0.592661043,0.0463921151,-0.2375947438
C,0,-0.1751352475,0.303539036,1.0867487926
H,0,-0.0146001709,0.2269750661,-1.1359967899
H,0,0.8798795964,0.2930861367,1.345573997
C,0,-1.2092984589,-0.350775227,1.986058133
C,0,-1.9368776819,-0.3994722721,-0.2441599027
C,0,-2.367232304,-0.4901118892,1.0507417536
H,0,-2.5365720317,-0.5171532985,-1.1382803638
H,0,-3.3751374932,-0.7356743627,1.366934932
C,0,-0.5170919049,2.1966890981,1.4148606814
C,0,-1.9229392678,2.378399751,1.3107854693
H,0,0.0339004725,2.545639378,0.5440658747
C,0,-2.4841915601,2.4010504346,0.0422024461
```

H,0,-2.5705666707,2.4607363523,2.1747624856
C,0,0.200746141,2.4433440296,2.6986492637
O,0,-1.7306351587,2.289577475,-0.9861381358
H,0,-3.5621570756,2.4551293757,-0.1136039013
B,0,-2.3347276814,1.9866874763,-2.4054249665
F,0,-2.2451657418,3.1358577868,-3.1301735249
F,0,-1.5384114723,0.9621618504,-2.8790629559
F,0,-3.635120661,1.5701648305,-2.1822624364
H,0,-1.4246633149,0.1736434204,2.9184417038
H,0,-0.850735211,-1.3559866294,2.252693523
C,0,1.5743688459,2.7092886755,2.6572617453
C,0,2.2917976122,2.9494739253,3.8231276464
C,0,1.6444373539,2.9243319935,5.0560984929
C,0,0.2781159492,2.6614634263,5.1116397205
C,0,-0.4379245358,2.4228083374,3.9427536241
H,0,2.0802021772,2.7344216938,1.6944761426
H,0,3.3552269003,3.1601217595,3.7694322503
H,0,2.2009775382,3.1128419318,5.9686675797
H,0,-0.2353421502,2.6465479517,6.067984151
H,0,-1.5054377495,2.2325313718,4.0065843125

DACPtranscinnaBF3 endo PDT B3LYP/6-31G*

E(RB3LYP) = -941.663549431

Zero-point correction= 0.258765 (Hartree/Particle)
Thermal correction to Energy= 0.274970
Thermal correction to Enthalpy= 0.275914
Thermal correction to Gibbs Free Energy= 0.212254
Sum of electronic and ZPE= -941.404785
Sum of electronic and thermal Energies= -941.388579
Sum of electronic and thermal Enthalpies= -941.387635
Sum of electronic and thermal Free Energies= -941.451295

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 172.546 62.865 133.983

C,0,-0.2202563604,-1.1990356888,0.2137866014
C,0,-0.0221105892,-0.5823251026,1.5871676843
H,0,0.5831399395,-1.4993053438,-0.4508508157
H,0,0.9146380664,-0.8118220756,2.0976260048
C,0,-1.3348086789,-1.0168369866,2.2722850909
C,0,-1.5291781015,-1.1495847498,-0.0733942967

```
C,0,-2.2277381179,-0.5141486459,1.1149331488
H,0,-2.0073039356,-1.3962250186,-1.0150917698
H,0,-3.305867715,-0.6633544146,1.2000926265
C,0,-0.2581535259,0.9809378217,1.3895714234
C,0,-1.8000879595,1.0415411382,1.1570500457
H,0,0.2482931157,1.2883318265,0.4718435087
C,0,-2.2622150349,1.7235941283,-0.07312546
H,0,-2.3308040575,1.4942437254,2.0011913312
C,0,0.2798374044,1.8468186497,2.5168627208
O,0,-1.5469355064,1.8711404206,-1.069235171
H,0,-3.3050413923,2.0631762812,-0.1305676416
B,0,-2.1795536614,2.5248356574,-2.5384617023
F,0,-1.3246882706,3.5439511312,-2.7753926525
F,0,-2.0913200097,1.4514469625,-3.3595683685
F,0,-3.4503490662,2.8890642706,-2.1884196212
H,0,-1.5287152409,-0.5238524576,3.2297067463
H,0,-1.4063732214,-2.1008931859,2.399035428
C,0,1.5060493868,2.502106888,2.3252658058
C,0,2.0798786642,3.2770155192,3.3326539423
C,0,1.4334306584,3.4183790685,4.5612075435
C,0,0.211028427,2.7787491778,4.7677934139
C,0,-0.357984891,2.0021704573,3.7569948337
H,0,2.0148311651,2.4057340088,1.3687762233
H,0,3.028587341,3.7758370778,3.1534807345
H,0,1.8744852484,4.0251044605,5.3471909848
H,0,-0.3062815598,2.8846416645,5.7177322569
H,0,-1.313594521,1.5222343341,3.9488863997
```

DACPtranscinnaUNCAT exo TS B3LYP/6-31G*

E(RB3LYP) = -617.044563659

Zero-point correction= 0.239683 (Hartree/Particle)
Thermal correction to Energy= 0.252087
Thermal correction to Enthalpy= 0.253032
Thermal correction to Gibbs Free Energy= 0.200561
Sum of electronic and ZPE= -616.804880
Sum of electronic and thermal Energies= -616.792476
Sum of electronic and thermal Enthalpies= -616.791532
Sum of electronic and thermal Free Energies= -616.844003

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 158.187 49.335 110.433
```

```
C,0,-0.9070006568,-0.8449230943,-0.0618096661
C,0,-0.3846319138,-0.5530705334,1.2168643092
H,0,-0.3144938856,-1.0379581402,-0.9489916087
H,0,0.6335306145,-0.7952302547,1.5067489155
C,0,-1.5468285512,-0.6397538424,2.1816758046
C,0,-2.2928261799,-0.6509562597,-0.0406113431
C,0,-2.678426819,-0.290378742,1.2559024338
H,0,-2.9453376231,-0.6718467932,-0.9074336801
H,0,-3.7038783194,-0.1585698503,1.5841302334
C,0,-0.3573567417,1.5450898815,1.2106042408
C,0,-1.7300693314,1.8904547533,1.2040778686
H,0,0.0995149952,1.6005088441,2.1972237404
C,0,-2.4089684099,2.2977940853,2.4292680503
H,0,-2.2090327052,2.2044862861,0.2820962957
C,0,0.5696277213,1.9044046715,0.107347661
O,0,-1.9815368017,2.1485664009,3.5697203285
H,0,-3.4025855883,2.7715254142,2.2682673639
H,0,-1.4732860956,-0.0267953571,3.0817946058
H,0,-1.6648055367,-1.6916599247,2.4923887966
C,0,1.930580096,2.096280047,0.3988918406
C,0,2.8435700579,2.4351723437,-0.5989473086
C,0,2.4148216023,2.5884250237,-1.9180784247
C,0,1.0647979931,2.4005789111,-2.2248443121
C,0,0.1532526864,2.0644280083,-1.2255156207
H,0,2.2726518708,1.9829841229,1.4253492492
H,0,3.8899513303,2.581932628,-0.3439568798
H,0,3.1226339016,2.8540884317,-2.6984923401
H,0,0.7184190784,2.5201331629,-3.2483450154
H,0,-0.8912027888,1.9208997759,-1.4867745385
```

DACPtranscinnaUNCAT endo TS B3LYP/6-31G*

B3LYP/6-31G*
E(RB3LYP) = -617.043362827

Zero-point correction= 0.239566 (Hartree/Particle)
Thermal correction to Energy= 0.252006
Thermal correction to Enthalpy= 0.252951
Thermal correction to Gibbs Free Energy= 0.200333
Sum of electronic and ZPE= -616.803796
Sum of electronic and thermal Energies= -616.791356
Sum of electronic and thermal Enthalpies= -616.790412
Sum of electronic and thermal Free Energies= -616.843030

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 158.136 49.386 110.743

C,0,-0.3917189541,-0.198051861,-0.1597700523
C,0,-0.0537351821,0.0593345992,1.1890587354
H,0,0.2884509229,-0.1184499651,-1.00087332
H,0,0.9682047268,0.0300907122,1.5546907485
C,0,-1.2157260929,-0.4603438342,2.0119417668
C,0,-1.7731559464,-0.3885210391,-0.2593731098
C,0,-2.3330155203,-0.2843622219,1.0177516424
H,0,-2.3278036158,-0.4568631739,-1.1879835911
H,0,-3.3797883455,-0.4428163116,1.2538981151
C,0,-0.5475835368,2.055552455,1.4329179744
C,0,-1.9600714,2.0534617042,1.323152219
H,0,-0.0476268258,2.4146432057,0.5373848664
C,0,-2.5780284719,2.4263026472,0.0595419703
H,0,-2.5940140749,2.0927035161,2.2040051255
C,0,0.1718529285,2.3982977622,2.6897861832
O,0,-1.9723881268,2.58034737,-0.9956807082
H,0,-3.6837594057,2.5471674924,0.0941508361
H,0,-1.35360078,0.0125623079,2.9850600063
H,0,-1.0657210885,-1.539328635,2.1841513473
C,0,1.5248913353,2.7745124874,2.6117390428
C,0,2.2519778168,3.1078673651,3.7524956882
C,0,1.6424905088,3.0714228123,5.0082903761
C,0,0.2992946818,2.7042865141,5.1049985022
C,0,-0.4271158656,2.3740686906,3.961107209
H,0,2.0068038477,2.8091669647,1.6370651675
H,0,3.2948290619,3.3999755034,3.6601147691
H,0,2.2057216707,3.3320114098,5.900131776
H,0,-0.1903762793,2.6815327448,6.0751866055
H,0,-1.4763469892,2.1126577776,4.0633671084

DACPtranscinnaUNCAT exo TS M06-2X/6-31G*

E(RM062X) = -616.772801140

Zero-point correction= 0.242150 (Hartree/Particle)
Thermal correction to Energy= 0.254363
Thermal correction to Enthalpy= 0.255307
Thermal correction to Gibbs Free Energy= 0.203410
Sum of electronic and ZPE= -616.530651
Sum of electronic and thermal Energies= -616.518439

Sum of electronic and thermal Enthalpies= -616.517494
Sum of electronic and thermal Free Energies= -616.569392

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 159.615 48.844 109.227

C,0,-0.8429383231,-0.7829198666,-0.0733846689
C,0,-0.355043044,-0.5663476622,1.2176100735
H,0,-0.2313285389,-0.9480606288,-0.9528193
H,0,0.6629499088,-0.7821240967,1.525203028
C,0,-1.5317340198,-0.6284027443,2.1511416784
C,0,-2.2271388645,-0.5628908367,-0.0788133055
C,0,-2.6336112335,-0.2298030121,1.2124524368
H,0,-2.8581970106,-0.540869197,-0.9603162505
H,0,-3.6657605181,-0.1017418535,1.5225380733
C,0,-0.3647634586,1.6031525615,1.2499206149
C,0,-1.7318178093,1.8925345026,1.2200269167
H,0,0.0879251506,1.6270001009,2.2405791483
C,0,-2.4372420005,2.2494755555,2.4548552074
H,0,-2.2026624142,2.2289849998,0.3018655817
C,0,0.5552598633,1.9250152351,0.1374399475
O,0,-2.0079273392,2.0809651306,3.5808739493
H,0,-3.4421033345,2.6960892282,2.306262306
H,0,-1.4545557133,-0.0382746212,3.0653011658
H,0,-1.6951434693,-1.6815756776,2.4288293774
C,0,1.9149529304,2.114156417,0.409589711
C,0,2.8164271269,2.4077570394,-0.6083214589
C,0,2.3739837296,2.5135111292,-1.9236876773
C,0,1.0226548069,2.3238892652,-2.2091922282
C,0,0.1224815599,2.0348134999,-1.1902583801
H,0,2.2640731613,2.0332022739,1.4363592329
H,0,3.8663426997,2.5543749083,-0.3729761036
H,0,3.0743672141,2.742661224,-2.7206973694
H,0,0.6679452688,2.4029431814,-3.2326308755
H,0,-0.9263133292,1.8790929443,-1.4292008311

DACPtranscinnaUNCAT endo TS M06-2X/6-31G*

E(RM062X) = -616.772204589

Zero-point correction= 0.242362 (Hartree/Particle)
Thermal correction to Energy= 0.254533
Thermal correction to Enthalpy= 0.255477

Thermal correction to Gibbs Free Energy= 0.203766
Sum of electronic and ZPE= -616.529843
Sum of electronic and thermal Energies= -616.517672
Sum of electronic and thermal Enthalpies= -616.516728
Sum of electronic and thermal Free Energies= -616.568439

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 159.722 48.767 108.836
```

```
 C,0,-0.3920409707,-0.1510345346,-0.1613146829
 C,0,-0.0155109952,0.0916463392,1.1661233967
 H,0,0.257472474,-0.0562837795,-1.0237084717
 H,0,1.0142896284,0.1182456528,1.5078003585
 C,0,-1.1460957647,-0.4068491855,2.0304748783
 C,0,-1.7749303581,-0.3614089401,-0.2156617427
 C,0,-2.2925532853,-0.2518094431,1.0710240169
 H,0,-2.3577545281,-0.4292359619,-1.1263829199
 H,0,-3.3289616027,-0.4220752062,1.3421347422
 C,0,-0.5784909238,2.1148785823,1.4205987804
 C,0,-1.9737327257,2.046376025,1.3227432606
 H,0,-0.0834572217,2.4667025606,0.5189097232
 C,0,-2.5883251824,2.3603431605,0.03583014
 H,0,-2.6148658412,2.079745941,2.198326146
 C,0,0.1478249543,2.4185192082,2.6785060938
 O,0,-1.9645110508,2.500962153,-0.9998837638
 H,0,-3.6957567817,2.4334467417,0.0379477467
 H,0,-1.2524710973,0.0856890693,2.9977137311
 H,0,-0.9921894396,-1.4820942781,2.2098152576
 C,0,1.5136311173,2.7266848716,2.6116709791
 C,0,2.2440097169,3.0165001595,3.7577047074
 C,0,1.6222547059,3.0037516162,5.0043058145
 C,0,0.2653029115,2.7036383154,5.0875705675
 C,0,-0.4639033563,2.4158929512,3.9379442254
 H,0,2.002351788,2.7376174694,1.6398651373
 H,0,3.3002862289,3.2549988602,3.6775780254
 H,0,2.1890913583,3.2308482079,5.9016958178
 H,0,-0.2325744744,2.7006324956,6.0526010414
 H,0,-1.5254462836,2.2029009483,4.0263749934
```

DACPtranscinnaUNCAT 33sigma TS M06-2X/6-31G*

E(RM062X) = -616.767714932

```
Zero-point correction= 0.243823 (Hartree/Particle)
Thermal correction to Energy= 0.255128
Thermal correction to Enthalpy= 0.256072
Thermal correction to Gibbs Free Energy= 0.206441
Sum of electronic and ZPE= -616.523892
Sum of electronic and thermal Energies= -616.512587
Sum of electronic and thermal Enthalpies= -616.511643
Sum of electronic and thermal Free Energies= -616.561274

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 160.095 47.182 104.457

 C,0,-0.6863963529,-0.0692727047,-0.3271177388
 C,0,-0.14121414,0.2819767182,1.0044882908
 H,0,-0.1227373285,-0.0142727158,-1.248779416
 H,0,0.9377885136,0.1433952423,1.1029567942
 C,0,-1.0293413485,-0.5145385721,1.9726507949
 C,0,-1.9553216296,-0.6332835982,-0.1743015232
 C,0,-2.2881212009,-0.5796243724,1.1627933311
 H,0,-2.6278897375,-0.8530637071,-0.994369911
 H,0,-3.2635655436,-0.812456624,1.5767117473
 C,0,-0.4557165447,1.8508154617,1.3746308703
 C,0,-1.9054278377,2.0695096303,1.2738655659
 H,0,0.0350071446,2.3857046725,0.5550191612
 C,0,-2.3830412466,2.1226006021,-0.0343406559
 H,0,-2.5356394788,2.3126379728,2.1205370702
 C,0,0.2255124949,2.1961869481,2.6792883785
 O,0,-1.6172870769,1.8490635769,-0.9964456005
 H,0,-3.4564958671,2.2890512325,-0.2187840393
 H,0,-1.1315703636,-0.0554775182,2.9565272676
 H,0,-0.6315720075,-1.5287653261,2.1092737879
 C,0,1.5968260902,2.4710978253,2.663056358
 C,0,2.2852742916,2.7787048708,3.831266652
 C,0,1.609096734,2.8191703818,5.0484933844
 C,0,0.2447752418,2.5500661708,5.0810175227
 C,0,-0.4393344728,2.2417143174,3.9071686133
 H,0,2.1279769856,2.4500052918,1.7134677795
 H,0,3.3490259926,2.9930835045,3.7903790967
 H,0,2.1413075552,3.0619620983,5.9629618795
 H,0,-0.2946638563,2.5815775969,6.0229605224
 H,0,-1.5052300106,2.0380670235,3.9565490162
```

DACPtranscinnaUNCAT exo PDT B3LYP/6-31G*

E(RB3LYP) = -617.092814743

Zero-point correction= 0.243903 (Hartree/Particle)
Thermal correction to Energy= 0.255692
Thermal correction to Enthalpy= 0.256636
Thermal correction to Gibbs Free Energy= 0.205052
Sum of electronic and ZPE= -616.848912
Sum of electronic and thermal Energies= -616.837123
Sum of electronic and thermal Enthalpies= -616.836179
Sum of electronic and thermal Free Energies= -616.887762

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      E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 160.449 47.806 108.566
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```
C,0,-0.8306426987,-1.2690852803,-0.0283400183
C,0,-0.4577244068,-0.8056885034,1.3712060837
H,0,-0.1576486082,-1.7668590835,-0.7181589405
H,0,0.3764742144,-1.3266454642,1.8463851737
C,0,-1.8369680963,-0.8843070199,2.0665327837
C,0,-2.0771060386,-0.8414877202,-0.2775062383
C,0,-2.5511295276,-0.085789854,0.9528397678
H,0,-2.6280294176,-0.909690352,-1.210424451
H,0,-3.6303121484,0.0625482166,1.0450237027
C,0,-0.2678909578,0.767798254,1.3440143781
C,0,-1.7014452464,1.2654848459,0.9868835446
H,0,-0.0720096484,1.0742083111,2.3766598018
C,0,-2.3038855244,2.2096680215,2.0045301832
H,0,-1.7597835675,1.7569503273,0.0098862507
C,0,0.8750207869,1.280365455,0.490709648
O,0,-1.9170079941,2.3645256096,3.1437549044
H,0,-3.2050155771,2.7559500047,1.6430258485
H,0,-1.8618722311,-0.3950770849,3.0460660024
H,0,-2.2143003407,-1.9079372467,2.149989858
C,0,2.0764925292,1.6473503603,1.1154909614
C,0,3.1716404006,2.0961885566,0.3770451603
C,0,3.0860458193,2.1920278133,-1.0124739205
C,0,1.8972864611,1.8347525928,-1.6503874869
C,0,0.8047179506,1.3848496704,-0.9073697802
H,0,2.1500851116,1.583429566,2.1990275922
H,0,4.0886739638,2.3768271578,0.8888467744
H,0,3.9346430699,2.5461305783,-1.591768094
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H,0,1.8166612355,1.9085064636,-2.7320879107
H,0,-0.1080825133,1.1058338042,-1.4246805792

DACPtranscinnaUNCAT endo PDT B3LYP/6-31G*

E(RB3LYP) = -617.090532829

Zero-point correction= 0.243633 (Hartree/Particle)
Thermal correction to Energy= 0.255510
Thermal correction to Enthalpy= 0.256454
Thermal correction to Gibbs Free Energy= 0.204358
Sum of electronic and ZPE= -616.846900
Sum of electronic and thermal Energies= -616.835023
Sum of electronic and thermal Enthalpies= -616.834079
Sum of electronic and thermal Free Energies= -616.886174

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 160.335 47.905 109.645

C,0,-0.4244496746,-0.5985977718,-0.2244467281
C,0,-0.0945912653,-0.3010997745,1.229725431
H,0,0.3120787818,-0.7649214294,-1.0041181378
H,0,0.8706876354,-0.6573950536,1.5945916611
C,0,-1.3659404969,-0.8512733136,1.9136022557
C,0,-1.7489179436,-0.4621925754,-0.3768720525
C,0,-2.3237766665,-0.0768420576,0.9792510557
H,0,-2.3133339687,-0.4989099117,-1.3029453136
H,0,-3.3969877042,-0.228496657,1.1180219037
C,0,-0.2948088551,1.2694395068,1.4020619006
C,0,-1.8413667505,1.405372504,1.2932797856
H,0,0.1528631656,1.774272031,0.5420127024
C,0,-2.3273451927,2.3922626599,0.2578767609
H,0,-2.2971806116,1.7036044157,2.2465884527
C,0,0.3601671829,1.8362977782,2.6506394195
O,0,-1.6311901233,2.9872634567,-0.5356766664
H,0,-3.4327680034,2.5370536355,0.2510581407
H,0,-1.4574354232,-0.5755910349,2.9691196077
H,0,-1.467779462,-1.9357999642,1.8085856422
C,0,1.6286509419,2.4258278661,2.5281745913
C,0,2.3113797654,2.9231726729,3.6374708013
C,0,1.735300154,2.8463368612,4.9064477578
C,0,0.4731823445,2.2698229017,5.0480185212
C,0,-0.2047200152,1.7715995945,3.9335391835

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H,0,2.0835463803,2.4983255851,1.5427398729
H,0,3.2908008938,3.3767560221,3.5086272629
H,0,2.2613197348,3.2362404943,5.7737118084
H,0,0.0089185343,2.2083114136,6.0290729583
H,0,-1.1889203578,1.3352211445,4.0790784212
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DACPtranscinnaUNCAT exo PDT M06-2X/6-31G*

```
E(RM062X) = -616.832714531

Zero-point correction= 0.246594 (Hartree/Particle)
Thermal correction to Energy= 0.258132
Thermal correction to Enthalpy= 0.259076
Thermal correction to Gibbs Free Energy= 0.208426
Sum of electronic and ZPE= -616.586121
Sum of electronic and thermal Energies= -616.574583
Sum of electronic and thermal Enthalpies= -616.573638
Sum of electronic and thermal Free Energies= -616.624288

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 161.980 47.121 106.602

C,0,-0.9461002562,-0.8776443889,-0.0851738631
C,0,-0.3584552175,-0.4180787196,1.2357692505
H,0,-0.3751289302,-1.2824858433,-0.9130091748
H,0,0.5928773911,-0.8662335669,1.5268576304
C,0,-1.5633908903,-0.6275348411,2.1703317288
C,0,-2.2440581516,-0.5562423074,-0.0805506925
C,0,-2.5377722841,0.1218691973,1.2431549051
H,0,-2.9505899011,-0.6442995535,-0.8988275389
H,0,-3.5870636105,0.1702192331,1.5435852767
C,0,-0.314552789,1.1557412038,1.2084724495
C,0,-1.8179433953,1.5297959448,1.16946706
H,0,0.0784722153,1.4828409001,2.1772370181
C,0,-2.2699912192,2.3539040265,2.3512937808
H,0,-2.115754514,2.0568866501,0.2573330222
C,0,0.5660090698,1.7314864684,0.1245944107
O,0,-1.6727320149,2.4590549457,3.3949875155
H,0,-3.2603548703,2.8412521335,2.2259508539
H,0,-1.4388093043,-0.1518801382,3.1484964083
H,0,-1.8327928793,-1.679985554,2.2882504778
C,0,1.8801841334,2.0880942315,0.4411543822
C,0,2.7500604563,2.5748161454,-0.5296362162
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C,0,2.3165329079,2.7179774879,-1.8446987469
C,0,1.0100694738,2.3696229377,-2.1751355131
C,0,0.1439620375,1.8807454184,-1.2006382315
H,0,2.2216466195,1.9848955363,1.4686229118
H,0,3.7649262688,2.8480341535,-0.2561744562
H,0,2.9897950298,3.1015891126,-2.6051955003
H,0,0.6602897766,2.4787291545,-3.1975554251
H,0,-0.868252152,1.603439032,-1.4804137237

DACPtranscinnaUNCAT endo PDT M06-2X/6-31G*

E(RM062X) = -616.829714542

Zero-point correction= 0.246374 (Hartree/Particle)
Thermal correction to Energy= 0.258042
Thermal correction to Enthalpy= 0.258986
Thermal correction to Gibbs Free Energy= 0.207750
Sum of electronic and ZPE= -616.583340
Sum of electronic and thermal Energies= -616.571673
Sum of electronic and thermal Enthalpies= -616.570729
Sum of electronic and thermal Free Energies= -616.621965

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 161.924 47.243 107.836

C,0,-0.4363482198,-0.5379255564,-0.2385624867
C,0,-0.0614677061,-0.229932774,1.1981437439
H,0,0.2733250246,-0.675458247,-1.0467876715
H,0,0.9280251988,-0.5506634408,1.5278751338
C,0,-1.2811100208,-0.8119395609,1.9332311393
C,0,-1.7660218811,-0.4514547743,-0.337840706
C,0,-2.2971792485,-0.08099879,1.03655717
H,0,-2.3632603341,-0.5049432239,-1.2413209604
H,0,-3.357391564,-0.264528912,1.2201710586
C,0,-0.3087154907,1.3198468446,1.3830090966
C,0,-1.8506694532,1.4102380434,1.2999619421
H,0,0.1190097347,1.8557693605,0.5308392878
C,0,-2.3657270359,2.3246412808,0.2172220827
H,0,-2.3018652197,1.7424261068,2.2428357939
C,0,0.341247283,1.8570056111,2.6413185987
O,0,-1.6827029704,2.8959113763,-0.5955023206
H,0,-3.4726336447,2.426205254,0.1874286582
H,0,-1.3354637048,-0.5210176302,2.9867749892

```
H,0,-1.351223837,-1.8986841098,1.8416385965
C,0,1.6443855398,2.3589834738,2.5450151236
C,0,2.330136106,2.8158303057,3.6646037834
C,0,1.7213957128,2.7830870291,4.9168611345
C,0,0.4258318046,2.2906240632,5.030885319
C,0,-0.2556958524,1.8324292158,3.9050856498
H,0,2.1230967706,2.3941642661,1.5690068525
H,0,3.3387927932,3.2035485299,3.5575119402
H,0,2.2505741352,3.1420582176,5.7941537925
H,0,-0.0627922717,2.2621978055,6.0003834072
H,0,-1.2681676481,1.4586422351,4.0287378512
```

Cyclohexanone SM

```
E(RM062X) =  -309.841420182

Zero-point correction= 0.151658 (Hartree/Particle)
Thermal correction to Energy= 0.158107
Thermal correction to Enthalpy= 0.159051
Thermal correction to Gibbs Free Energy= 0.121271
Sum of electronic and ZPE= -309.689762
Sum of electronic and thermal Energies= -309.683313
Sum of electronic and thermal Enthalpies= -309.682369
Sum of electronic and thermal Free Energies= -309.720150

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 99.214 24.674 79.516

Temperature=              298.150000 Pressure=                    1.000000
 E(ZPE)=                    0.150142 E(Thermal)=                  0.156644
 E(SCF)=                 -308.012447 DE(MP2)=                    -1.219084
 DE(CBS)=                   -0.117137 DE(MP34)=                    -0.065201
 DE(CCSD)=                  -0.034584 DE(Int)=                     0.039884
 DE(Empirical)=             -0.060655
 CBS-QB3 (0 K)=           -309.319083 CBS-QB3 Energy=            -309.312581
 CBS-QB3 Enthalpy=        -309.311637 CBS-QB3 Free Energy=       -309.349508

 O,0,-0.3158730384,-1.3587635314,-0.3791887868
 C,0,0.7828837839,-0.8500970619,-0.4631398933
 C,0,2.0431303726,-1.577510758,-0.053793164
 C,0,2.8864572027,-0.7212323192,0.9065026997
 C,0,3.1553390512,0.6633617848,0.3180050639
 C,0,1.8440046519,1.3808891509,-0.0002512513
```

C,0,0.9841597921,0.5579239348,-0.9749022769
H,0,1.774384128,-2.5412217098,0.3798859079
H,0,2.6227860807,-1.7597498,-0.9671619561
H,0,1.5113596769,0.4814039346,-1.9338919105
H,0,0.0106729947,1.0153187875,-1.1542306242
H,0,2.3515755429,-0.6137029143,1.8563625514
H,0,3.8227282258,-1.2394799941,1.1233877253
H,0,3.7477967692,0.561713325,-0.5987888416
H,0,3.7460089101,1.2584403491,1.0185089656
H,0,2.0349606493,2.3655985074,-0.4316530465
H,0,1.2835462063,1.5400133147,0.9273588373

PAA SM

E(RM062X) = -304.189993036

Zero-point correction= 0.065268 (Hartree/Particle)
Thermal correction to Energy= 0.071009
Thermal correction to Enthalpy= 0.071953
Thermal correction to Gibbs Free Energy= 0.035628
Sum of electronic and ZPE= -304.124725
Sum of electronic and thermal Energies= -304.118984
Sum of electronic and thermal Enthalpies= -304.118040
Sum of electronic and thermal Free Energies= -304.154365

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 44.559 18.248 76.453
```

```
Temperature=            298.150000 Pressure=                  1.000000
 E(ZPE)=                  0.064615 E(Thermal)=                0.070386
 E(SCF)=               -302.681908 DE(MP2)=                  -1.028525
 DE(CBS)=                -0.103642 DE(MP34)=                 -0.027396
 DE(CCSD)=               -0.026602 DE(Int)=                   0.031746
 DE(Empirical)=          -0.049111
 CBS-QB3 (0 K)=        -303.820823 CBS-QB3 Energy=         -303.815052
 CBS-QB3 Enthalpy=     -303.814108 CBS-QB3 Free Energy=    -303.850492
```

C,0,1.5183562123,0.6000187333,0.0940072405
C,0,0.0688565166,0.3050016595,-0.1071780027
O,0,-0.4737968727,-0.2684759957,0.9892926956
O,0,-1.8523007035,-0.5340107242,0.8307229762
O,0,-0.5965935652,0.5316490898,-1.0846714997
H,0,-2.0298312514,-0.2179296937,-0.0784549359

```
H,0,1.6365618766,1.6821872909,0.1678130509
H,0,2.0660796926,0.2510522748,-0.7802180994
H,0,1.8991000948,0.1283023654,0.9964015743
```

HydroniumIon

```
E(RHF) =  -304.719527360

Zero-point correction=                           0.106796 (Hartree/Particle)
Thermal correction to Energy=                    0.117505
Thermal correction to Enthalpy=                  0.118449
Thermal correction to Gibbs Free Energy=         0.071687
Sum of electronic and zero-point Energies=          -306.171421
Sum of electronic and thermal Energies=             -306.160712
Sum of electronic and thermal Enthalpies=           -306.159768
Sum of electronic and thermal Free Energies=        -306.206529

                E (Thermal)           CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total              73.735            33.712           98.418

Temperature=             298.150000 Pressure=                  1.000000
 E(ZPE)=                   0.105728 E(Thermal)=                0.116490
 E(SCF)=                -304.719527 DE(MP2)=                  -1.043642
 DE(CBS)=                 -0.106107 DE(MP34)=                 -0.028571
 DE(CCSD)=                -0.013524 DE(Int)=                   0.031986
 DE(Empirical)=           -0.054998
 CBS-QB3 (0 K)=         -305.828657 CBS-QB3 Energy=          -305.817894
 CBS-QB3 Enthalpy=      -305.816950 CBS-QB3 Free Energy=     -305.863844

  O  0.055963729664    -0.074566353850    -0.617697856146
  H  0.008814248414     0.885998079841    -0.281520732186
  H -0.755057243647    -0.602013296329    -0.295676968075
  H  0.911585677480    -0.521347473202    -0.291103529706
  O  2.181326585497    -1.248459895496     0.173226864466
  O -0.011249260255     2.349245158427     0.175503411655
  O -1.948531272879    -1.451755851143     0.145172837198
  H  2.858403476476    -1.286337713884    -0.511615575588
  H -0.454714459463     2.480253704545     1.020943247160
  H -2.669499832883    -1.446473680133    -0.494223292540
  H -2.338783260588    -1.176044456416     0.982008605261
  H -0.457308962676     2.935602206078    -0.445702328995
  H  2.600778574754    -0.819114428467     0.927414317494
```

Water2molecules

```
E(RM062X) =  -152.874946816
```

```
Zero-point correction=                      0.046471 (Hartree/Particle)
 Thermal correction to Energy=                0.051914
 Thermal correction to Enthalpy=              0.052858
 Thermal correction to Gibbs Free Energy=     0.020945
 Sum of electronic and zero-point Energies=        -152.828475
 Sum of electronic and thermal Energies=           -152.823033
 Sum of electronic and thermal Enthalpies=         -152.822089
 Sum of electronic and thermal Free Energies=      -152.854002
```

```
                E (Thermal)         CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
 Total             32.577          15.752          67.167
Temperature=            298.150000 Pressure=                 1.000000
 E(ZPE)=                  0.046007 E(Thermal)=               0.051470
 E(SCF)=               -152.140567 DE(MP2)=                 -0.518533
 DE(CBS)=                -0.054706 DE(MP34)=                -0.014044
 DE(CCSD)=               -0.006230 DE(Int)=                  0.016417
 DE(Empirical)=          -0.027625
 CBS-QB3 (0 K)=        -152.699282 CBS-QB3 Energy=        -152.693819
 CBS-QB3 Enthalpy=     -152.692875 CBS-QB3 Free Energy=   -152.724835
```

O	-1.47356	0.00012	-0.12045
H	-0.50787	-0.00002	-0.00045
H	-1.83438	-0.00077	0.77147
O	1.33111	-0.00009	0.10376
H	1.74084	0.76349	-0.3181
H	1.74101	-0.76288	-0.31939

TS1addition-paa TS

```
E(RHF) =  -763.255162776
```

```
Temperature=            298.150000 Pressure=                 1.000000
 E(ZPE)=                  0.277900 E(Thermal)=               0.295511
 E(SCF)=               -763.255163 DE(MP2)=                 -2.792178
 DE(CBS)=                -0.271309 DE(MP34)=                -0.104981
 DE(CCSD)=               -0.071950 DE(Int)=                  0.086872
 DE(Empirical)=          -0.136900
 CBS-QB3 (0 K)=        -766.267710 CBS-QB3 Energy=        -766.250099
 CBS-QB3 Enthalpy=     -766.249155 CBS-QB3 Free Energy=   -766.312306
```

```
H,0,-0.1667861755,0.0880886744,-0.1507830737
H,0,2.4720053135,-0.1023310391,0.5362554462
C,0,-0.2806973411,-3.1152936332,-2.8736659775
C,0,-0.3738472123,-1.6431682313,-2.653344814
O,0,-0.7641578855,-0.8073891238,-3.4173065251
O,0,0.1006822104,-1.3417693731,-1.4019276702
O,0,0.1008480677,0.0459982631,-1.1741636717
C,0,1.7698765643,1.9773531988,-0.6573146862
C,0,1.982894427,0.5974583757,-1.1867282368
O,0,2.5351338701,-0.3069040363,-0.4423703263
C,0,2.2594491541,0.4748818246,-2.6452438202
H,0,0.9481369709,2.4410133309,-1.2067746421
H,0,1.4472482769,0.9412831229,-3.2042434612
H,0,1.5319142308,1.9575212347,0.4077603521
H,0,2.3511226657,-0.5761625729,-2.9256531255
C,0,3.5722047867,1.2492228982,-2.8992853211
H,0,3.7897096424,1.2116779076,-3.9677029253
H,0,4.393580381,0.7489881622,-2.3768819324
C,0,3.080112622,2.7510931325,-0.9316258273
H,0,2.9414419936,3.7815424944,-0.6012932854
H,0,3.8844976043,2.316078061,-0.3296898562
C,0,3.4488227074,2.6935492276,-2.4137382801
H,0,2.6767652612,3.206657794,-2.9977471277
H,0,4.3900288503,3.2221590326,-2.5807919176
O,0,-0.4089943024,0.1669790211,1.2460658923
H,0,0.4604915027,0.1698707984,1.6928447068
O,0,2.2450612415,0.1550097727,2.1307434764
H,0,2.5794564835,-0.5451567082,2.7055076677
H,0,2.6307376051,0.9770174342,2.4597848977
H,0,-0.8738371671,-0.6145087359,1.5718191497
H,0,0.741247938,-3.3448926026,-3.1855591245
H,0,-0.9715578404,-3.3960662435,-3.6651643354
H,0,-0.4962895268,-3.6621502316,-1.9570839553
```

CriegeePAA Intermediate

E(RHF) = -610.701330618

Zero-point correction= 0.220838 (Hartree/Particle)
Thermal correction to Energy= 0.232862
Thermal correction to Enthalpy= 0.233806
Thermal correction to Gibbs Free Energy= 0.182889
Sum of electronic and ZPE= -613.838417
Sum of electronic and thermal Energies= -613.826393

```
Sum of electronic and thermal Enthalpies= -613.825449
Sum of electronic and thermal Free Energies= -613.876366

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 146.123 46.166 107.164

Temperature=            298.150000 Pressure=              1.000000
 E(ZPE)=                  0.218630 E(Thermal)=            0.230754
 E(SCF)=               -610.701331 DE(MP2)=              -2.265535
 DE(CBS)=                -0.220591 DE(MP34)=             -0.090137
 DE(CCSD)=               -0.063222 DE(Int)=               0.071253
 DE(Empirical)=          -0.109716
 CBS-QB3 (0 K)=        -613.160649 CBS-QB3 Energy=         -613.148525
 CBS-QB3 Enthalpy=     -613.147580 CBS-QB3 Free Energy=    -613.198691

 H,0,-0.9050071283,-2.0545328951,1.3073592124
 C,0,3.7256345377,0.545859293,0.5945776917
 C,0,2.5948555736,0.1936905948,-0.314293376
 O,0,2.3707075842,0.6366342558,-1.4066127657
 O,0,1.7939311751,-0.7288814442,0.2991605765
 O,0,0.6757707072,-1.0827254834,-0.4952284144
 C,0,-1.6195280702,-1.0128631043,-0.8372695054
 C,0,-0.5240550543,-0.5621395806,0.121827464
 O,0,-0.6647797164,-1.1226985104,1.3994628214
 C,0,-0.4712311184,0.9505944584,0.2703186464
 H,0,-1.3728537548,-0.6430045506,-1.8362846251
 H,0,-0.186443396,1.3682202194,-0.6992727796
 H,0,-1.6285978156,-2.106350156,-0.8710822276
 H,0,0.2979539075,1.2176536038,0.9997728178
 C,0,-1.834737927,1.5045879086,0.6924029284
 H,0,-1.7770149284,2.5944473798,0.7358071454
 H,0,-2.0749069659,1.1544721866,1.7012917057
 C,0,-2.9762392541,-0.4590389718,-0.3954057595
 H,0,-3.7371026557,-0.768674908,-1.1150467959
 H,0,-3.2505863988,-0.8945364317,0.5711147595
 C,0,-2.9329487074,1.0643910938,-0.2762290156
 H,0,-2.7384308387,1.4975168391,-1.2645808868
 H,0,-3.9021958397,1.4427297397,0.0579850845
 H,0,4.0931474946,-0.3363917015,1.1167759915
 H,0,3.3513921309,1.256958052,1.3355025655
 H,0,4.5174531072,1.011119673,0.0124234716
```

TS2migration-paa TS

```
E(RHF) =  -610.626296386

Zero-point correction= 0.216596 (Hartree/Particle)
Thermal correction to Energy= 0.228897
Thermal correction to Enthalpy= 0.229841
Thermal correction to Gibbs Free Energy= 0.178019
Sum of electronic and ZPE= -613.794638
Sum of electronic and thermal Energies= -613.782337
Sum of electronic and thermal Enthalpies= -613.781393
Sum of electronic and thermal Free Energies= -613.833215

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 143.635 46.364 109.069
Temperature=              298.150000 Pressure=                  1.000000
 E(ZPE)=                  0.214430 E(Thermal)=                0.226830
 E(SCF)=               -610.626296 DE(MP2)=                  -2.301314
 DE(CBS)=                -0.223520 DE(MP34)=                 -0.076982
 DE(CCSD)=               -0.073468 DE(Int)=                   0.072513
 DE(Empirical)=          -0.108702
 CBS-QB3 (0 K)=          -613.123339 CBS-QB3 Energy=            -613.110939
 CBS-QB3 Enthalpy=        -613.109995 CBS-QB3 Free Energy=        -613.162012

 O,0,0.2010929109,0.0772352417,0.0479242841
 C,0,0.2343599797,0.1296798531,1.4103113694
 H,0,2.2339023255,0.6451065894,1.6636072231
 O,0,1.4623287609,-2.130251455,1.8556150172
 O,0,-0.0130823992,-0.9777634398,2.0299505887
 H,0,1.1649139538,2.0305737304,1.4137934791
 H,0,0.1096923801,-0.8756389058,-0.1935892608
 C,0,1.3217838786,-2.8483887593,0.7954436365
 O,0,0.5494440941,-2.584352077,-0.1375862785
 C,0,1.2732721615,1.0856350379,1.9519086697
 C,0,-1.3399435158,0.6180182042,2.0308652589
 H,0,-1.3556348061,1.4871822968,1.3649978313
 H,0,-2.0795784908,-0.113161803,1.7187075275
 C,0,-1.324485578,0.9697476148,3.4915034925
 H,0,-2.2803240371,1.4670857914,3.6930813166
 H,0,-1.3025801999,0.0590039995,4.0941746111
 C,0,1.1807208206,1.2908976799,3.458453786
 H,0,1.9945260457,1.9505735793,3.7663832741
 H,0,1.3303733171,0.3341231879,3.9694220383
```

```
C,0,-0.1641177932,1.89312643,3.8613947438
H,0,-0.1843522566,2.0851422722,4.9358926404
H,0,-0.2932429371,2.8560352237,3.3548393599
C,0,2.1809417808,-4.0900911584,0.7666697332
H,0,2.2272169281,-4.4878627825,-0.24513356
H,0,3.1814540425,-3.871885654,1.1381763532
H,0,1.7257560841,-4.8312067674,1.4279306946
```

TFPAA SM

E(RHF) = -599.341240451

Zero-point correction= 0.042704 (Hartree/Particle)
Thermal correction to Energy= 0.050253
Thermal correction to Enthalpy= 0.051197
Thermal correction to Gibbs Free Energy= 0.008971
Sum of electronic and ZPE= -601.863945
Sum of electronic and thermal Energies= -601.856396
Sum of electronic and thermal Enthalpies= -601.855452
Sum of electronic and thermal Free Energies= -601.897678

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 31.534 24.882 88.873
```

```
Temperature=             298.150000 Pressure=                 1.000000
 E(ZPE)=                 0.042277 E(Thermal)=               0.049869
 E(SCF)=               -599.341240 DE(MP2)=                 -1.743207
 DE(CBS)=                -0.185751 DE(MP34)=                 -0.019098
 DE(CCSD)=                -0.037453 DE(Int)=                 0.050902
 DE(Empirical)=           -0.085010
 CBS-QB3 (0 K)=          -601.318581 CBS-QB3 Energy=          -601.310989
 CBS-QB3 Enthalpy=        -601.310044 CBS-QB3 Free Energy=        -601.352362
```

```
C,0,1.5004981649,0.5952701312,0.0809375339
C,0,0.0269279637,0.191458915,-0.1471063764
O,0,-0.5845066198,0.0822525256,1.0255524379
O,0,-1.950365679,-0.2453095778,0.9023882642
O,0,-0.4735733639,0.0244308325,-1.2149261109
H,0,-2.0875942385,-0.3327390572,-0.0617905227
F,0,1.5629109844,1.839816981,0.5493738163
F,0,2.1565563501,0.5359361116,-1.0651846288
F,0,2.0855784381,-0.2133228618,0.9584715865
```

TS1addition-tfpaa TS

E(RHF) = -1059.90993964

Zero-point correction= 0.256510 (Hartree/Particle)
Thermal correction to Energy= 0.275927
Thermal correction to Enthalpy= 0.276871
Thermal correction to Gibbs Free Energy= 0.207479
Sum of electronic and ZPE= -1064.816537
Sum of electronic and thermal Energies= -1064.797119
Sum of electronic and thermal Enthalpies= -1064.796175
Sum of electronic and thermal Free Energies= -1064.865568

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.147 70.826 146.049
```

```
Temperature=            298.150000 Pressure=                1.000000
 E(ZPE)=                  0.253945 E(Thermal)=              0.273506
 E(SCF)=              -1059.909940 DE(MP2)=                -3.510418
 DE(CBS)=                -0.353431 DE(MP34)=               -0.095983
 DE(CCSD)=               -0.083344 DE(Int)=                 0.106002
 DE(Empirical)=          -0.172763
 CBS-QB3 (0 K)=       -1063.765933 CBS-QB3 Energy=       -1063.746372
 CBS-QB3 Enthalpy=    -1063.745428 CBS-QB3 Free Energy=  -1063.815132
```

```
 H,0,-0.135444826,0.0349978995,-0.02307426
 H,0,2.4888711174,-0.0500201046,0.5586700102
 C,0,-0.3086052004,-3.0673597783,-2.9028826417
 C,0,-0.3874298498,-1.5461583278,-2.6319013965
 O,0,-0.8225163922,-0.760376874,-3.408164591
 O,0,0.1235703567,-1.3170843782,-1.4199786666
 O,0,0.1201412386,0.0560036972,-1.1190854349
 C,0,1.7729920611,1.9987262004,-0.675439138
 C,0,1.982573703,0.6074904902,-1.1739095503
 O,0,2.5520195158,-0.2751095323,-0.4122055626
 C,0,2.2551661848,0.4518819044,-2.6301003671
 H,0,0.9550315961,2.4540157501,-1.2371883061
 H,0,1.4428975944,0.9067874865,-3.1986536506
 F,0,-0.8651343594,-3.7627625277,-1.9139446193
 F,0,-0.941373683,-3.3489677341,-4.0307201528
 F,0,0.9623185138,-3.4521638344,-3.0200145887
 H,0,1.5329482477,2.0014323858,0.3896963615
 H,0,2.3489496363,-0.6052045895,-2.8872418746
```

```
C,0,3.5709938272,1.2159433914,-2.9023111844
H,0,3.7844294967,1.1571158588,-3.9705562943
H,0,4.3901374504,0.719027251,-2.3734877894
C,0,3.088039484,2.7593203392,-0.96297941
H,0,2.9533985415,3.7968598379,-0.6538772188
H,0,3.8883283021,2.3327730697,-0.3498776915
C,0,3.4583617704,2.6701045859,-2.4434284195
H,0,2.691431694,3.1782899649,-3.0381779713
H,0,4.4036881046,3.1884013552,-2.6188967226
O,0,-0.3630515123,0.0302734593,1.2496525557
H,0,0.501703044,0.0810878134,1.7135076457
O,0,2.2093244394,0.2035323772,2.1693322442
H,0,2.5866714342,-0.4592634299,2.7617578598
H,0,2.5074582504,1.0608429253,2.5001273866
H,0,-0.7805159613,-0.7961431625,1.5283540389
```

Criegee-tfpaa Intermediate

```
E(RHF) =  -907.360678496

Zero-point correction= 0.198325 (Hartree/Particle)
Thermal correction to Energy= 0.212278
Thermal correction to Enthalpy= 0.213222
Thermal correction to Gibbs Free Energy= 0.156448
Sum of electronic and ZPE= -911.578180
Sum of electronic and thermal Energies= -911.564227
Sum of electronic and thermal Enthalpies= -911.563283
Sum of electronic and thermal Free Energies= -911.620057

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 133.207 52.691 119.491

Temperature=             298.150000 Pressure=                 1.000000
 E(ZPE)=                   0.196342 E(Thermal)=               0.210407
 E(SCF)=                -907.360678 DE(MP2)=                 -2.981212
 DE(CBS)=                 -0.302658 DE(MP34)=                -0.081790
 DE(CCSD)=                -0.074258 DE(Int)=                  0.090405
 DE(Empirical)=           -0.145602
 CBS-QB3 (0 K)=         -910.659451 CBS-QB3 Energy=         -910.645386
 CBS-QB3 Enthalpy=      -910.644442 CBS-QB3 Free Energy=    -910.701441

 H,0,1.8365973516,1.3404016385,1.0747399245
 C,0,-3.240810383,-0.2758501628,0.3329832774
```

```
C,0,-1.9856474864,-0.2264906928,-0.5715537903
O,0,-1.911001681,-0.7837232993,-1.6178583622
O,0,-1.063977929,0.5177204242,0.0426860153
O,0,0.1238968346,0.608396487,-0.7265392333
C,0,2.3574678413,0.0498469577,-0.9944862602
C,0,1.1830032308,-0.1125756923,-0.0369731761
O,0,1.4044422628,0.4855522709,1.2066492754
C,0,0.8104897731,-1.5683520706,0.1880900606
H,0,2.0524144046,-0.3219988152,-1.9764975246
H,0,0.4591239063,-1.971982362,-0.7658903182
F,0,-3.6631754368,0.9478125044,0.643020018
F,0,-4.2165910978,-0.9151751282,-0.2930906797
F,0,-2.9684856555,-0.9225108257,1.4665107944
H,0,2.5920159446,1.1142598181,-1.087842697
H,0,-0.0070665045,-1.628456749,0.9113049947
C,0,2.0246244686,-2.3644524438,0.6755256516
H,0,1.742048063,-3.4142237145,0.7792202666
H,0,2.3176449374,-2.0092202086,1.668528574
C,0,3.5633329869,-0.7452588371,-0.4866576126
H,0,4.3812672612,-0.6411960956,-1.2025611269
H,0,3.9072373609,-0.3195997006,0.4616639863
C,0,3.2028520586,-2.217238727,-0.2876496228
H,0,2.9354550228,-2.6560234438,-1.2561417849
H,0,4.0680225651,-2.7675455319,0.0899736501
```

TS2addition-tfpaa TS

E(RHF) = -907.299656131

Zero-point correction= 0.194711 (Hartree/Particle)
Thermal correction to Energy= 0.208863
Thermal correction to Enthalpy= 0.209808
Thermal correction to Gibbs Free Energy= 0.152794
Sum of electronic and ZPE= -911.546335
Sum of electronic and thermal Energies= -911.532183
Sum of electronic and thermal Enthalpies= -911.531239
Sum of electronic and thermal Free Energies= -911.588252

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.064 53.085 119.995

Temperature=            298.150000 Pressure=            1.000000
 E(ZPE)=                0.192764 E(Thermal)=            0.207028
```

E(SCF)= -907.299656 DE(MP2)= -3.012456
DE(CBS)= -0.305593 DE(MP34)= -0.070084
DE(CCSD)= -0.084085 DE(Int)= 0.091559
DE(Empirical)= -0.144706
CBS-QB3 (0 K)= -910.632257 CBS-QB3 Energy= -910.617993
CBS-QB3 Enthalpy= -910.617049 CBS-QB3 Free Energy= -910.674288

O,0,0.1647489509,0.0699962704,0.0252154497
C,0,0.1787556317,0.1129869141,1.3947213809
H,0,2.210703007,0.52933316,1.6249749127
O,0,1.3678339448,-2.1110850179,1.881668752
O,0,-0.0785365796,-1.0069840818,2.0056456254
H,0,1.2022255636,1.9657097187,1.3926608955
H,0,-0.2528298986,-0.7623875048,-0.2535699095
C,0,1.2101308062,-2.8705342344,0.8674271589
O,0,0.3917301202,-2.8231022362,-0.0279923697
C,0,1.2750734533,1.013191014,1.9228754223
C,0,-1.3424339422,0.6620118237,2.0012018481
H,0,-1.35055143,1.5352495814,1.340375414
H,0,-2.1150041021,-0.0402879439,1.699591843
C,0,-1.3135494955,1.0064414808,3.4658320281
H,0,-2.2460083733,1.5427176871,3.6738192633
H,0,-1.3294422834,0.0915502723,4.0626032991
C,0,1.200686223,1.2139965308,3.4317434013
H,0,2.0455148602,1.8334842343,3.7386249548
H,0,1.3088692771,0.2479353294,3.9353992927
C,0,-0.1140483601,1.8735353529,3.84286104
H,0,-0.1232215593,2.0557342833,4.9192947523
H,0,-0.1993069533,2.8463747233,3.3459812078
C,0,2.2870246873,-3.993118815,0.8484024644
F,0,2.0934198017,-4.8352001317,-0.1621084667
F,0,3.5106724629,-3.4688233467,0.7182271122
F,0,2.2667714876,-4.6993085142,1.9823558073

Trifluoroacetic Acid PDT

E(RHF) = -524.572610991

Zero-point correction= 0.039179 (Hartree/Particle)
Thermal correction to Energy= 0.045376
Thermal correction to Enthalpy= 0.046320
Thermal correction to Gibbs Free Energy= 0.008036
Sum of electronic and ZPE= -526.758140
Sum of electronic and thermal Energies= -526.751944

```
Sum of electronic and thermal Enthalpies= -526.751000
Sum of electronic and thermal Free Energies= -526.789283

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 28.474 20.824 80.575

Temperature=             298.150000 Pressure=                 1.000000
 E(ZPE)=                 0.038788 E(Thermal)=              0.045021
 E(SCF)=              -524.572611 DE(MP2)=                 -1.504160
 DE(CBS)=                -0.162067 DE(MP34)=                 -0.015985
 DE(CCSD)=                -0.029543 DE(Int)=                 0.044192
 DE(Empirical)=            -0.074999
 CBS-QB3 (0 K)=          -526.276385 CBS-QB3 Energy=          -526.270152
 CBS-QB3 Enthalpy=        -526.269208 CBS-QB3 Free Energy=       -526.307563


 C,0,-1.3813394781,-0.1392907393,-0.0077065875
 C,0,0.1359029145,0.1367634312,-0.0697920151
 O,0,0.5749125473,1.2478271085,-0.1182164173
 O,0,0.800454981,-0.997023605,-0.055484217
 H,0,1.7585410683,-0.8284353968,-0.0894465742
 F,0,-1.7699020792,-0.8939180948,-1.0366665525
 F,0,-2.0608884597,0.9983011422,-0.0402524869
 F,0,-1.696019604,-0.784160656,1.1171491606
```

Example RRKM Input File

The text below shows an example input file for the QCPE RRKM program. The first two lines are the title for the example. In this example, rate constants were calculated with energies ranging from 57.73 kcal/mol in 0.5 kcal/mol increments up to 71.23 kcal/mol – this is relative to the molecule's zero-point level. The threshold energy barrier in this example is 12.87 kcal/mol; this is the difference between the zero-point level energies for the TS versus the primary ozonide, and is based in this case on the G4 energetics. A complete description of the parameters from the program can be found in: http://cdssim.chem.ttu.edu/nav/RRKM/Doc/RRKM_manual.pdf

```
run on cleavage A of primary ozonide with butyl
vinyl ether using G4 calcs
56.73,0.5,30,
0,
-1,0,1,218,
0,
-1,
-1,
1.0,
60,0,
37.3800,57.0782,83.5199,105.8121,128.1340,172.1397,238.7630
250.2691,286.1439,354.2613,427.4214,489.1129,595.9634,697.1219
737.5105,745.0248,786.6477,815.2104,882.7839,916.4730,930.9109
953.7442,982.3831,1000.8160,1025.4596,1042.4304,1073.6975,1108.0106
1136.9636,1165.3434,1194.3251,1242.2827,1252.5710,1291.6075,1310.2916
1313.9829,1325.4654,1339.5175,1372.8769,1392.4979,1413.7177,1442.6131
1488.0680,1492.2285,1496.3558,1500.0643,1509.9878,1525.7511,2971.1375
3014.2502,3016.6213,3028.6132,3032.4458,3037.8867,3041.5173,3056.7262
3077.0158,3099.1195,3104.7500,3132.6360
606.8,606.8,1131.7
0,
12.87,
59,0,
35.4633,55.1796,87.9562,116.4529,133.4028,151.7836,248.9667
251.4219,287.0760,366.5845,400.4870,433.4861,499.4323,596.9726
673.9981,743.9371,771.8165,808.9730,870.9221,918.1055,941.6053
949.6107,991.6754,1039.5077,1065.4122,1073.3109,1128.5998,1141.4087
1183.9219,1190.3490,1219.3122,1251.2061,1261.7202,1292.1871,1308.1146
1318.4736,1325.2342,1386.3031,1398.5033,1412.6072,1424.2184,1470.8778
1487.8256,1495.7059,1500.1126,1509.2570,1523.2487,2955.1096,3012.0584
3015.7781,3026.9780,3031.3907,3040.4521,3051.4762,3076.7419,3097.3577
3097.5369,3103.2562,3216.2472
557.9,557.9,978.4
0,
```

Listing of Dynamics Programs for Program Suite PROGDYN

Program progdynstarterHP

```
#!/bin/bash
# This is the master control program for dynamics, in the form of a Unix Shell Script.
#
# Necessary input files:
# freqinHP         - This is the standard output from a Gaussian 98 or 03 frequency calculation using
freq=hpmodes.
# progdyn.conf – This is a file giving a variety of configuration options, called on by many of the
subprograms.
#
# Optional input:
# isomernumber     - A number in file isomernumber provides a start for numbering runs.
# detour – A signal file that, by existing, signals the program to do a side calculations
# nogo – A signal file that, by existing, signals the program to stop between points
#
# Programs called:
#  proggenHP     - An awk program that starts a trajectory, giving each mode its zero point energy (if a
quasiclassical calculation) plus random additional excitations depending on the temperature.
#  prog1stpoint – Awk program that creates the first Gaussian input file for each run
#  prog2ndpoint – Awk program that creates the second Gaussian input file for each run
#  progdynb – Creates subsequent Gaussian input files until run is completed, used the awk
# proganal – A program to analyze the latest point and see if a run is done.  This program must be redone
for each new system.  Elaborate changes are often programmed into proganal, such as the automatic
changing of configuration variables.
# randgen – A program that generates random numbers between 0 and 1.  These are generated all at once
and stored in a file for use by proggenHP.
#
# Output files
# isomernumber – A running tab of the run number
# geoRecord – A record of all the starting positions and velocities.
# geoPlusVel – Created by proggen, this gives starting position and velocities for current run.
# g03.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input
#       file for Gaussian03 for current run and latest point.
# olddynrun and olderdynrun – files containing the last two outputs from Gaussian, for creation
# of the next point
# dyn  - A record of all of the Gaussian outputs.
# dynfollowfile – A short record of the runs and their results.
# skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run.
# diagnostics – optional output that follows which subprograms are running and configuration variables,
decided by variable in progdyn.conf
# vellist – optional output that list the velocities of each atom, decided by variable in progdyn.conf
# A number of files starting with 'temp' are created then later erased.


#progdynstarterHP, made to use high-precision modes from Gaussian output with freq=hpmodes
#updated to create a random number file temp811 that is used by proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn putting it under control of progdynb
#version Feb 2008 moves variables like the scratch directory and location of randgen to the beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run twice in checking for complete runs
#version May 2009 Echeck catches bad energies after only one point, other lines written simpler, triple
while loop, revised comments
#version Aug 2010 isomernumber adds words to ease parsing, increased elements up to bromine,
runpointnumber checked for more appropriate restarts
```

```
#
#LIMITATIONS - standard version only handles elements up to bromine, must change program to do
higher atomic numbers
#   only handles up to 4000th excited state for modes - this could start to affect the initialization of
classical modes or transition vectors at
#    extremely high temperatures
#   The routine that checks whether the actual energy approximately equals the desired energy checks for
lines containing "SCF Done" or "EUMP2 =" or " Energy="
#   This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculatons but the routine in
prog2ndpoint would have to be changed for other calcs.
#
#                              OUTLINE
# A. initilize to perform Gaussian jobs and know where we are
#    start loop
# B. if no file named "skipstart" then generate a new isomer.  Instructions: Get rid of skipstart to start new
isomer.
#    the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and second points, and
sets up for continuous loop
# C. loop over propagation steps
#
#  AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system and assigned here
or by program calling this one
export LC_ALL=C
echo $1
scratchdir=$1
export g09root=/apps/lms/g09_A02_XEON
. $g09root/g09/bsd/g09.profile
origdir=`pwd`
cd $origdir
logfile=docslog
randdir=~/bin
cp /scratch/d-singleton/binall700/* /tmp/$PBS_JOBID
proggramdir=/tmp/$PBS_JOBID
freqfile=/scratch/d-singleton/binall700/freqinHP
echo ORIGDIR:
echo $origdir
echo SCRATCHDIR:
echo $scratchdir
echo PROGGRAMDIR:
echo $proggramdir

rm -f nogo    # assume that if someone is starting a job, they want it to go.
rm -f diagnostics # contains extra info from start of progFS

#### Triple 'while' loop - will have to break multiple times to get out, but advantage is ability to control
starting over
while (true)
do

# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f goingwell
while (true)
do
#  BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
   if (test -f skipstart) then
      echo "skipping start and continuing from previous runs"
   else
#  B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1 generate
geoPlusVel and first input file
      if [ `cat runpointnumber` = "1" ]; then
```

```
      echo "XXXX did not complete first point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "2" ]; then
      echo "XXXX did not complete second point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "3" ]; then
      echo "XXXX did not complete third point so new isomer started" >> dynfollowfile
    fi
    cd $origdir
    $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
    awk '/        1         2         3         4/,/Harmonic frequencies/ {print}' $freqfile > temp401
    awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 > tempfreqs
    awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 > tempredmass
    awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 > tempfrc
    awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
    awk '/has atomic number/ {print}' $freqfile > tempmasses
    awk '/Standard orientation:/,/tional const/ {if ($3==0) print}' $freqfile > tempstangeos
    awk -f $proggramdir/proggenHP $freqfile > geoPlusVel
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533 > isomernumber
      rm temp533
    else
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm g09.com
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
#  B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2  if first
part successfule then clean up and run the first input file, otherwise die
    if (test -s g09.com) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses temp401 temp811
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cat $scratchdir/g09.log >> dyn
        cp $scratchdir/g09.log olderdynrun
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
#  B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3 if B2
worked then you are here.  create 2nd point, run it, and set up for propagation loop
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
# before we decide to run this, check the energy
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    tail -1 dynfollowfile | awk '/XXXX/ {print}' > tempdone
    if (test  -s tempdone) then
```

```
      rm -f dyn
      rm -f traj
      echo 0 > runpointnumber
      break
    fi
    if (test -s g09.com) then
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olddynrun
        cat $scratchdir/g09.log >> dyn
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   / {print}' > old
        awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   / {print}' > older
        echo 3 > runpointnumber
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a start, so lets skipstart until instructed otherwise
    echo "forward" > skipstart
  fi
# Reverse trajectories starter routine
  if [ `cat skipstart` = "reverserestart" ]; then
    cd $origdir
    rm g09.com
    echo 1 > runpointnumber
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
    if (test -s g09.com) then
      rm -f goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olderdynrun
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    if (test -s g09.com) then
      rm -f goingwell
      cd $scratchdir
```

```
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > goingwell
      if (test -s goingwell) then
        cp $scratchdir/g09.log olddynrun
        cat $scratchdir/g09.log >> dyn
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   / {print}' > old
        awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   / {print}' > older
        echo 3 > runpointnumber
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
    echo "reverse" > skipstart
  fi

#
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___
END_of_B___

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
propagation loop
  while (true)
  do
#increment runpointnumber
    cp runpointnumber temp533
    awk 'BEGIN {getline;i=$1+1;print i}' temp533 > runpointnumber
    rm temp533
    rm -f goingwell
    cd $scratchdir
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
    cd $origdir
    grep 'Normal termination' $scratchdir/g09.log > goingwell
    if (test -s goingwell) then
      mv olddynrun olderdynrun
      cp $scratchdir/g09.log olddynrun
      awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/   0   / {print}' > old
      awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/   0   / {print}' > older
      awk -f $proggramdir/progdynb olddynrun > g09.com
      rm -f old older
    else
      cp $scratchdir/g09.log $origdir/g09.log
      break
    fi

# here is a cool link that lets you interupt the dynamics with a short job, then
# it automatically goes back to the dynamics  just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test  -f detour) then
      rm detour
      date >> $logfile
```

```
      cat run.com >> $logfile
      cp run.log temp.log
      cd $scratchdir
      $g09root/g09/g09 $origdir/run.com > $origdir/run.log
      cd $origdir
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > tempdone
    if (test  -s tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ]; then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olderdynrun
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
          mv dyn dyn$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olderdynrun
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
        mv dyn dyn$a
      fi
      break
    fi
  done
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done

  if (test  -f nogo) then
    break
```

```
  fi
  if (test  -s goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0
```

Program proggenHP

```
BEGIN {
# Aut 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification of displacement
on particular modes
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file cannontraj, so
one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without changes needed
# updated June 2008 to incorportate new method for choosing displacements with initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorportates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
```

```
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a point that is not a
freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting proggen *****************" >> "diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print "classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it from tempmasses
when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
```

```
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets you isotopic
substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print "atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >>
"diagnostics"
  if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "diagnostics"
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
```

```
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes unless classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6; mode[i+3,$2,$1]=$7;
mode[i+4,$2,$1]=$8
      }
    }
  }
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >> "modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside random number
generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
  getline < "temp811"; randArrC[i]=$1
}
# for a QM distribution for a harmonic oscillator in its ground state, we want to generate a set of random
numbers
#between -1 and 1 weighted such that numbers toward the center are properly more common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction for the motion of
each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
```

```
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]      #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when classical but the spacing
is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
  if (temp<10) vibN[i]=0        # avoids working with very small temperatures - if the temp is too low, it
just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#    get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Ansgroms for compatability with
Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]    #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]         #no zpe when classical
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but hopefully that bug is
killed and you can use disMode 0
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatability
  if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
```

```
  if ((diag>1) && (i==1)) print "zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >>
"diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i] >> "diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
    }
  }

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5        # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a saddle point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction, the rest go in a
random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
  }

# if controlphase is being used, set the velocity on particular modes as positive or negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based on 1/2RT in
degree of freedom
if (classical==2) {
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
  kinEnCart=100000*cartEn
```

```
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
      if (DRP==1) velArr[i,j]=0
      }
    }
  }

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*canno
nArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 + cannonvelArr[j,2]^2 +
cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance)) multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) && (KEinittotal>(KEinitmodes+cannonball-
tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1]; velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
    }
  }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use this for other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140, keeping momenta the
same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667; velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f \n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
  }

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
  }

#anything else I add to the file will not affect the trajectories but will keep a record and be good for
analysis
for (i=1;i<=numFreq;i++) {
```

```
  if (initialDis==0) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i], randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==1) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i], randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==2) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i], randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
  }
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"   KE initial total=",KEinittotal
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"    maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol  E + zpe=",zpePlusE,"  potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}
```

Program prog1stpoint

```
BEGIN {
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
#     removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
```

```
numAtoms=0; atomnumber=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag==1) print "***************** starting prog1stpoint *****************" >> "diagnostics"
if (diag==1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag==1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag==1) print "processors,checkpoint,title" >> "diagnostics"
if (diag==1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

getline < "isomernumber"
isomernum = $1
#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities not needed for 1st point
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
```

```
    }
  }

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
# make the title four words exactly, leaving out spaces if necessary
print title1,title2,title3,title4
print "runpoint 1"
print "runisomer ", isomernum
print ""
print charge,multiplicity
}

END {
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
print ""
}
```

Program prog2ndpoint

```
BEGIN {
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that DRP does not
check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
etolerance=1
```

```
#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="DRP") DRP=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="etolerance") etolerance=$2
  if ($1=="reversetraj") reversetraj=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting prog2ndpoint *****************" >> "diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

#get the isomer number from file
getline < "isomernumber"
isomernum = $1

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
```

```
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster, sometimes
not
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print title1,title2,title3,title4
print "runpoint 2"
print "runisomer ", isomernum
print ""
print charge,multiplicity

# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
# so we need to set up arrays for position, velocity, and force

#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    arr[i,j]=velArr[i,j]+geoArr[i,j]
    if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
    }
  if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
  if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
  }

#pull out other information useful for testing whether total energy is right or bad
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
    }
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
  }
#get initial geometry into file traj
print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
```

```
  print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
  }
#added by Samae on 102910
scfcount=0
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if (($1=="SCF") && (scfcount==0)) newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
newPotentialEK=(newPotentialE-potentialE)*627.509
if ($1=="SCF") {
  if (scfcount==0) {
    pddga=$5
    }
  if (scfcount==1) {
    qm=$5
    }
  if (scfcount==2) {
    pddgb=$5
    pddgc=(pddga-pddgb)
    newPotentialE=(qm+pddgc)
    newPotentialEK=(newPotentialE-potentialE)*627.509
    }
  scfcount++
  }
}

# now we go ahead and translate the forces and add them
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /      8    / || /      9
/
|| /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /     15    / || /     16    / || /     17    / || /
18
/ || /     19    / || /     20    / || /     21    / || /     22    / || /     23    / || /     24    / || /     25    / || /     26    / ||
/     27
 / || /     28    / || /     29    / || /     30    / || /     31    / || /     32    / || /     33    / || /     34    / || /     35    /)
&& length($3
) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >> "diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#put out Echeck but only if not a DRP
if (DRP==0) {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK,"   point 1 kinetic E=",KEinittotal,"
Total=",newPotentialEK+KEinittotal >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinittotal)>(desiredModeEnK+etolerance)) print "XXXX bad total Energy" >>
"Echeck"
```

```
  if ((newPotentialEK+KEinittotal)<(desiredModeEnK-etolerance)) print "XXXX bad total Energy" >> "Echeck"
  }
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
    if (DRP==1) forceArr[i,j]=0
    arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
    if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4)) arr[i,j]=geoArr[i,j]
    }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >> "diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
print ""
#get second geometry into file traj
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint 2 ","runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
  }
}
```

Program progdynb

```
BEGIN { #this is the main routine for generating new .com files by the Verlet algorithym
# Aug 2010 increased elements handled automatically but only up to bromine!
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
```

```
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
damping=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
OFS="     "

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="keepevery") keepevery=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="damping") damping=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting progdynb *****************" >> "diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
```

```
# get number of atoms and weights from geoPlusVel, and previous geometries from old and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5; atSym[i]=$1
  }

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
  }

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
  }

#for DRPs read in oldAdjForces and maxAtomMove
if (DRP==1) {
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

# record atom velocities for IVR analysis.  This is actually the velocity in the previous run, which is the
easiest to calculate.
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1
if (diag==3) print "runpoint ",runpointnum-1,"runisomer ",isomernum >> "vellist"
for (at=1;at<=numAtoms;at++) {
  atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2 +(oldarr[at,3]-
olderarr[at,3])^2)^.5
  KEatomstotal=KEatomstotal+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
  if (diag==3) print atomVel >> "vellist"
  }
apparentTemp=KEatomstotal*2/(3*RgasK*numAtoms)
if (diag==4) print "KEatomstotal",KEatomstotal,"apparent Temperature",apparentTemp >> "vellist"
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
}

#must adjust next line for weird atoms
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /      8    / || /      9
/
```

```
|| /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /     15    / || /     16    / || /     17    / || /
18
/ || /     19    / || /     20    / || /     21    / || /     22    / || /     23    / || /     24    / || /     25    / || /     26    / ||
/      27
 / || /     28    / || /     29    / || /     30    / || /     31    / || /     32    / || /     33    / || /     34    / || /     35    /)
&& length($3
) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >> "diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
############routine for DRPs#############
if (DRP==1) {
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time (s^s) and
divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(avNum*1
000))
      oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
      if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
      if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3])  > "oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3])  >> "oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }
########

############normal routine for Verlet #############
if (DRP==0) {
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time (s^s) and
divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(avNum*1
000))
```

```
      if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >> "diagnostics"
      if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
      newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4)) newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
      if (boxon==1) {
        if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j]) newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-
oldarr[i,j])+forceArr[i,j]
        if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        }
      }
    }
  }
########

if ((runpointnum % keepevery)==0) system("cat g09.log >> dyn")
print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(maxcycle=200) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster, sometimes
not
print "pop=none "
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print  title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ",isomernum
if (DRP==1) print "maxForce and forceMult and maxAtomMove",maxForce,forceMult,maxAtomMove
print ""
print charge,multiplicity
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
  print "" >> "traj"
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
  print ""
  if (length(meth5)>2) print meth5
  if (length(meth6)>2) print meth6
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
      print $0
      }
    }
  print ""
}
```

Program randgen

```
#include <stdio.h>
```

```
#include <stdlib.h>

int a,b,c;
double d;

int product(int x, int y);

int main(void)
{
  int count=1;
  srand48(time (0));
  while (count<=10000)
  {
    d = drand48();
    printf ("%.20f\n", d);
    count++;
  }
  return 0;
}

/* Function returns the product of the two values provided
int product(int x, int y)
{
    return (x * y);
}
*/
```

Program proganal

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ MVE/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<30)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }

END {
  C1C2=Distance(1,2)
  C2O6=Distance(2,6)
  O4O5=Distance(4,5)
  O5O6=Distance(5,6)
  C1O4=Distance(1,4)
  printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f
","C1C2",C1C2,"C2O6",C2O6,"O4O5",O4O5,"O5O6",O5O6,"C1O4",C1O4)
  if (runpoint>500) {
    print "Too many points.  XXXXMT"
    }
  if ((C2O6>2.5) && (C1O4>2.5)) {
    print "Reformed Starting Material  XXXXMR"
```

```
     }
   if ((C1C2>2.1) && (O4O5<1.5) && (O5O6>2)) {
      print "CaseA - Formed major products XXXXMA"
      }
   if ((C1C2>2.1) && (O5O6<1.5) && (O4O5>2)) {
      print "CaseB - Formed minor products XXXXMB"
      }
   system("date '+%b:%d:%Y %T'")
   system("tail -1 Echeck | grep XXXX")
   }

function Distance(Atom1,Atom2) {
  return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
   value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distance(Atom1,
Atom2)*Distance(Atom2,Atom3)))
   return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
   B1x=A[Atom2]-A[Atom1]
   B1y=B[Atom2]-B[Atom1]
   B1z=C[Atom2]-C[Atom1]
   B2x=A[Atom3]-A[Atom2]
   B2y=B[Atom3]-B[Atom2]
   B2z=C[Atom3]-C[Atom2]
   B3x=A[Atom4]-A[Atom3]
   B3y=B[Atom4]-B[Atom3]
   B3z=C[Atom4]-C[Atom3]
   modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
   yAx=modB2*(B1x)
   yAy=modB2*(B1y)
   yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
   CP2x=(B2y*B3z)-(B2z*B3y)
   CP2y=(B2z*B3x)-(B2x*B3z)
   CP2z=(B2x*B3y)-(B2y*B3x)
   termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
   CPx=(B1y*B2z)-(B1z*B2y)
   CPy=(B1z*B2x)-(B1x*B2z)
   CPz=(B1x*B2y)-(B1y*B2x)
   termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
  dihed4=(180/3.141592)*atan2(termY,termX)
  return dihed4
}

function killdyn(isomer) {
   system("rm -f dyn")
}
```

progdyn.conf

```
#This is the configuration file for PROGDYN.  This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method ONIOM(BLYP/6-31G*:PDDG)
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 restricted
charge 0
multiplicity 1
processors 2
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 200mw
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother, use
killcheck 1
killcheck 1
#checkpoint dyn20.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
title MVE ozonolysis oniom 218dis2
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that
# those at the end by 1/e
initialdis 2
#*** timestep -- this is the time between points in the trajectory.  Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 218.15
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,Solvent=water)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
```

```
method3 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
method4 IOp(3/76=1000001970)IOp(3/77=0800008000)IOp(3/78=0700010000)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary
frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian
frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be
made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir negative
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave
it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target,
such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the
vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following
cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the
first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading
time.
keepevery 1000
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 9
linkatoms 1
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.  This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
```

```
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
boxon 0
boxsize 7.5
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0
#displacements 11 0
#displacements 12 0
#displacements 13 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 3 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
#reversetraj true


#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj
```

Program progKE

This awk program takes the "traj" files output by PROGDYN, determines the kinetic energy in a subset of atoms, and outputs that energy for each point in a trajectory. The version show here is made for the R=octyl system, and minor modifications would have to be carried out for other alkyl groups.

```
BEGIN {
line=0
pointcount=0
for (i=1;i<=34;i++) {
  for (j=1;j<=3;j++) {
    oldarr[i,j]=0
    }
  }
}

(/C / || /H / || /O /) {
line++
if ($1=="C") mass[line]=12
if ($1=="H") mass[line]=1.00783
if ($1=="O") mass[line]=15.9994
newarr[line,1]=$2
newarr[line,2]=$3
newarr[line,3]=$4
if (line==34) {
  pointcount++
  for (i=1;i<=34;i++) {
    for (j=1;j<=3;j++) {
      velarr[i,j]=newarr[i,j]-oldarr[i,j]
      }
    }
  energy=0
  if (pointcount>250) {
    for (i=10;i<=34;i++) {
      for (j=1;j<=3;j++) {
        energy=energy+(1E30/4.184E26)*mass[i]*0.5*(velarr[i,j]^2)
        }
      }
    printf(" %.4f,",energy)
    }
  line=0
  for (i=1;i<=34;i++) {
    for (j=1;j<=3;j++) {
      oldarr[i,j]=newarr[i,j]
      }
    }
  }
}
END {
if (pointcount>250) print "}
```