

Alkyl end group effects on the thermal decomposition of oxymethylene ether fuel additives

An improvement on high-level theory-based studies

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Abstract

Efforts to improve the efficiency of internal combustion engines continue, and with them so do the investigations of fuel additives with favorable properties that reduce harmful emissions. One potential additive is dimethoxymethane (DMM), the simplest oxymethylene ether (OME), its high oxygen to carbon ratio is ideal for reducing engine soot formation. However, major disadvantages like low cetane number, low lower heating value (LHV), and high water solubility may impede DMM from being widely adopted. Although OMEs with more oxymethylene units and higher cetane numbers have been explored as alternatives, drawbacks regarding their low energy density, oxidative stability, and poor sealing material compatibility remain.

Recent studies have shown that OMEs with longer alkyl end groups like diethoxymethane (DEM) and dipropoxymethane (DPM) have better diesel compatibility, higher energy densities, and remain environmentally friendly. This work seeks to elucidate the initiation chemistry of DEM and DPM by quantifying the primary reactions that occur during the onset of the combustion. To do this, a chemical kinetic investigation was carried out to study the pyrolysis of DEM, DPM, and the most relevant radicals formed from their thermal decomposition. High-level electronic structure calculations at the (CCSD(T)/cc-pV ∞ Z//M06-2X/cc-pVTZ) level of theory were leveraged in conjunction with master equation theory to quantify the rates of reaction. The predicted temperature and pressure-dependent rate constants showed that single-step soot precursor-forming reactions in DEM and DPM have low importance at ignition temperatures, instead these soot precursors likely form through radical decomposition reactions. In addition, it was found that H-atom abstraction radicals from DEM favor the production of ethyl formate and acetaldehyde. Although similar compounds were produced by equivalent radicals for DPM, the results suggest that these radicals are also prone to generate abundant amounts of formaldehyde at high temperatures. This is the first comparison of the pyrolysis of different OME end groups and is the first high-level ab initio study of DPM. Lastly, python codes were developed and integrated with existing software to automate the computational process. The improved computational pipeline was leveraged to expedite the application of quantum mechanical methods to compute rates for DEM and DPM.

I would like to dedicate this work to my mother, sister and partner who have been with me in presence and mind over the last two years. Thank you all for always giving me unconditional love and support.

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Chapter 1

Introduction

Combustion has played a vital role in our society for thousands of years. Although it is a highly complex process involving diffusion, reaction kinetics, turbulence, and heat transfer, we have learned to harness the power of combustion for a wide range of scientific and engineering applications. One key application is in the transportation sector [1], where for the last two centuries combustion has been used as a means for power generation via internal combustion engines. During that time, fossil fuels, comprised mainly of hydrocarbons, have been the primary combustion fuels due to their high energy density, accessibility, and portability. Today, hydrocarbons still comprise more than 80% of combustion fuels used for transportation [1].

However, this source cannot be used indefinitely as fossil fuels cannot be replenished at the rate at which they are being consumed. Additionally, burning hydrocarbons contributes to global warming and produces harmful CO_2 , CO, and particulate matter emissions [2, 3]. Additionally, the formation of major hazardous air pollutants such as formaldehyde have been shown to be a degradation product from biogenic volatile organic compounds reacting with traffic emissions [4, 5]. Consequently, electric vehicles have seen a surge in popularity over the last decade, specifically in the light-duty market. Heavy-duty electric vehicles (marine, terrestrial, and air crafts) have not been as prominent as current lithium-ion batteries lack the necessary energy density to power these vehicles for long periods [6]. These markets will continue to rely on cleaner alternatives to traditional fossil fuels for the foreseeable future [7]. Thus, researching alternative fuels or fuel additives that blend naturally into current engine technology is essential to mitigate the consequences of this continuous oil dependency and meet future emission regulations.

1.1 Detailed kinetic mechanisms elucidate fuel breakdown

In the past, fuel breakdown was studied using practical engine simulations, which only measured global parameters (such as ignition delay times, laminar flame speeds, pollutant concentrations at exhaust) to capture reactivity trends. This led to the hasty adoption of new liquid fuel systems that seemed to improve a specific property (i.e. efficiency, pollutant formation),

while ignoring other properties. This shortsightedness led to irreversible implications on human health and the environment [8, 9]. Thus, exhaustive and comprehensive studies of the underlying chemistry using predictive simulations of combustion systems are a necessity to achieve true clean engine design and understand the sources of pollutant formation.

Predictive simulations of combustion systems have become feasible with the development of high-power computing over the last two decades. These simulations combine multiple disciplines and various temporal and spatial scales in an attempt to capture strongly coupled chemical and physical processes (such as heat transfer, reaction kinetics, diffusion, and turbulence) across a wide range of temperatures, pressures, and concentrations. Within this frame, the role of chemical kinetic models is to provide a detailed understanding of the complex combustion chemistry of fuels. The diagram shown in Fig. 1.1 highlights the multiple levels of information required to fully understand the combustion behavior of a fuel.

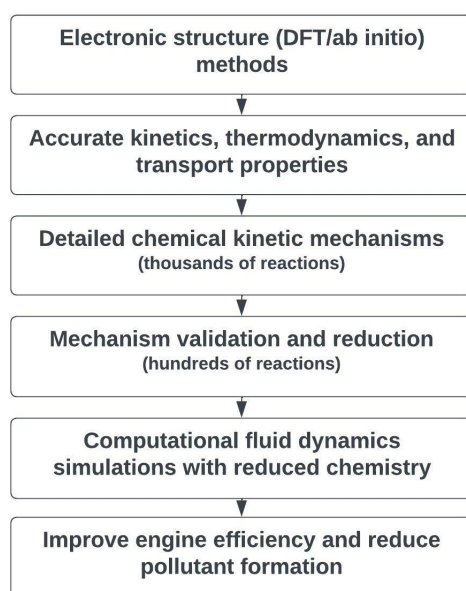


Fig. 1.1 Diagram of the layers of understanding for the simulation of combustion systems.

Electronic structure calculations provide detailed information about individual atoms and molecules which can be used to elucidate reaction mechanisms by providing accurate elementary reaction rates for the most relevant species. These results are coupled with thermodynamic parameters and transport properties to construct detailed kinetic models that describe fuel breakdown. The calculation results can be validated by experimental setups that measure global fuel properties, e.g. ignition delay times and flame speeds. However, comprehensive kinetic mechanisms that include this important chemistry may be quite extensive, and thus mechanism reduction techniques (that still accurately predict global properties) are essential. These reduced mechanisms are incorporated into computational fluid dynamics simulations to model the coupling of chemical and physical effects. Then, these simulations can be paired with engine experiments to provide a more holistic understanding of the fuel combustion in real

world applications. This work focuses on optimizing, expediting, and testing the application of electronic structure methods to efficiently produce accurate reaction kinetics that will enhance the performance of chemical kinetic mechanisms.

Chemical kinetic mechanisms have been successful at modeling the ignition of multiple types of fuels [10, 11] and play a vital role in the prediction of flame structures and pollutant formation [12]. These mechanisms can be quite extensive as they contain reaction rate information for all species in the system. For instance, the simple oxidation of hydrogen requires eight species and ~ 30 reactions, while the mechanism for methane requires ~ 30 species and over 200 reactions [13]. These numbers increase exponentially proportional to the number of heavy atoms in a molecule [14]. Not only are these reactions nonlinearly coupled, but also they occur on vastly different timescales which presents other simulation challenges. While the development of kinetic mechanisms should strive for a comprehensive understanding of the underlying chemistry, engineers need simpler kinetic models to produce engine simulations within reasonable time frames. Thus, finding ways to significantly reduce the size of these mechanisms while maintaining chemical fidelity and producing accurate global parameter predictions is an active area of research [14].

Even though reduced mechanisms contain only a fraction of the original number of species and reactions, their construction still requires reaction rate constants for potentially hundreds of reactions. This information is not always readily available, which leads to the use of estimation-based techniques such as group additivity [15], rate rules [16, 17] and analogy-based methods [18] to capture reaction rate constants. Although they expedite mechanism development, these techniques are valid only for restricted ranges of temperature, pressure, and concentration; their use beyond these regimes could lead to widely erroneous predictions [14]. Quantum mechanical calculations and high-level electronic structure methods present a potential solution as they are capable of measuring reaction rates more precisely across a wide range of conditions, improving model accuracy. However, these calculations take time to produce as they are computationally expensive.

1.1.1 Automation of kinetic mechanism generation

There has been significant research effort towards automating kinetic mechanism generation since mechanism development is one of the major bottlenecks in combustion modeling. Some of the first solutions to automated mechanism generation relied on representing reaction networks as square matrices and applying matrix transformations to simulate chemical reactions [19, 20]. These approaches paved the way for more sophisticated methods that leveraged cheminformatics and graph theoretical algorithms that use reaction rules to identify new reaction pathways, mechanisms, and lumps of isomers [21]. Reaction Mechanism Generator, or RMG, is one of these graph-based approaches. Developed by Gao et al. [22], it is written in Python and constructs mechanisms for C, H, O, S, and N containing species. RMG can estimate thermodynamic and kinetic parameters, as well as compute pressure-dependent rate constants from quantum

chemistry calculations. Codes like RMG build new mechanisms by calculating thermodynamic, transport and reaction rate parameters; however, they all have different termination criteria. In the case of RMG, it adds reaction families and their corresponding products to the *core* of the mechanism iteratively until the rate of product formation falls below a user-specified threshold. Although different mechanism generators have different termination criteria, none of them attempt to calculate high-level individual rate constants for every single reaction as that would be unfeasible for practical time frames. Thus, the few that don't use estimation-based methods employ cheaper electronic structure methods to calculate the large number of unknown reaction rate constants.

The accuracy of these kinetic mechanism generators may be improved significantly if high-level rate constants are calculated only for the most important reactions in a system. However, the current process of performing high-level quantum mechanical rate constant calculations (described in detail in Ch. 2) is time-consuming as it requires extensive file management and constant use of graphical user interfaces.

The first part of this work seeks to expedite the development of accurate kinetic mechanisms. To achieve this, a code that automates the process of performing high-level rate constant calculations was developed. The code requires minimal user intervention and, by combining it with existing codes, streamlines potential energy surface generation, hindered rotors scans, conformer analysis, ground-state energy calculations, and the leverage of master equation theory to produce rate constants. This improved computational pipeline was leveraged to study the high-temperature unimolecular rates diethoxymethane (DEM) and dipropoxymethane (DPM). DEM and DPM are biofuels, specifically diesel additives, studied due to their ideal blending properties and potential to significantly reduce engine emissions.

1.2 Application of automated kinetics to biofuel design

Biofuels are considered a more environmentally friendly alternative to traditional fossil fuels, as their low carbon to oxygen ratio has been shown to directly reduce soot by decreasing the formation of hydrocarbon intermediates [23, 24]. Additionally, when used as fuel additives, they provide fuel stability by increasing the octane number. Since they are made from biomass (i.e. plants, algae material, or animal waste), biofuels are easily replenishable. Biofuels degrade biologically, and their use turns bio residues into income instead of useless disposal. Moreover, biomass is an available source of energy in most countries, implementing biofuels into engine systems worldwide would meet strategy needs [25]. Common biofuels used today include various alcohols, ethers, and esters, with the most well-known being light alcohols (methanol and ethanol) and biodiesel, the latter of which is comprised of long-chain fatty acid esters derived from vegetable oils and animal fats. Biodiesel specifically is close to 100% renewable, which justifies the small CO₂ emissions from biodiesel combustion and has a large effect on the reduction of greenhouse gas emissions [26]. Efficient and inexpensive synthesis methods for these oxygenated biofuels are still under investigation, as it is challenging to turn the biomass into

fuels with the correct ignition characteristics. Most oxygenates, however, are currently obtained through either fermentation processes or catalytic reactions. Biodiesel is commonly produced through catalyzed transesterification in the presence of triglycerides (vegetable oil) and alcohol [27], whereas ethanol and other alcohols can be produced through anaerobic fermentation of corn-derived sugars or glycerol [28].

Unfortunately, not all oxygenates have the necessary properties that an ideal biofuel needs. A prime example of this is methyl tert-butyl ether (MTBE). MTBE was the petroleum industry's gasoline additive of choice in the 1980s due to its affordability, knock prevention, and blending properties. However, the use of MTBE proved controversial after it was shown to be sparingly soluble in water in the early 2000s. This is problematic because MTBE does not biodegrade easily, which makes it difficult and expensive to remove from wells and other sewage systems [29]. As a result of the environmental risks and public health concerns, most states in the USA decided to impose a complete or partial ban on MTBE. Additionally, the combustion of other oxygenates has also been shown to promote the formation of carbonyl pollutants such as aldehydes and ketones, which play an important role in the formation of photochemical smog [30]. Thus, simply relying on knowledge of a fuel's global parameters such as octane number, ignition delay times, and sooting propensity is not sufficient to reliably predict the combustion processes and decomposition of biofuels across a wide range of conditions. To prevent mass production of potentially harmful fuel and fuel additives, a thorough investigation of the biofuel's ignition, kinetics, and thermochemical properties and more must be carried out.

As a biofuel is subject to elevated temperatures, highly reactive radicals and meta-stable products begin to form as the fuel molecules decompose. These radicals drive the ignition chemistry by further breaking down the parent molecules, reacting with other short-lived species, and promoting subsequent oxidation reactions. The molecular structure variations among biofuels leads to the production of different intermediates, which alters the rate of reaction and the final decomposition products [31]. Incorporating a deep understanding of this phenomena into a detailed combustion mechanism is essential to quantitatively assess pollutant formation and biofuel efficiency.

The high-temperature decomposition in the absence of oxygen (pyrolysis) plays a key role in the development of reaction mechanisms and in the combustion modeling of fuel-rich regions ($\phi \rightarrow \infty$) inside an internal combustion engine (here ϕ refers to the *equivalence ratio*, or the ratio of fuel to air). These fuel-rich pockets are more prominent in compression ignition (CI) engines as the fuel-air mixture is less homogeneous than in spark ignition (SI) engines. This causes incomplete combustion and is responsible for the increase sooting seen in CI engines compared to SI engines. Additionally, sooting tendency has been shown to be proportional to temperature [32], and becomes significant at temperatures high enough for the fuel molecules energize and unimolecularly dissociate into radicals. Therefore, studying the high-temperature unimolecular pyrolysis and subsequent radical decomposition of biofuel candidates will show the impact of individual bond strengths and the presence of oxygen in the molecule, thus providing insights into the chemistry responsible for their sooting promoting or inhibition properties. Additionally,

the extension of experimental techniques to study key pyrolysis reactions in isolation being carried out in parallel to the application of robust computational models will help validate theoretical findings. This complementary experimental-theoretical approach can enrich the insight obtained from pyrolysis studies to more complex combustion reactions.

1.2.1 OMEs as fuel additives

Oxymethylene ethers (OMEs, $\text{CH}_3 - (\text{OCH}_2)_n - \text{CH}_3$) are biofuels that have garnered attention in the last two decades as they provide almost soot-free combustion. Dimethoxymethane (DMM) is the simplest OME (where $n=1$), and 42% of its molecular weight comes from oxygen. The lack of C-C bonds in its molecular structure drastically reduces the amount of soot precursors formed during its pyrolysis. Engine tests with DMM/fossil fuel blends have reported significant reduction in soot formation with increasing DMM content [33]. Additionally, DMM has been shown to have a higher impact on engine efficiency compared to other oxygenates as it enhances cetane number and lubricity [34]. However, concerns with their low energy density and high water solubility have inhibited the widespread adoption of DMM and longer methyl-terminated OMEs. Recently, Bartholet et al. [35] showed that the most optimal OME structures are those with extended alkyl end groups, these OMEs provide substantial reduction in soot formation while retaining or improving diesel blending properties. Diethoxymethane (DEM) and dipropoxymethane (DPM) have the same molecular structure as DMM but with ethyl and propyl end groups, respectively. DEM and DPM show promise as viable diesel additives [35]. While the first stage high-temperature unimolecular decomposition of DEM has been investigated before both experimentally [36] and computationally [37], its subsequent unimolecular radical decomposition has not been studied thoroughly. In addition, the high temperature pyrolysis of DPM has not been investigated at this point in time. Thus, DEM and DPM serve as excellent candidates to apply and demonstrate the developed computational process.

The second part of this work seeks to apply the optimized computational pipeline described in Subsection 1.1.1 to perform high-level rate constant calculations for the unimolecular and subsequent radical decomposition of DEM and DPM. The goal is to elucidate the high-temperature unimolecular pyrolysis of these molecules and provide accurate rate constants for the key reactions that may inhibit or promote soot formation in the ignition of DEM and DPM. This work hopes to be incorporated into future mechanisms that predict the decomposition of these diesel additives.

1.3 Research Objectives & Thesis Overview

Detailed kinetic mechanisms are key to predict the sooting tendencies of potential biofuels. The time of production of these mechanisms must be expedited to be able to produce combustion simulations of increasingly larger (more realistic) fuels within engineering time frames. The first objective of this work is to reduce the time required to produce theory-based mechanisms

by automating the computational pipeline used to calculate high-level rate constants for unimolecular reactions in gas-phase systems. The second objective of this work is to apply this optimized computational pipeline to theoretically explore the pyrolysis of two potential biofuel additives: DEM and DPM. These two biofuels have the capacity to reduce soot emissions while maintaining high energy density, low water solubility, and good oxidative stability [35]. Important reactions for the unimolecular and subsequent radical pyrolysis of DEM and DPM are filtered from an automatically constructed potential energy surface, while the relaxed geometries and frequencies are found using electronic structure theory. The final ground-state energies were acquired via high-level *ab initio* calculations and are used to calculate pressure- and temperature-dependent rate constants for the most relevant unimolecular reactions.

The thesis outline is presented below:

- Ch. 2 provides an overview of kinetic modeling, and explores the computational process in detail while outlining the different software used to filter important reactions and to calculate reaction rate constants. Finally, a brief description of various experimental techniques used to validate combustion simulations is presented.
- Ch. 3 describes the utility and functionality of all the python scripts developed in this work to optimize the computational pipeline for calculating high-level rate constants. These scripts have been integrated to work with the RMACC supercomputing resources of CU Boulder.
- Ch. 4 provides a comprehensive description of the most relevant work available in the literature regarding the oxidation, high temperature decomposition, and reaction mechanism development of oxymethylene ethers (OMEs). DEM and DPM are OME variations with longer alkyl end groups, and the literature available on these molecules is also explored in this chapter.
- Ch. 5 presents the results of the computational modeling work on DEM and DPM pyrolysis. The results include potential energy surfaces of the unimolecular decomposition of DEM and DPM. In addition, temperature- and pressure-dependent rate constants for the most relevant reaction channels are presented. The effects the different alkyl end groups have on the decomposition rate and product formation is also investigated in this chapter. Finally, the potentially significant role of chemically activated reactions in the high-temperature decomposition of these diesel additives is discussed.
- Ch. 6 explores the decomposition of the most relevant DEM and DPM fuel radicals formed during pyrolysis. The results show that different oxygenated products form during the combustion of DEM and DPM. In DEM pyrolysis, ethyl formate, ethylene, acetaldehyde, and formaldehyde are abundantly produced, while DPM pyrolysis is prone to generate more formaldehyde, propyl formate, propanal, and propylene. The relevance of the difference in product distribution and its impact in the sooting tendencies and future mechanism development of DEM and DPM is also discussed in this chapter.

- Finally, Ch. 7 provides an overview of the work done in this thesis and suggests future research directions regarding the study of OMEs.

Chapter 2

Computational chemistry to improve the accuracy of kinetic sub-mechanisms

Combustion modeling is far from an easy feat, as it requires the connection of multiple disciplines including chemistry, physics, fluid dynamics, thermodynamics, mathematics and computer science. The process of describing and predicting complex ignition phenomena integrates multiple levels of understanding from electronic structure theory describing the molecular reactions, to kinetic modeling development predicting the main intermediates and products of combustion, to computational fluid dynamic (CFD) simulations and engine experiments describing the macroscopic properties of ignition. This work relates specifically to the development of kinetic models, which must contain the reactions representing the reactive and energy transferring steps that take place during ignition. The degree to which kinetic models capture the underlying combustion chemistry greatly affects the accuracy of subsequent CFD and engine simulations.

2.1 Overview on kinetic modeling

To accurately simulate combustion phenomena and capture fuel properties and behavior, gas-phase kinetic models must contain transport properties like viscosity, thermal conductivity, thermal diffusivity (especially for problems where diffusion is important) for all included species, thermodynamic parameters (enthalpies, entropies, specific heats, etc.) for all included species, and a detailed reaction mechanism including all possible elementary reaction rates connecting all species. These components will be discussed in greater detail in the following sections.

2.1.1 Transport properties

Transport properties describe collisional energy transfer and are vital for kinetic models that attempt to solve problems involving diffusion. These properties are driven by temperature, momentum, and density gradients in the chemical mixture and can be described using Fourier's, Newton's, and Fick's laws, respectively. Not only do transport properties govern the rate at which energy is transferred, but they also have a profound impact on flame profile shapes,

velocities, and pollutant formation [38]. Precise calculations of transport properties are pivotal for the overall accuracy of a combustion model.

Transport properties are calculated using isotropic, spherically-averaged intermolecular potentials, such as the Lennard-Jones (LJ) potential shown in (2.1).

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{-12} - \left(\frac{\sigma}{r} \right)^{-6} \right] \quad (2.1)$$

Here, r is the intermolecular distance, while ϵ and σ represent the potential's well depth and the distance at which the potential energy vanishes, respectively. Potentials like the LJ are used to model single-point electric charges, thus their usages mean this interpretation is being extended to larger molecules. This approximation has shown to be reasonable for small molecules [39, 40], but breaks down for larger molecules where the isotropic assumption of the potentials breaks down [41]. Jasper and Miller proposed a way to get around this issue by modeling collisional rate from LJ parameters obtained by averaging over multiple molecular orientations [42]. Their results showed good agreement between the predicted and experimentally tabulated collision rates. Their collision rate expression can be used to evaluate collision integrals that predict transport properties using classical mechanics of binary collisions [43].

2.1.2 Thermodynamic parameters

In addition to transport properties, kinetic models also need an accurate thermodynamics database containing enthalpies, entropies, and specific heats for each species to model energy conservation and capture the exothermicity/endothermicity of the chemical reactions in the system.

Benson group additivity [15, 44] has been a widely used approach to acquire thermodynamic parameters. This method assigns contributions for thermodynamic properties to individual molecular functional groups to create an additive method for deriving thermodynamics properties based on structure. However, additive methods do not consistently capture molecular thermochemistry, rendering this method inconsistently accurate. Nevertheless, many reaction mechanism generators used today, such as RMG [22], use Benson-style group additivity to estimate thermochemical parameters.

More accurate thermodynamics parameters may be acquired via high-level electronic structure calculations using computational chemistry software such as Gaussian [45, 46]. Gaussian and other computational chemistry codes use electronic structure methods to calculate individual partition functions for the translational, electric, rotational, and vibrational components of molecular motion. Then, parameters such as entropy and internal energy may be derived as a function of these partition function components using the well-known thermodynamic relations. Eqns. 2.2 and 2.3 show the entropy S and internal energy E relation to any component of the partition function q , which is a function of volume and temperature. N and k_B denote moles and

the Boltzmann constant, respectively. Finally, the heat capacity C_V , and Gibbs free energy G may be calculated using the internal energy and entropy derivations (2.4).

$$S = Nk_B + Nk_B \ln \left(\frac{q(V, T)}{N} \right) + Nk_B T \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (2.2)$$

$$E = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (2.3)$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N, V} \quad G = E - TS + PV \quad (2.4)$$

Thermodynamic properties can be passed into a kinetic modeling software (i.e. CHEMKIN [47]) using NASA polynomial format [48]. These are polynomial fits for the specific heat at constant pressure C_p , enthalpy H , and entropy S in terms of temperature T_k and fitting constants a_{ik} . The NASA polynomials are shown in Eqns. 2.5-2.7.

$$\frac{C_p}{R} = a_{1k} + a_{2k} T_k + a_{3k} T_k^2 + a_{4k} T_k^3 + a_{5k} T_k^4 \quad (2.5)$$

$$\frac{H}{RT} = a_{1k} + \frac{a_{2k}}{2} T_k + \frac{a_{3k}}{3} T_k^2 + \frac{a_{4k}}{4} T_k^3 + \frac{a_{5k}}{5} T_k^4 + \frac{a_{6k}}{T_k} \quad (2.6)$$

$$\frac{S}{R} = a_{1k} \ln T_k + a_{2k} T_k + \frac{a_{3k}}{2} T_k^2 + \frac{a_{4k}}{3} T_k^3 + \frac{a_{5k}}{4} T_k^4 + a_{7k} \quad (2.7)$$

A recent publication by Keçeli et al. [49] proposed another code (PACT) to calculate accurate thermochemistry specifically for combustion chemistry applications, which works with current versions of RMG. PACT extracts geometries from RMG and converts them to 3D structures using Openbabel [50], a cheminformatics tool, to leverage high-accuracy quantum chemical methods to compute the complete partition function.

2.1.3 Kinetic mechanism development

Finally, kinetic models require a comprehensive reaction rate description involving all of the species considered in the model, this information is encapsulated in kinetic mechanisms. Kinetic mechanisms are complex as myriads of chemical reactions occur during the ignition of a fuel/air mixture (an average kinetic mechanism may involve hundreds of species and

reactions [51], while for larger mechanisms these numbers can be in the thousands [13]). As the mixture is subjected to elevated temperatures, reactive radicals and meta-stable species begin to form from the breakage of weak molecular bonds within the molecule. This pool of radicals promotes subsequent chemical reactions creating more radicals and driving ignition and/or flame propagation. The rate of ignition is determined by the types of radicals formed during initial stages of fuel decomposition.

For most flames, radicals may be formed from either H-atom abstraction or thermal decomposition reactions. Radicals formed from H-abstraction may undergo O₂ addition, the product is a peroxy radical (RO₂) that can either eliminate HO₂ directly, or internally abstract a H-atom (changing the location of the radical site) to form a QOOH compound. The QOOH may then react in various ways including another molecular oxygen addition, HO₂ elimination, and heterocycle formation + OH. On the other hand, radicals formed via thermal decomposition may further decompose, directly eliminating alkenes and producing more radicals. All of these radical reactions occur on a unimolecular surface. Thus, studying unimolecular reaction may unveil much of the significant chemistry from ignition (with the exception of abstraction reactions) including pyrolysis, abstraction, and RO₂ chemistry.

Historically, chemical kinetic mechanisms have had impressive accuracy at modeling fuel combustion. In 1984, the Gas Research Institute mechanism (GRI-Mech) was published by Frenklach et al. [52] It was open-source and predicted emissions from natural gas mixtures well. Another widely used mechanism was that of Miller et al. [53], which described the combustion of various nitrogen compounds.

Traditionally, all of these kinetic mechanisms have been built manually, and can take several years to produce. Thus, several automatic model generation codes have been published in the last decades to alleviate this effort [19, 22, 54]. These codes use graph-theoretical analysis to model reactions and most of them calculate rate constants and thermodynamic parameters using estimation-based methods. The following is an overview of different estimation-based methods used in the past to construct kinetic mechanisms.

2.1.3.1 Estimation-based methods used to calculate rate constants

The fundamental concept behind estimation-based methods is the idea that the reactive moiety is similar for various reactions within a reaction family. Thus, rate constants may be estimated based on a combination of the contribution of the reactive moiety and the specific kinetics of the reaction.

Rates from similar reaction families: One example of an estimation-based method that draws upon previous empirical data is given in Eqn. 2.8.

$$\ln(k_i(T)) = \ln(k_0(T)) + m(x_i - x_0) \quad (2.8)$$

Here, $k_0(T)$ is the rate of a known reaction in the same family, m is a reaction family parameter, and x is a known property of the species of reaction i , this could be enthalpy.

Rates from TST and thermodynamic parameters: Another estimation-based approach is to derive rate coefficients using transition state theory (TST) and thermodynamic parameters (calculated using Benson group additivity [15, 44]):

$$k(T) = n_e \kappa(T) \frac{k_B T V_m}{h} \exp\left(\frac{\Delta S^\ddagger}{k_B}\right) \exp\left(-\frac{\Delta H^\ddagger}{k_B T}\right) \quad (2.9)$$

Here, ΔS^\ddagger and ΔH^\ddagger are the activation entropy and enthalpy, respectively, k_B is Boltzmann's constant, V_m is the molar volume at standard pressure, and κ is a non-classical factor that accounts for quantum mechanical tunneling in the system. The number of single events n_e of the reaction (also known as reaction path degeneracy) is a function of the total rotational symmetry number and the number of optical isomers. Since this method draws upon group additivity measurements for thermodynamic parameters, its accuracy is a function of the accuracy of the group additivity method for the specific molecules in hand. This method provides a fast, computationally inexpensive approach to capture rate coefficients. Thus it is the method of choice of multiple reaction mechanism generators such as RMG [22].

Rates from known Arrhenius fit parameters: However, similar group additivity schemes that don't depend on thermodynamic parameters have been utilized in the past [55, 56]. Instead, these methods rely on Arrhenius fit parameters. The Arrhenius equation (2.10) shows the dependence of a rate constant as a function of temperature T , activation energy E_a , and a pre-exponential factor A . This equation is often used to model rate constants acquired via experimental and theoretical methods.

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (2.10)$$

The group additivity schemes described above rely on the Arrhenius fit parameters for reactions from the same reaction family plus a structural difference contribution to derive new rate constants. The structural contribution is made up of a sum of all sub molecular groups within the reactive moiety, and is known as the group additivity value (GAV). For instance, if a reactive moiety is composed of N atoms, the pre-exponential factor and activation energy for a new reaction can be calculated as follows.

$$\log \tilde{A} = \log \tilde{A}_{ref} + \sum_{i=1}^N \Delta \text{GAV}_{\log \tilde{A}}(X_i) \quad (2.11)$$

$$E_a = E_{a,ref} + \sum_{i=1}^N \Delta GAV_{E_a}(X_i) \quad (2.12)$$

Where $\log \tilde{A}_{ref}$ and $E_{a,ref}$ are the pre-exponential factor and activation energy for the reference reaction, respectively. ΔGAV is the group additivity value (GAV) of the reactive moiety. Then, the new reaction rate constant may be calculated using the newly acquired Arrhenius parameters ($\log \tilde{A}$ and E_a) and may be paired with a tunneling factor κ . Finally, the GAVs for a reaction family may be determined from previous theoretical or experimental calculations and are a function of the relative bonding structures.

Rates from rate rules: Finally, another way to represent rates of reaction is through previously derived correlations, or rate rules. The idea behind this method is to use the chemically active components of the molecule to derive rate coefficients based on previous combinations of these components. In the case of a hydrogen abstraction reaction (i.e. $XH + \dot{Y} \leftarrow \dot{X} + YH$), X and Y are the chemically active groups. Reaction mechanism generators like RMG [22] then approximate the reaction rate as that of a transition state supergroup, of the form XHY , in existing databases composed of rates derived from quantum mechanics calculations, experiments, or transition state theory. If data is not available for a XHY supergroup, then the rates of supergroups close to it in the database are averaged.

2.1.3.2 Overview of the computational process used to calculate high-level rate constants

Although estimation-based methods to calculate rates are ideal for expediting semi-accurate rate constant calculations for the hundreds of reactions involved in a mechanism, they all rely on preexisting empirical data and on preset molecular structure rules. This is an issue because when empirical data is not available, or when a molecule doesn't follow such rules, the subsequent assumptions made by these methods are a major detriment to the kinetic model's accuracy. In addition, past experiments have shown that many important reaction types have pressure-dependent rate coefficients [57], however most of these methods do not include any pressure dependence and often derive rate constant expressions only for the high pressure limit.

This is where modern quantum mechanical calculations of rate constants have a significant impact in the field of combustion chemistry. The coupling of high-level quantum mechanical rate constant calculations with experimentally validated C₀-C₄ sub mechanisms has played a vital role in improving the predictive capability of kinetic models in recent decades [13]. Fig. 2.1 shows a general outline of the main steps involved in employing quantum mechanical calculations to measure reaction rate constants.

The remainder of this chapter will start by providing a brief description of the main reactions that occur in fuel breakdown. Then, an overview of the software tools used to measure the energies, molecular geometries, and vibrational modes of the most relevant species involved in unimolecular reactions is provided. Then, Section 2.4 will describe how the energies of these

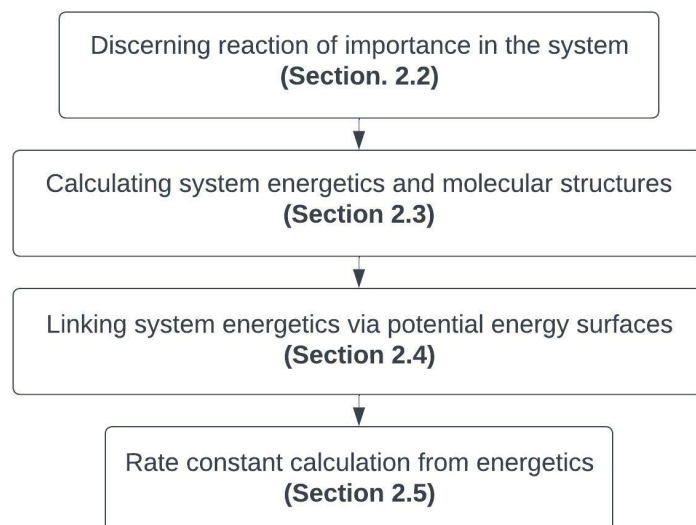


Fig. 2.1 Generalized computational steps required to calculate reaction rate constants from quantum mechanical principles.

products and reactants are interconnected in higher-dimensional potential energy surfaces, and how the surfaces related to internal rotation coordinates are modeled to search for lower energy conformers. This is followed by a description of the theories (classical trajectory, transition state, RRKM, and master equation) employed to measure rate constants from accurate energetic calculations. Finally, the main experimental setups used for kinetic modeling validation in this work are described.

2.2 Reaction classes

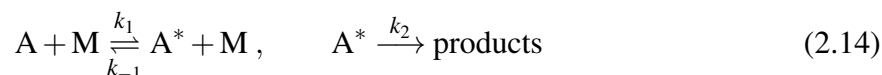
Kinetic mechanisms are composed of various types of reactions, but most fall within the umbrella of unimolecular or bimolecular reactions. This work focuses mainly on unimolecular reactions but a brief description of the latter will be provided since they are quite relevant in driving and promoting ignition.

2.2.1 Unimolecular reactions

Due to the fast and complex nature of combustion chemistry, many reactions which were thought to be simple one-step, unimolecular reactions, turned out to be part of composite mechanisms involving other radicals. An example of this is dinitrogen pentoxide (N_2O_5). N_2O_5 was originally thought to decompose via Eqn. 2.13.



However, it was discovered that several radicals such as NO_2 are part of the composite decomposition of dinitrogen pentoxide [58]. This led to the idea that molecules are allowed to react after they have acquired some amount of energy (activation energy) to decompose. About a century ago, Lindemann and Christiansen [59] formalized this idea by hypothesizing that unimolecular reactions proceed via a collisional energy transfer (from a third body M).



Then, the energized reactant, A^* , may transfer its energy in subsequent collisions or may redistribute the excess energy throughout its internal modes and react to form products. At high temperatures, the most relevant unimolecular reactions include homolytic fissions, β -scission, isomerizations, and pericyclic reactions.

Homolytic fissions happen when the covalent bonds are broken and each molecular group keeps an unpaired electron, creating two free radicals. An example of a homolytic fission in the decomposition of DPM is shown in Eqn. 2.15. The products are a ethyl radical and a long oxygenated hydrocarbon radical.



These reactions tend to have lower rates at low temperatures, but they quickly become important at higher temperatures as the internal bond stretching modes acquire excess energies from collisions and break apart.

Free radicals are the reactants in β -scission reactions. Free radicals are extremely reactive and short-lived (low activation energies) species, β -scissions happen when the unpaired electron disturbs a neighboring bond, stealing one of the bonded electrons and forming a double bond. This process produces alkenes in hydrocarbon chains (or possibly aldehydes in molecules with an oxygenated backbone) plus another radical. An example of a β -scission for an important radical in the pyrolysis of DPM forming propaldehyde and methoxymethyl radical is shown below.



Isomerization reactions are chemical processes in which a molecules reacts into any of its isomeric forms (i.e. compounds with the same chemical composition but different structure). Isomerization reactions tend to be relevant at low temperatures, but their relative importance decreases for higher temperatures as the rate of homolytic fissions increases with the number of collisions. A relevant type of isomerization reactions is an internal hydrogen transfer reaction.

These reactions are common in long chain radicals, where the charged site steals a hydrogen atom (usually from an alkyl group) on the other side of the molecule.



Finally, pericyclic reactions happen in tight rings where multiple molecular orbitals overlap. In these reactions, the molecular structure is rearranged, in a fashion in which bonds form and break simultaneously. The most common pericyclic reactions in unimolecular pyrolysis are cyclo-elimination reactions. Eqn. 2.2 shows a potential cyclo-elimination reaction in DPM. It is also known as a four-center reaction since the interchange of electrons is happening between four heavy atoms. These reactions may occur also for larger and smaller rings.

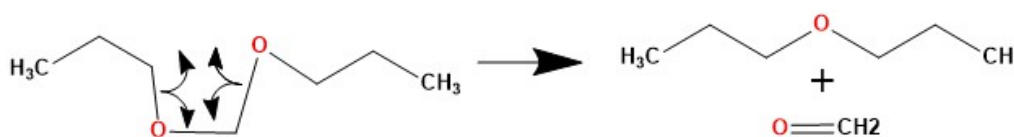


Fig. 2.2 Pericyclic reaction forming formaldehyde and dipropyl ether from DPM.

2.2.2 Bimolecular reactions

According to collision theory, atom/molecule *A* and atom/molecule *B* may interact via an elastic collision (internal state and arrangements of both *A* and *B* stays invariant), an inelastic collision (the internal states of both molecules changes but their arrangements remain invariant), or a reactive collision (the two molecules react to form two new complexes) [60]. Bimolecular reactions that go through a transition state (see Section 2.3) onto the products are part of the latter interaction. These reactions can be reversible or irreversible and the rate of reactions depends on the concentration of the reactants. An important type of bimolecular reactions in fuel combustion are hydrogen atom abstraction reactions. These reactions occur when a reactive free radical ($\dot{\text{R}}$) approaches a molecule and steals a hydrogen atom.



Reactions like Eqn. 2.18 have a high impact on ignition since they are a major source of fuel radicals.

2.3 Energies and molecular structures from quantum mechanical methods

The first step in generating theory-based rate constants involves calculating properties of individual atoms and molecules using quantum chemistry principles. This includes information such as molecular structure, energetics, vibrational frequencies, and more. This information is essential to model single-step reactions and calculate rate constants from classical trajectory, and master equation theory (see Section 2.5). Nowadays this can be done by employing quantum mechanical calculations on molecular structures with computational chemistry software such as Gaussian [45]. The following subsections will cover the theory behind these calculations and the way Gaussian is leveraged to acquire molecular geometries and energies from such theory.

2.3.1 Analytical solutions to Schrödinger's equation

The foundations of computational chemistry lie in the advancements made in quantum mechanics throughout the last century. The dawn of quantum physics took place in the early 1900s, when the classical view of the world was left behind and scientists turned to answer questions related to the microscopic, subatomic world. Max Planck, a German physicist, was the first person to use a quantum (discrete) hypothesis to explain the experimental results of blackbody radiation as a function of frequency and temperature. Planck's assumption that the oscillator's energy levels were discrete, instead of continuous, turned out to be surprisingly accurate, and revolutionized our understanding of electromagnetic radiation.

Some twenty-five years later, Erwin Schrödinger, an Austrian physicist, formulated the following mathematical expression that predicts the time and space evolution of the wave equation ψ , or probability density, of a quantum system with a mass of interest m in a potential field V .

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right] \psi(x,t) \quad (2.19)$$

Schrödinger's formulation, a linear partial differential equation, completely specifies the state of a system and can be rearranged and expressed as an eigenvalue problem. This allows linear, Hermitian operators like the Hamiltonian and momentum operators to be applied to Schrödinger's equation to predict observable quantities such as the total energy, linear, and angular momentum of the system.

The hydrogen atom is the simplest system to predict using Schrödinger's equation, this system is governed by the Coulomb potential between the electron and the proton.

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (2.20)$$

Where e is the electric charge, and ϵ_0 is the vacuum permittivity. After substituting Eqn. 2.20 into Eqn. 2.19 and rewriting it in spherical coordinates, we get:

$$-\hbar \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \hat{L}^2 \psi + 2m_e r^2 \left[-\frac{e^2}{4\pi\epsilon_0 r} - E \right] \psi(r, \theta, \phi) = 0 \quad (2.21)$$

Here, the operator \hat{L}^2 , which only depends on the azimuthal and polar coordinates, arises from the conversion of the Laplacian operator from spherical coordinates. This equation can be seen as an operator acting on ψ , whose first and third components only depend on the radial coordinate, and whose second component comes out to be $\hbar^2 l(l+1)$, derived from the spherical harmonics $Y_l^{m_l}(\theta, \phi)$ [61]. Here, l and m_l are the angular momentum and magnetic quantum numbers, respectively. The leftover terms from Eqn. 2.21 depend only on r , and can be solved using Plank's ingenious idea of energy discretization.

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2} \quad n = 1, 2, 3, \dots \quad (2.22)$$

The final r-dependent wave functions, or radial wave functions, are only a function of n and l , and are described in terms of Laguerre polynomials L_{n+l}^{2l+1} :

$$R_{nl}(r) = -\left\{ \frac{(n-l-1)!}{2n[(n+1)!]^3} \right\} \left(\frac{2}{na_0} \right)^{l+\frac{3}{2}} r^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right) \quad (2.23)$$

The complete expression for the wave functions of the hydrogen atom is given by the combination of the radial wave functions given by Eqn. 2.23 and the spherical harmonics. Thus, the wave functions, and energy states, of the hydrogen atom only depend on the three quantum numbers n , l , and m_l .

$$\psi_{nlm_l}(r, \theta, \psi) = R_{nl} Y_l^{m_l}(\theta, \phi) \quad (2.24)$$

2.3.2 DFT and ab initio methods

The next quantum system of interest is the Helium atom, however, this three-body system cannot be solved analytically using Schrödinger's equation. The difficulty lies in the non-linearity presented by the inter-electronic repulsion term between three particles. Thus, the hydrogen atom is the only quantum system that can be fully determined, and modeling of more complex systems relies on approximation methods such as perturbation theory or the variational method. Perturbation theory consists of adding weak perturbation terms to the operators applied to a simpler system with a known solution to get an approximation of the observable quantities for a more complex system. The variational method, on the other hand, is based on estimating an upper bound for the ground-state energy of a system.

The variational principle and perturbation theory became the foundations of modern quantum chemistry and molecular orbital theory. Today, ab initio (or from first principles) quantum

chemistry methods attempt to solve Schrödinger's equation using these approximations. The simplest ab initio method is the Hartree-Fock method, also known as the self-consistent field (SCF) method [62], which proposes the use of special types of antisymmetric wave functions ψ that satisfy Pauli's exclusion principle for electrons in the same orbital while also accounting for their location and spin. However, this method relies on other approximations like the Born-Oppenheimer, independent electron, and the linear combination of atomic orbitals approximations, and thus fails to capture the electron correlation accurately for heavier molecules. Several post-Hartree-Fock ab initio methods have been proposed in an attempt to capture electron correlation more effectively. Among them are the Møller-Plesset perturbation theory methods (MP n) [63], which rely on systematic improvements of the HF wave function through Rayleigh-Schrödinger perturbation theory of the n -th order. Unfortunately, MP n methods have shown convergence issues at large n and do not account for dynamic electron correlation. In the 1950s however, coupled cluster theory (originally developed for nuclear physics applications) was formulated for electronic structure modeling [64] and found great success at modeling electron correlation. Couple-cluster methods are now considered the "gold standard" ab initio methods today for calculating ground-state energies.

Density Functional Theory (DFT) has been thoroughly investigated over the last thirty years as it yields accurate results at a much lower computational cost than coupled-cluster and other ab initio methods. The origins of DFT go back to the 1960s when Pierre Hohenberg and Walter Kohn showed that the ground-state energy can be expressed in terms of an electron density integral [65].

$$E = E[\rho] \quad (2.25)$$

Here, ρ denotes the electron density and the square bracket is a special notation indicating an integral over the whole space $\rho(x, y, z)$. DFT proposes an entirely different approach to the electron correlation problem by bypassing wave function approximations in favor of electron densities. Various approximations of $E[\rho]$, or functionals, have been proposed as they serve as an upper bound for the real ground-state energy. DFT is not considered ab initio as the most widely used and successful functionals contain empirical parameters. In today's calculations, these semi-empirical functionals are paired with basis sets (for modeling molecular orbitals) to produce accurate ground-state energy predictions for larger molecules.

Every ab initio or semi-empirical DFT method is paired with a basis set that models atomic orbitals and turns the partial differential wave equations into algebraic notations that can be numerically solved by computers. The origin of basis sets dates back to 1930, when the American physicist John Slater proposed a special type of functions to describe the atomic orbitals of complex molecules. The orbitals described by a linear combination of these basis functions, overall called a basis set, became known as Slater-type orbitals (STO). This was considered an improvement on the traditional method of superimposing hydrogen-like orbitals for the estimation of the ground-state energies. In general, larger basis sets do a better job at

approximating a molecule's electronic structure, but they require higher computational power. Minimal basis sets, or basis sets that contain only one basis function to describe each orbital, provide the simplest atomic orbital representation. One such basis set is STO-3G, which describes each orbital as a Slater-type orbital using three Gaussian functions, also known as Gaussian-type orbitals (GTOs were proposed in 1950 by Samuel Francis Boys, a British theoretical chemist, and became widely used as they reduced the overall computational time when compared to the previously used STOs). Split-valence basis sets, or basis sets where a different number of Gaussian functions is used to describe the core and valence orbitals, are more accurate than minimal basis sets. The notation shown below for split-valence basis sets was introduced by British theoretical chemist John Pople.

$$X - YZg \quad (2.26)$$

Where X represents the number of Gaussian functions (also called primitive Gaussians) comprising the atomic core orbitals, Y represents the number of Gaussians comprising for the first basis function of the atomic valence orbital, and Z represents the number of Gaussians comprising the second basis function of the atomic valence orbital. The presence of two numbers after the hyphen implies a double-zeta basis set, implying that the valence orbitals are described by two basis functions. Accuracy can be further improved by adding polarization functions (terms that include an asymmetric component) and diffuse functions (terms that better approximate the inter-molecular bonding far away from the nuclei). Unfortunately, a theoretical Hartree-Fock limit is reached after superimposing multiple Slater type orbital (STO) functions, where the best value for the ground-state energy is reached using one-electron wave functions that do not account for all electron interactions. Figure 2.3 is commonly used to visualize the limitations on the combinations of methods and basis sets.

		Electron Correlation					Full configuration interaction
		HF	MP2	MP3	MP4	CCSD(T)	
Basis Set Type	Minimal						
	Split-valence						...
	Polarized						
	Diffuse						
	
		HF Limit					... Schrödinger Eqn.

Fig. 2.3 Limits for basis set types vs. electron correlation for ab initio methods [66].

Here, the more accurate basis sets and methods are lower and farther to the right, respectively. The lower right corner represents a fully deterministic combination and is equated to the solution to Schrödinger's equation. The lowest row corresponds to the HF limit and the right-most column corresponds to the full configuration interaction (CI). Full CI is a linear variational approach in which all Slater determinants are included in the variational procedure for modeling

all possible electrons orbitals and virtual excitation orbitals. Unsurprisingly, this is a limiting case since the computational time of Full CI with reasonable basis sets is too large, as it involves millions of electron configurations.

2.3.3 Computational chemistry software, quantum mechanical methods and basis sets used in this work

The arrival of computers as fast numerical solvers has brought forth significant leaps in knowledge over the last 30 years. Nowadays, supercomputers can solve computational chemistry methods in a matter of hours, a feat that was impossible before as this meant solving eigenvalue problems with $N \times N$ matrices where N is the number of basis functions, which for large molecules and accurate methods can be in the millions. Software that optimize these computations include Gaussian [45], Avogadro [67] and Molpro [68]. In this work, DFT methods were employed using Gaussian [45] to calculate molecular structures and frequencies, as well as to scan potential energy surfaces (see Section 2.4) for internal rotation modes. Most DFT methods implemented with Gaussian utilize the Berny algorithm as the default molecular optimization technique. It is a gradient descent algorithm written by H.B.Schlegel in 1982 [69]. In the most updated version, the Hessian is computed from the force field for each step of the optimization and linear searches are leveraged for finding lower points on the PES. Quintic, quartic, cubic polynomial fits for the energy and first derivative are utilized if second derivatives are available at both points and convergence has not been reached. Any gradient vector components associated with frozen degrees of freedom are set to zero; these constraints are often used to get cleaner-looking potential energy scans for internal rotation vibrations.

Optimizations and frequency calculations were done at the B3LYP/6-311++G(d) and M06-2X/cc-pVTZ levels of theory. B3LYP [70] is one of the most famous hybrid functional methods, it developed in the 80s by combining ideas from previous functionals proposed by Axel D. Becke, Chengteh Lee, Weitao Yang, and Robert Ghormley Parr. It is called a hybrid method because its calculation involves both exact methods to account for exchange correlation, and DFT methods to account for dynamic electron correlation. The basis set of choice is 6-311++G(d), which is a triple-zeta basis set with diffuse functions on both heavy atoms and hydrogen, as well as a polarization function on heavy atoms. M06-2X is one of the M06 functionals, or Minnesota Functionals, developed by the Truhlar research group at the University of Minnesota [71]. It is a semi-empirical hybrid meta-exchange correlation functional parametrized specifically for nonmetals and has found success in gas-phase kinetics and thermochemistry applications. The cc-pVTZ basis set, on the other hand, was developed by Thom H. Dunning [72] in the late 1980s when he was working at Argonne National Laboratories. It is a polarized, valence-only, triple zeta correlation-consistent basis set, and has been shown to yield excellent results when paired with ab initio and DFT methods. [73].

If employing master equation theory (see Section 2.5) to calculate rate coefficients, molecular geometry and frequency calculations must be performed not only for all species in the reaction

system, but also for all transition state structures connecting reactants to products. This is because master equation theory relies on transition state theory (TST) to predict rates of reaction. Transition state structures are defined as the chemical structure located at a saddle point in the PES (see Section 2.4) connecting the reactant and the products. Transition state theory predicts this structure is at a quasi-equilibrium (exists classically), and thus includes it in its subsequent derivation for the reaction rate by accounting for its concentration. Gaussian allows for molecular optimization, frequency and energy calculations for transition state structures.

All Gaussian calculations were submitted to the RMACC supercomputer [74]. When a calculation runs successfully, the requested parameters (optimized geometries, frequencies, energies, thermochemistry, etc.) will be outputted to a *.log* file. Gaussian input files have a simple format and contain three main sections: the route section, the title section, and the molecular geometry section. The route section contains specifications about the computational resources required to run the calculation, this is a function of the level of theory that is being requested. In addition, it contains the level of theory, details about the integration grid used for minimization, and other optional parameters. The title section just contains a title, defined by the user for file management purposes. Finally, the geometry section contains the initial molecular structure, which can be given in either Cartesian or Z-matrix format.

An example of Cartesian vs. Z-Matrix descriptions for methyl ($\dot{\text{C}}\text{H}_3$) is presented in Fig. 2.4.

Z-Matrix	-----	Cartesian	-----
C	-	C	0.00000000 0.00000000 0.00000000
H 1 B1	-	H	0.00000000 1.07652900 0.00000000
H 1 B2 2 A1	-	H	0.93230200 -0.53826500 0.00000000
H 1 B3 3 A2 2 D1	-	H	-0.93230200 -0.53826500 0.00000000
	-		
B1	-		
B2	-		
B3	-		
A1	-		
A2	-		
D1	-		

Fig. 2.4 Z-matrix (left) and Cartesian (right) descriptions for methyl radical.

Cartesian coordinates describe a three-variable (XYZ) location in space relative to an origin, where $3N$ variables must be accounted for to describe an N atom molecule. Z-matrix (internal) coordinates are based on relative positions, and describe the length, planar angles, and torsion angles between atoms in the molecule. Since Z-matrices stay invariant to three-dimensional rotation and translation, only $3N-6$ variables are necessary to describe the molecule ($3N-5$ for linear molecules).

Z-Matrices formatted for Gaussian are composed of two main sections: the connectivity and variable sections. Each row in the connectivity section is defining a new atom i based on previously defined atoms (with the exception of the first row). Bond lengths, planar angles, and torsion angles are stored in the variables B, A, and D, respectively and their values are specified in the variable section.

2.4 Potential energy surfaces link system energetics

The calculated energetics for all reactants, products, and transition states are interconnected by reaction coordinates in a three-dimensional potential energy surface (PES), which is a set of ground-state energy solutions as a function of spatial coordinates. Transition state structures connect reactants to products/wells and exist at saddle points on the PES, located at the maxima in the direction of reaction coordinates and at a minima along all other coordinates. Fig. 2.5 shows the planar projection of a PES for different unimolecular reactions created using PESViewer (see Subsection 2.4.1). Here, bimolecular products, isomers, and transition state structures are shown in red, blue, and green, respectively. Notice that isomerization reactions and concerted reactions are have transition states (at energies 69.1 and 60.2 kcal/mol), while homolytic fissions reactions (with products located at 84.1 and 78.1 kcal/mol) do not.

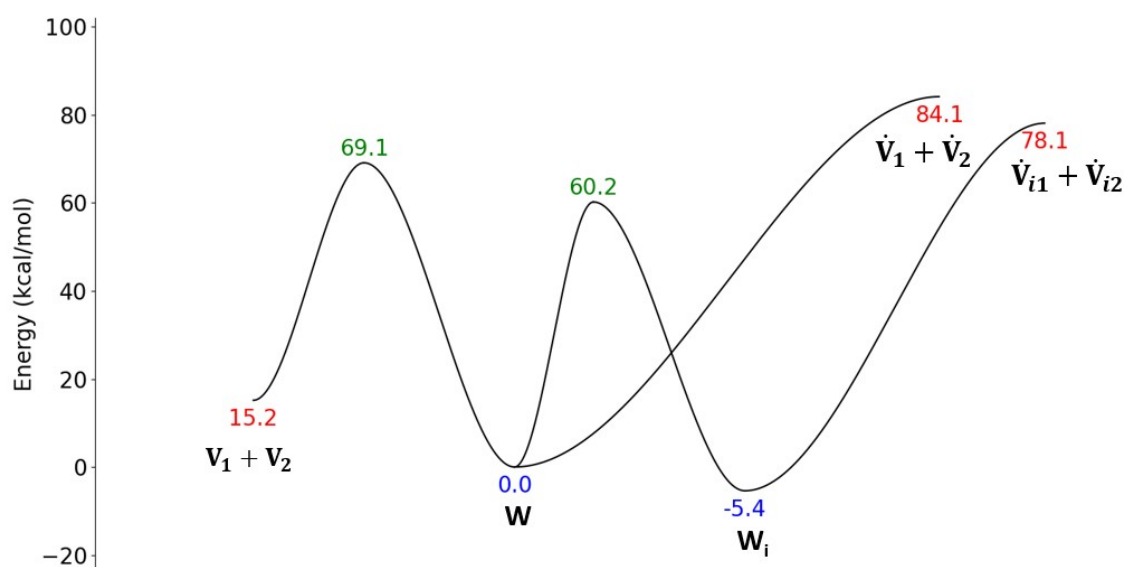


Fig. 2.5 Two-dimensional projections of the PES along a reaction coordinate for isomerization, elimination, and dissociation reactions. Free radicals are marked by a dot, and isomers are shown with a subscript i .

2.4.1 KinBot for automatic reaction search

The process of finding all the relevant reactions in a system is time-consuming, even for experienced computational chemists. A simple molecule with 4-5 heavy atoms may contain dozens of potentially relevant unimolecular reactions, and one must consider the energetics of all of them to find the reaction channels with the lowest activation energies. Additionally, modeling transition state structures with Gaussian is a tedious process it may require multiple optimizations to converge to the saddle point without unintentionally converging to a local minima nearby on the PES. To speed up the process, we utilized KinBot [75]. KinBot is a code developed at Sandia National Laboratories that automates Gaussian, and characterizes kinetically important stationary points on a PES for C, H, O, and S-containing species. The code works by iteratively

changing the geometry of the reactant to obtain saddle points corresponding to the most relevant reactions that fall within the predefined reaction classes within the software. Once it has found all possible reactions, KinBot generates Gaussian calculations at a requested level of theory (B3LYP/6-311++G(d) for this work) for the energies and vibrational frequencies for the reactant, products, and transition states. In addition, it performs intrinsic reaction coordinate (IRC) calculations, which are used to verify that the transition state structures are connecting the appropriate products to the reactant. Once a job runs successfully, KinBot labels output files based on the corresponding molecule's reaction class (these include simple H-migrations, H₂ eliminations, and Diels-Alder) or a unique ChemID [75]. Additionally, all optimized molecular structure filenames and species' relative energies are stored in an input file called *pesviewer.inp*.

Three files are necessary to run a KinBot calculation: a shell script (loads the required modules and specifies number of nodes and cores necessary to execute the program), a JSON file (specifies KinBot reaction search parameters), and a text file (specifies the amount of computing resources for the additional Gaussian calculations that KinBot spawns). KinBot has additional dependencies aside from Gaussian including Python 3, RDKit, OpenBabel [50]. RDKit is an open-source cheminformatics toolkit written in C++, and OpenBabel is a software used to inter-convert chemical file formats. To visualize KinBot's output, one can use the PESViewer module. PESViewer is a Python code written by Ruben Van de Vijver, one of the developers of KinBot. It takes an input file (such as *pesviewer.inp*) that contains references to geometries and relative energies and constructs 2-D projection of the PES of the system.

Although it saves a considerable amount of time, KinBot also has some drawbacks. The main one is that it may fail to find concerted reactions such as four-center or six-center pericyclic reactions and can miss reactions that fall outside of the built-in reaction classes the code searches. This is an issue particularly for long chain molecules where these types of reactions have low activation energies and are likely to dominate the unimolecular decomposition at low temperatures.

2.4.2 Hindered rotor scans reveal lower energy conformers

Once KinBot has optimized all molecular structure, a potential energy scan for the hindered rotors (HR) of the molecule is necessary to find lower energy conformers and to capture the contributions of internal rotational energy for master equation calculations (see Section 2.5). A HR is a vibrational frequency for internal rotation and a full scan of each rotation is necessary since energized molecules are available to access most internal rotation states. These PES scans are done along a torsional coordinate from a re-optimized structure at the M06-2X/cc-pVTZ level of theory [76]. An example of a M06-2X/cc-pVTZ Gaussian HR scan revealing a lower energy conformer for DPM is shown in Fig. 2.6. Here, a conformer with a calculated ground-state energy 0.2 kcal/mol below the initial optimized structure was found after changing the torsion angle between atoms 9 and 6 by 230°. Multiple iterations of optimizations and HR scans are done with M06-2X/cc-pVTZ until no lower energy conformers are found.

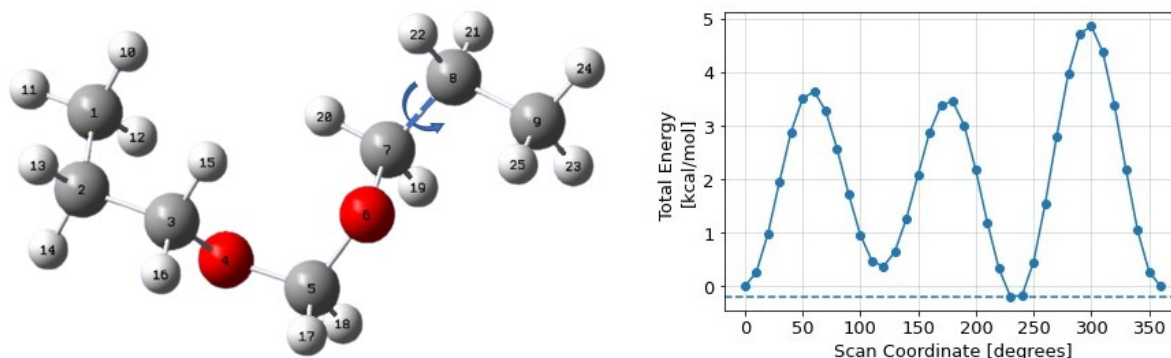


Fig. 2.6 Hindered rotor scan for the 7-8 bond of DPM, rotating a methyl group and the two hydrogen atoms attached to C8.

Once the lowest energy conformers for each structure are found at the M06-2X/cc-pVTZ level of theory, ab initio coupled cluster methods with the inclusion of triple excitations [77] were paired with correlation consistent polarized-valence (double- ζ and triple- ζ) basis sets to calculate high-level energies (CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ) for the lowest energy molecular configuration. The infinite basis set limit [78] is estimated via the extrapolation (2.27) of the obtained ground-state energies. In addition, zero-point energy corrections evaluated at the M06-2X/cc-pVTZ level are incorporated into the final value of the high-level energies. A similar extrapolation has been applied before to estimate high-level energies for C_3H_4 reactions [79].

$$E_{high-level} = E_{zero-point}[M06-2X/cc-pVTZ] + E[CCSD(T)/cc-pVTZ] + 0.4628 \times \{E[CCSD(T)/cc-pVTZ] - E[CCSD(T)/cc-pVDZ]\} \quad (2.27)$$

2.4.3 Morse Potential

The Morse potential is a mathematical expression that reflects the anharmonicity of a chemical bond by reproducing its dissociation energy as a function of separation (similar to the Lennard-Jones potential). Its formulation is given by Fig.

$$V_{Morse}(r) = BDE(1 - e^{\alpha(r-r_0)})^2 \quad (2.28)$$

The Morse potential is a function of the bond dissociation energy (BDE), the equilibrium bond length r_0 , and the curvature parameter α . The BDE is the energy required to break a molecular bond, and the equilibrium bond length is the average distance of the atoms at the lowest energy level. The curvature parameter is a function of the system's reduced mass μ , the BDE, and the averaged harmonic oscillator frequency ν :

$$\alpha = 2\pi\nu\sqrt{\frac{\mu}{2\text{BDE}}} \quad (2.29)$$

Since it reproduces the effect of bond breaking, it is used in this work to model homolytic fissions using a phase space theory model in the MESS code (see Subsection 2.5.3) when calculating rate constants. An example of the Morse potential function modeling a C-O homolytic fission in DEM is shown in Fig. 2.7

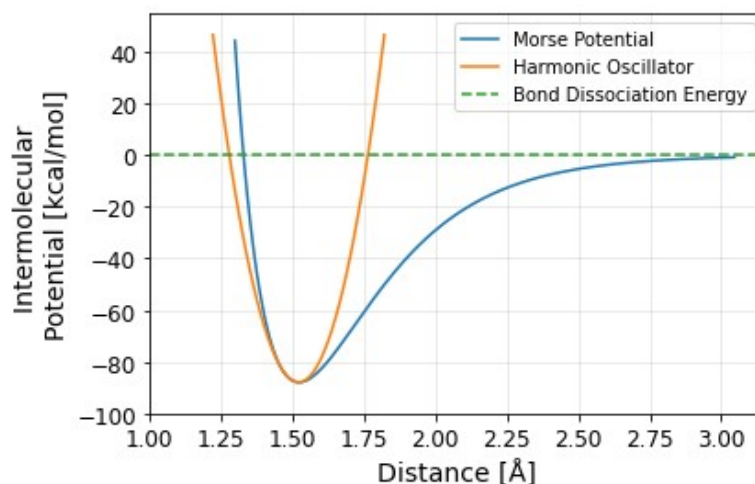


Fig. 2.7 Morse potential, harmonic oscillator approximation, and bond dissociation energy for the following DEM bond fission reaction: $\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{O}\dot{\text{C}}\text{H}_2 + \dot{\text{O}}\text{C}_2\text{H}_5$.

Here, the potential is shifted down by 88.0 kcal/mol, which is the reaction's bond dissociation energy, to be able to capture the dissociation profile with a negative exponential fit (2.38) (see Subsection 2.5.3). The harmonic oscillator is included for comparison, showing that the Morse potential approximates it reasonably near the equilibrium bond length.

2.5 Rate constants from quantum mechanical calculations

2.5.1 Transition State and RRKM theory

Transition state theory (TST), proposed in 1935 by Henry Eyring [80], provides the foundation for modern reaction rate calculations. TST is a semi-classical theory that assumes equilibrium energy distribution for all states along the reaction coordinate. Furthermore, it only holds if all arrangements that enter transition state from the reactant go on to the products, which means that the rate constant expression given in TST is an upper bound for the real value. This expression is a function of the Boltzmann distribution and is given below.

$$k_{rate} = \frac{kT}{h} e^{\frac{-\Delta G}{RT}} \quad (2.30)$$

Where k is Boltzmann's constant, and ΔG is the Gibbs free energy between the transition state and the reactants. Some forms of Eqn. 2.30 include a transmission coefficient κ to account for quantum tunneling [81]. Although tunneling effects are relevant at low temperatures, κ is usually within the range [0.5, 2] and larger errors introduced in the calculation of ΔG dominate the uncertainties of TST calculated rate constants.

One major source of error for TST lies in its assumption that the reactant is in thermal equilibrium with the environment, this may not always be the case, especially for low-pressure gas-phase unimolecular reactions. A workaround is a TST formulation in terms of the total energy of the system, this is known as microcanonical TST or Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Starting from the assumption that no re-crossings occur, (situations in which the molecule is reflected to the reactants after passing through the transition state) RRKM theory starts by defining the production rate in terms of variables from the following two reactions.



Eqn. 2.31 shows the forward and reverse rate constants going from the reactant A to its energized state A^* , where the energy transfer happened through a collider M . Eqn. 2.32 shows the forward rate constants going from the energized reactant to the transition state A^\ddagger and from the transition state to the products P , the key assumption here is that $k^\ddagger \gg k_2$. Now, the expression for the rate of production can be derived from rate equations in terms of the concentration of the reactant $[A]$.

$$\frac{d[P]}{dt} = k_2 \frac{k_1 [M][A]}{k_{-1}[M] + k_2} = k_{total}[A] \quad (2.33)$$

Where the fraction term is the concentration of the transition state $[A^*]$. Now, the total unimolecular reaction rate constant can be rewritten in a differential expression in terms of energy.

$$k_{total}(E + dE) = \frac{(dk_1(E)/k_{-1})k_2(E)}{1 + k_2(E)/k_{-1}[M]} \quad (2.34)$$

Eqn. 2.34 implies that k_1 and k_2 are both a function of the energy E . The concentration of the collider is a function of pressure, and the term $k_{-1}[M]$ is the collision frequency deactivation factor. The differential term in parenthesis represents the probability of A^* to be in a state with energy E , modeled by a Boltzmann distribution. At the high-pressure limit, when $k_{-1}[M] \rightarrow \infty$,

Eqn. 2.34 reduces to Eqn. 2.30. Since $k_2(E)$ is determined by the vibrational quantum states for A^\ddagger , the unimolecular rate proposed by RRKM theory is a function of the geometries and vibrational frequencies of the reactant and transition state. Finally, Variational Transition State Theory (VTST) treats transition states as saddle points on a Gibbs free energy surface (ΔG), which takes into account temperature and entropy effects when predicting the geometry of the transition state.

2.5.2 Master equation theory

A master equation is a set of integrodifferential equations that describe the rates of loss and production of chemical species as a function of energy. These coupled equations are all a function of angular momentum J , total energy E , and time t . However, the former is treated as a constant for most thermal unimolecular reactions when the system is in pseudo-steady state. Furthermore, the angular momentum is often ignored for simplicity, yielding the one-dimensional master equation, only in terms of E .

The main form of the master equation assumes that the density of states is large, and thus individual quantum states cannot be resolved. Therefore, the energy is treated as a continuous, as opposed to a quantized, variable. This approximation is accurate for all but diatomic reactants. The continuous time-dependent master equation for any species concentration x is given below.

$$\frac{\partial x(E,t)}{\partial t} = [M] \int_0^\infty [R(E,E')x(E',t) - R(E',E)x(E,t)] dE' - k(E)x(E,t) \quad (2.35)$$

Where the change in concentration is the integral summation of gain/loss of collisional energy states between the infinitesimal range $(E', E' + dE')$. The terms $R(E, E')$ and $R(E', E)$ are the rate coefficients for collisional energy transfer to and from all other energy levels E' , respectively. The $k(E)x(E, t)$ term denotes the species concentration loss due to reaction. Eqn. 2.35 can also be written in a finite-difference form for numerical solutions. In such form, the first term on the right-hand side of Eqn. 2.35 is usually denoted as \mathbf{J} , and its matrix form is outlined below.

$$J_{ij} = [M] \delta E R_{ij}, \quad i \neq j \quad (2.36)$$

$$J_{ii} = -k_i - \sum_{j \neq i} [M] \delta E R_{ji} \quad (2.37)$$

All the diagonal terms of \mathbf{J} are negative because of the off-diagonal terms being positive. It can be shown that the unimolecular reaction rate coefficient k_{uni} is given by the the largest (or least negative) eigenvalue of the matrix \mathbf{J} .

2.5.3 MESS code for unimolecular rate constant calculations

This work leverages the Master Equation System Solver (MESS) [82] developed at Argonne National Lab to calculate unimolecular rate constants. MESS input files generally have two main sections: the global section, and the model section. The global section contains condition parameters such as the temperature and pressure ranges, method parameters (for solving the master equation), energy grid parameters (or discretization parameters), and cut-off parameters (these are for sanity checks, and method evaluation purposes). The model section consists of the statistical descriptions of all species in the model which are defined as wells, bimolecular products, and barriers. The energy transfer between species is described with a Lennard-Jones (LJ) collisional frequency model. This model describes the inter-molecular potential and involves the parameters ϵ (a measure of the inter-molecular potential's well depth) and σ (the distance at which the inter-molecular potential vanishes) which can be measured experimentally and can be retrieved from online databases such as RMG [22].

In addition, a symmetry factor must be specified for all species included in the model. The symmetry factor for MESS is defined as the ratio of the symmetry number for external rotations σ_{rot} and the number of enantiomers m . The symmetry number for external rotations may be obtained from online databases and is a function of the molecule's point group, while the number of enantiomers is given by 2^n , where n is the number of chiral centers (atoms bonded to four different chemical groups) present in the molecule. To model bond fissions, MESS employs phase space theory (PST) to estimate the number of states. In its PST model, MESS simulates potential energy as a function of distance R (in units of bohr) using the following expression.

$$V = \frac{-C_n}{R^n} \quad (2.38)$$

Where C_n is the potential prefactor and n is the potential power exponent. In this work, these parameters are found by fitting the negative power law (2.38) to the Morse potential (2.28) as a function of the parameters of a specific bond fission. The harmonic oscillator frequency in the Morse potential was approximated by averaging all symmetric and asymmetric bond stretching modes for bond. An example of this for an important bond fission in the pyrolysis of DEM is shown in Fig. 2.8.

It is immediately clear that the negative power law (2.38) is not able to capture the Morse potential near the equilibrium bond length, and instead fits better the far field potential. In practice, the negative power law parameters (C_n and n) are changed in order to fit a region between 30% and 50% increase of the equilibrium bond length to model bond fissions [51]. However, these ranges may vary slightly to adjust predictions to match rates coefficients obtained from experiments (if available).

Lastly, MESS input files require all final vibrational frequencies, molecular structures, hindered rotor scans, and ground-state energies in the system. This information is often scattered in dozens of Gaussian output *.log* files and makes input MESS files extensive (often up to 5000

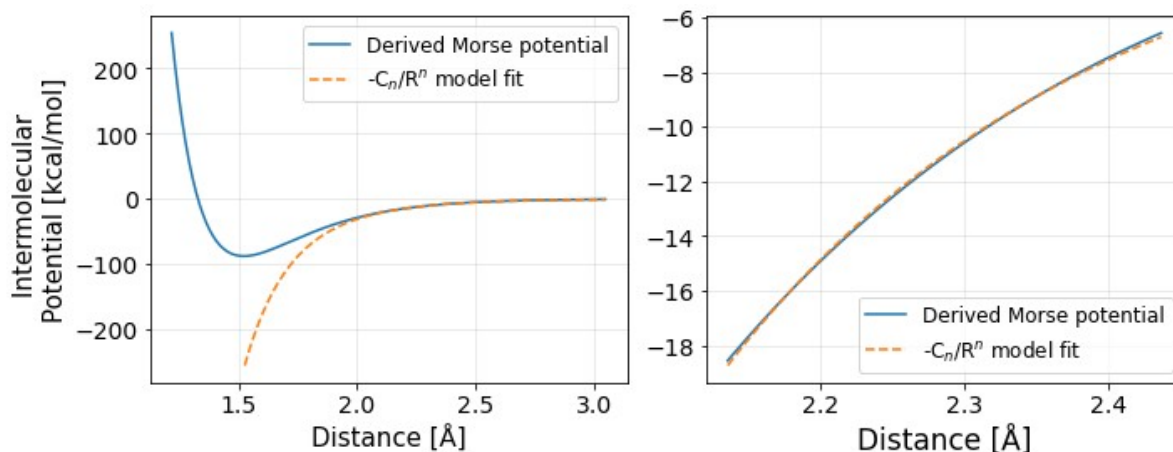


Fig. 2.8 Derived Morse potential and negative power law fit for modeling the following DEM bond fission reaction: $\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{O}\dot{\text{C}}\text{H}_2 + \dot{\text{O}}\text{C}_2\text{H}_5$. A zoomed in plot is shown on the right.

rows of text). Thus, constructing an input file for MESS may take several days depending on the complexity of the system.

2.5.4 Reaction rate constant expressions

Once rate constants are acquired by MESS, it is useful to capture their behavior into mathematical models that kinetic modeling software (i.e. CHEMKIN) are able to understand. The most basic mathematical expression for a rate constant was an exponential introduced by Svante Arrhenius in the early 1900s [2]. His mathematical formulation (2.10) is derived from the integration of species concentrations and is still used today to model basic forward reactions. However, for reaction rates that are more sensitive to temperature, various tweaks for the traditional Arrhenius equation have been proposed over the years [83]. The modified Arrhenius expression (2.39) includes a temperature factor in the front raised to the n power, where n is another fitting constant. For rates that have a more complex temperature dependency, the double Arrhenius expression (2.40) is useful as it adds an additional exponential term to better model the growth/decay of the rates.

$$k(T) = AT^n \exp\left(\frac{-E_a}{RT}\right) \quad (2.39)$$

$$k(T) = A_1 T^{n_1} \exp\left(\frac{-E_{a1}}{RT}\right) + A_2 T^{n_2} \exp\left(\frac{-E_{a2}}{RT}\right) \quad (2.40)$$

However, under some conditions the reaction rate may be quite sensitive to pressure, and Arrhenius equations by themselves do not capture pressure dependency. About a century ago, Frederick Lindemann proposed a pressure dependent falloff rate expression that extrapolates

rate constants from other known rate constants at an upper k_∞ and lower k_0 pressure limit [59]. The expression is in terms of a reduced pressure P_r and the mixture concentration $[M] \sim \frac{P}{RT}$, and is shown below.

$$k(T, P) = k_\infty \left(\frac{P_r}{1 + P_r} \right) \quad P_r = \frac{k_0[M]}{k_\infty} \quad (2.41)$$

In the early 1980s, Gilbert et al. [84] expanded this expression for a more refined pressure-dependency treatment. They introduced a broaden factor F .

$$k(T, P) = k_\infty \left(\frac{P_r}{1 + P_r} \right) F, \quad \log F = \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1} \log F_{cent} \quad (2.42)$$

Here, c , n , and d are known parameters, all given in terms of F_{cent} by the following expressions:

$$c = -0.4 - 0.67 \log F_{cent}, \quad n = 0.75 - 1.27 \log F_{cent}, \quad d = 0.14 \quad (2.43)$$

Finally, the expression for F_{cent} is given in terms of the four Troe parameters α , T^{***} , T^* , and T^{**} .

$$F_{cent} = (1 - \alpha) \exp\left(\frac{-T}{T^{***}}\right) + \alpha \exp\left(\frac{-T}{T^*}\right) + \exp\left(\frac{-T^{**}}{T}\right) \quad (2.44)$$

This is known as the Troe formalism, and it is particularly useful to describe rate constants that are affected by third body colliders. A different fitting method was proposed by Miller and Lutz [85] (known as a PLOG fit). PLOG is based on a logarithmic interpolation of the reaction rates from a higher and a lower pressure. PLOG yields more accurate results than the Troe formalism if the gas mixture does not change, and fails if third body collisions are important [13]. The PLOG expression is given in Eqn. 2.45.

$$\ln k = \ln k_i + (\ln k_{i+l} - \ln k_i) \frac{\ln P - \ln P_i}{\ln P_{i+l} - \ln P_i} \quad (2.45)$$

Where, k_i and k_{i+l} are the rates at a lower and higher pressure, respectively.

Finally, Chebyshev polynomials, first introduced by Venkatesh et al. [86], are another type of fit based on Chebyshev expansions [87], aimed to capture the temperature and pressure dependence of multiple-well reactions (which other methods have trouble capturing [86]).

Chebyshev polynomials attempt to capture the logarithm of the rate constant, as shown in Eqn. 2.46 within N and M basis functions along the temperature and pressure axes, respectively.

$$\log k(\tilde{T}, \tilde{P}) \approx \sum_{i=1}^N \sum_{j=1}^M a_{ij} \varphi_i(\tilde{T}) \varphi_j(\tilde{P}) \quad (2.46)$$

Chebyshev polynomials of degree $i - 1$ are given in Eqn. 2.47. The arc-cosine constraints the input space of the polynomials within the closed interval $[-1, +1]$. Thus, the temperature and pressure spaces must be mapped to the unit square using Eqns. 2.48 and 2.49.

$$\varphi_i(x) = \cos[(i - 1)\arccos(x)], \quad i = 1, 2, 3, \dots, \quad (2.47)$$

$$\tilde{T} \rightarrow \frac{2T^{-1} - T_{min}^{-1} - T_{max}^{-1}}{T_{min}^{-1} - T_{max}^{-1}} \quad (2.48)$$

$$\tilde{P} \rightarrow \frac{2\log P - \log P_{min} - \log P_{max}}{\log P_{max} - \log P_{min}} \quad (2.49)$$

The uniform mapping does not affect the rate constant [86]. The fit coefficients, a_{ij} in Eqn. 2.46, may be acquired by applying a minimization algorithm such as least-squares. The authors [86] note that the data points from the \tilde{P} and \tilde{T} spaces should be the roots of the higher-order Chebyshev polynomial to ensure a uniform approximation of the temperature and pressure domain. Finally, the accuracy increases proportional to the amount of basis functions utilized along the pressure and temperatures axes.

2.6 Experimental techniques for kinetic modeling validation

The combustion models used to describe the decomposition of large molecules are complex as they involve strongly coupled chemical and physical processes such as heat transfer, reaction kinetics, and diffusion. The development of such models relies heavily on experimental setups that minimize such complexities and maximize measurement accuracy. Shock tubes, rapid compression machines, and flow reactors (plug-flow, and jet stirred) are effective techniques used to study global fuel properties such as ignition delay times, flame speeds, and extinction strain rate over a wide range of conditions (temperature, pressure, equivalence ratios, re-circulation rates, initial concentrations). By leveraging different experimental setups, one can probe fuels at most engine-like conditions.

2.6.1 Shock tubes to measure global and local flame properties

Shock tubes are a type of batch reactor that can be used to measure both global and detailed combustion properties (ignition delay, speciation, and reaction rate constants). They are useful for gas-phase kinetics studies since high temperatures can be produced in a short amount of time and subsequent reactions can be isolated from low concentration mixtures between reactants and inert gases. Shock tubes are typically several meters long and are composed of the driver (high pressure), and the driven (low pressure) sections, separated by a diaphragm of metal foil or cellophane. The reactants start in the driven section while the driver section is filled with inert gas (He, Ar, etc.). After the diaphragm bursts, a shock wave forms and propagates at supersonic speeds towards the low-pressure region, heating and compressing the reactants. Strong shock waves raise the temperature enough for molecules to begin dissociating into radicals, and bond dissociation rates can be measured using precise laser diagnostics.

One of the best methods to validate high-level quantum mechanical rate constant calculations is to compare it to available shock tube data in the literature. Then, flexible parameters in the buffer gas' energy relaxation model (ΔE_{down} model) of MESS can be tweaked to correct inconsistencies in the theoretical methods. Fig. 2.9 shows how the ΔE_{down} parameters were systematically changed to match the total rate of decomposition for DEM measure by the single pulse shock tube studies carried out by Herzler et al. [36].

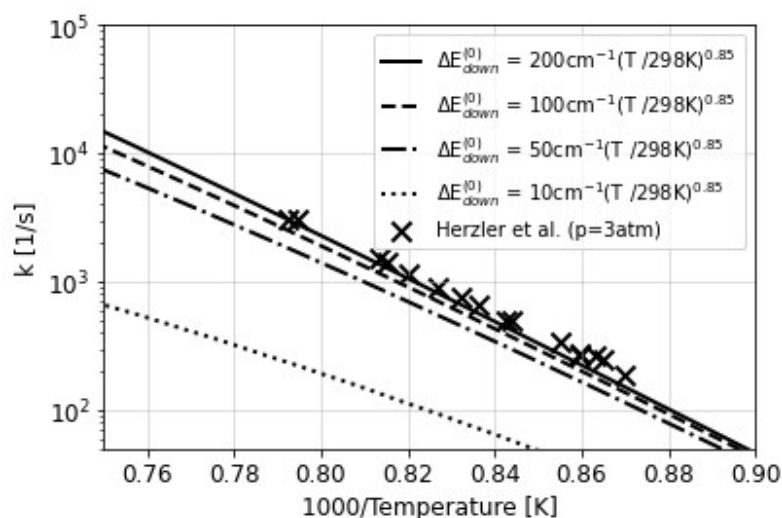


Fig. 2.9 Total experimental vs. theoretical rate of decomposition of DEM with different values for the ΔE_{down} energy relaxation model.

Significant research efforts are allocated into optimizing shock-tube experiments because they are one of the few setups used to validate rate coefficients. Recently, researchers from the Argonne National Laboratory introduced a miniature high-repetition-rate shock tube with a tunable synchrotron-generated photoionization time-of-flight mass spectrometer. They used the script to probe the pyrolysis of dimethyl ether (DME) at temperatures between 1400-1700 K; and pressures between 3-16 bar [88]. This setup is compact, automated, repeatable, and has a fast cycle rate, which helps match synchrotron beam times easily.

2.6.2 Flow reactors to measure intermediate and product species concentrations

Flow reactors are useful for measuring species concentrations for oxidation and pyrolysis in gas-phase kinetic studies. They usually operate at temperatures and pressures below 1500 K and 50 bar, respectively. Plug-flow reactors (PFR) are a type of flow reactor that operate at a steady state and are assumed to have axial gradients but no radial gradients. Reactants are continuously fed into the reactor and are modeled as a series of infinitely thin coherent “plugs”. Each plug has a uniform radial composition, and the residence time is derived from the plug’s position in the reactor. Laminar flow reactors (LFR) are similar to PFR, however the no-slip boundary condition is not neglected and thus the velocity profile is modeled as parabolic instead of constant. Species concentrations can be obtained via gas chromatography or infrared (IR) analysis. Recently, a new analytical expression for measuring first stage ignition delays of DME in a PFR setup was published [89]. The ignition delay times were determined based on the distance between the fuel inlet and the location where the reactor wall temperature increases by a few degrees.

Although flow reactors deliver useful insights about key intermediates and products, possible complications such as surface reactions may arise and should be considered. In addition, flow reactor experiments required much larger fuel quantities compared to shock tube and RCM experiments.

2.6.2.1 Photoionization mass spectrometry to reveal isomeric product branching and onset of combustion in microreactor experiments.

Mass spectrometry measures the mass-to-charge ratio (m/z) of charged particles and, outputs a spectrum of the charged ion’s signal as a function of m/z . In photoionization mass spectrometry (PIMS), a high frequency photon is used to ionize low concentrations of gas-phase molecules in a bath gas (such as He or Ar), this allows for the detection of relevant combustion intermediates. In addition, a synchrotron light source enables selective tuning of the photon energy, allowing for isomer resolution and evaluation, and preventing fragmentation. Synchrotron vacuum ultraviolet (VUV) photoionization mass spectrometry, known as SVUV-PIMS, has been widely used to study the thermal decomposition, low-temperatures oxidation, and radical distribution of gas-phase molecules [90]. We utilized a VUV-PIMS setup paired with a SiC micro-reactor to validate the theoretical findings from the studies outlined in Ch. 5 and 6, a schematic of the experiment is shown below.

In this setup, the ionization source has a fixed energy of 10.487 eV which comes from the Spectra-Physics Quanta-Ray Pro 30 Hz pulsed neodymium-doped yttrium aluminum garnet (Nd: YAG) laser. The primary output from this laser (1064 nm) is frequency tripled in a gas mixture of argon and xenon to produce photons at 118.2nm (10.487 eV). A silicon carbide microreactor is used to heat up the fuel/bath gas mixture to temperatures ranging from 300 - 1600 K. When combined with the reflectron time-of-flight mass spectrometer, this system

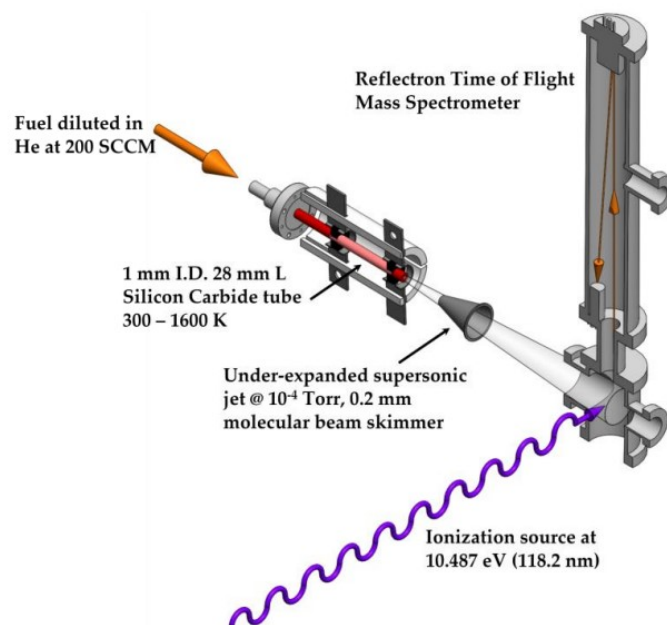


Fig. 2.10 Reflectron photoionization time-of-flight mass spectrometer with fixed ionization source of 10.487 eV.

can observe early kinetic processes by discerning thermal decomposition products formed at timescales of $\sim 100\mu\text{s}$. Some of the molecules whose pyrolysis has been studied using this experiment include acetaldehyde [91], furan [92], and propionic acid [93].

Chapter 3

Computational pipeline optimization with python

Over the last two decades, the field of computational chemistry has made significant leaps, allowing for major improvements of the chemical kinetic models used in combustion simulations [13]. Part of this success is due to the implementation of high-level theoretical methods to obtain rate parameters. These parameters improved the accuracy of detailed kinetic mechanisms that describe the most important rates of reaction and reaction pathways that occur during the decomposition of a molecule. The general method used to compute rate coefficients from quantum mechanical calculations was described in detail in Ch. 2.

Although this method yields rate constants competitive in accuracy with experiments [41], it remains a considerable time expense even for experienced computational chemists. High-level calculations of rate constants are time-consuming partly because some may take more than a week to complete (especially if dealing with large molecules), and partly because of the substantial amount of time spent in file management. This is because the process of acquiring accurate molecular properties through the combination of different DFT/ab initio methods requires computational chemists to spend countless hours manually extracting information from long *.log* files or setting up multiple input files for software that performs electronic structure calculations (i.e. Gaussian [45]). The process is tedious and begs for automation methods that have the potential to minimize input errors (typos, which waste computational resources), and expedite the overall rate constant calculation time.

This chapter addresses the first goal of this thesis exploring several python automation projects developed in this work to optimize the computational pipeline used to calculate high-level rate constants for gas-phase reactions. Fig. 3.1 revisits the steps involved in calculating rate coefficients and highlights the automated using the codes developed in this work. Overall, four different codes were developed: the KinBot reaction filtration code, the hindered rotor identification code, the MESS input file generation code, and the computational pipeline automation code. Each section in this chapter will detail the logic, purpose, advantages, and future improvement ideas of each code developed herein.

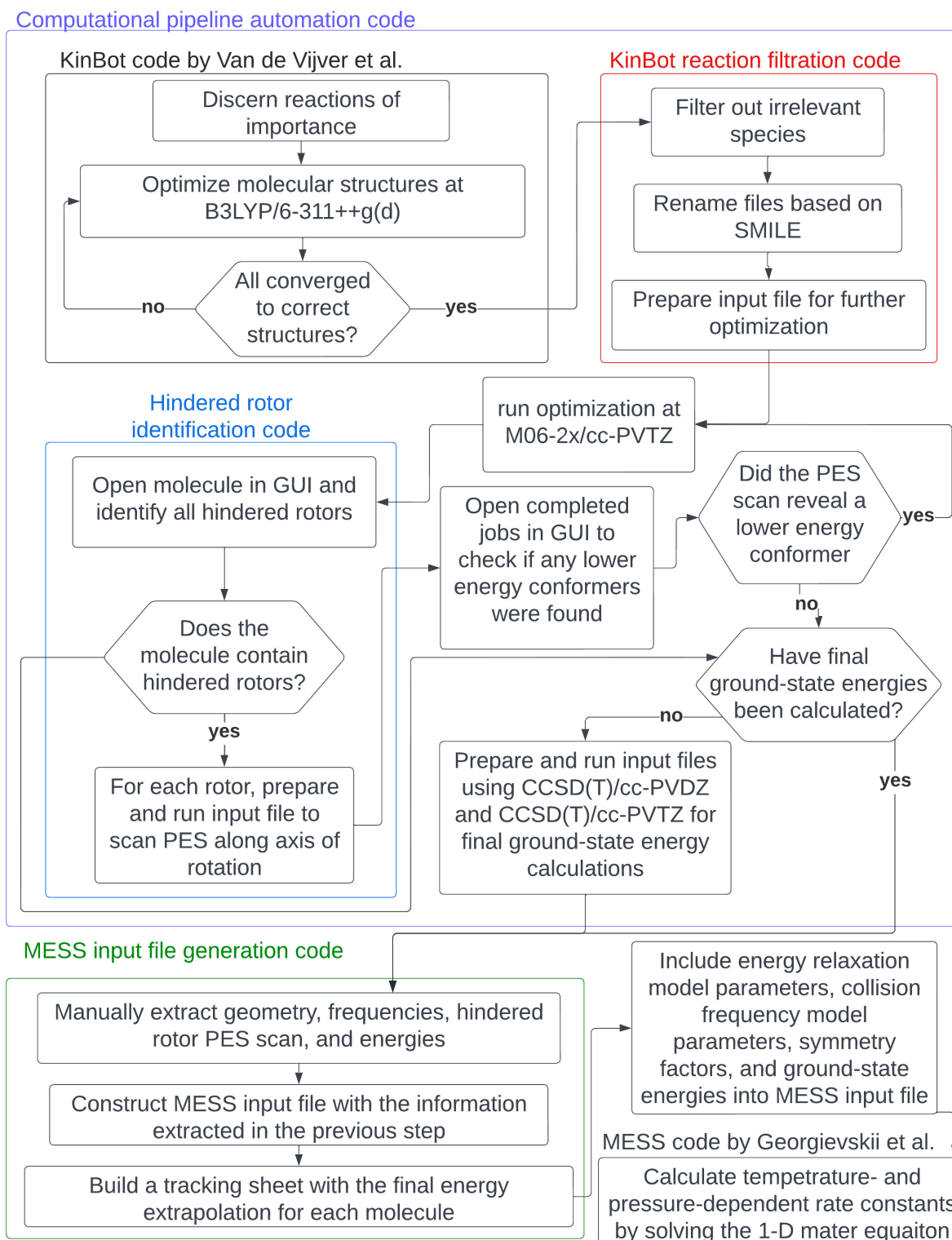


Fig. 3.1 Flow chart of the methods used in this work (that leverage previously developed codes and software [45, 75, 82, 94]) to calculate high-level rate coefficients, and the computational steps captured by the automation codes (in red, blue, green, and purple) developed in this work.

3.1 KinBot reaction filtration code

Traditionally, one of the most time-intensive tasks in theory-based rate generation is to manually find transition state structures of such reactions. This is because optimization in a PES (via gradient descent) may easily miss saddle points and instead converge into local minima. Consequently, multiple jobs must be submitted with small differences in the initial molecular structure with the hope that it will converge into the correct saddle points between reactants and products. KinBot [75] is an incredibly useful code that not only determines reactions of importance based on its PES search, but also automatically finds and optimizes relevant transition state structures at any given level of theory using Gaussian [45]. The resulting KinBot PES can be visualized using the PESViewer module. An example of a KinBot-generated PES for $\text{CH}_3\text{CH}_2\text{OCH}_2\dot{\text{O}}$, a relevant radical in DEM pyrolysis, is shown in Fig. 3.2.

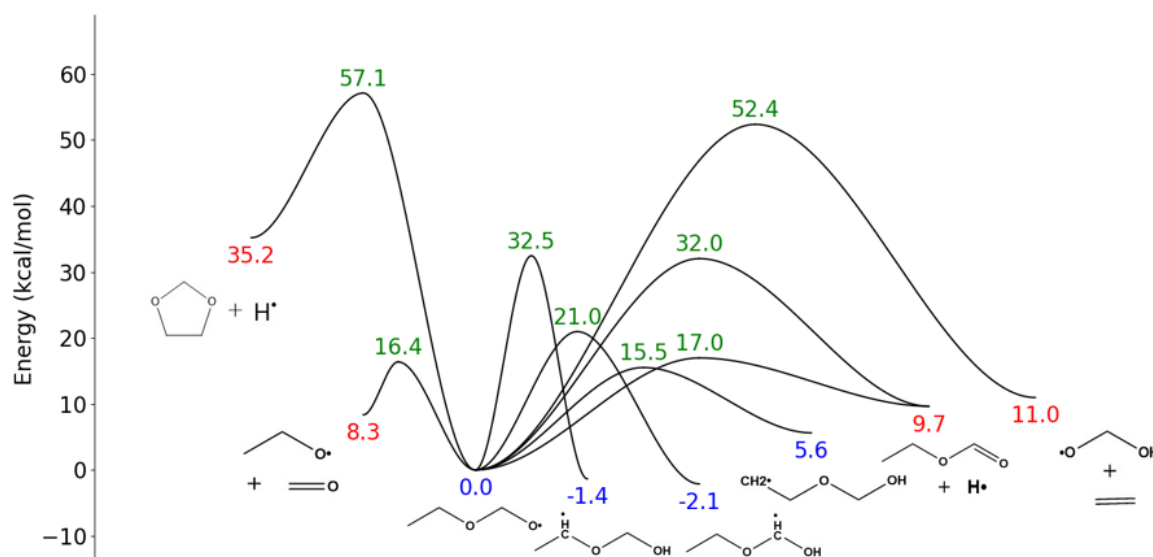


Fig. 3.2 KinBot-generated PES for $\text{CH}_3\text{CH}_2\text{OCH}_2\dot{\text{O}}$ with a cutoff of 60.0 kcal/mol. Isomerization, β -scission, and transition state energies are shown in blue, red, and green respectively.

KinBot has various reaction search parameters, one of which is used to only keep in *pesviewer.inp* the species and transition states that have calculated energies (at B3LYP/6-311++G(d)) below a specified energy cutoff. This allows KinBot to disregard unlikely reactions with high activation energies. However in practice, one would only perform further energetic calculations on a subset of the reactions found by KinBot, as high-accuracy DFT and ab initio calculations are computationally expensive, and often times the reactions with the lowest activation energies will take 99% of the unimolecular reaction flux. In the case of Fig. 3.2, this means that the transition states and products related to the activation energies of 57.1 kcal/mol and 52.4 kcal/mol may be considered negligible in the unimolecular decomposition of $\text{CH}_3\text{CH}_2\text{OCH}_2\dot{\text{O}}$.

Another issue with KinBot is that it labels optimization files corresponding to bimolecular products and wells based on the species' unique ChemID [75] (i.e. methoxy radical is labeled as 310670570000000000002_well), and transition states based on the atom numbering in the

specified geometry (i.e. a transition state corresponding to an internal hydrogen transfer reaction between atom 2 and atom 4 is labeled as 461341380780180000001_intra_H_migration_2_4). For a computational chemist, it would be more useful to name the files based on unique species identifier system such as the simplified molecular-input-line-entry system (SMILES) [95–97]. SMILES are a chemical species identifier developed to provide a human/machine language interface, they provide a user- and machine-friendly approach to label molecules based on their chemical graph structure. Naming files with SMILES would allow molecules to be readily identified and would aid in keeping a clean file structure.

The KinBot reaction filtration code (provided in Appendix A) aims to solve these two problems. These scripts extract the optimized geometries of the reactant, products, and transition states for reactions below a specified energy cut-off from the KinBot-generated PES. For instance, a cutoff of 33 kcal/mol would disregard the two reactions with activation energies of 52.7 and 57.1 kcal/mol from Fig. 3.2 and would only extract the optimized geometries of species related to reactions with an activation energy below 33 kcal/mol. Then, the scripts label each species' filename using SMILES, and writes Gaussian input files for the second round of optimizations and frequency calculations (at M06-2X/cc-pVTZ). The following subsection provides a detailed explanation of the logic behind these scripts

3.1.1 Algorithm explanation

There is an additional bash script that is executed when running KinBot, it is called *Transfer.sh*. This script triggers once the KinBot search finishes and, among other tasks, it is responsible for moving all of the Gaussian output *.log* and machine-readable *.chk* files into a folder called *Log_Chk_files* within a parent *Transfer* folder which also has the *pesviewer.inp* file. Thus, the *Log_Chk_files* folder contains information about the geometry, vibrational frequencies, and energy for all species that KinBot considered.

The KinBot reaction filtration code is composed of five scripts, two written in bash and three in python: *get_input_gjf.py*, *newzmat.sh*, *parsingPesviewer.py*, *run_all_gjfs.sh*, and *xyz2mol.py*. These scripts are meant to be placed inside the *Transfer* folder, in the same directory as the *Log_Chk_files* folder and *pesviewer.inp* file. Then, the scripts may be executed by running *parsingPesviewer.py* with python3, this file is composed of three main functions: *get_valid_logFiles()*, *create_input_files(validFilesTS)*, and *setupJobs(xyzFilesTS, procs)*.

The *get_valid_logFiles()* function is responsible querying the user for a maximum energy cutoff and extracting (from *pesviewer.inp*) the ChemID for the species whose corresponding reaction lies below the cutoff. Then, the *Log_Chk_files* folder is accessed and, using the ChemID of the filtered species, it identifies their corresponding *.log* files. The *.log* files are then opened, and the *TS* keyword is searched within its input file's route section (see Subsection 2.3.3) to check if the species is a transition state structure. Finally, the function returns a hashmap (*validFilesTS*) where the keys are the ChemID, and the values are a list of length two where the

zeroth item contains a Boolean that specifies whether the corresponding species is a transition state structure, and the first item contains the energy (B3LYP/6-311++G(d)) of the specie.

Next, the *create_input_files(validFilesTS)* function is called with the hashmap (*validFilesTS*) as its argument. For every *.log* file in the hashmap (*validFilesTS*), *create_input_files(validFilesTS)* creates a dummy *.xyz* file containing the Cartesian coordinates of the species, and feeds this file to the *xyz2mol.py* script [98] to obtain the species' SMILES structure. In addition, the input *.gjf* file template is created (with Z-matrix format) by passing in the *.log* file as an argument to *get_input_gjf.py*. The *get_input_gjf.py* script utilizes the *newzmat* utility from Gaussian to obtain Z-matrix representations of the optimized geometries from the machine-readable *.chk* files (it assumes the *.chk* file is identically named to the *.log* file). This is useful since having molecular structures in terms of internal coordinates allows to perform PES scans for internal rotational modes, which will be done later. Then, the function loops through all the newly created *.gjf* files in the directory and prepares the for the next round of optimizations by setting up their route section with the desired number of processors for each optimization job. In addition, it renames the *.gjf* using SMILES and their (B3LYP/6-311++G(d)) energy according to the following format: *SMILES_Eenergy.gjf*, with the energy being specified with a hyphen instead of a dot. For instance, if dimethyl ether was one of two bimolecular products at energy 4.5 kcal/mol, its Gaussian input filename would be: *COC_E4-5.gjf*. The *create_input_files(validFilesTS)* function returns two hashmaps, one (*xyzFilesTS*) is identical to *validFilesTS* but stores *.gjf* files instead of *.log* files, and the other (*procs*) stores information about the number of processors to use for each species in the next round of (M06-2X/cc-pVTZ) optimizations (taken as user input).

Finally, the *setupJobs(xyzFilesTS, procs)* function takes in these hashmaps as its arguments and is responsible for setting up the shell scripts (*run_all_gjfs.sh*) that will be used to run each species' subsequent (M06-2X/cc-pVTZ) optimization. To avoid overloading a specific allocation in the RMACC supercomputer, the function rotates through the currently available allocations. If an allocation is changed in the future, the *allocation* directory should be modified accordingly. Lastly, the shell script/input *.gjf* file pair will be placed inside a folder named after the SMILES of the corresponding specie.

Although the automatic SMILE labeling aspect of these scripts is a nice feature, their true value lies in filtering species from reactions with an activation energy below a specific energy cutoff. This is because a standard KinBot output may spawn thousands of files, all named with different ChemIDs. Thus, finding specific files and utilizing a Gaussian GUI to save each file with the correct geometry format and job specifications is a time-consuming task.

There are some disadvantages to the current version of these scripts, the main one being the working implementation of the RDKit molecule object is not able to provide SMILES labels for radical molecules. This is an issue since most species in unimolecular decomposition are radicals. This matter may be addressed in future updates to the RDKit library, or may be avoided all-together by leveraging another python cheminformatics library. Finally, a suggestion for a future improvement is to assign the number of processors per node and time limit to each job based on the number of heavy atoms present in the molecule, instead of taking these values from

user input. This small improvement would not have a great impact in the overall time saved but would reduce human intervention thus minimizing the number of typos given to the scripts.

3.2 Hindered rotor identification code

Once subsequent (M06-2x/cc-pVTZ) molecular optimizations have been run, hindered rotor scans are performed in the search for lower energy conformers (see Subsection 2.4.2). Hindered rotors can be visualized easily using a GUI such as Gaussview [94].

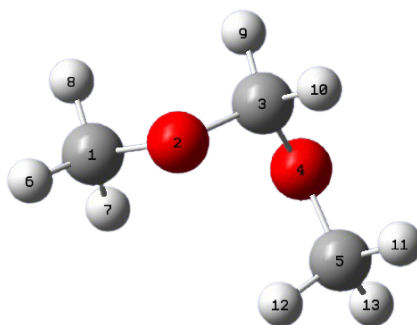


Fig. 3.3 Ball-and-stick model of dimethoxymethane using GaussView6.

Fig. 3.3 shows the optimized molecular structure model for dimethoxymethane (DMM). DMM has four rotors, corresponding to rotations of the 1-2, 2-3, 3-4, and 4-5 axes. Thus, to scan the potential energy surface associated with internal rotational degree of freedom, four different dihedrals must be scanned by 360° . One can do this with 144 *.gjf* input files, where 36 input files are assigned to each dihedral, and each file scans 1 step in 10° increments.

Setting up 144 files manually can be easily avoided by writing a script that loops through the files and performs some basic string parsing. However, this requires the user to preemptively know which dihedrals to look for, in other words, it requires to user to know what axes on the molecule correspond to its hindered rotors. As shown in Fig. 3.3, visually spotting a molecule's hindered rotors is straightforward, but creating a program that identifies them given a Z-matrix or Cartesian geometries is more complicated.

This is the problem that the rotor identification code (Appendix B) aims to solve. These scripts unify bond modeling ideas (using covalent radii) with some basic graph theory concepts to capture the hindered rotors present in a molecular structure. First, the code defines the molecule's bond graph, which is a two-dimensional array where the i^{th} term contains an array of all atoms bonded to atom i . Then, the code identifies all atoms in the bond graph that are bonded to only one other atom and eliminates them. Additionally, it also rules out any two atoms with a bond length short enough to be considered a double/triple bond. Finally, the code identifies rotors as all axes left on the final bond graph that don't form part of a cyclic structure. The following subsection will describe the process in more detail.

3.2.1 Algorithm explanation

The rotor identification code has 2 python scripts and one bash script: *get_geometry.py* (inspired by [99]), *get_rotors.py*, and *run_all_gjfs_array.sh*. Furthermore, these scripts assume that *get_input_gjf.py* has been employed to create a *.gjf* template from the previous optimization's *.log* and *.chk* files. To run the code, one must call *get_rotors.py* with python3 in the same directory as the template *.gjf* files.

The *get_rotors.py* script only has one function (*main*), this function is called when the scripts are executed. First, *main* loops through the *.gjf* files in the same directory and feeds them to *get_gView_format(file_name)* (which is a function inside *get_geometry.py*). This is done to convert the comma-separated *.gjf* files (from the *newzmat* utility) into space-separated input *.gjf* like the ones created by GaussView6. Then, the function loops through the newly converted files and extracts information about the species' multiplicity, geometry, and whether or not it is a transition state structure. Then, the *.gjf* file is fed to the *get_file_string_array* to get an two-dimensional array representation of the input Z-matrix, this template will be useful later on when creating copies of 100+ input files. After the Z-matrix template has been retrieved, another two-dimensional array containing the Cartesian coordinates of the species is created (*xyz_array*) with information extracted from the *.log* file. This array is passed into the *get_geom(xyz_array)* function which returns another two-dimensional array *geom* with a description of the Cartesian geometry that is easier to handle.

Then, *geom*, along with a *bond_threshold* parameter is passed to the *get_bond_graph()* function which is responsible for creating the molecule's bond graph. The *get_bond_graph()* function uses *get_r12(coords1, coords2)* to obtain the Euclidean distance (3.1) between any two points in three-dimensions.

$$dist_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2} \quad (3.1)$$

Then, it determines whether atoms are bonded based on the inequality shown in Eqn. 3.2 [100]. This condition labels any two atoms as bonded if their bond length is less than or equal to the sum of their covalent radii [101] times a *bond_threshold* parameter. This parameter is tuned in an attempt to capture the correct bonding of optimized transition state structures. In addition, a similar inequality with a tighter condition (3.3) is utilized to find any two atoms that have a double/triple bond, these axes cannot be rotors.

$$dist_{ij} \leq 1.2[cov(i) + cov(j)] \quad (3.2)$$

$$dist_{ij} \leq 1.2[0.73 * cov(i) + 0.73 * cov(j)] \quad (3.3)$$

The bond graph of a molecule is a two-dimensional array that described its connectivity. As mentioned earlier, the i^{th} term in a bond graph contains a list of all atoms bonded to atom i . For instance, the following bond graph describes DMM (shown in Fig. 3.3).

$$[[2, 6, 7, 8], [1, 3], [2, 4, 9, 10], [3, 5], [4, 11, 12, 13], [1], [1], [1], [3], [3], [5], [5], [5]]$$

Once the bond graph is obtained, it is used, along with *geom* to obtain all of the possible planar angles and torsion angles in the molecule using the *get_angles(geom, bond_graphs)* and *get_torsions(geom, bond_graphs)* functions. The former calculates the planar angles using Eqn. 3.4

$$\theta_{ijk} = \cos^{-1}(r_{ij} \cdot r_{jk}) \quad (3.4)$$

Where r_{ij} is the unit vector between atoms i and j , which is calculated using the Euclidean distance and basic linear algebra principles using the *get_u12* function. The *get_torsions(geom, bond_graphs)* function calculates torsion angles using Eqn. 3.5, where $n_{ijk} = \left[\frac{r_{ji} \times r_{jk}}{\sin(\theta_{ijk})} \right]$ is the normal vector to the plane described by atom i , j , and k .

$$\phi_{ijkl} = \cos^{-1}(n_{ijk} \cdot n_{jkl}) = \cos^{-1} \left[\frac{(r_{ji} \times r_{jk}) \cdot (r_{kj} \times r_{kl})}{\sin(\theta_{ijk}) \sin(\theta_{jkl})} \right] \quad (3.5)$$

Information about the torsion angles is passed to the *get_rotor_dihedrals_method_2* function, along with other arguments including the two-dimensional array containing the input Z-matrix (*zmat_array*), and the bond graph (*bond_graph*). This function gets the rotor axes from *get_all_rotors(bond_graph)* (see 3.2.1.1); and finds their corresponding dihedral label within the Z-matrix template (*zmat_array*). It returns two lists, one containing all of the dihedrals identified as rotors, and the other containing the labels of the four atoms that define the dihedral that corresponds to each rotor. Finally, multiple copies of the original *.gif* file are created (using *create_gjf_copies(new_dir, zmat_file, rotor_dihedrals)*), each one with the correct Gaussian PES scan command and the appropriate route section (the number of processors (*numProc*) to be used for each file is take from user input). These files are placed inside a folder named after their respective dihedral, all within another folder named after the species' SMILES. Finally, a bash script (*run_all_gjfs_array.sh*) that runs all 36 jobs in parallel (using slurm arrays) is placed inside each dihedral's folder.

3.2.1.1 Function logic: *get_all_rotors(bond_graph)*

The *get_all_rotors(bond_graph)* function performs multiple transformations of bond graph to get the rotor axes. First, it constructs the molecule's heavy atom bond graph (*heavy_heavy_atoms*)

by eliminating all *singly-bonded* atoms (mostly hydrogen and double-bonded oxygen). In addition, these atoms will also be removed from other atom's bonding entries. The following is an example of a heavy atom bond graph for DMM shown in Fig. 3.3.

$$[[2], [1, 3], [2, 4], [3, 5], [4]]$$

Then, through a subsequent transformation, a two dimensional array (*axes*) where the elements are the general axes of heavy atoms is acquired. For the example of DMM, the general axes are:

$$[[1, 2], [2, 3], [3, 4], [4, 5]]$$

These represent the axes between the heavy atoms. Then, it is passed as an argument to the (*include_cyclics_branched(axes)*) function which enters a loop where, if it finds an axis where one vertex (atom) is not bonded to any other atom in the graph, it classifies it as a rotor and eliminates it from (*axes*). More specifically, it is looping through (*axes*) and classifying every axis that is not part of a cyclic structure as a rotor. For the case of DMM, the series of mutations to (*axes*) would be as follows.

$$[[1, 2], [2, 3], [3, 4], [4, 5]] \xrightarrow{[1,2] \text{ is a rotor}} [[2, 3], [3, 4], [4, 5]] \xrightarrow{[2,3] \text{ is a rotor}} [[3, 4], [4, 5]] \dots$$

For the case of DMM, since it does not contain any cyclic structures, every axis will be classified as a rotor. For demonstration purposes, let us consider the case of toluene (SMILES: CC1=CC=CC=C1).

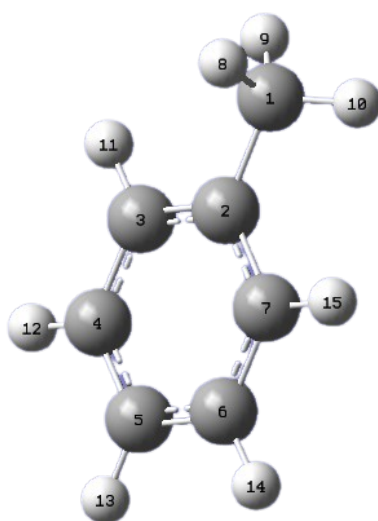


Fig. 3.4 Ball-and-stick model of toluene using GaussView6.

The bond graph and generalized (*axes*) for toluene as depicted in Fig. 3.4 are the following:

```
bondgraph :[[2, 8, 9, 10], [1, 3, 7], [2, 4, 11], [3, 5, 12], [4, 6, 13], [5, 7, 14], [2, 6, 15],  
           [1], [1], [1], [3], [4], [5], [6], [7]]
```

```
generalizedaxes : [[1, 2], [2, 3], [2, 7], [3, 4], [4, 5], [5, 6], [6, 7]]
```

Now, when the generalized (*axes*) for toluene are passed to the *include_cyclics_branched* function, it will only rule the [1,2] axis as a rotor. This is because all of the other atoms left (*axes*) after [1,2] has been eliminated are bonded to two different atoms, thus the code rules it out as a transition state structure. The drawback of this method is that it would fail to recognize rotors that connect cyclic structures. For instance, if there was another benzene group bonded to Carbon 1, then the code would not recognize the [1,2] axis as a rotor because it would rule it out as being part of a larger cyclic ring.

These scripts are highly accurate for closed-shell molecules. However, they occasionally mislabel or miss hindered rotors altogether in radicals and transition states. It is evident that the script heavily relies on the accuracy of the bond graph to determine the rotors, and these bond graphs are a function of constant parameters. However, the bond lengths that they model are not constant. In the case of some radicals and transition states, the effective bond lengths may be significantly shorter or longer than the covalent bond length, and the scripts break down by either incorrectly labeling double bonds, or incorrectly labeling bonds between atoms that are not supposed to be bonded. Different thresholds have been tested with little success.

However, a solution to this problem has recently been published by Gaussian Inc. They have made available a feature that identifies the internal rotation modes during the harmonic vibrational analysis. At the moment of writing this thesis, we are testing the accuracy of this new feature and will include it in all automation scripts moving forward.

3.3 MESS input file generation code

The MESS code [82] is leveraged in this work to produce rate coefficients. It solves the one-dimensional master equation and produces temperature- and pressure-dependent rate coefficients for multi-well (unimolecular) systems. To do this, a MESS input file must contain information on the vibrational frequencies, molecular structure, hindered rotor scans, and ground-state energy for all species in the system. This information is often scattered in dozens of Gaussian output *.log* files and makes input MESS files extensive (often thousands of rows long). Thus, constructing an input file for MESS may take several days depending on the number of reactions included in the system.

The MESS input file generation code (Appendix E) aims to automate the construction of a MESS input file by searching through numerous *.log* files, extracting the necessary information, and appending it to a MESS input file with the correct format. The scripts require the user to place all Gaussian output *.log* files corresponding to isomerizations, eliminations, and bond fissions reaction products (along with their transition states) in different folders following a similar *wells-bimolecular-barrier* file management as the one in the model section (see 2.5.3) of the MESS input file. Then, the scripts access all these files systematically, extract the necessary data (namely Cartesian geometries, vibrational frequencies, hindered rotor scans, internal rotational modes, and ground-state energies), and append it to a newly created MESS input file. During the process, the scripts log onto the terminal the files they are currently scanning for debugging purposes. The following subsection will describe the logic used in the code in detail.

3.3.1 Algorithm explanation

The MESS input file generation code is composed of four core python files: *geometryInfo.py*, *get_energies.py*, *messParsing.py*, and *writeMessFile.py*, but it also leverages the utilities provided in *get_geometry.py*. To run the code, one must execute the *writeMessFile.py* (using python3) in the same directory as the *wells* and *products* folders which contain the required *.log* files. The *writeMessFile.py* script calls the *writeMessFile()* function which is the core of the code. Once called, this function runs *write_Header()*, which writes the model section (see 2.5.3) of the MESS file. Then, it loops through the *wells* and *products* folders (saved in the *pathways* variable) and does the following.

1. Identifies the *.log* which contains the molecular optimization, and vibrational frequencies based on the naming and stores the filename in the *m062xFileName* variable.
2. Then the Cartesian geometry, frequencies, charge and multiplicity for the species are acquired via the *get_xyzGeom(m062xFileName)*, and *get_frequencies(m062xFileName)* functions from the *.log* file. These functions are located in *geometryInfo.py*. They access *m062xFileName* and perform string parsing using the *regex* library to extract the optimized Cartesian geometry, frequencies, charge, and multiplicity from various sections of the *.log* file. Then, the *get_rotors(geom, m062xFileName, bond_thresh)* function leverages the hindered rotor identification code (Section 3.2) to identify the axes corresponding to each hindered rotor's dihedral. This is done because with our naming scheme, the hindered rotor's dihedral is used to identify each *.log* rotor calculation, but the MESS input file identifies the rotors based on the group and axis of rotation in *Rotor* segment of the global section.
3. Then, the script accesses the each rotor *.log* file corresponding to the species and extracts the peaks and valleys (using the *get_peaks_valleys(dihedrals, m062xFileName)* function) of the PES scan. These values are stored in the *rotorEnergies* variable.

4. Next, depending on the type of species (well, transition state, bimolecular product), the script will write the MESS *Barrier* and *Bimolecular* sections with the information gathered in the previous steps.
5. Finally, the script calls the *write_energies_spreadsheet* function which is defined in the *get_energies.py* script. This function is responsible for creating the Microsoft Excel sheet containing the relative energies for all species in the system, as well as the final energy extrapolation calculations. The function takes in four arguments, the first (*energiesDictionary*) is a hashmap that contains species' names as keys, and a list of the zero point corrections, ab initio (CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ) energies, and T1 diagnostic (measure of multi-reference electron correlation) for each species. These values will be used in the final energy extrapolation equation (2.27). The other three arguments are lists that identify species as transition state structures, bimolecular products, and products of dissociation reactions (i.e. homolytic fissions).

The newly created MESS input file still requires some user intervention to specify parameters for the LJ collisional frequency model, the symmetry factors, and the hindered rotor's rotation group. In addition, the user must also exclude the internal rotation frequencies from the vibrational modes section, and specify the potential prefactor, and the potential power exponent (see 2.5.3 and 2.4.3) for phase space theory.

3.3.2 Future improvements

These scripts have, without a doubt, the most impact on the computational workflow of all of the automation scripts outlined in this work. Not only because they reduce work that can potentially take at least a week down to less than a day, but mainly because they significantly reduce the amount of human intervention in the creation of MESS input files. This minimizes undesired errors and typos which can be quite frequent on input files that are thousands of lines long. However, there is significant room for improvement, some suggestions for future work are outlined below.

- The SMILES for the parent molecule may be fed from the file name into an online database (i.e. RMG) using browser automation tools such as *selenium* to extract the LJ parameters of any given molecule. Alternatively, these parameters may also be extracted from the NIST database.
- Symmetry factors are a function of the molecule's point group and number of chiral centers. While the point groups may be extracted from online data bases with a similar method as the one described above, publicly available codes that attempt to find the number of chiral centers in a molecule given its Cartesian coordinates have yielded little success. However, such a script may be developed from an accurate molecular bond graph.

- The information on the hindered rotor's rotation group and vibrational frequency can be obtained from the output *.log* file and incorporated into the MESS input file using the new Gaussian feature (*HinderedRotor* option in the *Freq* command) outlined in Section 3.2.
- Finally, the current version of the scripts generate a MESS input file for a reaction system involving one well and all of its products. A useful upgrade would be to edit the logic to allow the construction of a MESS input file for multiple-well reaction systems.

3.4 Computational pipeline automation code

Although the previous automation scripts significantly optimize the computational chemistry process of calculating theory-based rate constants, major time sinks still exist in the use of GUI (such as GaussView) to read and write *i/o* files for every Gaussian calculation. In addition, humans are checking these files only during their work hours, which is a third of the day, on average. This means that if files finish running overnight, they stay untouched for several hours before its output can be used in subsequent calculations. Thus, automating this computational process would save a considerable amount of time. This section describes the first iteration of a comprehensive automation of the entire computational pipeline for calculating the ground-state energies of gas-phase reaction systems with high-level DFT and *ab initio* calculations using the Gaussian software and the resources of the RMACC supercomputer. The intention of this work is to combine the KinBot, hindered rotors, and MESS python scripts to produce a robust python automation pipeline with the aim of saving researcher's time and minimizing undesired human input errors leading to the waste of computational resources.

These pipeline automation scripts are made to be run from a RMACC *compile* node by activating a custom python environment (*labbeDev*) that contains the necessary dependencies (mainly those required by the KinBot and MESS codes). The future goal of these scripts is to start with KinBot's reaction search and end with an input MESS file for the reaction system. However, the current working version of the code ends after the final ground-state energies are calculated (using CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ), as shown in Fig. 3.1. A more simplified flow chart that encapsulates the pipeline automation code is depicted in Fig. 3.5

The pipeline's automation is designed to have only two user intervention steps (UIS). The first one happens once the KinBot reaction search runs successfully, the user must download *pesviewer.inp* along with 2-D molecule drawings (stored in a folder called *xyz*) to visualize the system's potential energy surface and choose an energy cut-off, only keeping the most relevant reactions in the system. Then, the user can fire the KinBot reaction filtration scripts using the specified cutoff to set up geometry optimization and frequency calculation jobs using the M06-2X/cc-pVTZ method and basis set. The second UIS happens once all of the DFT jobs are prepared, here the user has the option to add any additional transition states and products not considered in the system. This step is essential since KinBot may miss important 4-center and 6-center pericyclic reactions in closed-shell molecule systems. In addition, the KinBot reaction

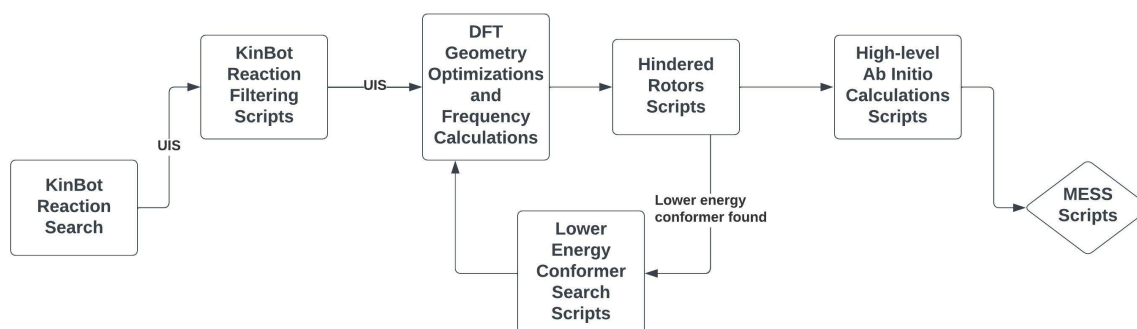


Fig. 3.5 Flow chart of the automation of the computational pipeline. UIS stands for user intervention step. The diamond-shaped box denotes the scripts that have not been integrated into the pipeline's automation at the moment of writing this thesis.

filtration code also fire the hindered rotor scripts internally and show all of the rotors found for each molecule preemptively, storing them in a *rotors_found.txt* file. This file will later be used by the hindered rotor scripts, and its purpose is to let the user verify that the rotors found are related to the correct axes. Additionally, this gives the user the option to add or delete any missing or additional rotors and correct inconsistencies from the hindered rotor identification code (this part will be omitted if the *HinderedRotors* feature of Gaussian is found to work properly for all molecules).

Once all molecules and hindered rotors are verified, the scripts may be called to perform the DFT geometry optimization, frequency calculations and hindered rotor scans in a loop until no lower energy conformers are found. If a lower energy conformer is found, an additional script that retrieves the lower energy geometry and sets up a new round of optimizations will fire. Finally, when the scripts exit the lower energy conformer loop, an additional script that prepares and runs high-level ab initio calculations using the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ methods and basis sets will fire to get more accurate estimates of the ground-state energies of the fully optimized molecular structures.

3.4.1 Algorithm explanation

The core of computational pipeline automation code (Appendix D) is comprised of six python files: *run_iter.py*, *searchLowConf.py*, *start_pipeline.py*, *start_rotor_run.py*, *startHighEnergyCalcs.py*, and *startSearchLowConf.py*, but the code requires all of the files included in the KinBot reaction filtration code and the hindered rotor identification code. This code may be called after a successful KinBot run, and requires all of the necessary python and bash scripts to be placed inside the *Transfer* folder. The code starts by executing the KinBot reaction filtration code by calling *parsingPesviewer.py* (see 3.1). Once that runs successfully, each species' folder will contain the Gaussian input *.gif* file for the next round of (M06-2X/cc-pVTZ) optimizations and frequency calculations along with a series of python scripts. In addition, it will generate *rotors_found.txt*. Once the user has verified that all of the relevant species are included

and that the hindered rotors have been correctly identified for each species, the entire code may be executed and will run without any further user intervention by calling the *start_pipeline.py* script.

This script goes into each species' folder and executes *run_iter.py*. This python file in turn is responsible for executing the shell script (*run_all_gjfs.sh*) that runs the (M06-2X/cc-pVTZ) optimization, and the *start_rotor_run.py* script. This last python script has a function that scans the directory every five minutes (times out after a day) to check if any *slurm.out* files have been created (if yes, then this is a sign that the job is not in queue anymore and has started the calculations). Then, it will open the bash script (*run_all_gjfs.sh*) and extract the job time for the calculation from the *sbatch* resources section and use that as the new timeout. Next, it will open the *slurm.out* file every ten minutes (until timeout) to check if the optimization calculations are over. If the calculations have run successfully, *get_input_gjf.py* will be called to obtain the new *.gjf* input files from the output *.log* file (see 3.1.1).

The next steps is where the the looping begins. First, if the newly created *.gjf* input file corresponds to a species that has no rotors, then the *startHighEnergyCalcs.py* script will be called. This script has a single function with no arguments, *runHighECalcs()*, that is executed upon call. This function is responsible for creating a directory called *HighEnergyCalcs* which will hold copies of the *.gjf* input file with the route section changed such that it requests ab initio (CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ) calculations instead. Then, the accompanying bash script will start the Gaussian calculation

Now, if the newly created *.gjf* input file corresponds to a species that has rotors, the rotor identification code will be called using *rotors_found.txt* (see Subsection 3.2.1) as an argument. This will create all of the new input *.gjf* files required to perform hindered rotor calculations and place them inside the corresponding dihedral folder. Then, the function will loop through these folders and run *run_all_gjfs_array.sh* which, by leveraging *slurm* arrays jobs, provides the utility to perform all 36 PES scan jobs in parallel. Next, the *wait_for_rotors()* function (within the *startSearchLowConf.py* script) will be called. The purpose of this function is similar to that of the *start_rotor_run.py*, which is to open for the slurm files every 5 minutes to check if the PES scanning calculations have started. A similar method is employed to check if the calculations have finished. Once the rotor calculations have finished, the *low_conf()* function within the *searchLowConf.py* script is called. This function is responsible for opening all 36 *.log* files and checking if any of them showed a lower energy conformer from modifying the corresponding dihedral. If no lower energy conformers were found from the hindered rotor scans, then the *startHighEnergyCalcs.py* script will be called.

However, if a lower energy conformer is found (that is, a geometry with a calculated energy at least 0.01 kcal/mol below that energy of the starting optimization), then the *.log* and *.chk* files (along with all of the necessary python files) are moved into a newly created folder within the species' directory called *it2*. Using these two files, a new input *.gjf* file is created with the *get_input_gjf.py* script, and then reformatted using the *get_gView_format(fileName)* function. Finally, a new iteration begins with the *fireIter()* function in *run_iter.py* being called.

3.4.2 Future improvements

The computational pipeline automation code sets the foundations for fully automated electronic structure calculations. The addition of some improvements would allow this code to run by itself and be able to, in a matter of several days, perform all the necessary calculations (which would usually take several weeks) to obtain high-level rate coefficients.

One of the major setbacks of the current working version of the code is that it does not have any error handling algorithm, thus when and if a calculation fails, the entire pipeline for that specific species halts. Thus, an important improvement to the code is to have a function that runs every time a calculation ends. The purpose of such a function would be to first verify that the calculation finished successfully, and second to address any convergence problems that may potentially arise. In addition, the RMACC supercomputer, which is currently used to perform the all calculations, shuts down the first Wednesday of every month for maintenance. Thus, a useful feature to include would be to take the current date into account in the calculations and pause any jobs that would run past maintenance (since they would be terminated), then pick up the calculations again the Thursday after the first Wednesday of every month.

Finally, it would be useful to integrate the MESS input file generation code into this work. One idea to do so would be to loop through each molecule in the system and ask the user to input whether the molecule is a well, barrier, or fragment. Then, the script would reorganize all output files into a structure ready to be fed into the MESS input file generation code. Alternatively, a feature could be integrated into the KinBot reaction filtering scripts that saves the type of molecule (well/barrier/fragment) for each filtered species and passes this data structure all the way down to the MESS input file generation code, this would eliminate user input. However, the downside of the latter solution is that it would not work for multiple-well reaction systems since KinBot searches single-well reactions.

Chapter 4

Previous work on oxymethylene ethers (OMEs)

The global pressures to decrease emissions from the transportation sector are continuously increasing with emission regulations becoming more strict. Although the recent rise in popularity of private electric vehicles is beginning to address this issue, the electrification of light-duty vehicles alone will not meet future regulation targets [102]. This requires the electrification of heavy-duty vehicles (freight, marine, aviation) as well. Freight transportation alone is responsible for the increasing volumes of pollutants and emissions seen in cities [103, 104]. However, the technology required for the economically favored electrification of heavy-duty engines may be several years away from being developed. Thus, alternative liquid fuels and fuel additives have been investigated extensively in recent years in an attempt to reduce emission from heavy-duty engines.

Oxymethylene ethers (OMEs) have been widely studied over the last two decades due to their potential to reduce emissions and improve engine efficiency in compression ignition (diesel) engines. Some OMEs can be produced from syngas, a product from the gasification of biomass [105]; they can also be synthesized from methanol and formaldehyde [106]. Dimethoxymethane (DMM), the simplest OME, is composed of an oxymethylene unit bonded to an oxygen with methyl end groups. Larger OMEs can be produced by either increasing the number of oxymethylene units (i.e. 2,4,6 trioxaheptane or $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_3$), or extending the end groups (i.e. diethoxymethane or $\text{CH}_3\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_3$). Examples of these variations are shown in Fig. 4.1

Most OME work in the literature has been focused on performing engine tests and studying the kinetics of smaller OMEs, such as DMM, while little work has been done on larger OMEs. However, in a recent publication, Bartholet et al. [35] predicted that the OMEs with the best diesel-blending properties are those with extended alkyl chains. Diethoxymethane (DEM) and dipropoxymethane (DPM) are examples of such OMEs with ethyl and propyl end groups respectively. Seeing that the theory-based reaction kinetics of DEM and DPM has been barely investigated, these two molecules serve as ideal test cases to apply the automation methods described in Ch. 3. In addition, calculating high-level rate constants for the pyrolysis of DEM

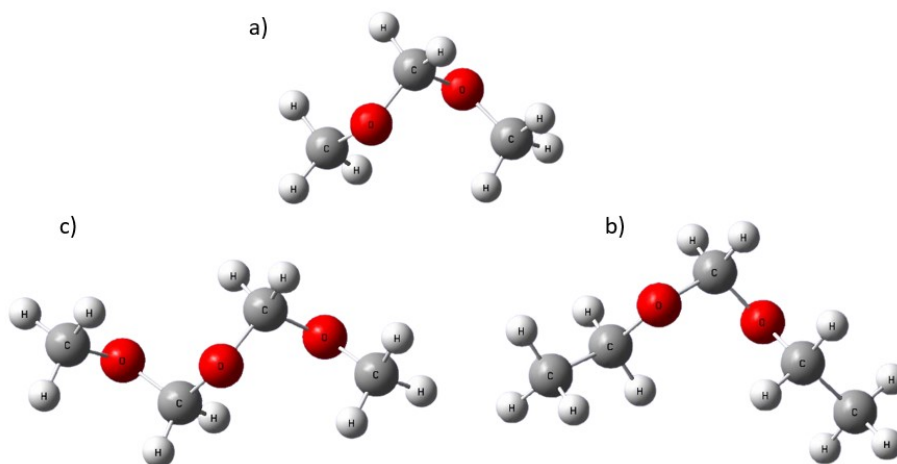


Fig. 4.1 Ball-and-stick models of dimethoxymethane (a), diethoxymethane (b), and 2,4,6-trioxahexane (c) highlighting possible extended OME structures (b) and (c) from (a), the simplest OME

and DPM will help elucidate the high temperature chemistry of these potential additives in fuel-rich regions inside engines.

To help set the stage of these studies (further described in Ch. 5 and 6), this chapter will walk through an brief overview of the work that has been done on oxymethylene ethers (OMEs).

4.1 Dimethoxymethane as a diesel additive

Previous studies have shown the promise of OMEs as diesel additives for emissions control. It has been reported that 20% OMEs in diesel blends reduces PM and NO_x production by up to 90% by 50%, respectively [107]. As such, previous chemical kinetic and experimental analysis has focused on the simplest OME, DMM, and its performance in diesel blends. Here we briefly discuss the history of DMM kinetics studies.

Molera et al. [108–110] were the first to study the low temperature (218–685 K) gas-phase oxidation of DMM, and concluded that hydroperoxides and peroxy radicals play a vital role in its DMM oxidation. Fernandez Sanchez et al. [111] studied the subsequent decomposition of H-abstraction radicals for DMM under the absence of oxygen, and suggested that $\text{CH}_3\text{O}\dot{\text{C}}\text{HOCH}_3$ breaks down into either methyl formate and methyl radical, or into 3 products: carbon monoxide, methane and methoxy radical. Additionally, they suggested that $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OCH}_3$ decomposes into either methoxymethyl radical and formaldehyde, or to formyl radical, methane, and formaldehyde.

In the early 2000s, Daly et al. [112] developed a kinetic mechanism for the oxidation of DMM using a jet-stirred reactor at 5.07 bar, at 800 to 1200 K, for various equivalence ratios ranging from 0.444 - 1.778. The parameters in their mechanism relied on analogies to reactions of hydrocarbons, dimethyl ether (DME), and diethyl ether (DEE). Their mechanism was adopted

by Dias et al. [113–115] to developed a new kinetic scheme for lean and rich DMM flames. To validate their scheme, Marrodan et al. [116, 117] conducted high-pressure oxidation experiments in a plug-flow reactor at temperatures between 573 to 1373 K, and at various equivalence ratios. In a more recent study, Vermiere et al. [118] developed a new kinetic model for the low- and intermediate-temperature oxidation and pyrolysis of DMM by investigating PES at the CBS-QB3 level of theory. They validated their model using the data by Marrodan et al. and concluded that the methoxymethoxymethyl radical ($\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OCH}_3$) either unimolecularly decomposes into formaldehyde and methoxymethyl radical or adds to molecular oxygen; while dimethoxymethyl radical ($\text{CH}_3\text{O}\dot{\text{C}}\text{HOCH}_3$) undergoes a fast β -scission forming methyl radical and methyl formate. More recent results have shown that H-abstraction likely happens from the central carbon [119]. As a consequence, a high production of methyl formate is expected in the ignition of DMM.

Shock-tube experiments have also been carried out for DMM/Ar/O₂ and DMM/n-heptane mixtures to investigate their ignition delay times. [120, 121]. In particular, Hu et al. [121] found that the ignition delay time for DMM was inversely proportional to the equivalence ratio, the opposite behavior is seen for n-heptane. Through sensitivity analysis, they showed that Eqns. 4.1 and 4.2 are the most important ignition-promoting reactions, and argued that higher concentrations of DMM would increase the peak mole fraction of combustion-driving hydroxyl radicals in the system, which would in turn reduce the ignition delay times.



More recently, Peukert et al. and Golka et al. [122, 123] measured unimolecular rate constants for the high-temperature decomposition of DMM with shock tube experiments using Hydrogen Atomic Resonance Absorption Spectrometry (H-ARAS) and high-repetition-rate time-of-flight mass spectrometry as detection techniques. To further validate their results, Golka et al. published a subsequent study the following year [124], where they performed quantum chemical calculations at the CCSD(F12*)(T*)/cc-pVQZ-F12//B2LYP-D3/def2TZVPP level of theory. Their results showed that the terminal C-O bond fission forming $\text{CH}_3\text{OCH}_2\dot{\text{O}} + \text{CH}_3$ dominates the unimolecular decomposition of DMM. This was also suggested by the mechanism developed by Vermiere et al. [118] To further contribute to the accuracy of the previously developed mechanisms for DMM, Kopp et al. [119] investigated the kinetics and thermo-chemistry of DMM using ab initio methods at the CCSD(T)/aug-cc-pV(D+T)Z//B2PLYPD3BJ/6-311++g(d,p) level of theory. They investigated hydrogen abstraction reactions by $\dot{\text{H}}$ and $\dot{\text{C}}\text{H}_3$, and concluded that abstraction from the central carbon is always favored, promoting the production of methyl formate.

4.2 OMEs with more oxymethylene units have better diesel-blending properties

Although promising for considerably reducing engine emissions, DMM lacks the necessary properties of an ideal diesel additive. For one, its low flash point, viscosity, and lower heating value would require modifications to the current engine injector systems [125, 126]. Moreover, it has been shown that DMM could be a potential environmental hazard due to its high water solubility [35].

OMEs with the number of oxymethylene units varying from $n = 3-5$, have shown promise as diesel additives as they have a higher viscosity and cetane number, as well as lower vapor pressure [125, 127, 128]. Longer OMEs ($n > 6$) have a high melting point and risk condensation at low temperatures, which may clog filters within fuel injector systems [127]. In their work, Liu et al. [125] tested 10%, 20%, and 30% $\text{OME}_{n=3-5}$ by volume in diesel in a light-duty direct injection compression engine. They found P20 (20% by volume) was the optimal choice as it produced almost soot-free combustion and did not produce as much NO_x as P30. As an effect of an overall higher cetane number, the addition of P20 also showed a slight increase in the brake thermal efficiency (BTE). Lastly, they found that that combustion duration was shortened with the addition of $\text{OME}_{n=3-5}$. Shortly after, in a dual experimental and theoretical study, He et al. [129] developed a kinetic mechanism for the low- and intermediate-temperature combustion of $\text{OME}_{n=3}$. Sun et al. [130] complemented the mechanism by studying the high temperature combustion chemistry via synchrotron ultra-violet photo ionization mass spectrometry (SUV-PIMS) and also measured laminar burning velocities in a spherical combustion vessel at various equivalence ratios. They concluded that the combustion of $\text{OME}_{n=3}$ is highly driven by hydrogen abstractions, the resulting radicals break down quickly, forming abundant amounts of formaldehyde via β -scission reactions. Li et al. [126] also measured ignition delay time, adiabatic flame temperature, and premixed laminar flame speed of $\text{OME}_{n=3}$ and found that temperature has the highest impact on the ignition delay time, followed by equivalence ratio and pressure, respectively. In their study, they compared $\text{OME}_{n=3}$ to n-heptane and saw faster, and less temperature- and pressure-sensitive flames for $\text{OME}_{n=3}$ than for n-heptane, which helped sustain flame propagation at idle and low load conditions.

Interestingly, in a recent study, Lin et al. [131] conducted engine experiments on $\text{OME}_{n=3}$ and diesel blends at various engine loads and found that at 50% load, the total particle number concentrations (PNC) increased by 71.2% for P20 compared to diesel due to a large amount of nucleation mode particles (ultra-fine particles), also known as NMPs, being produced at these conditions. NMPs are considered harmful since they are present in large quantities and can easily enter the circulatory system and even the cellular organelles [132]. Since medium loads are unavoidable in most vehicle engines, this proves to be a major setback for the widespread adoption of $\text{OME}_{n=3}$ as a diesel additive. However, it still holds potential for power generation engines, where there is a narrower set of operating conditions.

4.3 The effect of the extension of the alkyl end groups in OMEs

Other concerns regarding the combustion of methyl-terminated OMEs include its low energy density, high water solubility, and poor oxidative stability. Recently, Bartholet et al. [35] showed that most optimal OME structures (while accounting for both combustion and fuel handling properties) include extended alkyl end groups. Ethyl-, propyl- and butyl-terminating OMEs have an overall higher energy density and hydrophobicity. These molecules can be synthesized from bio-based feed stock [133] and although the presence of C-C bonds in these molecules promotes the formation of soot precursors, it has been shown that even dibutoxymethane (i.e. $C_4H_9OCH_2OC_4H_9$) has eight times less sooting tendency than conventional diesel [35]. There have been significantly fewer studies on OMEs with extended end groups. What studies are available focused primarily on DEM. The following is a summary of the kinetic studies published to date on OMEs with extended end groups.

Experimentally-derived rate coefficients for the ethyl-, and propyl-terminating OMEs + OH reactions have been reported by Thüner et al. [134] and Vovelle et al. [135]. These studies provided some of the first experimental rate expression for these reactions which drive the ignition of DEM and DPM. In another study, Tajima et al. [136] examined the metastable decomposition of DEM through mass-analyzed ion kinetic energy (MIKE) spectrometry and proposed fragmentation mechanisms based on the observed spectra. Dias and Vandoreen [115] developed one of the first kinetic models describing the flat flame stabilization of a rich DEM/ethylene/oxygen/argon fuel mixture at a low pressure of 50 mbar. Then, Zhang et al. [137] measured the ignition delay times of DEM/oxygen/argon mixtures at various pressures, temperatures, and equivalence ratios. They proposed a high-temperature oxidation mechanism based on their experimental data and derived rate constants for important unimolecular channels of DEM by analogy to a preexisting dimethyl carbonate (DMC) mechanism [138]. Ignition delay times were also measured via RCM and shock-tube experiments by Lehrheuer et al. [133] for the 590 - 1190 K temperature range. More recently, Li et al [139] developed chemical kinetic mechanism for DEM oxidation for low to high temperatures by comparing its auto-ignition characteristics to those of n-heptane.

The first experimentally acquired conformations of DEM were obtained by Venkatesan et al [140] using matrix isolation infrared spectroscopy. They supported their work using DFT methods (B3LYP/6-31++G**). In another quantum chemical study, Kroger et al. [141] provided high-level ab initio reaction rate constants for DEM H-abstraction reactions by \dot{H} , $\dot{C}H_3$, and \dot{C}_2H_5 radicals. They also calculated unimolecular rate constants for the subsequent β -scission reactions at the CCSD(T)/aug-cc-pV(T+D)Z//B2PLYPD3BJ/6-311++(d,p) level of theory. They concluded that β -scission pathways leading to the formation of ethylene are of minor importance, which explains the low sooting tendency of DEM compared to other C-C bond containing species.

The high temperature unimolecular decomposition of DEM has first studied in the late 90s by Herzler et al. [36] using a single pulse shock tube experiment. They used Argon as their bath gas, and tracked the production and destruction of ethylene, ethanol, and DEM to derive molecular and bond fission rate coefficients. They found that 1.2 ethylene and 0.5 ethanol were produced for every DEM molecule destroyed. They also found that the ethylene/ethanol ratio increased for higher temperatures. Recently, Jacobs et al [51] published a comprehensive study of DEM combustion, they measured ignition delay times, extinction strain rates, and laminar burning velocities. In addition, they developed a detail kinetic model to describe the pyrolysis and oxidation of DEM at low and high temperatures. Their model includes high-level ab initio calculations at the DLPNO-CCDD(T)/CBS//B3LYP-D3BJ/def2-TZVP level of theory and rate constants derived by the master equation system solver (MESS).

Although the pyrolysis of DEM was studied by Jacobs et al. [51], no similar study has been done to date on DPM. In addition, empirical setups such as micro reactor experiments coupled with photoionization mass spectrometry (PIMS) detection techniques have not been used to isolate initiation reactions and validate dominant pathways predicted by theoretical findings. As a result, further work is necessary to fully understand the initiation chemistry and thermal decomposition of DEM and DPM.

Chapter 5

End group effects on the pyrolysis of oxymethylene ethers

5.1 Introduction

Improving the emissions from internal combustion engines has been one of the major challenges faced by the modern transportation industry. Global efforts to improve the operation of these engines have led to the study of alternative fuels and fuel mixtures that reduce the formation of particulate matter (PM), soot and nitric oxides (NO_x). In this context, oxygenated hydrocarbons have garnered attention recently as alternative fuels and blending agents for diesel. Specifically, oxymethylene ethers (OMEs) have shown promise as viable diesel additives to reduce soot production from engines due to their high oxygen to carbon ratio and ease of manufacturability from renewable feedstock and biomass. As described in Ch. 4, OMEs with extended alkyl end groups have proved to substantially reduce soot emissions while retaining ideal diesel blending properties such as biodegradability, energy density, and sealing material compatibility.

In this work, we investigate the unimolecular thermal decomposition OMEs with ethyl and propyl end groups during the first stages of combustion, discerning the main reaction channels that take place for each OME end group. This will unveil the effects of chemistry structure, specifically the effect of terminal carbon chain length in OMEs. Pressure (0.01atm – 100atm) and temperature (500K-2000K) dependent reaction rate constants were calculated for various bond fission and isomerization-decomposition reactions for diethoxymethane, and dipropoxymethane using quantum chemical calculations at the CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. We validate our results with previous experimental and computational work.

5.2 Methodology

The simplest OME, dimethoxymethane ($\text{CH}_3\text{O}[\text{CH}_2\text{O}]_n\text{CH}_3$ where $n=1$), is comprised of one oxymethylene unit bonded to an oxygen with terminating methyl groups. For the work

presented in Ch. 5 and 6, dimethoxymethane will be labeled as M-1-M, where the letters refer to the alkyl end group type, and the number refers to the amount of oxymethylene units present in the molecule. Thus, diethoxymethane and dipropoxymethane are referred to E-1-E and P-1-P, respectively here on. In addition, the oxymethylene unit carbon will be labeled as δ , and subsequent carbons to the left or right as α , β and γ , respectively.

5.2.1 Theoretical Methods

A theoretical study from first principles was performed for M-1-M, E-1-E and P-1-P to determine the most important reactions that take place during ignition by comparing the ground energies of reactants, transition states, and products. The electronic structure calculations were performed using Gaussian [45] to validate and complement the PIMS results. Reaction pathways on the potential energy surface (PES) and initial structure geometries for all species were generated at the B3LYP/6-311++g(d) level of theory and with a barrier threshold of 100kcal/mol using KinBot [75], an automated PES explorer developed at Sandia National Laboratory. KinBot expedites the identification of potential transition state reactions by iteratively changing the geometry of the reactant to obtain initial guesses for reactive saddle points which are then optimized into transition states using Gaussian.

Next, the methods outlined in Ch. 3 were leveraged to obtain geometry optimizations, rovibrational frequencies calculations and hindered rotor scans for all relevant reactants, transition states and products using the M06-2X/cc-pVTZ density functional theory (DFT) method and basis set [71] with tight convergence criteria and an ultrafine grid. Relaxed scans of 10-degree steps were performed on the hindered rotors in search for lower energy conformers. Higher level energy estimates for the stationary points were calculated by extrapolating energies obtained at the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory to approximate an infinite basis set [78, 79]. The PESs with the all final for E-1-E, P-1-P, and their subsequent products are shown in Figs. 5.1 and 5.2, respectively. The extent of the multi-reference characteristic was determined by calculating the T1 diagnostic for each species and transition state; no species had a T1 diagnostic larger than the generally accepted threshold of 0.02 for closed shell systems. Intrinsic reaction coordinate (IRC) calculations at M06-2X/cc-pVTZ were done to confirm transition state structures.

Finally, pressure and temperature-dependent rate constants were evaluated using the Master Equation System Solver (MESS) [82] developed at Argonne National Laboratories. The energy relaxation model was used in all rate calculations, with an expectation value for $\Delta E_{down}^{(0)} = 200cm^{-1}(T/298K)^{0.85}$. The collisional frequency model was employed using the Lennard-Jones potential with Ar as a collider to model Herzler et al. [36]. The modeling for all bond fissions is similar to what was done by Jacob et al. [51], where the phase space theory parameters for the MESS code were acquired by fitting a negative power law to the Morse potential:

$$V_{Morse}(r) = \text{BDE}(1 - e^{\alpha(r-r_0)})^2 \quad (5.1)$$

Here, the Morse potential is a function of r in terms of the bond dissociation energy (BDE), the equilibrium bond length r_0 , and the curvature parameter α . The curvature parameter, in turn, is a function of the reduced mass μ , the BDE, and the averaged harmonic oscillator frequency ν for the corresponding symmetric and asymmetric bond stretching modes:

$$\alpha = 2\pi\nu\sqrt{\frac{\mu}{2\text{BDE}}} \quad (5.2)$$

The MESS parameters were chosen from a fit that matches the Morse potential between 30-50% increase of the equilibrium bond length r_0 . These parameters reproduce the total E-1-E rates for Herzler et al. [36] for the temperature range 1150-1260 K. All transition state rate constants include the Eckart tunneling correction factor. Rate constants were calculated for temperatures between 500 and 2000 K in 10 K intervals and for pressures between 10^{-5} - 100 atm in one order of magnitude intervals.

5.2.2 Experimental Methods

Photoionization mass spectrometry (PIMS) measurements coupled with microreactor experiments are used to characterize the decomposition products and support theoretical results. The details of these experiments can be found in previous work [142–145]; a brief description is provided here. Microreactor pyrolysis experiments are carried out with a silicon carbide (SiC) tube 28 mm long with a 1 mm inner diameter. SiC is suitable for high-temperature flow studies because it has a high melting point and is chemically inert in vacuum environments. It is resistively heated up to 1800 K, and the surface temperature is measured using a ThermoIMAGER TIM M-1 camera with a 16 mm focusing lens. This device measures temperature by characterizing the radiation produced by the heated silicon carbide reactor. The reactor temperature uncertainty is estimated to be ± 50 K, and measurements were obtained at steady temperatures in 100 K increments along a temperature range of 300–1800 K.

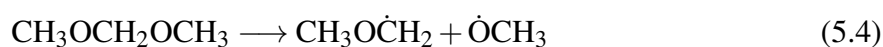
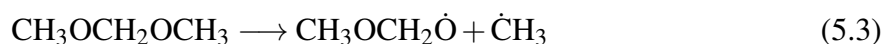
The dimethoxymethane sample evaluated in this work was purchased from Sigma Aldrich at a purity of $\geq 99.5\%$. Diethoxymethane and dipropoxymethane were produced by the transacetalization reaction of methyl terminated OMEs with higher alcohols. This resulted in compounds with a purity of $>95\%$. Each of these molecules were entrained in a helium carrier gas, (AirGas; UHP $\geq 99.999\%$) for PIMS and diluted to $\leq 0.2\%$ to limit bimolecular reactions. The diluted mixture was then flowed through the microreactor at approximately 200 SCCM, where the pressure drops from the inlet pressure, roughly 300 Torr, to vacuum pressure (104 Torr) at the exit. The residence time is roughly 100 μs . In helium, the gas centerline temperature reaches within 100 K of the measured wall temperature after traveling through approximately

one third of the reactor length. Products exit the microreactor into a high vacuum environment and enter a 0.2 mm diameter molecular beam skimmer. The ninth harmonic of a Nd:YAG laser (118.2 nm or 10.487 eV) intersects the molecular beam downstream, and resulting ions are accelerated into a Jordan reflectron time-of-flight mass spectrometer. Mass spectra are averaged over 1000 scans, with a mass resolution $\Delta m/m$ of roughly 400. The number of species detectable by the PIMS is limited only by the ionizing 10.487 eV VUV light, species with a higher ionization energy cannot be detected.

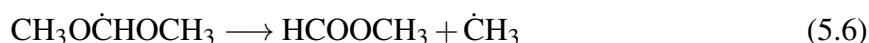
5.3 Results and Discussion

5.3.1 Overview of previous M-1-M work

M-1-M has been studied extensively both experimentally and computationally. Golka et al. [123, 124] investigated the pyrolysis of M-1-M behind reflected shock waves in the 1100-1600 K temperature range and at two different pressures 0.4, and 4.7 bar utilizing hydrogen atom resonance absorption spectroscopy (H-ARAS). They inferred the unimolecular rate coefficients for the C–O bond fission reactions from the recorded $[H](t)$ -profiles. In their work, they did not find any competition by molecular reactions, and further validated their findings using quantum chemical calculations at the CCSD(F12*)(T*)/cc-pVQZ-F12//B2PLYP-D3/def2-TZVPP level of theory. In addition, their calculated temperature and pressure dependent rate coefficients for the unimolecular channels for M-1-M showed that the terminal C-O bond fission (5.3) dominates under pyrolytic conditions $T > 1000\text{K}$, and the central C-O bond fission (5.4) comprises less than 10% of the reaction flux.



Further analysis on the hydrogen abstraction pathways from M-1-M and subsequent isomerization and β -scission reactions were computed by Kopp et al. [119]. They showed that the central carbon site is always favored for hydrogen abstraction (5.5), and that the subsequent radical decomposes into methyl formate and methyl radical (5.6).



Finally, the unimolecular decomposition of the M-1-M, M-2-M, and M-3-M radicals formed via bond fission reactions is currently being investigated by Morehead et al. (to be submitted) and their results suggest that long aldehydes and formaldehyde are prominent products in the pyrolysis of methyl-terminated OMEs.

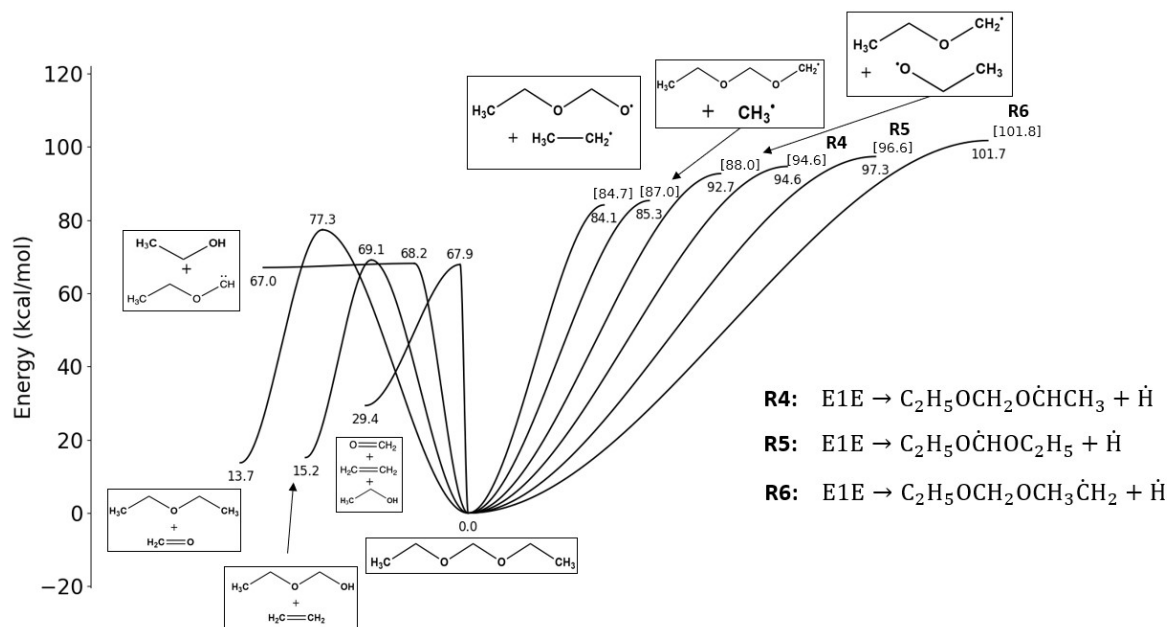


Fig. 5.1 Potential Energy Surface of unimolecular decomposition of E-1-E calculated at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. The zero point energy is located at the parent E-1-E molecule. Ground-state energies calculated by Jacobs et al. [51] are shown in square brackets.

5.3.2 Comparison of the E-1-E and P-1-P rate coefficients to the literature

The first molecular and bond fission rates for E-1-E were measured by Herzler et al. [36] using a single-pulse shock-tube experiment for pressures and temperatures between 2-4 bar and 1150-1260 K, respectively. They found that for every E-1-E molecule destroyed, 1.2 and 0.5 molecules of ethylene and ethanol were formed, respectively. They used the formation of ethanol as a measure for the total rate from molecular channels and subtracted this rate from the total E-1-E rate of destruction to derive the total rate coming from bond fission channels. Argon was used as a bath gas in their setup, and the error range from their Arrhenius fits is presented in Fig. 5.3.

More recently, Jacobs et al. [51] published a comprehensive study of E-1-E, measuring ignition delay times, laminar burning velocities, and extinction rates. They used these results to develop a kinetic reaction mechanism for E-1-E that includes *ab initio* calculations describing the unimolecular decomposition of E-1-E. Their electronic structure, and single point energy calculations were carried out at the calculations were down at the at the DLPNO-CCDD(T)/CBS//B3LYP-D3BJ/def2-TZVP level of theory, their calculated BDEs for E-1-E

are shown in square brackets in Fig. 5.1. The comparison of the total rate constant for the unimolecular decomposition of E-1-E predicted in this study to those calculated by Jacobs et al. [51] and Herzler et al. [36] is shown in Fig. 5.3.

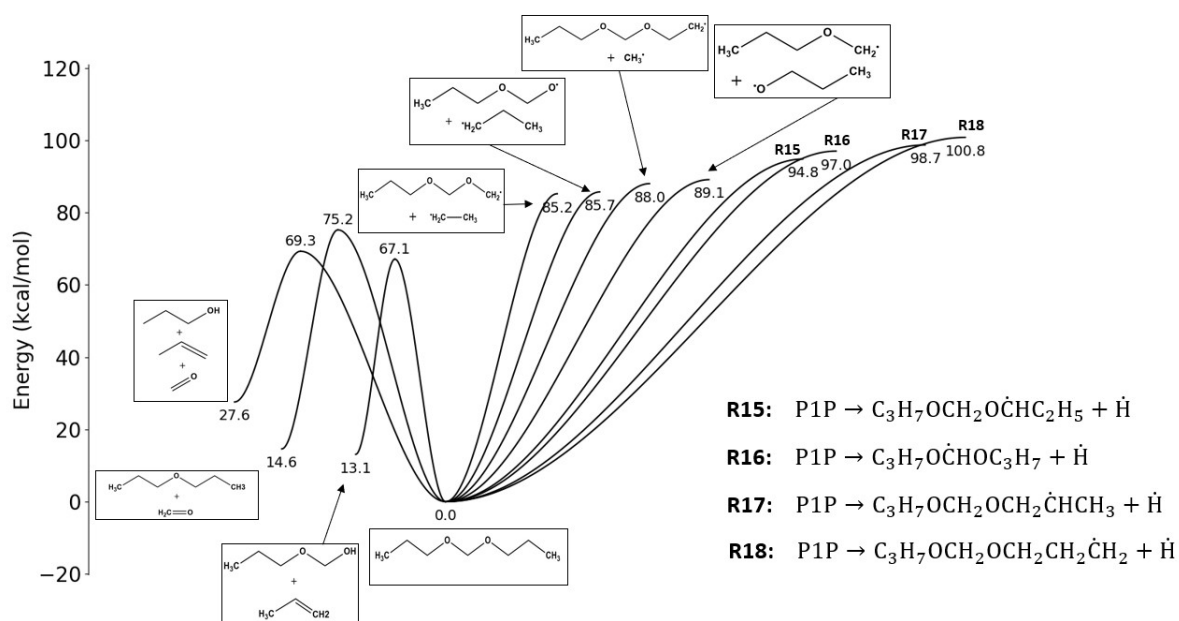


Fig. 5.2 Potential Energy Surface of unimolecular decomposition of P-1-P calculated at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. The zero point energy is located at the parent P-1-P molecule. Molecular and bond fission reactions are shown on the left and right, respectively.

Excellent agreement is seen between the presently calculated rates and the experimental results from Herzler et al. [36]. The mean and maximum difference between our model and their experimental data are 88.32 and 236.14 1/s, respectively. The predicted rates show a strong turn-over at temperatures above 1600 K, which was not seen before. At lower temperatures, the predicted rates slightly undershoots the experimental data.

The total rate from Jacobs et al. [51] was acquired through $\log P$ [85] interpolation of their Arrhenius fits using pressures of 1 and 10 atm. We suspect that the discrepancies with their results may be due to the use of different methods for calculating single point energies. Although the difference in BDE for the α C-O bond fission in their study and this work was found to be only 0.6 kcal/mol, our predicted rate for this reaction is an order of magnitude larger for most relevant temperatures.

This complementary study validates the findings from Jacobs et al [51] and shows a discrepancy in the magnitude of the rate constant of the primary channel of decomposition, namely the α C-O bond fission. Since this rate heavily influences the total rate of consumption of E-1-E, further experimental calculations are vital for developing accurate sub mechanisms describing the decomposition of this molecule.

To our knowledge, this is the first study of the unimolecular pyrolysis of P-1-P. However, our results follow an analogous pattern to those of E-1-E, and the calculated BDEs show similar

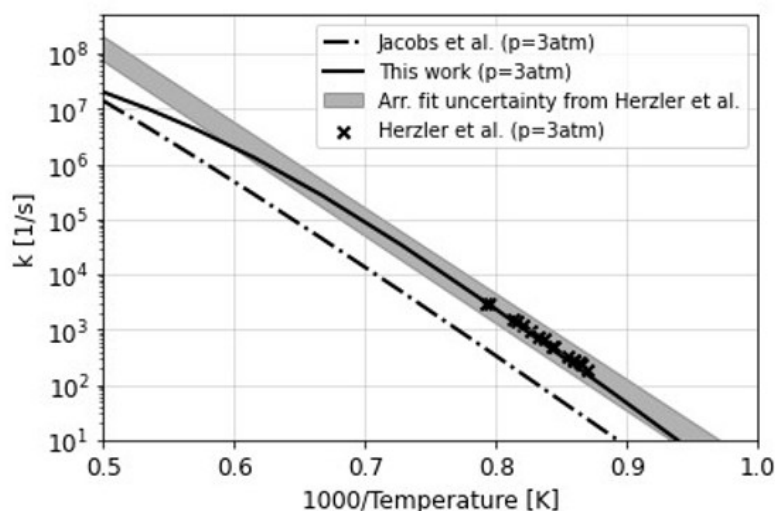
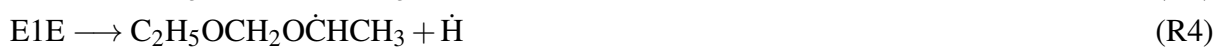


Fig. 5.3 Total rate coefficient of E-1-E calculated in this work compared to previous shock-tube and theoretical studies.

trends to the ones calculated by Cheng et al. [146, 147] for dipropyl ether (DPE). The α β C-C bond is the weakest and the β γ C-C bond is the strongest for both P-1-P and DPE; moreover, the molecular reaction forming propylene + alcohol was found to dominate the unimolecular decomposition of both molecules at low temperatures.

5.3.3 End group effect on product distribution and total reactivity

A total of twenty-one unimolecular reactions were considered for modeling the pyrolysis of E-1-E and P-1-P, fourteen bond fissions and seven molecular reactions. In addition, microreactor experiments coupled with PIMS were leveraged to validate the main reaction channels.





5.3.3.1 Unimolecular decomposition of diethoxymethane (E-1-E)

The extension of the alkyl end group in E-1-E and P-1-P increases their flexibility and opens more possibilities for molecular reaction channels. The results from Fig. 5.4 show that at low temperatures ($T < 800\text{K}$), the decomposition of E-1-E is dominated by the alcohol cleavage reaction forming ethanol and a carbene (R9).

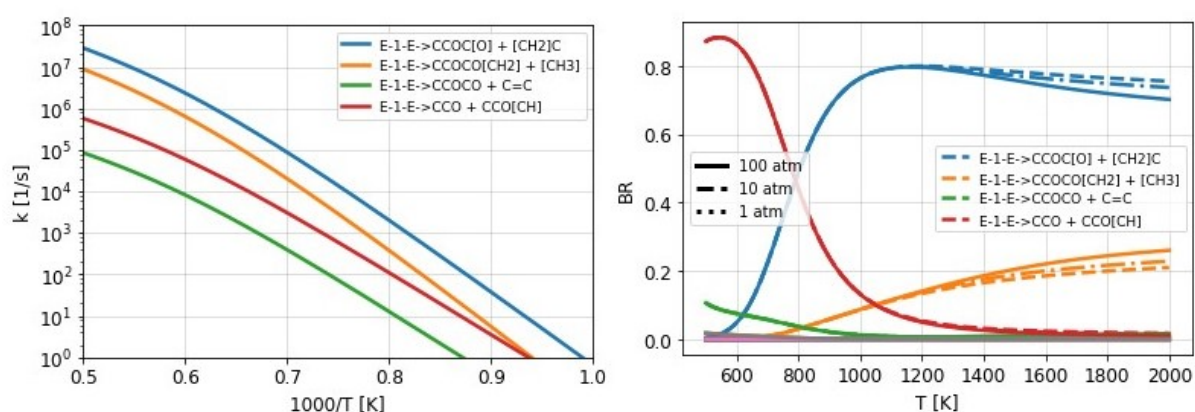


Fig. 5.4 Unimolecular rate constants at $p = 10$ atm (left) and branching ratios (right) for E-1-E. The four reaction channels shown here hold at least 1% of the total unimolecular reaction flux of E-1-E.

At pyrolytic temperatures above 1000 K, the most relevant reactions become the α C-O bond fission (R1), followed by the α β C-C bond fission (R2) forming ethyl and methyl radicals, respectively. Traces of these radicals are also seen to peak at high temperatures in Fig. 5.5, methyl is seen at m/z 15 and ethylene (a product of ethyl radicals undergoing fast β -scissions) is seen at m/z 28. The increase production of ethylene at high temperatures was also seen by Herzler et al. [36]. Other larger, short-lived radicals break down mostly forming ethylene and formaldehyde (m/z 30), although the latter is not ionizable at 10.487 eV. Finally, these bond fission reactions are more pressure-sensitive for E-1-E than for P-1-P, especially at the higher temperatures.

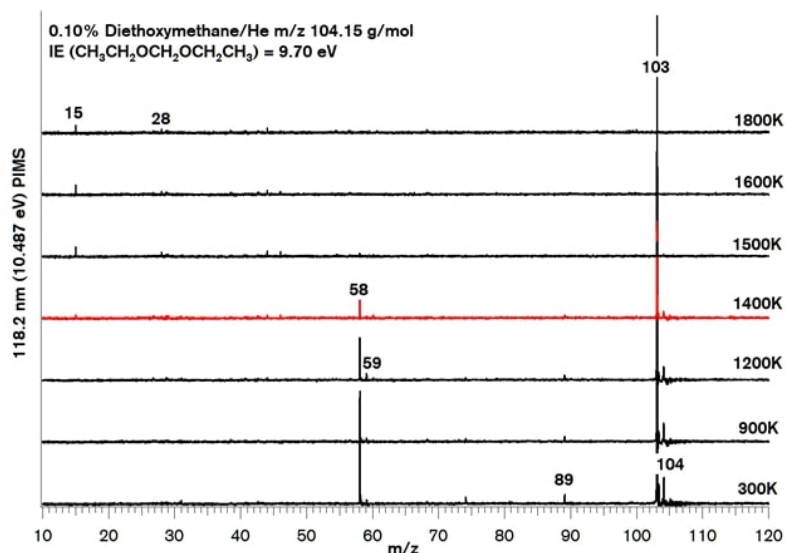


Fig. 5.5 PIMS of 0.1% diethoxymethane (E-1-E) in He in the micro reactor at 200 SCCM heated from 300 to 1700 K and ionized by 118.2 nm (10.487 eV) photons.

5.3.3.2 Unimolecular decomposition of dipropoxymethane (P-1-P)

The molecular channel for propylene elimination dominates the decomposition of P-1-P at the lower temperatures ($T < 700$ K). At higher temperatures, α β C-C bond fission (R11) takes over $\sim 75\%$ of the total reaction flux, forming ethyl radical and a longer radical (i.e. $C_3H_7OCH_2O\dot{C}H_2$). PIMS for this molecule (provided in Appendix E) shows that the latter peaks (m/z 102) at low and intermediate temperatures. The α C-O bond fission (R12) forming propyl radicals is the second most important channel. The addition of the third carbon to the end groups has the effect of spreading out the electron density, thus weakening the δ C-O bond (89.1 kcal/mol for P-1-P as opposed to 92.7 kcal/mol in E-1-E).

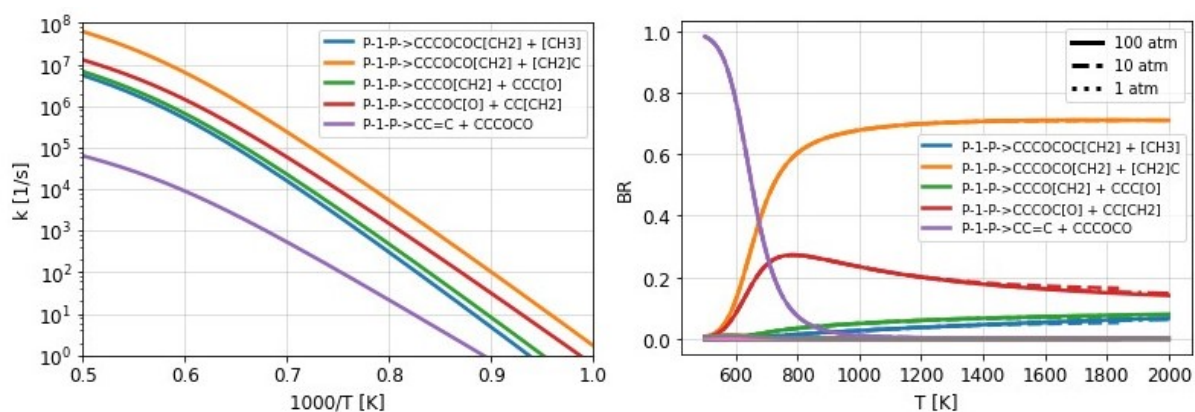


Fig. 5.6 Unimolecular rate constants at $p = 10$ atm (left) and branching ratios (right) for P-1-P.

As a consequence, this reaction, along with the β γ C-C bond fission reaction forming methyl radicals, become competitive and slightly relevant at the highest temperatures. Lastly, these results show that any formaldehyde seen in the system is not formed via molecular reactions from the parent molecule, rather it is mainly formed via subsequent radical decomposition.

5.3.3.3 Total reactivity and trends for different end groups

Figs. 5.1 and 5.2 show that the BDE of the α C-H bond is at least 2 kcal/mol lower than for the other C-H bonds, which suggests that H-abstraction reactions by radicals such as $\dot{\text{H}}$, $\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}_2\text{H}_5$ likely occur at the α carbon for both E-1-E and P-1-P. Moreover, since the C-H bonds have a considerably higher BDEs than the C-O and C-C bonds, it is not surprising to see that the fragments of C-H bond cleavage are not favorable unimolecular products.

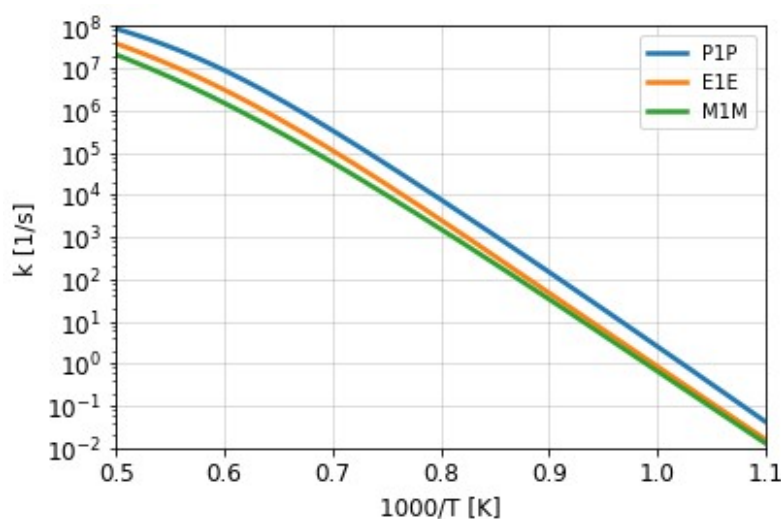


Fig. 5.7 Total rate constant for M-1-M, E-1-E, and P-1-P at p=10 atm.

The overall rate constants for the different end groups are compared in Fig. 5.7. P-1-P is significantly faster than E-1-E and M-1-M. This result was validated with PIMS as methyl (m/z 15), a combustion-sustaining radical, peaks at lower temperatures for P-1-P than for E-1-E, showing that the onset of combustion happens earlier for propyl end groups. This makes P-1-P the most favorable additive as it not only has a higher energy density than M-1-M and E-1-E, but it also ignites faster and produces larger combustion-sustaining radicals. This comes at the cost of a higher peak mole fraction of propylene, a soot precursor produced in P-1-P which is not a likely product in E-1-E's high temperature decomposition. Further studies on the total yield sooting index (YSI) of these molecules are needed to balance their costs and benefits.

5.3.4 Relevant well-skipping reactions

The energetic calculations displayed in Fig. 5.1 show that the H-abstraction radicals formed through (R4-R6) are located high on the potential energy surface, at least 15-20 kcal/mol above the products from the most accessible bond fission (R1). These radicals may break down via β -scission reactions, eliminating smaller complexes such as ethyl radicals, ethylene, and acetaldehyde; or they can undergo chemically activated (well-skipping) reactions, in turn increasing the total reaction flux towards the products of R1. The plots in Fig. 5.8 compare the total well-skipping rate coming from the radicals formed by H-abstraction from the α and β carbons to the theoretical unimolecular β -scission rates calculated by Kroger et al. [141]. A

concentration of H-atom of 1% by volume [148] was utilized to convert the bimolecular rate units of the well-skipping reactions into unimolecular rate units. The effect well-skipping for the radical formed by H-abstraction from the central δ carbon (R5) was found to have little importance, that radical likely undergoes β -scission forming ethyl radical and ethyl formate.

However, the well-skipping reactions for the other two α and β radicals were found to be relevant and even dominant were compared to the unimolecular radical decomposition rates. The results in Fig. 5.8 show that at all temperatures, both the well-skipping and radical decomposition rates increase with pressure. However, we would like to note that radical decomposition rates have a slower turn-over at high temperatures than well-skipping reaction rates. Consequently at high temperatures, we would expect well-skipping rates to be more competitive at lower pressure. Further investigations of the relevance of well-skipping in these systems must be carried out, however, these preliminary results suggest that these reactions must be considered in the construction of future mechanisms for E-1-E.

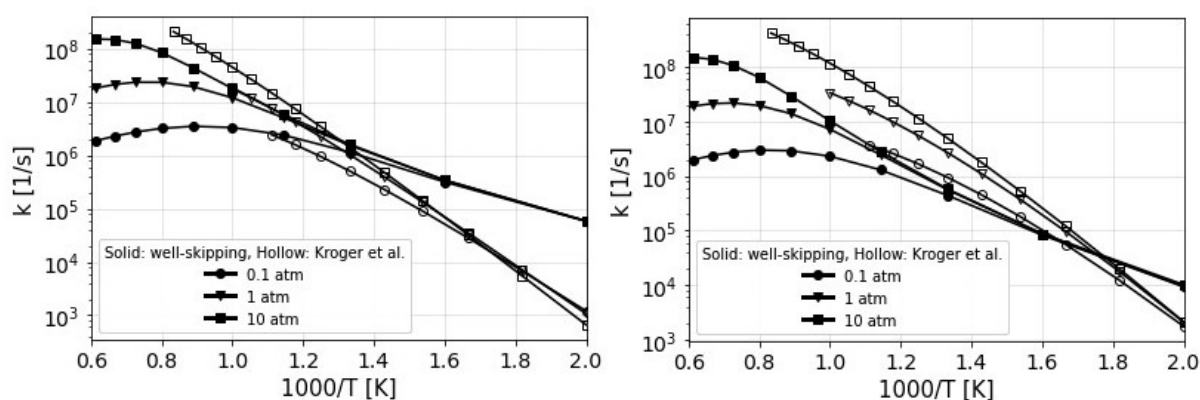


Fig. 5.8 Total well-skipping vs. β -scission rate constant for the decomposition of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{OCH}_2\dot{\text{C}}\text{H}_2$ (left), and $\text{CH}_3\text{CH}_2\text{OCH}_2\dot{\text{C}}\text{HCH}_3$ (right) at multiple pressures.

5.4 Conclusion

We have explored the thermal decomposition of E-1-E and P-1-P, two viable alternatives to M-1-M as diesel additives, through quantum mechanical calculations at the CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. Temperature and pressure-dependent rate constants for their unimolecular decomposition were calculated using transition state theory and master equation theory.

Our investigation shows that the α C-O and α β C-C bond fissions dominate the pyrolysis of both E-1-E and P-1-P, producing ethyl radicals and long oxygen radicals (for E-1-E), or β carbon radicals (for P-1-P). Further studies on the decomposition of these radicals as well as on the combustion driving radical H-abstraction reactions is necessary to complement this study and build a comprehensive mechanism for both E-1-E and P-1-P. At higher temperatures, P-1-P shows more competition from other bond fission reactions as the electron density is more spread out, yielding overall lower BDEs. The effect of extending the alkyl end groups results

in an overall faster unimolecular rate. Additionally, the onset of combustion happens at lower temperatures for P-1-P compared to E-1-E, as dissociation products such as methyl and propyl radicals appear earlier for P-1-P on the PIMS. Additionally, well-skipping reactions were found to be relevant and competitive with radical decomposition reactions in the H-atom abstraction radicals from the α and β carbon sites, implying that chemically activated pathways require further study in the kinetic models of these OMEs.

Both E-1-E and P-1-P have passed previous environmental screenings and have been shown to be ideal diesel blend stocks [35]. The results from this work suggest that P-1-P is slightly superior because it combusts faster, potentially yielding lower ignition delay times than E-1-E. However, it has been shown before that the amount of hydrocarbons intermediates and soot precursors depend greatly on the C/O ratio (2.5 for E-1-E, and 3.5 for P-1-P) [23]. Thus, both OMEs have potential, further experimental work determining the combustion characteristics of these additives blended with diesel is compulsory for balancing their advantages and disadvantages.

Chapter 6

High-temperature decomposition of relevant radicals formed from diethoxymethane and dipropoxymethane pyrolysis

6.1 Introduction

As noted in Ch. 5, E-1-E and P-1-P have received increased attention in the last couple of years due to their favorable diesel-blending properties. The unimolecular decomposition, oxidation, and ignition delay of E-1-E have been studied through shock-tube experiments and quantum chemical calculations [23, 36, 133, 137, 140]. In addition, low- and high-temperature kinetic mechanisms for E-1-E pyrolysis and oxidation have been proposed by Li et al. [139] and Jacobs et al. [51] using analogies to reaction rate constants from n-heptane, diethyl ether, and dimethoxymethane. However, little to no work has been done on the unimolecular decomposition of the fuel radicals of E-1-E and P-1-P formed via H-loss or H-atom abstraction. To date, Kroger et al. [141] are the only group to calculate high-level ab initio rate constants for the subsequent radical decomposition of E-1-E. They employed quantum chemical calculations at the CCSD(T)/aug-cc-pV(T+D)Z//B2PLYPD3BJ/6-311++(d,p) level of theory and found that the central (δ) and α (non-terminal) carbons are the most favored for radical H-abstraction. They further concluded that the low sooting tendency of E-1-E might be explained by the minor importance of β -scission pathways from such radicals leading to the formation of ethylene.

Nevertheless, the work from Kroger et al. [141] focused on the unimolecular rate constant calculations for the H-abstraction radicals of E-1-E, and no results were produced for the oxygen and carbon radicals formed via alkyl end group cleavage. It has been shown that these radicals are dominant products in the unimolecular decomposition of E-1-E and P-1-P. Thus, the environmental and atmospheric impact of the high-temperature combustion of E-1-E and P-1-P inside diesel engines will depend on the fate of these oxygen and carbon radicals. The

calculation of accurate rate coefficients for the decomposition of these radicals is compulsory for the development of detailed chemical kinetic models necessary to understand emissions and sooting propensity of these potential biofuels.

In this work, we explore the subsequent radical decomposition of E-1-E and P-1-P using high-level ab initio and DFT calculations at the CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. Specifically, pressure- (0.01atm - 100atm) and temperature- (500K - 2000K) dependent rate coefficients were calculated for the radical bi products of several alkyl end group cleavage reactions, (namely C₂H₅OCH₂Ö, C₂H₅OCH₂OÖH₂, C₃H₇OCH₂OÖH₂, C₃H₇OCH₂Ö). In addition, we further explore the isomerization-decomposition pathways of E-1-E and P-1-P radicals formed via H-atom abstraction, which were shown to favor chemically activated reactions over β -scission reactions in Ch. 5.

6.2 Theoretical Methods

A theoretical study from first principles was performed for the radical bi products of E-1-E and P-1-P pyrolysis. The electronic structure calculations were performed using the combination of the Gaussian software [45] and the python scripts developed in Ch. 3. Reaction pathways on the potential energy surface (PES) and initial structure geometries for all species were generated at the B3LYP/6-311++g(d) level of theory and with a barrier threshold of 60kcal/mol using KinBot [75].

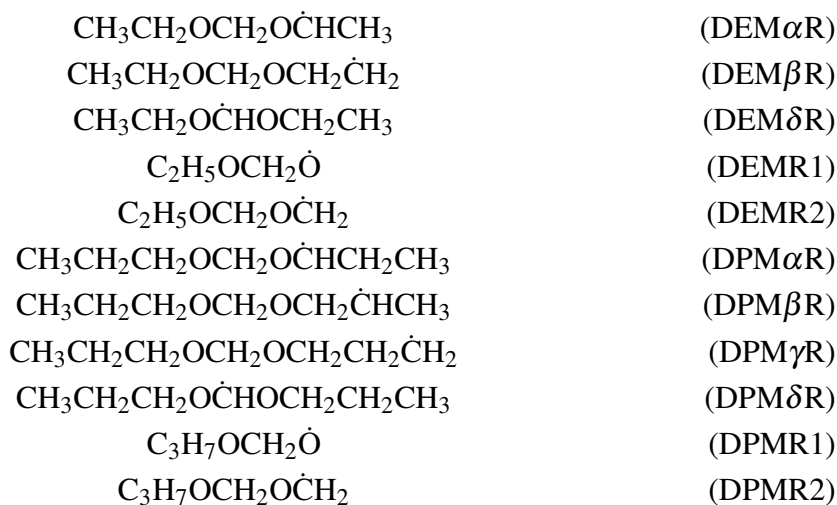
Geometry optimizations, vibrational frequencies calculations, and hindered rotor scans for all relevant reactants, transition states and products were performed using the M06-2X/cc-pVTZ density functional method (DFT) and basis set [71] with tight convergence criteria. Relaxed scans of 10-degree steps were performed on the hindered rotors in search for lower energy conformers. Higher level energy estimates for the stationary points were obtained using the CCSD(T)/cc-pV ∞ Z method by extrapolating optimized energies from the CCSD(T)/cc-pVDZ, and CCSD(T)/cc-pVTZ levels of theory [78, 79]. The extent of the multi-reference characteristic was determined by calculating the T1 diagnostic for each species and transition state; no species had a T1 diagnostic larger than the generally accepted threshold of 0.03 for opened shell systems.

Finally, pressure and temperature-dependent rate constants were evaluated using the Master Equation System Solver (MESS) [82] developed at Argonne National Labs. The Energy Relaxation model was used in all rate calculations, with an expectation value for $\Delta E_{down}^{(0)} = 200cm^{-1}(T/298K)^{0.85}$. The collisional frequency model used was based on the Lennard-Jones potential with Ar as a collider to match previous computational studies [141].

6.3 Results and Discussion

Throughout this discussion we will be analyzing the decomposition of the following radicals, which are products of the most relevant bond cleavage and H-atom abstraction reactions for E-1-E and P-1-P. The radicals are labeled based on their parent molecule (DEM for E-1-E, and

DPM for P-1-P), and those formed via H-atom abstraction are represented using the Greek letters δ , α , β , and γ which correspond to the different carbon sites with unpaired electrons (see Section 5.2):



6.3.1 H-abstraction radicals

The bimolecular H-abstraction reactions from the parent molecules by highly reactive radicals drive the decomposition of E-1-E and P-1-P. For the case of E-1-E, H-abstraction reactions may yield three possible radicals: DEM α R, DEM β R, and DEM δ R. Kroger et al. [141] showed that H-abstraction reactions by $\dot{\text{H}}$, $\dot{\text{C}}\text{H}_3$, and $\dot{\text{C}}\text{H}_2\text{CH}_3$ happen at similar rates forming DEM α R and DEM δ R, while H-abstraction reactions from the β carbon have a lower rate. In addition, Kroger et al. [141] calculated molecular geometries, energies and unimolecular rates of reaction for DEM α R, DEM β R, and DEM δ R. The energies predicted in this work are all within 1 kcal/mol of those calculated by Kroger et al. [141], as depicted in Fig. 6.1. The one exception being the energy for the transition state structure connecting DEM α R to DEM β R, where a lower energy conformer was found in this work.

The increased contribution of this isomerization reactions (DEM α R to DEM β R) at low temperatures explains the discrepancies between the total rate of decomposition of DEM β R predicted in this work to the one calculated by Kroger et al. [141] (shown in the top right plot of Fig. 6.2). However, the branching ratio plot in the bottom right of Fig. 6.2 shows that at high temperatures (above 1000 K), the β -scission reaction forming ethylene and $\dot{\text{O}}\text{CH}_2\text{OC}_2\text{H}_5$ (DEMR1) takes over. Additionally, this plot shows that chemically activated (well-skipping) reactions towards the products of DEM α R and DEM δ R are relevant reaction pathways in the decomposition of DEM β R. However, little information about these reactions is known at higher temperatures, especially at the lower pressures, since at these conditions radicals modeled with MESS become chemically-ill defined. This effect has been seen in similar studies [119], and the reason for this is due to the inseparability of chemical and collisional eigenvalues of the master equation in these conditions [149, 150]. The total isomerization-decomposition rate for

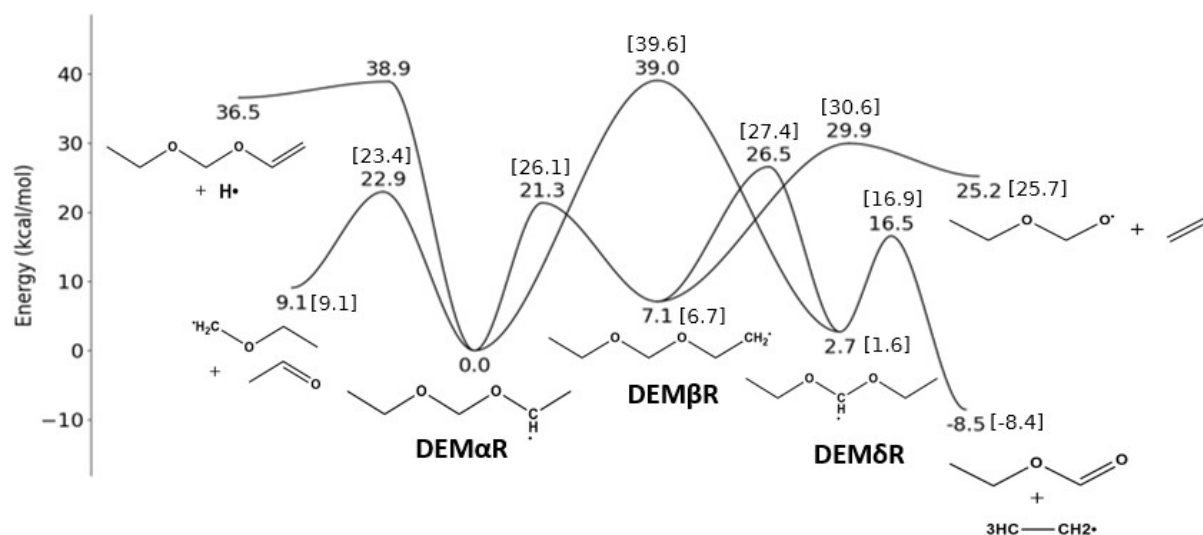


Fig. 6.1 PES of unimolecular decomposition of the E-1-E H-atom abstraction radicals calculated at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory. The energy of W1.1 is used for reference. Ground-state energies calculated by Kroger et al. [141] are shown in brackets.

DEM α R predicted in this work compared to those of Kroger et al. [141] is shown in the top left plot of Fig. 6.2. The rates predicted in this work are slightly slower across all temperatures and pressures.

Given that the same energy relaxation and collisional model parameters were used in both studies, we believe the reason for the difference may be due to a combination of the how one-dimensional hindered rotors were modeled in both studies and the discrepancies in the final energies shown in Fig. 6.1.

The branching ratios in the bottom left of Fig. 6.2 show that if DEM α R is formed, its unimolecular decomposition does not vary significantly at different pressures and is dominated by the β -scission reaction forming acetaldehyde and C₂H₅O \dot{C} H₂. Acetaldehyde has been shown to decompose into methyl and formyl radicals at high temperatures [151], while C₂H₅O \dot{C} H₂ forms formaldehyde and ethyl radicals via a β -scission reaction. It is safe to assume that if DEM δ R is formed, it will quickly decompose into ethyl formate and ethyl radical via β -scission due to the low activation energy of this channel compared to the isomerization reactions. Overall, the results show that isomerization reactions are not likely to play a significant role in the high-temperature unimolecular decomposition of these radicals, even though their energy barriers are comparable to those of β -scission reactions. In addition, well-skipping reactions are expected to contribute to the final product distribution, especially at atmospheric pressures. However, further work is required to characterize these rates at high temperatures. Finally, the rates from DEM α R and DEM β R exhibit major pressure fall-off which is more prominent at higher temperatures, this has been observed in similar studies of M-1-M radicals [119].

For P-1-P, four different radicals may be formed from H-atom abstraction (DPM α R, DPM β R, DPM γ R, and DPM δ R), and the PES for their isomerization-decomposition reactions is shown in Fig. 6.3.

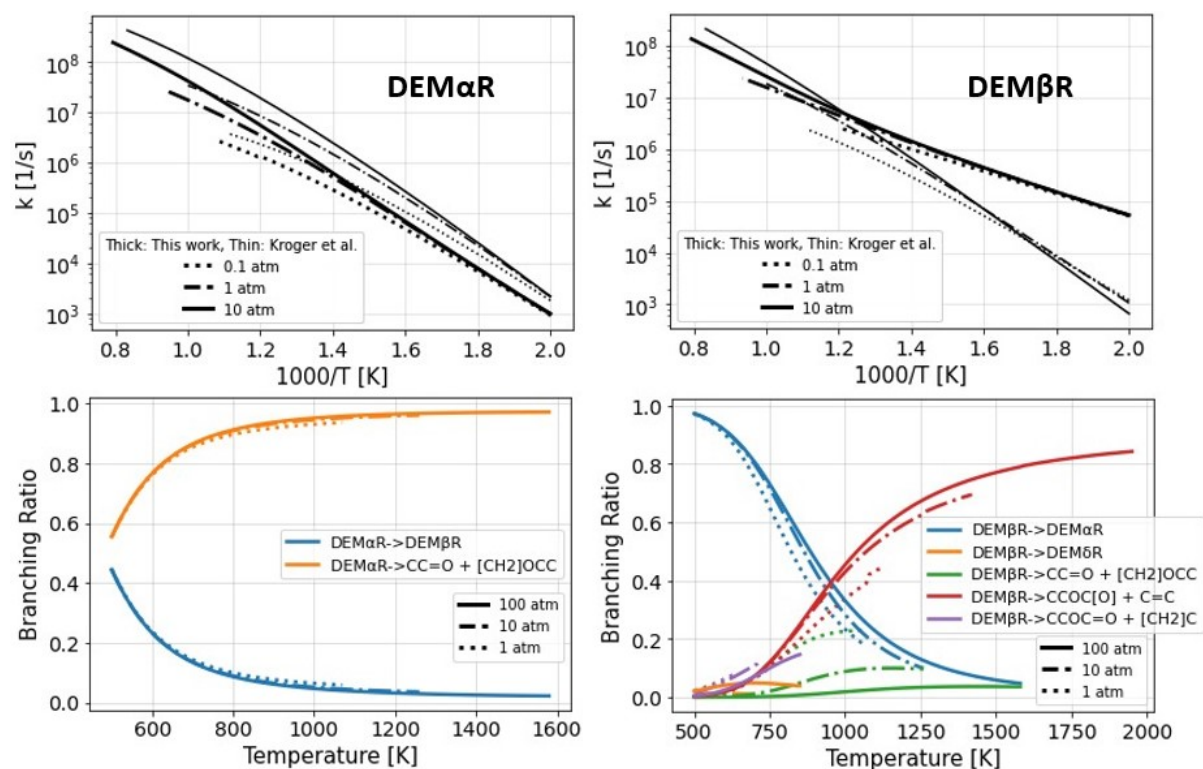


Fig. 6.2 Total isomerization-decomposition rate constant (top left, top right) and branching ratio (bottom left, bottom right) for the decomposition of $DEM\alpha R$ and $DEM\beta R$ at multiple pressures.

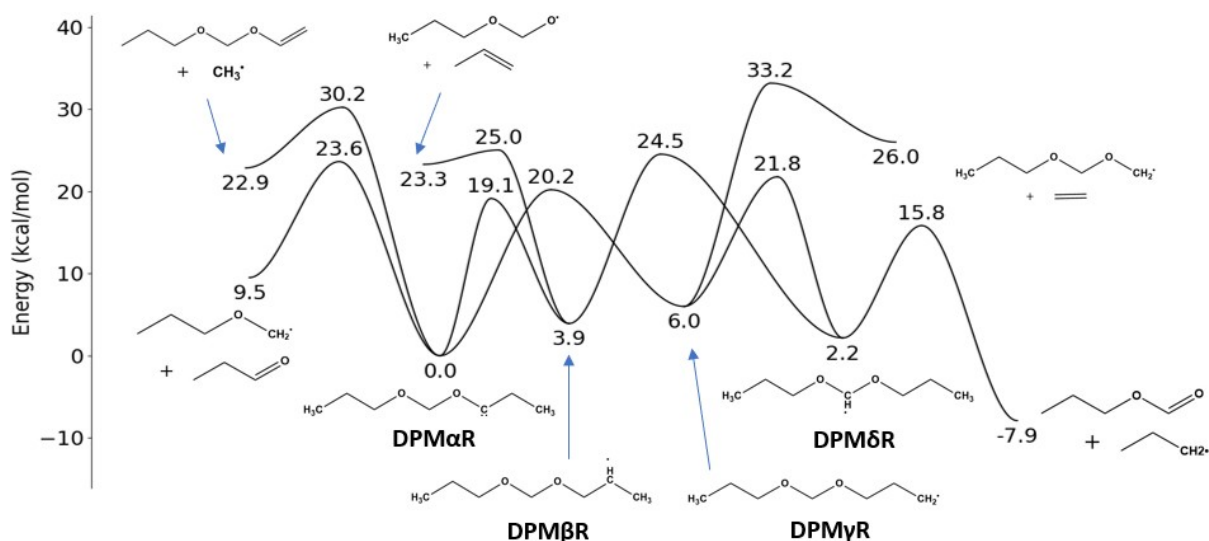


Fig. 6.3 PES of unimolecular decomposition of the P-1-P H-atom abstraction radicals calculated at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory.

First, we note that the isomerization energy barriers are lower than the β -scission barriers in Fig. 6.3 compared to Fig. 6.1. This is due to the longer carbon chain length of the P-1-P fuel radicals. Although this has little impact on the decomposition of $\text{DPM}\delta\text{R}$ (which is still heavily dominated by the low barrier of the β -scission reaction), it raises the rate of the isomerization reaction of $\text{DPM}\alpha\text{R}$ (which forms $\text{DPM}\beta\text{R}$) compared to that of $\text{DEM}\alpha\text{R}$ at low temperatures. Nevertheless, the high-temperature decomposition of $\text{DPM}\alpha\text{R}$ is dominated by its β -scission reaction forming propanaldehyde and $\text{C}_3\text{H}_7\text{O}\dot{\text{C}}\text{H}_2$, the latter of which is a source of formaldehyde and propyl radicals.

Fig. 6.4 shows the predicted rates and product distribution for the other two potential radicals formed via H-atom abstraction ($\text{DPM}\beta\text{R}$ and $\text{DPM}\gamma\text{R}$). The branching ratios in the bottom show that $\text{DPM}\beta\text{R}$ is more likely to isomerize (into $\text{DPM}\alpha\text{R}$) than $\text{DPM}\gamma\text{R}$, especially at low temperatures and high pressures.

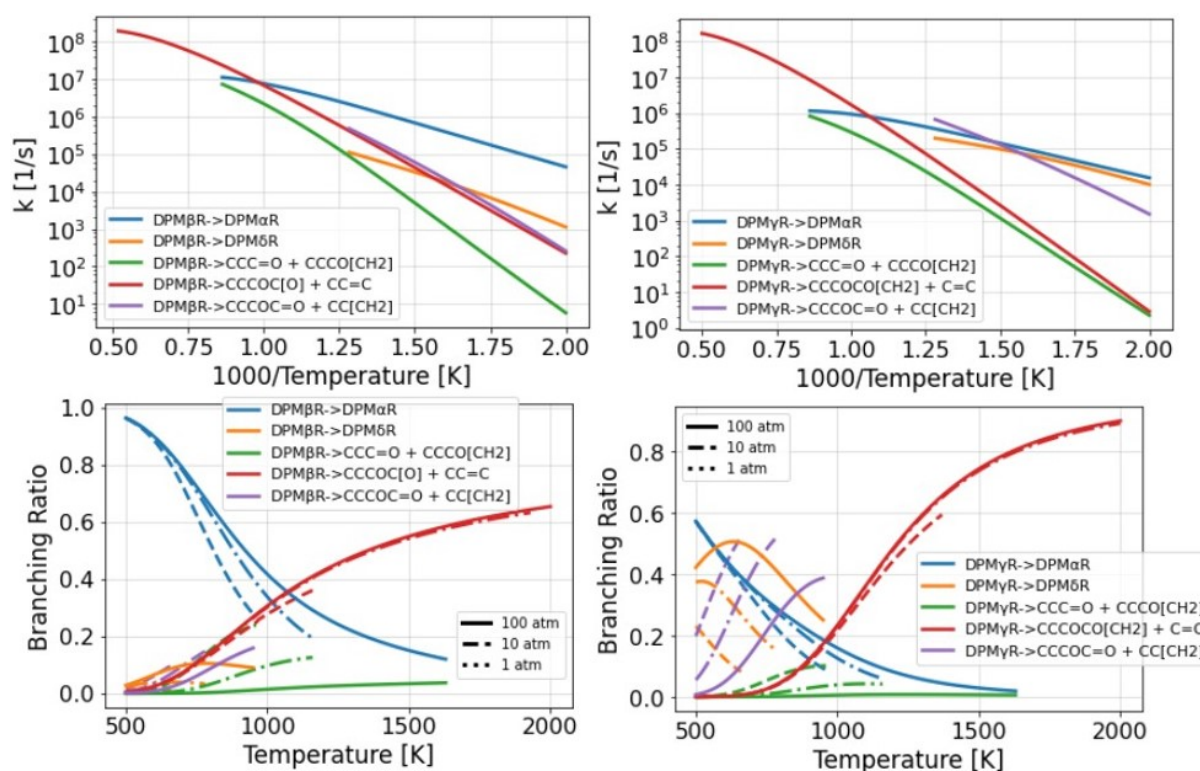


Fig. 6.4 Isomerization-decomposition rate constants (at atmospheric pressure) and corresponding branching ratio of $\text{DPM}\beta\text{R}$ (left) and $\text{DPM}\gamma\text{R}$ (right) at multiple pressures.

At higher temperatures, $\text{DPM}\beta\text{R}$ and $\text{DPM}\gamma\text{R}$ decompose into propylene and DPMR1 , and ethylene and DPMR2 , respectively. This reveals that $\text{DPM}\beta\text{R}$ is potentially one of the main sources of propylene (a soot precursor) in the system, as propylene is unlikely to form via molecular reactions from the parent (P-1-P) molecule. Additionally, the extra carbon present in the P-1-P H-abstraction radicals allows for the formation of DPMR2 , which starts a series of chain reactions that eliminate formaldehyde from the methylenedioxy group (similar to the decomposition of methoxymethyl in methyl-terminated OMEs [152]). The E-1-E equivalent of DPMR2 ($\text{DEM}\text{R2}$) is only formed from bond fissions (by cleaving off a methyl group). The

increased prospect of DPMR2 radicals appearing in the subsequent decomposition of P-1-P suggests that P-1-P ignition is more likely to show high peak mole fractions of formaldehyde. Formaldehyde is hazardous to human health. In high concentrations, formaldehyde irritates skin, eyes, and nasal membrane, and is known to be neurotoxic and carcinogenic [153, 154]. Thus, further species concentration studies are required to assess if formaldehyde is being produced in dangerous amounts from the auto ignition of OMEs. Finally, like DEM β R, chemically activated reactions through DPM α R and DPM δ R show significant relevance at low temperatures for DPM β R and DPM γ R, but further studies are required to predict these rates at higher temperatures.

6.3.2 The CH₃CH₂OCH₂Ö and CH₃CH₂CH₂OCH₂Ö radicals

The oxygen radicals (DEM α R1 and DPM α R1) are formed from the OME's end group cleavage. For E-1-E, this is the dominant reaction pathway (accounting for more than 75% of the reaction flux), while for P-1-P this accounts for ~40% of the total reaction flux.

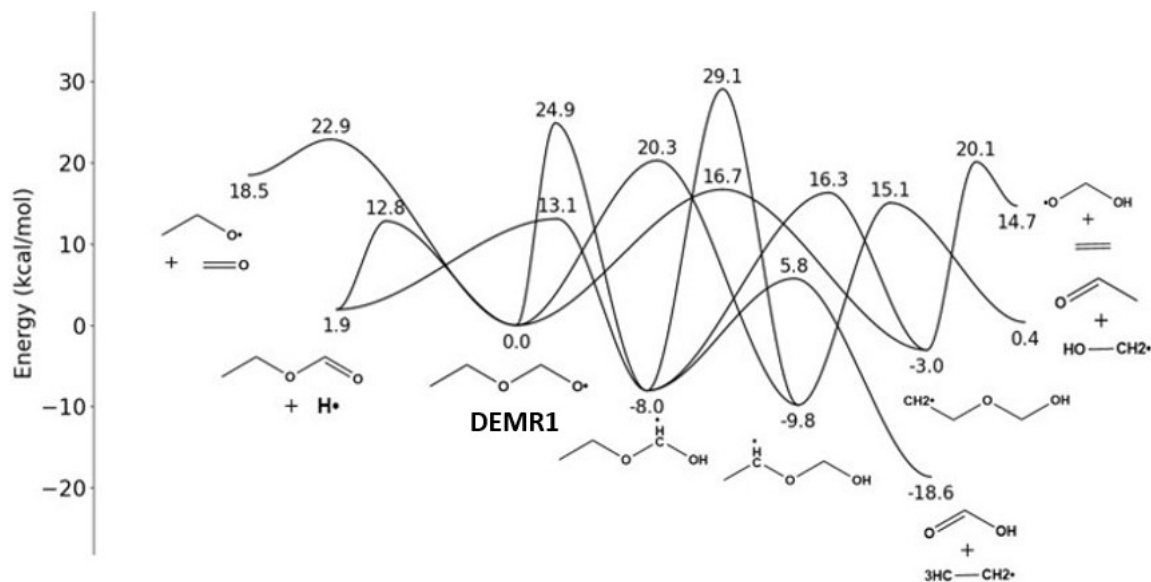


Fig. 6.5 PES of unimolecular decomposition of the oxygen radical and alcohol radical isomers for E-1-E calculated at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory.

As shown in Fig. 6.5, these radicals may isomerize into different carbon radical alcohols. For the case of DEMR1, the predicted difference in energy barrier between the most accessible isomerization and the lowest β -scission reaction is 3.9 kcal/mol. For the longer DPMR1 (in Fig. 6.6), the difference for the equivalent reactions was calculated to be only 0.3 kcal/mol. However, the calculated rates depicted in Fig. 6.7 show that DEMR1 and DPMR1 will undergo a β -scission reaction, eliminating a hydrogen atom and forming ethyl formate and propyl formate, respectively. This β -scission reaction is dominant over a wide range of pressures and temperatures. In the case of DPMR1, the isomerization pathways are slightly more competitive but are still overshadowed by the β -scission reaction which is almost two orders of magnitude faster.

These results are not surprising since previous high-level ab initio and experimental investigations have concluded that the equivalent reaction is also dominant for most pressures and temperatures for the methoxy ($\text{CH}_3\dot{\text{O}}$) and methoxy-methoxy ($\text{CH}_3\text{OCH}_2\dot{\text{O}}$) radicals [155, 156]. In addition, seeing that ethyl formate and propyl formate are also direct products of DEM δ R and DPM δ R, we would expect to see traces of ethyl and propyl formate and their products in reaction isolation studies. The high temperature unimolecular decomposition of ethyl formate was investigated in the past [157, 158] in a combined ab initio and shock-tube study. Their predicted unimolecular rates for ethyl formate, for the pressure and temperature ranges of 1-100 atm and 500-2000 K, showed that ethyl formate decomposes mainly via the following reaction:



The reaction 6.1, which forms formic acid and ethylene, dominates over bond fissions even at high temperatures and pressures because it may be formed via two different molecular channels (four-center and six-center reactions). Little work has been done on the unimolecular pyrolysis of propyl formate. Its decomposition may be similar to that of ethyl formate, in which case it would decompose into formic acid and propylene via three different concerted reactions. However, the rates may not be as dominant and instead compete with C-C bond fission rates since those should be lower than in ethyl formate due to the weakening of the BDE from a more spread-out electron density.

6.3.3 The $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OC}_2\text{H}_5$ and $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OC}_3\text{H}_7$ radicals

The carbon radicals in E-1-E (DEMR2) are formed from a methyl group cleavage. In E-1-E, this reaction accounts for about a quarter of the total unimolecular reaction flux (see Fig. 5.4). The equivalent radical in P-1-P (DPMR2), forms from an ethyl group cleavage and accounts for most of the unimolecular reaction flux of P-1-P (see Fig. 5.6). Figs. 6.8 and 6.9 show the calculated energies for the isomers of DEMR2 and DPMR2 and their products of decomposition.

For both DEMR2 and DPMR2, the isomerization pathways have a lower energy barrier than the β -scission channel. For DEMR2, the difference is only 1.9 kcal/mol, while for DPMR2 the difference increases to 6.4 kcal/mol. The most accessible isomer for both DEMR2 and DPMR2 is the one with the radical at the α carbon (located at energies -1.2 and -1.0 kcal/mol, respectively). Fig. 6.10 shows the predicted rates constants from DEMR2 (left) and DPMR2 (right). The predicted rates are only defined up to 1000 K at atmospheric pressures, however, at high temperatures one might expect the flux towards isomerization reactions to decrease as most of the reactants decompose via fast β -scissions. Based on this assumption, it is likely that the decomposition of DEMR2 at high temperatures will be heavily dominated by the β -scission reaction forming formaldehyde and a smaller carbon radical (which also decomposes into formaldehyde and ethyl radical). Since isomerization reaction to $\text{C}_2\text{H}_5\dot{\text{C}}\text{HOCH}_2\text{OCH}_3$ is more accessible for DPMR2, it is dominant at low temperatures and stays relevant even at 1000 K.

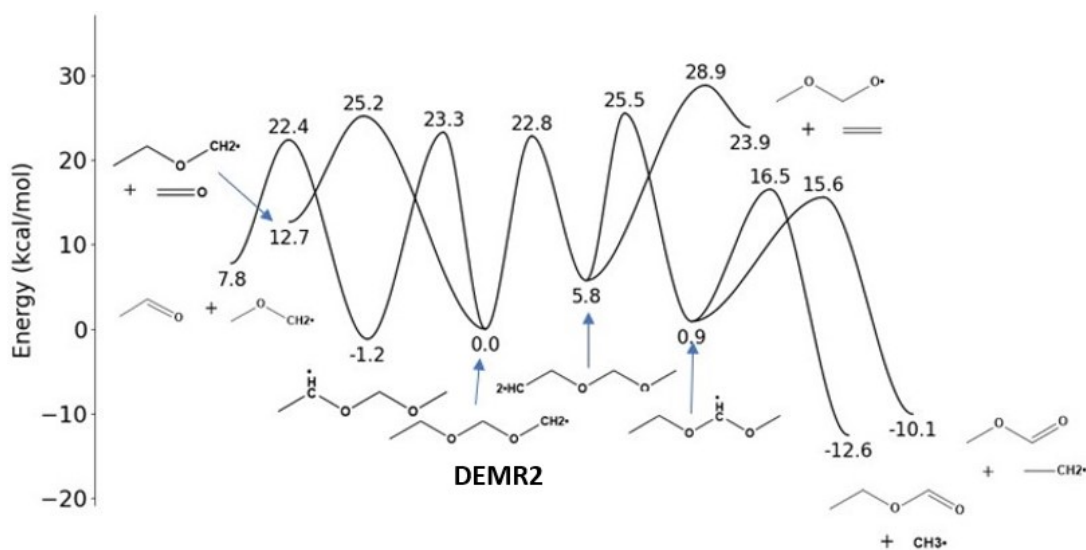


Fig. 6.8 PES of unimolecular decomposition of DEMR2 at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory.

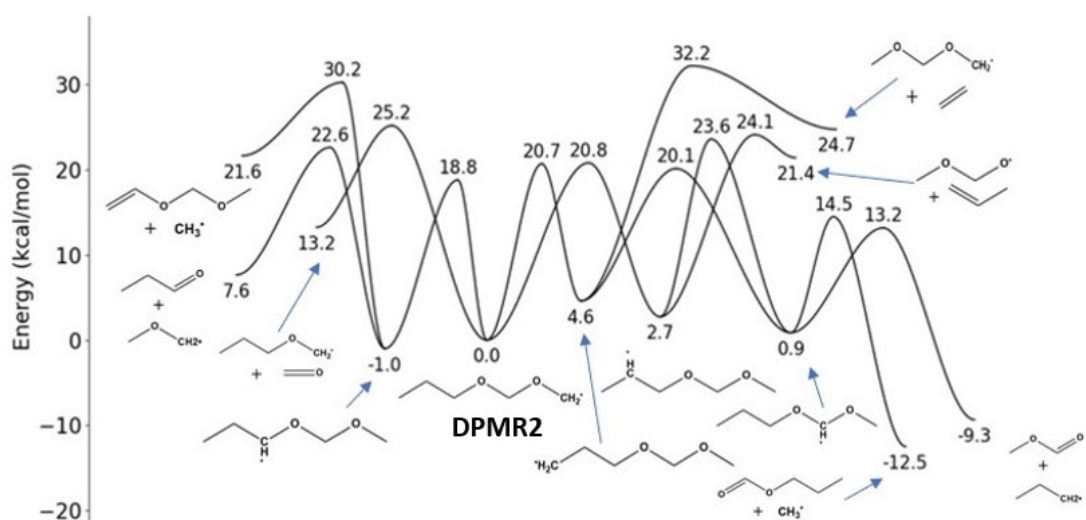


Fig. 6.9 PES of unimolecular decomposition of DPMR2 at the coupled-cluster CCSD(T)/cc-pV ∞ Z/M06-2X/cc-pVTZ level of theory.

Additionally, the chemically activated reaction that skips through $C_2H_5\dot{C}HOCH_2OCH_3$ towards methoxymethyl radical and propanaldehyde is also a competitive pathway at intermediate temperatures and atmospheric pressures but was found to decrease in importance at higher pressures. The results displayed in the bottom plot in Fig. 6.10 suggest that at intermediate temperatures the final products of DPMR2 will include formaldehyde, ethyl radical, methyl radical and propanal. At higher temperatures, the decomposition of DPMR2 will be dominated by its β -scission reaction and is expected to favor formaldehyde production more heavily.

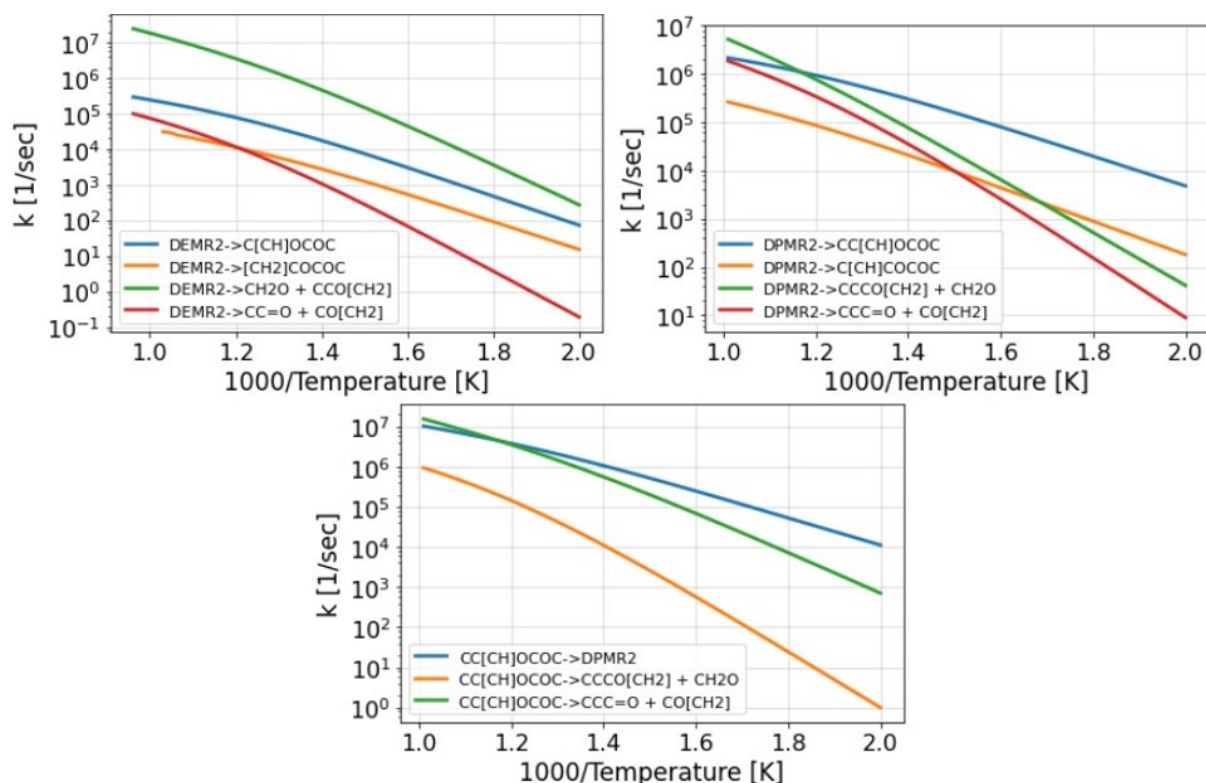


Fig. 6.10 Isomerization-decomposition rate constants (at atmospheric pressure) of DEMR2 (left), DPMR2 (right), and $C_2H_5\dot{C}HOCH_2OCH_3$ (bottom).

6.3.4 Chemically activated reactions

In Ch. 5, it was shown that $CH_3CH_2OCH_2O\dot{C}HCH_3$ ($DEM\alpha R$) and $CH_3CH_2OCH_2OCH_2\dot{C}H_2$ ($DEM\beta R$) have the potential to react with H-atom and undergo a chemically activated (well-skipping) reaction forming bond fission products. The bimolecular rates of these well-skipping reactions were converted to unimolecular rate units using a H-atom concentration of 1% by volume [148], and directly compared with the radical decomposition rates calculated by Kroger et al. [141]. Fig. 6.11 shows a similar comparison but with the radical decomposition rates calculated in this work.

The top plots of Fig. 6.11 show that for both $DEM\alpha R$ and $DEM\beta R$, well-skipping reactions become relevant at around 1000 K for pressures lower than 10 atm. At lower temperatures, most of the rate of reaction goes towards recombination, forming the parent (E-1-E) molecule.

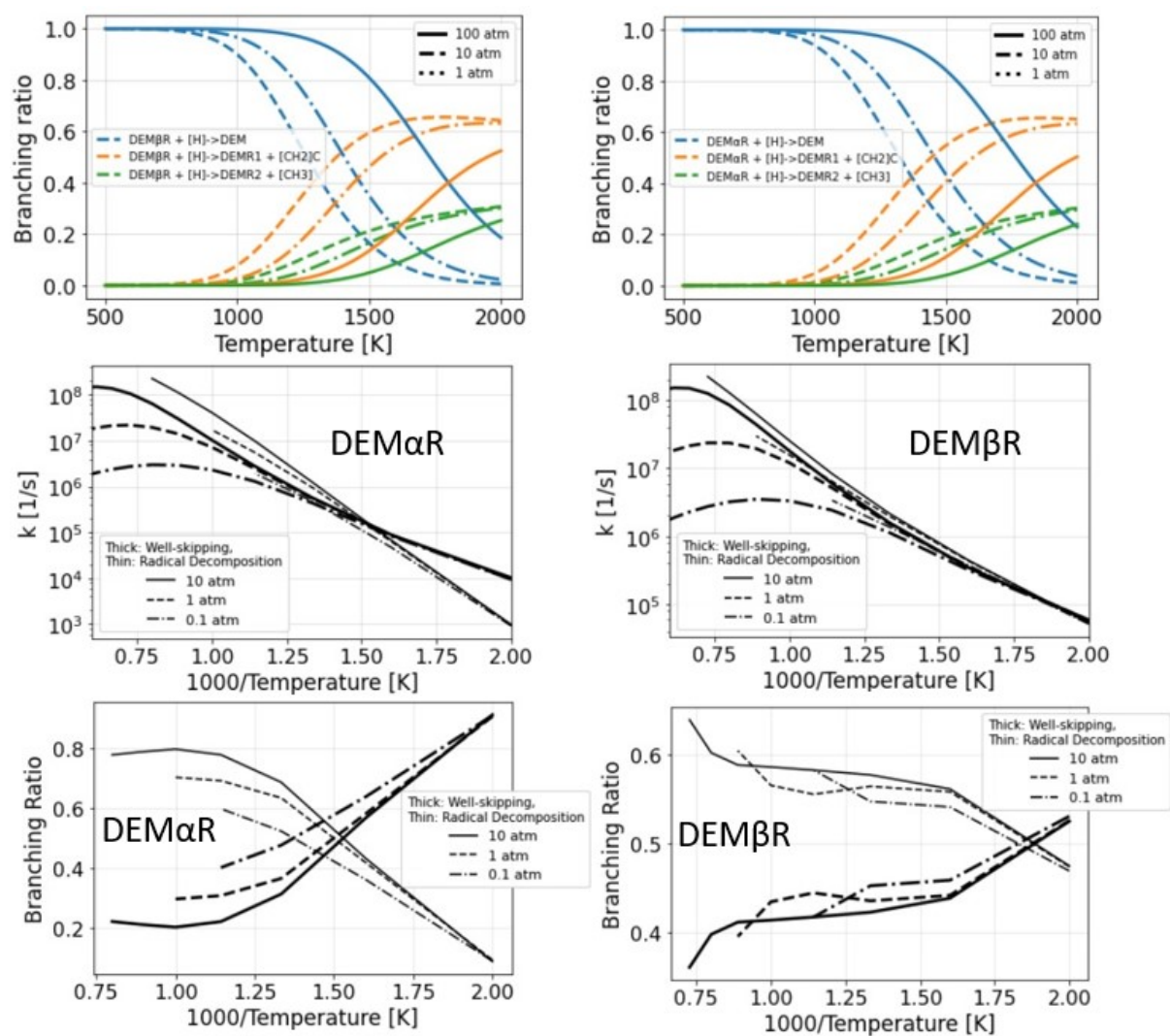


Fig. 6.11 Total well-skipping rates vs. radical decomposition rates for DEM α R (mid left) and DEM β R (mid right) at multiple pressures. The bottom row shows the branching ratio of the rates in the middle row, while the top row shows branching ratio comparing the recombination rate vs. well-skipping rate for the bimolecular reaction of DEM α R (left) and hydrogen atom, and DEM β R (right) and hydrogen atom.

The mid plots of Fig. 6.11 predict that the well-skipping rates slow down significantly at 1000 K, and are even negatively affected at higher temperatures. Nevertheless, they still stand on similar orders of magnitude as the radical decomposition rates for all pressures at intermediate temperatures. These results suggest that the bond fission products (i.e. ethyl, methyl, $\dot{\text{O}}\text{CH}_2\text{OC}_2\text{H}_5$ (DEM β R), and $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OC}_2\text{H}_5$ (DEM α R)) will be produced in higher quantities at intermediate temperatures by accounting for well-skipping reactions in future kinetic mechanisms for E-1-E. Lastly, the branching ratios on the bottom row of Fig. 6.11 shows that for DEM β R, at intermediate temperatures, the proportion of the radical decomposition rates is slightly higher than that of the well-skipping rates, however, this is expected to change rapidly as the well-skipping rates have a sharp turn-over at temperatures above 1000 K. For the case of DEM α R, the proportion of radical decomposition rates increases rapidly at earlier temperatures, and is more pronounced at higher pressures. The collapse at 1000 K for pressures of 0.1 atm in both plots is due to the insufficiency of data for radical decomposition (this was discussed in Subsection 6.3.1).

6.4 Conclusion

We have explored the unimolecular decomposition of the most relevant fuel radicals of E-1-E and P-1-P through quantum mechanical calculations at the CCSD(T)/cc-pV ∞ Z//M06-2X/cc-pVTZ level of theory. The final energetics for each fuel radical, transition state, and products were calculated and presented in various potential energy surfaces to visualize the most accessible channels for each radical. Temperature- and pressure-dependent rate constants have been calculated using transition state theory and master equation. The MESS input files used in this work, which contain geometries, frequencies, internal rotor scans, and modeling parameters, can be found in Appendix E.

The results showed that the E-1-E H-atom abstraction radicals favor the production of ethyl, ethyl formate (from DEM β R and DEM δ R) and acetaldehyde (from W1.1). While the P-1-P H-atom abstraction radicals also produce the equivalent compounds (propyl, propyl formate, propanaldehyde) through similar channels, they are also prone to generate $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OC}_3\text{H}_7$ (DPMR2) whose equivalent radical ($\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OC}_2\text{H}_5$ (DEM α R)) is not formed from the E-1-E H-atom abstraction radicals. Since DPMR2 forms abundant amounts of formaldehyde at high temperatures, it is expected that P-1-P auto-ignition will produce more formaldehyde than E-1-E. Additionally, the results show that the oxygen radicals, $\dot{\text{O}}\text{CH}_2\text{OC}_3\text{H}_7$ (DEM γ R) and $\dot{\text{O}}\text{CH}_2\text{OC}_2\text{H}_5$ (DEM β R), will primarily decompose into aldehydes, which likely further decompose into soot precursors such as ethylene and propylene via concerted reactions. These studies show that most alkenes seen in E-1-E and P-1-P flames likely come from radical decomposition rather than molecular reactions from the parent molecule. Finally, the well-skipping was confirmed to be relevant at intermediate temperatures for E-1-E. We hypothesize that these (well-skipping) reactions will not be as relevant in P-1-P auto-ignition as the P-1-P H-atom abstraction radicals are slightly faster than their E-1-E counterparts.

Chapter 7

Conclusions and Future Work

7.1 Thesis Overview

Modern heavy-duty vehicles continue to rely on liquid fuel engine systems. Clean fuel alternatives or fuel additives that blend into current engine technology are vital to keep heavy-duty engine pollution levels low and meet future emission regulations. Predictive simulations of potential fuels involve the union of multiple disciplines. In particular, chemical kinetic models connect the physical and chemical state of the system to the rates of consumption/formation of chemical species. This is useful to predict product formation from fuel ignition, and to better understand the underlying combustion chemistry. A detailed kinetic model must include transport properties (that capture diffusion and energy transfer), thermodynamic parameters (that capture macroscopic energy states), and a comprehensive kinetic mechanism (that captures the rate of product formation and reactant consumption).

Traditionally, kinetic mechanism rates and thermodynamic parameters were calculated using estimation-based methods such as Benson group additivity. Although these methods provide reasonable results and speed up mechanism development, they are inaccurate and introduce systematic errors into the models. With the advent of high-power computers, quantum mechanical methods have proved to be a better option for calculating rates of reaction as they greatly improved the accuracy of kinetic mechanisms. However, the process of performing high-level rate constant calculations via electronic structure methods takes time, and requires significant human intervention.

The first goal of this thesis is to help alleviate this issue with the development of automation scripts that speed up the computational pipeline required to calculate high-level rate constants by minimizing human intervention. Three main codes were developed and have been partially integrated into a computational pipeline automation code. This code filters reactions, and automatically sets up and runs Gaussian [45] calculations for molecular geometry optimizations, vibrational frequencies, ground-state energies, and potential energy surface scans for internal rotational modes in gas-phase systems. This is achieved with minimal user intervention, saving weeks of work and significantly reducing the potential of user input errors leading to the waste

of computational resources. These codes are built to work with other renowned software in the field (i.e. KinBot [75] and MESS [82]) used to automatically find saddle points and compute temperature- and pressure-dependent macro-canonical rate constants.

The automated computational pipeline was then applied to contribute towards the accurate kinetic mechanism generation of soot reducing biofuels. In specific, these methods were leveraged to study the pyrolysis of diethoxymethane (E-1-E) and dipropoxymethane (P-1-P), and their most relevant radicals produced during initiation. This work unveils the nature of the primary reactions that occur during the onset of combustion, these reactions describe the thermal decomposition of E-1-E and P-1-P through high-level rate constant calculations using quantum mechanical methods and master equation theory.

The results of this application of concept were split into two chapters. First, the findings in Ch. 5 showed that the most important reaction channels for E-1-E pyrolysis were ethyl and methyl cleavage, while for P-1-P pyrolysis these were ethyl and propyl cleavage. In addition to producing alkyl radicals, these reactions also form longer oxygen and carbon radicals (i.e. $C_2H_5OCH_2\dot{O}$, $C_2H_5OCH_2O\dot{C}H_2$, $C_3H_7OCH_2O\dot{C}H_2$, $C_3H_7OCH_2\dot{O}$) whose subsequent decomposition dictates the intermediate and final products in the auto-ignition of E-1-E and P-1-P. Additionally, chemically activated reactions (modeled with 1% by volume concentration of H-atom) starting from the H-atom abstraction radicals were shown to be relevant in the production of fuel radicals in E-1-E.

Similarly in Ch. 6, the automated computational pipeline was applied to explore the subsequent decomposition of $C_2H_5OCH_2\dot{O}$, $C_2H_5OCH_2O\dot{C}H_2$, $C_3H_7OCH_2O\dot{C}H_2$, $C_3H_7OCH_2\dot{O}$ as well as that of the H-atom abstraction radicals from E-1-E and P-1-P. The results showed that E-1-E H-atom abstraction radicals favor the production of ethyl formate and acetaldehyde. While similar products (propyl formate, propanaldehyde) are seen for the P-1-P H-atom abstraction radicals, they also produce formaldehyde, especially at high temperatures. The oxygen radicals show a trend of breaking down into stable aldehydes via β -scission reactions, whereas the carbon radicals are prone to produce formaldehyde at high temperatures and some propanaldehyde at intermediate temperatures. Finally, the production of alkenes is seen only in radical decomposition as its formation via molecular reactions is unlikely at temperatures relevant to pyrolysis.

The efforts described in this work strive to improve and expedite the process of acquiring high level rate constants for gas-phase kinetics applications, while also refining the accuracy of future sub mechanisms describing the rates of reaction involved in the auto-ignition of E-1-E and P-1-P.

7.2 Future work

Recommendations for future improvements regarding the automation methods developed have been described in detail in Ch. 3. However, suggestions regarding further research on E-1-E and P-1-P have not been described in detail. While Ch. 5 and Ch. 6 of this thesis addressed

the high-temperature unimolecular decomposition of E-1-E and P-1-P and some of their most relevant fuel radicals, the decomposition of additional molecules that play a relevant role in the pyrolysis E-1-E and P-1-P is still largely unknown.

One such molecule is propyl formate, which is a direct product of both H-atom abstraction and oxygen ($C_3H_7OCH_2\dot{O}$) radicals in P-1-P. Although, Ning et al. [157] developed a mechanism that models the decomposition of ethyl formate at intermediate temperatures, no such work has been done for the decomposition of propyl formate. The little work that has been done on propyl formate (also known as formic acid propyl ester) involves investigations of its decomposition via bimolecular reactions by measuring the rates of H-atom abstraction by difluoroamino radicals [159]. Additionally, the only study, to date, to measure the thermal decomposition of propyl formate was done in 1943 by Anderson et al. [160]. Their work was focused for the temperature range of 360° - 400°C and using a 280-cc. Pyrex flask reaction vessel submerged in molten tin, they were able to reproduce rate expressions for the total unimolecular decomposition of propyl formate. However, modern techniques may complement this study by calculating reaction rates for the individual unimolecular decomposition channels of propyl formate. The resulting rates and product distribution from such a study will greatly affect the intermediates and final products seen in P-1-P ignition and improve the accuracy of future P-1-P mechanisms.

On another note, much of the relevant combustion chemistry in realistic engine conditions also occurs via abstraction reactions. These reactions occur in a bimolecular surface and typically involve highly unstable reactive radicals and fuel molecules. Calculating high-level rate constants for these bimolecular reaction systems will also improve mechanism accuracy. One of the most promising tools for predicting bimolecular rates is EStokTP, developed by Cavallotti et al. [161]. EStokTP may be coupled with Gaussian [45] and MESS [82] to model abstraction and addition reactions. In its most recent version, EStokTP explores one reaction per submitted job. This involves considerable amounts of manual input, including optimized geometries, frequencies, and 1-D hindered rotor scans. A similar automation method as the MESS input file generation code may be developed to expedite EStokTP calculations and even include them in the computational pipeline automation code.

Finally, other OMEs have been identified as promising diesel additives with the potential to substantially reduce emissions while retaining or improving fuel properties [35]. These include $C_4H_9OCH_2OC_4H_9$ (B-1-B), $C_3H_7OCH_2OCH_2OC_3H_7$ (P-2-P), and $C_2H_5OCH_2OCH_2OC_4H_9$ (E-2-B). Mechanisms for these molecules may be built by analogy to future mechanism for E-1-E or P-1-P. B-1-B has an additional alkyl group over P-1-P, which means its combustion is prone to generate more soot precursors, however, it has a higher energy density and a lower flash point which make it a more favorable additive in terms of integration into current engine systems. On the other hand, P-2-P and E-2-B have a longer oxymethylene backbone which suggests they are prone to produce abundant amounts of formaldehyde at high temperatures. However, further studies on their pyrolysis are necessary to address how these changes in molecular structure affect the overall decomposition.

7.3 Acknowledgements and funding

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Appendix A

Python scripts | KinBot reaction filtration code

A.1 newzmat.sh

```
1 #!/bin/bash
2 #SBATCH --partition=shas
3 #SBATCH --qos=long
4 #SBATCH --nodes=1
5 #SBATCH --ntasks-per-node=1
6 #SBATCH --time=00:10:00
7 #SBATCH --job-name=NZM
8 #SBATCH --account=ucb147_summit3
9
10 module purge
11 module load "gaussian/16_avx2"
12
13 newzmat -ichk -rebuildzmat -step 999 TS_C_CO_E82-99.chk TS_C_CO_E82-99.
    gjf
14
15 echo "Z-Matrix has been generated!"
```

A.2 run_all_gjfs.sh

```
1 #!/bin/bash
2 #SBATCH --partition=shas
3 #SBATCH --qos=normal
4 #SBATCH --nodes=1
5 #SBATCH --ntasks-per-node=11
6 #SBATCH --time=24:00:00
7 #SBATCH --job-name=83.35
8 #SBATCH --account=ucb146_summit3
9
10 module purge
```

```

11 module load "gaussian/16_avx2"
12
13 FILES=*.gjf
14 for f in $FILES
15 do
16   name=$(echo "$f" | cut -f 1 -d '.')
17   g16 <$name.gjf> $name.log
18   echo "Processing $name file..."
19 done
20 echo "Finished all jobs."

```

A.3 get_input_gjf.py

```

1 import os, subprocess
2
3 # .log, .chk and newzmat.sh files must be in the same directory
4 def main(logfile, num_process=0, job='m062x'):
5     # edits newzmat shell script and creates a gjf for each log file
6     with open('newzmat.sh') as newzmatSC:
7         scLines = newzmatSC.readlines()
8         newzmatSC.close()
9     gjfFile = logfile.replace('.log', '.gjf')
10    for i, line in enumerate(scLines):
11        if 'newzmat' in line:
12            currentCHK = [item for item in line.split() if item.
13endswith('.chk')][0]
14            currentGJF = [item for item in line.split() if item.
15endswith('.gjf')][0]
16            scLines[i] = line.replace(currentCHK, logfile.replace('.log
17', '.chk')).replace(currentGJF, gjfFile)
18            newzmatFile = open(f'newzmat.sh', 'w')
19            newzmatFile.writelines(scLines)
20            newzmatFile.close()
21
22            subprocess.run(['sh', 'newzmat.sh'])
23
24            # extracts route section informatino from log file
25            lfile = open(logfile, 'r')
26            lfileString = lfile.read()
27            lfile.close()
28            jobTitle = lfileString.split("#")[1].split('
-----
29') [0]
30            optTitle = jobTitle.split('opt')[-1]
31            if 'ts' in optTitle.lower():
32                ts = True
33            else:
34                ts = False

```

```

31     procsLine = lfileString.split("%")[1].split('
-----
') [0]
32     numProc = int(procsLine.split()[0].split('=')[-1])
33     # adds route section to gjf file
34     outputgjfFile = open(gjfFile, 'r')
35     gjfLines = outputgjfFile.readlines()
36     outputgjfFile.close()
37
38     if job.lower() == 'M062X'.lower():
39         if ts:
40             gjfLines[0] = '\n#opt=(calcall,tight,ts) freq m062x/cc-pvtz
maxdisk=500GB\n'
41         else:
42             gjfLines[0] = '\n#opt=(calcall,tight) freq m062x/cc-pvtz
maxdisk=500GB\n'
43     elif job.lower() == 'E'.lower():
44         gjfLines[0] = '\n# ccSD(t,t1diag)/cc-pvdz maxdisk=500GB int=
ultraFine\n'
45     elif job.lower() == 'E1'.lower():
46         gjfLines[0] = '\n# ccSD(t)/cc-pvtz maxdisk=500GB int=ultraFine\
n'
47
48     gjfLines.insert(0, f'\n%chk={gjfFile[:-4]}.chk')
49     gjfLines.insert(0, '\n%mem=700MW')
50     gjfLines.insert(0, f'%nprocshared={numProc + num_process}')
51     outputgjfFile = open(gjfFile, 'w')
52     outputgjfFile.writelines(gjfLines)
53     outputgjfFile.close()
54     #
55
56     return gjfFile
57
58 if __name__ == '__main__':
59     main(logfile='', num_process=0, job='m062x')

```

A.4 parsingPesviewer.py

```

1 #!/usr/bin/env python
2 # coding: utf-8
3
4 # In[1]:
5
6
7 # beginning of program
8
9 # -- Dependencies -- #
10 import os, shutil

```



```
54         else:
55             if float(energyBarrier) < allTSProds[prods]:
56                 allTSProds[prods] = float(energyBarrier)
57                 del groundEnergies[allTSReacts[prods]]
58                 groundEnergies[reacts] = energyBarrier
59                 allTSReacts[prods] = reacts
60
61         reactsProds[key] = allTSReacts.values()
62     else:
63         for k in entries:
64             groundEnergies[k.split(' ')[0]] = k.split(' ')[1]
65             reactsProds[key] = [j.split(' ')[0] for j in entries]
66
67     # script assumes parent well is at the reference '0.0' energy
68     parentWell = [energy for energy in groundEnergies if groundEnergies
69                   [energy]=='0.0'][0]
70
71     lowestTSEnergy = min([float(groundEnergies[value]) for value in
72                           reactsProds["ts"]])
73     print("Enter TS Energy cut-off: ")
74     cutOff = float(input())
75     minEnergy = lowestTSEnergy + cutOff
76
77     allTSReacts = {v: k for k, v in allTSReacts.items()}
78
79     # filters out products of TS with barriers larger than minimum
80     energy
81     for mol in list(groundEnergies.keys()):
82         if float(groundEnergies[mol]) > minEnergy:
83             del groundEnergies[mol]
84             if mol in allTSReacts:
85                 if allTSReacts[mol] in groundEnergies:
86                     del groundEnergies[allTSReacts[mol]]
87
88     validEnergies = list(groundEnergies.values())
89     validMolecules = list()
90     # -- potential bug, assumes only Bimolecular products have 1 '_' in
91     # their kinbot-generated name -- #
92     for i in range(len(validEnergies)):
93         molecule = list(groundEnergies.keys())[list(groundEnergies.
94               values()).index(validEnergies[i])]
95         if len(molecule.split("_"))==2:
96             validMolecules.append(molecule.split("_")[0])
97             validMolecules.append(molecule.split("_")[1])
98         else:
99             validMolecules.append(molecule)
100
101     # removes duplicates
102     validMolecules = list(dict.fromkeys(validMolecules))
```

```
97
98 # extracts only files of interest from Log_Chk_files directory
99 os.chdir("./Log_Chk_files")
100 validFiles = dict()
101 validFiles[parentWell+'_well.log'] = '0.0'
102
103 for molecule in validMolecules:
104     for file in os.listdir():
105         if molecule in file and file.endswith('.log') and molecule
106 != parentWell and "IRC" not in file:
107             for key in groundEnergies:
108                 if molecule in key:
109                     validFiles[file] = groundEnergies[key]
110
111 validFilesTS = dict()
112 for file in validFiles:
113     fl = open(file, 'r')
114     flLines = fl.readlines()
115     fl.close()
116     isTS = False
117     for line in flLines:
118         if line.startswith(' #') and 'TS,' in line:
119             isTS = True
120             break
121     if isTS:
122         validFilesTS[file] = [True, validFiles[file]]
123     else:
124         validFilesTS[file] = [False, validFiles[file]]
125 os.chdir("../..")
126
127 return validFilesTS
128
129 def create_input_files(validFilesTS):
130     """
131     :arg
132     :returns:
133     """
134
135     validFiles = validFilesTS.keys()
136     xyzFilesTS = dict()
137     xyzGeoms = dict()
138     for logfile in validFiles:
139         # copies newzmat shell script into folder with .chk files
140         base_dir = os.getcwd()
141         shutil.copy(base_dir+"/newzmat.sh", base_dir+"/Log_Chk_files/
142 newzmat.sh")
143         # creates .xyz file and parses in required information
```

```
143     xyzFile = open('xyzFile.xyz', 'w')
144     os.chdir("Log_Chk_files")
145     geom = get_xyzGeom(logfile)
146     vibrations = get_frequencies(logfile) #frequencies, charge and
multiplicity
147     charge = vibrations[-1][0]
148     xyzFile.write(str(len(geom))+f'\ncharge={charge}=\n')
149     for coord in geom:
150         split = coord.split(',')
151         xyzFile.write(split[0]+9*' ' +split[1]+9*' ' +split[2]+9*' ' +
split[3]+' \n')
152     xyzFile.close()
153     # edits newzmat shell script and creates a gjf for each log
file
154     gjfFile = get_input_gjf.main(logfile)
155
156     # moves gjfs back to Transfer directory
157     shutil.move(f"{os.getcwd()}/{gjfFile}", f"{base_dir}/{gjfFile}"
)
158     os.chdir("../..")
159
160     # convert cartseian coords to smile structure using xyz2mol
project. Renames all files to SMILES str.
161     SMILE = subprocess.check_output(f'python xyz2mol.py xyzFile.xyz
', shell=True).decode("utf-8").split('\r')[0].replace('.', '_').
replace("\\", "").replace("/", "").replace('\n', '')
162     # -- potential bug, assumes only TS products have more than 1 '
_' in their kinbot-generated name -- #
163     if SMILE != '':
164         if len(logfile.split("_"))>2:
165             os.remove('xyzFile.xyz')
166             os.rename(gjfFile, f'TS_{SMILE}.gjf')
167             xyzFilesTS[f"TS_{SMILE}.gjf"] = [validFilesTS[logfile
][0], validFilesTS[logfile][1]]
168             # stores logfile xyz geometries for each gjf file (will
send this to get_rotors.py)
169             xyzGeoms[f'TS_{SMILE}.gjf'] = geom
170         else:
171             os.remove('xyzFile.xyz')
172             os.rename(gjfFile, f'{SMILE}.gjf')
173             xyzFilesTS[f"{SMILE}.gjf"] = [validFilesTS[logfile][0],
validFilesTS[logfile][1]]
174             xyzGeoms[f'{SMILE}.gjf'] = geom
175     # xyz2mol seems to only work for closed shell molecules.
Queries user for SMILES for unnamed molecules
176     else:
177         SMILE = input(f"Enter SMILES for {logfile}: ")
178         os.remove('xyzFile.xyz')
```

```
179         os.rename(gjfFile, f'{SMILE}.gjf')
180         xyzFilesTS[f"{SMILE}.gjf"] = [validFilesTS[logfile][0],
validFilesTS[logfile][1]]
181         xyzGeoms[f'{SMILE}.gjf'] = geom
182
183     # adds route section to gjf files and moves them to corresponding
directory
184     procs = dict()
185     for file in os.listdir():
186         if file.endswith(".gjf"):
187             print(file)
188             with open(file, 'r') as f:
189                 zmat = f.readlines()[4:] #reads file starting from its
charge and multiplicity
190                 f.close()
191             # adds route section
192             fileName, fileExtension = os.path.splitext(file)
193
194             energy = xyzFilesTS[file][1].replace(".", "-")
195             if xyzFilesTS[file][0]:
196                 zmat.insert(0, '\n#opt=(calcall,tight,ts) freq m062x/cc
-pvtz maxdisk=500GB int=ultrafine\n')
197             else:
198                 zmat.insert(0, '\n#opt=(calcall,tight) freq m062x/cc-
pvtz maxdisk=500GB int=ultrafine\n')
199                 zmat.insert(0, f'\n%chk={fileName}_E{energy}.chk')
200                 zmat.insert(0, '\n%mem=700MW')
201                 numProc = input(f"How many of processors shared for {
fileName}: ")
202                 procs[file] = numProc
203                 zmat.insert(0, f'%nprocshared={numProc}')
204
205                 zmatFile = open(file, 'w')
206                 zmatFile.writelines(zmat)
207                 zmatFile.close()
208                 if not os.path.isdir(f'{fileName}_E{energy}'):
209                     os.mkdir(f'{fileName}_E{energy}')
210                     os.chdir(f'{fileName}_E{energy}')
211                     os.mkdir('it1')
212                     os.chdir('../')
213                 destination = f'{fileName}_E{energy}/it1/{fileName}_E{
energy}.gjf'
214
215                 source = f'{fileName}.gjf'
216                 shutil.move(source, destination)
217                 #copies required files to each molecule directory
218                 shutil.copy('geometryInfo.py', f'{fileName}_E{energy}/it1/
geometryInfo.py')
```

```
219         shutil.copy('get_geometry.py', f'{fileName}_E{energy}/it1/
get_geometry.py')
220         shutil.copy('get_rotors.py', f'{fileName}_E{energy}/it1/
get_rotors.py')
221         shutil.copy('search_rotors.py', f'{fileName}_E{energy}/it1/
search_rotors.py')
222         shutil.copy('start_rotor_run.py', f'{fileName}_E{energy}/
it1/start_rotor_run.py')
223         shutil.copy('get_input_gjf.py', f'{fileName}_E{energy}/it1/
get_input_gjf.py')
224         shutil.copy('newzmat.sh', f'{fileName}_E{energy}/it1/
newzmat.sh')
225         shutil.copy('searchLowConf.py', f'{fileName}_E{energy}/it1/
searchLowConf.py')
226         shutil.copy('startSearchLowConf.py', f'{fileName}_E{energy}/
it1/startSearchLowConf.py')
227         shutil.copy('run_iter.py', f'{fileName}_E{energy}/it1/
run_iter.py')
228         shutil.copy('startHighEnergyCalcs.py', f'{fileName}_E{energy
}/it1/startHighEnergyCalcs.py')
229
230     return xyzFilesTS, procs, xyzGeoms
231
232 def setupJobs(xyzFilesTS, procs):
233     """
234     :args:
235     :returns:
236     """
237
238     moleculeDirectories = xyzFilesTS.keys()
239     # copies directory_creator.py and run_all_gjfs.sh into each rotor
240     folder
241     base_dir = os.getcwd()
242     jobAllocation = '1'
243     for file in os.listdir():
244         fileName = file
245         if "E" in file:
246             fileName = file.split("_E")[0]
247         if f'{fileName}.gjf' in moleculeDirectories:
248             # updates batch scripts - must be in parent directory!
249             bFile = open('run_all_gjfs.sh', 'r')
250             bArrayFile = open('run_all_gjfs_array.sh', 'r')
251             bLines = bFile.readlines()
252             bArrayLines = bArrayFile.readlines()
253             bFile.close()
254             bArrayFile.close()
255             allocations = {'1': 'ucb140_summit4', '2': 'ucb140_summit5',
, '3': 'ucb146_summit3', '4': 'ucb147_summit3'}
```

```

255     jobQOS = 'normal'
256     print(f"For {file}: \n")
257     jobNodes = str(int(procs[f'"{fileName}.gjf'])+1)
258     jobTime = input("Enter time= ")
259     jobName = xyzFilesTS[f'"{fileName}.gjf'] [1]
260     if int(jobTime)>24:
261         jobQOS = 'long'
262         bLines [2] = bLines [2].split('=')[0]+'='+jobQOS+'\n'
263         bArrayLines [2] = bArrayLines [2].split('=')[0]+'='+jobQOS+'\n'
264
265         bLines [4] = bLines [4].split('=')[0]+'='+jobNodes+'\n'
266         bArrayLines [4] = bArrayLines [4].split('=')[0]+'='+str(int(
267             jobNodes)-3)+'\n' # used 3 nodes less for rotor jobs
268         bLines [5] = bLines [5].split('=')[0]+'='+jobTime+':00:00\n'
269         bArrayLines [5] = bArrayLines [5].split('=')[0]+'='+jobTime+':00:00\n'
270         bLines [6] = bLines [6].split('=')[0]+'='+jobName+'\n'
271         bArrayLines [6] = bArrayLines [6].split('=')[0]+'='+jobName+'
272         _rotors'+'\n'
273         bLines [7] = bLines [7].split('=')[0]+'='+allocations [
274             jobAllocation]+''\n'
275         bArrayLines [7] = bArrayLines [7].split('=')[0]+'='+
276         allocations [jobAllocation]+''\n'
277         # recycles through allocations
278         if jobAllocation=='4':
279             jobAllocation = '1'
280         else:
281             jobAllocation = str(int(jobAllocation)+1)
282         updatedBFile = open('run_all_gjfs.sh', 'w')
283         updatedBArrayFile = open('run_all_gjfs_array.sh', 'w')
284         updatedBFile.writelines(bLines)
285         updatedBArrayFile.writelines(bArrayLines)
286         updatedBFile.close()
287         updatedBArrayFile.close()
288
289         source = base_dir+'/run_all_gjfs.sh'
290         source_array = base_dir+'/run_all_gjfs_array.sh'
291         # print(os.listdir())
292         destination = f"{base_dir}/{file}/it1/run_all_gjfs.sh"
293         destination_array = f"{base_dir}/{file}/it1/
294         run_all_gjfs_array.sh"
295         shutil.copy(source, destination)
296         shutil.copy(source_array, destination_array)
297         print('\n -----')
298
299 # Function Calling

```

```
296 validFilesTS = get_valid_logFiles()
297 xyzFileTS, procs, xyzGeoms = create_input_files(validFilesTS)
298 setupJobs(xyzFileTS, procs)
299 # runs search rotors within each molecule folder
300 base_dir = os.getcwd()
301 for fileName in os.listdir():
302     if '_E' in fileName:
303         os.chdir(f'{base_dir}/{fileName}/it1')
304         search_rotors.main(xyzGeoms)
305         os.chdir(base_dir)
306
307 # end of program
```

A.5 xyz2mol.py

```
1 """
2 Module for generating rdkit molobj/smiles/molecular graph from free
3 atoms
4
5 Implementation by Jan H. Jensen, based on the paper
6
7 Yeonjoon Kim and Woo Youn Kim
8 "Universal Structure Conversion Method for Organic Molecules: From
9 Atomic Connectivity
10 to Three-Dimensional Geometry"
11 Bull. Korean Chem. Soc. 2015, Vol. 36, 1769-1777
12 DOI: 10.1002/bkcs.10334
13
14 """
15
16 import copy
17 import itertools
18
19 from rdkit.Chem import rdmolops
20 from rdkit.Chem import rdchem
21 try:
22     from rdkit.Chem import rdEHTTools #requires RDKit 2019.9.1 or later
23 except ImportError:
24     rdEHTTools = None
25
26 from collections import defaultdict
27
28 import numpy as np
29 import networkx as nx
30
31 from rdkit import Chem
32 from rdkit.Chem import AllChem, rdmolops
33 import sys
```

```
32
33 global __ATOM_LIST__
34 __ATOM_LIST__ = \
35     ['h', 'he',
36      'li', 'be', 'b', 'c', 'n', 'o', 'f', 'ne',
37      'na', 'mg', 'al', 'si', 'p', 's', 'cl', 'ar',
38      'k', 'ca', 'sc', 'ti', 'v', 'cr', 'mn', 'fe', 'co', 'ni', 'cu',
39      'zn', 'ga', 'ge', 'as', 'se', 'br', 'kr',
40      'rb', 'sr', 'y', 'zr', 'nb', 'mo', 'tc', 'ru', 'rh', 'pd', 'ag',
41      'cd', 'in', 'sn', 'sb', 'te', 'i', 'xe',
42      'cs', 'ba', 'la', 'ce', 'pr', 'nd', 'pm', 'sm', 'eu', 'gd', 'tb',
43      'dy',
44      'ho', 'er', 'tm', 'yb', 'lu', 'hf', 'ta', 'w', 're', 'os', 'ir',
45      'pt',
46      'au', 'hg', 'tl', 'pb', 'bi', 'po', 'at', 'rn',
47      'fr', 'ra', 'ac', 'th', 'pa', 'u', 'np', 'pu']
48
49 global atomic_valence
50 global atomic_valence_electrons
51
52 atomic_valence = defaultdict(list)
53 atomic_valence[1] = [1]
54 atomic_valence[5] = [3,4]
55 atomic_valence[6] = [4]
56 atomic_valence[7] = [3,4]
57 atomic_valence[8] = [2,1,3]
58 atomic_valence[9] = [1]
59 atomic_valence[14] = [4]
60 atomic_valence[15] = [5,3] #[5,4,3]
61 atomic_valence[16] = [6,3,2] #[6,4,2]
62 atomic_valence[17] = [1]
63 atomic_valence[32] = [4]
64 atomic_valence[35] = [1]
65 atomic_valence[53] = [1]
66
67 atomic_valence_electrons = {}
68 atomic_valence_electrons[1] = 1
69 atomic_valence_electrons[5] = 3
70 atomic_valence_electrons[6] = 4
71 atomic_valence_electrons[7] = 5
72 atomic_valence_electrons[8] = 6
73 atomic_valence_electrons[9] = 7
74 atomic_valence_electrons[14] = 4
75 atomic_valence_electrons[15] = 5
76 atomic_valence_electrons[16] = 6
77 atomic_valence_electrons[17] = 7
78 atomic_valence_electrons[32] = 4
```



```
78 atomic_valence_electrons[35] = 7
79 atomic_valence_electrons[53] = 7
80
81
82 def str_atom(atom):
83     """
84     convert integer atom to string atom
85     """
86     global __ATOM_LIST__
87     atom = __ATOM_LIST__[atom - 1]
88     return atom
89
90
91 def int_atom(atom):
92     """
93     convert str atom to integer atom
94     """
95     global __ATOM_LIST__
96     #print(atom)
97     atom = atom.lower()
98     return __ATOM_LIST__.index(atom) + 1
99
100
101 def get-UA(maxValence_list, valence_list):
102     """
103     """
104     UA = []
105     DU = []
106     for i, (maxValence, valence) in enumerate(zip(maxValence_list,
107 valence_list)):
108         if not maxValence - valence > 0:
109             continue
110         UA.append(i)
111         DU.append(maxValence - valence)
112     return UA, DU
113
114 def get_BO(AC, UA, DU, valences, UA_pairs, use_graph=True):
115     """
116     """
117     BO = AC.copy()
118     DU_save = []
119
120     while DU_save != DU:
121         for i, j in UA_pairs:
122             BO[i, j] += 1
123             BO[j, i] += 1
124
```

```
125     BO_valence = list(BO.sum(axis=1))
126     DU_save = copy.copy(DU)
127     UA, DU = get_UA(valences, BO_valence)
128     UA_pairs = get_UA_pairs(UA, AC, use_graph=use_graph)[0]
129
130     return BO
131
132
133 def valences_not_too_large(BO, valences):
134     """
135     """
136     number_of_bonds_list = BO.sum(axis=1)
137     for valence, number_of_bonds in zip(valences, number_of_bonds_list)
138     :
139         if number_of_bonds > valence:
140             return False
141
142     return True
143
144 def charge_is_OK(BO, AC, charge, DU, atomic_valence_electrons, atoms,
145 valences,
146 allow_charged_fragments=True):
147     # total charge
148     Q = 0
149
150     # charge fragment list
151     q_list = []
152
153     if allow_charged_fragments:
154         BO_valences = list(BO.sum(axis=1))
155         for i, atom in enumerate(atoms):
156             q = get_atomic_charge(atom, atomic_valence_electrons[atom],
157 BO_valences[i])
158             Q += q
159             if atom == 6:
160                 number_of_single_bonds_to_C = list(BO[i, :]).count(1)
161                 if number_of_single_bonds_to_C == 2 and BO_valences[i]
162 == 2:
163                     Q += 1
164                     q = 2
165                 if number_of_single_bonds_to_C == 3 and Q + 1 < charge:
166                     Q += 2
167                     q = 1
168
169             if q != 0:
170                 q_list.append(q)
```

```
169     return (charge == Q)
170
171 def BO_is_OK(BO, AC, charge, DU, atomic_valence_electrons, atoms,
172             valences,
173             allow_charged_fragments=True):
174     """
175     Sanity of bond-orders
176
177     args:
178         BO -
179         AC -
180         charge -
181         DU -
182
183     optional
184         allow_charges_fragments -
185
186
187     returns:
188         boolean - true of molecule is OK, false if not
189     """
190
191     if not valences_not_too_large(BO, valences):
192         return False
193
194     check_sum = (BO - AC).sum() == sum(DU)
195     check_charge = charge_is_OK(BO, AC, charge, DU,
196                                atomic_valence_electrons, atoms, valences,
197                                allow_charged_fragments)
198
199     if check_charge and check_sum:
200         return True
201
202     return False
203
204 def get_atomic_charge(atom, atomic_valence_electrons, BO_valence):
205     """
206     """
207
208     if atom == 1:
209         charge = 1 - BO_valence
210     elif atom == 5:
211         charge = 3 - BO_valence
212     elif atom == 15 and BO_valence == 5:
213         charge = 0
214     elif atom == 16 and BO_valence == 6:
```

```

215     charge = 0
216 else:
217     charge = atomic_valence_electrons - 8 + BO_valence
218
219     return charge
220
221
222 def clean_charges(mol):
223     """
224     This hack should not be needed anymore, but is kept just in case
225
226     """
227
228     Chem.SanitizeMol(mol)
229     #rxn_smarts = ['[N+:1]=[*:2]-[C-:3]>>[N+0:1]-[*:2]=[C-0:3]',
230     #             '[N+:1]=[*:2]-[O-:3]>>[N+0:1]-[*:2]=[O-0:3]',
231     #             '[N+:1]=[*:2]-[*:3]=[*:4]-[O-:5]>>[N
+0:1]-[*:2]=[*:3]-[*:4]=[O-0:5]',
232     #             '[#8:1]=[#6:2](!-:6))
[*:3]=[*:4][#6-:5]>>[*-:1][*:2](*:6)=[*:3][*:4]=[*+0:5]',
233     #             '[0:1]=[c:2][c-:3]>>[*-:1][*:2][*+0:3]',
234     #             '[0:1]=[C:2][C-:3]>>[*-:1][*:2]=[*+0:3]']
235
236     rxn_smarts = ['[#6,#7:1]1=[#6,#7:2][#6,#7:3]=[#6,#7:4][CX3-,NX3
-:5][#6,#7:6]1=[#6,#7:7]>>',
237     #             '[#6,#7:1]1=[#6,#7:2][#6,#7:3]=[#6,#7:4][-0,-0:5]=[#6,#7:6]1[#6-,#7-:7]
',
238     #             '[#6,#7:1]1=[#6,#7:2][#6,#7:3](=[#6,#7:4])
[#6,#7:5]=[#6,#7:6][CX3-,NX3-:7]1>>',
239     #             '[#6,#7:1]1=[#6,#7:2][#6,#7:3]([#6-,#7-:4])
=[#6,#7:5][#6,#7:6]=[-0,-0:7]1']
240
241     fragments = Chem.GetMolFragments(mol, asMols=True, sanitizeFragments=False)
242
243     for i, fragment in enumerate(fragments):
244         for smarts in rxn_smarts:
245             patt = Chem.MolFromSmarts(smarts.split(">>")[0])
246             while fragment.HasSubstructMatch(patt):
247                 rxn = AllChem.ReactionFromSmarts(smarts)
248                 ps = rxn.RunReactants((fragment,))
249                 fragment = ps[0][0]
250                 Chem.SanitizeMol(fragment)
251             if i == 0:
252                 mol = fragment
253             else:
254                 mol = Chem.CombineMols(mol, fragment)
255

```

```
256     return mol
257
258
259 def B02mol(mol, BO_matrix, atoms, atomic_valence_electrons,
260           mol_charge, allow_charged_fragments=True):
261     """
262     based on code written by Paolo Toscani
263
264     From bond order, atoms, valence structure and total charge,
265     generate an
266     rdkit molecule.
267
268     args:
269         mol - rdkit molecule
270         BO_matrix - bond order matrix of molecule
271         atoms - list of integer atomic symbols
272         atomic_valence_electrons -
273         mol_charge - total charge of molecule
274
275     optional:
276         allow_charged_fragments - bool - allow charged fragments
277
278     returns
279         mol - updated rdkit molecule with bond connectivity
280
281     """
282     l = len(BO_matrix)
283     l2 = len(atoms)
284     BO_valences = list(BO_matrix.sum(axis=1))
285
286     if (l != l2):
287         raise RuntimeError('sizes of adjMat ({0:d}) and Atoms {1:d}
288         differ'.format(l, l2))
289
290     rwMol = Chem.RWMol(mol)
291
292     bondTypeDict = {
293         1: Chem.BondType.SINGLE,
294         2: Chem.BondType.DOUBLE,
295         3: Chem.BondType.TRIPLE
296     }
297
298     for i in range(l):
299         for j in range(i + 1, l):
300             bo = int(round(BO_matrix[i, j]))
301             if (bo == 0):
302                 continue
```

```
302         bt = bondTypeDict.get(bo, Chem.BondType.SINGLE)
303         rwMol.AddBond(i, j, bt)
304
305     mol = rwMol.GetMol()
306
307     if allow_charged_fragments:
308         mol = set_atomic_charges(
309             mol,
310             atoms,
311             atomic_valence_electrons,
312             BO_valences,
313             BO_matrix,
314             mol_charge)
315     else:
316         mol = set_atomic_radicals(mol, atoms, atomic_valence_electrons,
317                                   BO_valences)
318
319     return mol
320
321 def set_atomic_charges(mol, atoms, atomic_valence_electrons,
322                       BO_valences, BO_matrix, mol_charge):
323     """
324     """
325     q = 0
326     for i, atom in enumerate(atoms):
327         a = mol.GetAtomWithIdx(i)
328         charge = get_atomic_charge(atom, atomic_valence_electrons[atom
329 ], BO_valences[i])
330         q += charge
331         if atom == 6:
332             number_of_single_bonds_to_C = list(BO_matrix[i, :]).count
333             (1)
334             if number_of_single_bonds_to_C == 2 and BO_valences[i] ==
335             2:
336                 q += 1
337                 charge = 0
338                 if number_of_single_bonds_to_C == 3 and q + 1 < mol_charge:
339                     q += 2
340                     charge = 1
341
342             if (abs(charge) > 0):
343                 a.SetFormalCharge(int(charge))
344
345     #mol = clean_charges(mol)
346
347     return mol
```

```
346
347 def set_atomic_radicals(mol, atoms, atomic_valence_electrons,
348 BO_valences):
349     """
350     The number of radical electrons = absolute atomic charge
351     """
352     for i, atom in enumerate(atoms):
353         a = mol.GetAtomWithIdx(i)
354         charge = get_atomic_charge(
355             atom,
356             atomic_valence_electrons[atom],
357             BO_valences[i])
358
359         if (abs(charge) > 0):
360             a.SetNumRadicalElectrons(abs(int(charge)))
361
362     return mol
363
364
365
366 def get_bonds(UA, AC):
367     """
368     """
369     bonds = []
370
371     for k, i in enumerate(UA):
372         for j in UA[k + 1:]:
373             if AC[i, j] == 1:
374                 bonds.append(tuple(sorted([i, j])))
375
376     return bonds
377
378
379
380 def get_UA_pairs(UA, AC, use_graph=True):
381     """
382     """
383
384     bonds = get_bonds(UA, AC)
385
386     if len(bonds) == 0:
387         return [()]
388
389     if use_graph:
390         G = nx.Graph()
391         G.add_edges_from(bonds)
392
```

```
393     UA_pairs = [list(nx.max_weight_matching(G))]
394     return UA_pairs
395
396     max_atoms_in_combo = 0
397     UA_pairs = [()]
398     for combo in list(itertools.combinations(bonds, int(len(UA) / 2))):
399         flat_list = [item for sublist in combo for item in sublist]
400         atoms_in_combo = len(set(flat_list))
401         if atoms_in_combo > max_atoms_in_combo:
402             max_atoms_in_combo = atoms_in_combo
403             UA_pairs = [combo]
404
405         elif atoms_in_combo == max_atoms_in_combo:
406             UA_pairs.append(combo)
407
408     return UA_pairs
409
410
411 def AC2BO(AC, atoms, charge, allow_charged_fragments=True, use_graph=
True):
412     """
413
414     implemenation of algorithm shown in Figure 2
415
416     UA: unsaturated atoms
417
418     DU: degree of unsaturation (u matrix in Figure)
419
420     best_BO: Bcurr in Figure
421
422     """
423
424     global atomic_valence
425     global atomic_valence_electrons
426
427     # make a list of valences, e.g. for CO: [[4],[2,1]]
428     valences_list_of_lists = []
429     AC_valence = list(AC.sum(axis=1))
430
431     for i,(atomicNum, valence) in enumerate(zip(atoms, AC_valence)):
432         # valence can't be smaller than number of neighbours
433         possible_valence = [x for x in atomic_valence[atomicNum] if x
>= valence]
434         if not possible_valence:
435             print('Valence of atom',i,'is',valence,'which bigger than
allowed max',max(atomic_valence[atomicNum]),'. Stopping')
436             sys.exit()
437         valences_list_of_lists.append(possible_valence)
```



```
438
439 # convert [[4],[2,1]] to [[4,2],[4,1]]
440 valences_list = itertools.product(*valences_list_of_lists)
441
442 best_BO = AC.copy()
443
444 for valences in valences_list:
445
446     UA, DU_from_AC = get-UA(valences, AC_valence)
447
448     check_len = (len(UA) == 0)
449     if check_len:
450         check_bo = BO_is_OK(AC, AC, charge, DU_from_AC,
451                             atomic_valence_electrons, atoms, valences,
452                             allow_charged_fragments=allow_charged_fragments)
453     else:
454         check_bo = None
455
456     if check_len and check_bo:
457         return AC, atomic_valence_electrons
458
459     UA_pairs_list = get-UA_pairs(UA, AC, use_graph=use_graph)
460     for UA_pairs in UA_pairs_list:
461         BO = get_BO(AC, UA, DU_from_AC, valences, UA_pairs,
462                    use_graph=use_graph)
463         status = BO_is_OK(BO, AC, charge, DU_from_AC,
464                           atomic_valence_electrons, atoms, valences,
465                           allow_charged_fragments=allow_charged_fragments
466                          )
467
468         charge_OK = charge_is_OK(BO, AC, charge, DU_from_AC,
469                                  atomic_valence_electrons, atoms, valences,
470                                  allow_charged_fragments=
471                                  allow_charged_fragments)
472
473         if status:
474             return BO, atomic_valence_electrons
475         elif BO.sum() >= best_BO.sum() and valences_not_too_large(
476             BO, valences) and charge_OK:
477             best_BO = BO.copy()
478
479     return best_BO, atomic_valence_electrons
480
481 def AC2mol(mol, AC, atoms, charge, allow_charged_fragments=True,
482           use_graph=True):
483     """
484     """
```

```
480 # convert AC matrix to bond order (BO) matrix
481 BO, atomic_valence_electrons = AC2BO(
482     AC,
483     atoms,
484     charge,
485     allow_charged_fragments=allow_charged_fragments,
486     use_graph=use_graph)
487
488 # add BO connectivity and charge info to mol object
489 mol = B02mol(
490     mol,
491     BO,
492     atoms,
493     atomic_valence_electrons,
494     charge,
495     allow_charged_fragments=allow_charged_fragments)
496
497 # If charge is not correct don't return mol
498 if Chem.GetFormalCharge(mol) != charge:
499     return []
500
501 # B02mol returns an arbitrary resonance form. Let's make the rest
502 mols = rdchem.ResonanceMolSupplier(mol, Chem.UNCONSTRAINED_CATIONS,
503     Chem.UNCONSTRAINED_ANIONS)
504 mols = [mol for mol in mols]
505
506 return mols
507
508 def get_proto_mol(atoms):
509     """
510     """
511     mol = Chem.MolFromSmarts("[#" + str(atoms[0]) + "]")
512     rwMol = Chem.RWMol(mol)
513     for i in range(1, len(atoms)):
514         a = Chem.Atom(atoms[i])
515         rwMol.AddAtom(a)
516
517     mol = rwMol.GetMol()
518
519     return mol
520
521
522 def read_xyz_file(filename, look_for_charge=True):
523     """
524     """
525
526     atomic_symbols = []
```

```
527 xyz_coordinates = []
528 charge = 0
529 title = ""
530
531 with open(filename, "r") as file:
532     for line_number, line in enumerate(file):
533         if line_number == 0:
534             num_atoms = int(line)
535         elif line_number == 1:
536             title = line
537             if "charge=" in line:
538                 charge = int(line.split("=")[1])
539         else:
540             atomic_symbol, x, y, z = line.split()
541             atomic_symbols.append(atomic_symbol)
542             xyz_coordinates.append([float(x), float(y), float(z)])
543
544 atoms = [int_atom(atom) for atom in atomic_symbols]
545
546 return atoms, charge, xyz_coordinates
547
548
549 def xyz2AC(atoms, xyz, charge, use_huckel=False):
550     """
551
552     atoms and coordinates to atom connectivity (AC)
553
554     args:
555         atoms - int atom types
556         xyz - coordinates
557         charge - molecule charge
558
559     optional:
560         use_huckel - Use Huckel method for atom connectivity
561
562     returns
563         ac - atom connectivity matrix
564         mol - rdkit molecule
565
566     """
567
568     if use_huckel:
569         return xyz2AC_huckel(atoms, xyz, charge)
570     else:
571         return xyz2AC_vdW(atoms, xyz)
572
573
574 def xyz2AC_vdW(atoms, xyz):
```

```
575
576     # Get mol template
577     mol = get_proto_mol(atoms)
578
579     # Set coordinates
580     conf = Chem.Conformer(mol.GetNumAtoms())
581     for i in range(mol.GetNumAtoms()):
582         conf.SetAtomPosition(i, (xyz[i][0], xyz[i][1], xyz[i][2]))
583     mol.AddConformer(conf)
584
585     AC = get_AC(mol)
586
587     return AC, mol
588
589
590 def get_AC(mol, covalent_factor=1.3):
591     """
592
593     Generate adjacent matrix from atoms and coordinates.
594
595     AC is a (num_atoms, num_atoms) matrix with 1 being covalent bond
596     and 0 is not
597
598     covalent_factor - 1.3 is an arbitrary factor
599
600     args:
601         mol - rdkit molobj with 3D conformer
602
603     optional
604         covalent_factor - increase covalent bond length threshold with
605         facto
606
607     returns:
608         AC - adjacent matrix
609     """
610
611     # Calculate distance matrix
612     dMat = Chem.Get3DDistanceMatrix(mol)
613
614     pt = Chem.GetPeriodicTable()
615     num_atoms = mol.GetNumAtoms()
616     AC = np.zeros((num_atoms, num_atoms), dtype=int)
617
618     for i in range(num_atoms):
619         a_i = mol.GetAtomWithIdx(i)
620         Rcov_i = pt.GetRcovalent(a_i.GetAtomicNum()) * covalent_factor
```

```
621     for j in range(i + 1, num_atoms):
622         a_j = mol.GetAtomWithIdx(j)
623         Rcov_j = pt.GetRcovalent(a_j.GetAtomicNum()) *
covalent_factor
624         if dMat[i, j] <= Rcov_i + Rcov_j:
625             AC[i, j] = 1
626             AC[j, i] = 1
627
628     return AC
629
630
631 def xyz2AC_huckel(atomicNumList, xyz, charge):
632     """
633
634     args
635         atomicNumList - atom type list
636         xyz - coordinates
637         charge - molecule charge
638
639     returns
640         ac - atom connectivity
641         mol - rdkit molecule
642
643     """
644     mol = get_proto_mol(atomicNumList)
645
646     conf = Chem.Conformer(mol.GetNumAtoms())
647     for i in range(mol.GetNumAtoms()):
648         conf.SetAtomPosition(i, (xyz[i][0], xyz[i][1], xyz[i][2]))
649     mol.AddConformer(conf)
650
651     num_atoms = len(atomicNumList)
652     AC = np.zeros((num_atoms, num_atoms)).astype(int)
653
654     mol_huckel = Chem.Mol(mol)
655     mol_huckel.GetAtomWithIdx(0).SetFormalCharge(charge) #mol charge
arbitrarily added to 1st atom
656
657     passed, result = rdEHTTools.RunMol(mol_huckel)
658     opop = result.GetReducedOverlapPopulationMatrix()
659     tri = np.zeros((num_atoms, num_atoms))
660     tri[np.tril(np.ones((num_atoms, num_atoms), dtype=bool))] = opop #
lower triangular to square matrix
661     for i in range(num_atoms):
662         for j in range(i+1, num_atoms):
663             pair_pop = abs(tri[j, i])
664             if pair_pop >= 0.15: #arbitrary cutoff for bond. May need
adjustment
```

```
665         AC[i,j] = 1
666         AC[j,i] = 1
667
668     return AC, mol
669
670
671 def chiral_stereo_check(mol):
672     """
673     Find and embed chiral information into the model based on the
674     coordinates
675
676     args:
677         mol - rdkit molecule, with embeded conformer
678
679     """
680     Chem.SanitizeMol(mol)
681     Chem.DetectBondStereochemistry(mol, -1)
682     Chem.AssignStereochemistry(mol, flagPossibleStereoCenters=True,
683     force=True)
684     Chem.AssignAtomChiralTagsFromStructure(mol, -1)
685
686     return
687
688 def xyz2mol(atoms, coordinates,
689            charge=0,
690            allow_charged_fragments=True,
691            use_graph=True,
692            use_huckel=False,
693            embed_chiral=True):
694     """
695     Generate a rdkit molobj from atoms, coordinates and a total_charge.
696
697     args:
698         atoms - list of atom types (int)
699         coordinates - 3xN Cartesian coordinates
700         charge - total charge of the system (default: 0)
701
702     optional:
703         allow_charged_fragments - alternatively radicals are made
704         use_graph - use graph (networkx)
705         use_huckel - Use Huckel method for atom connectivity prediction
706         embed_chiral - embed chiral information to the molecule
707
708     returns:
709         mols - list of rdkit molobjects
710
711     """
```

```
711
712     # Get atom connectivity (AC) matrix, list of atomic numbers,
molecular charge,
713     # and mol object with no connectivity information
714     AC, mol = xyz2AC(atoms, coordinates, charge, use_huckel=use_huckel)
715
716     # Convert AC to bond order matrix and add connectivity and charge
info to
717     # mol object
718     new_mols = AC2mol(mol, AC, atoms, charge,
719         allow_charged_fragments=allow_charged_fragments,
720         use_graph=use_graph)
721
722     # Check for stereocenters and chiral centers
723     if embed_chiral:
724         for new_mol in new_mols:
725             chiral_stereo_check(new_mol)
726
727     return new_mols
728
729
730 def main():
731
732
733     return
734
735
736 if __name__ == "__main__":
737
738     import argparse
739
740     parser = argparse.ArgumentParser(usage='%(prog)s [options] molecule
.xyz')
741     parser.add_argument('structure', metavar='structure', type=str)
742     parser.add_argument('-s', '--sdf',
743         action="store_true",
744         help="Dump sdf file")
745     parser.add_argument('--ignore-chiral',
746         action="store_true",
747         help="Ignore chiral centers")
748     parser.add_argument('--no-charged-fragments',
749         action="store_true",
750         help="Allow radicals to be made")
751     parser.add_argument('--no-graph',
752         action="store_true",
753         help="Run xyz2mol without networkx dependencies")
754
```

```
755 # huckel uses extended Huckel bond orders to locate bonds (requires
RDKit 2019.9.1 or later)
756 # otherwise van der Waals radii are used
757 parser.add_argument('--use-huckel',
758     action="store_true",
759     help="Use Huckel method for atom connectivity")
760 parser.add_argument('-o', '--output-format',
761     action="store",
762     type=str,
763     help="Output format [smiles,sdf] (default=sdf)")
764 parser.add_argument('-c', '--charge',
765     action="store",
766     metavar="int",
767     type=int,
768     help="Total charge of the system")
769
770 args = parser.parse_args()
771
772 # read xyz file
773 filename = args.structure
774
775 # allow for charged fragments, alternatively radicals are made
776 charged_fragments = not args.no_charged_fragments
777
778 # quick is faster for large systems but requires networkx
779 # if you don't want to install networkx set quick=False and
780 # uncomment 'import networkx as nx' at the top of the file
781 quick = not args.no_graph
782
783 # chiral comment
784 embed_chiral = not args.ignore_chiral
785
786 # read atoms and coordinates. Try to find the charge
787 atoms, charge, xyz_coordinates = read_xyz_file(filename)
788
789 # huckel uses extended Huckel bond orders to locate bonds (requires
RDKit 2019.9.1 or later)
790 # otherwise van der Waals radii are used
791 use_huckel = args.use_huckel
792
793 # if explicit charge from args, set it
794 if args.charge is not None:
795     charge = int(args.charge)
796
797 # Get the molobjs
798 mols = xyz2mol(atoms, xyz_coordinates,
799     charge=charge,
800     use_graph=quick,
```



```
801     allow_charged_fragments=charged_fragments ,
802     embed_chiral=embed_chiral ,
803     use_huckel=use_huckel)
804
805     # Print output
806     for mol in mols:
807         if args.output_format == "sdf":
808             txt = Chem.MolToMolBlock(mol)
809             print(txt)
810
811         else:
812             # Canonical hack
813             isomeric_smiles = not args.ignore_chiral
814             smiles = Chem.MolToSmiles(mol, isomericSmiles=
isomeric_smiles)
815             m = Chem.MolFromSmiles(smiles)
816             smiles = Chem.MolToSmiles(m, isomericSmiles=isomeric_smiles
)
817             print(smiles)
818             # return smiles
```

Appendix B

Python scripts | Hindered rotor identification code

B.1 get_geometry.py

```
1 # program begins
2
3 import sys, math, os, shutil
4 from collections import Counter
5 from io import open
6 import numpy as np
7
8 ## -- CONSTANTS -- ##
9
10 # threshold beyond average of covalent radii to determine bond cutoff
11 bond_thresh = 1.2
12
13 # conversion from radians to degrees and vice versa
14 rad2deg = 180.0 / math.pi
15 deg2rad = 1.0 / rad2deg
16
17 # covalent (or ionic) radii by atomic element (Angstroms) from
18 # "Inorganic Chemistry" 3rd ed, Housecroft, Appendix 6, pgs 1013-1014
19 cov_rads_original = { 'H' : 0.37, 'C' : 0.77, 'O' : 0.73, 'N' : 0.75,
20                       'F' : 0.71,
21                       'P' : 1.10, 'S' : 1.03, 'Cl' : 0.99, 'Br' : 1.14, 'I' : 1.33, 'He' :
22                       0.30,
23                       'Ne' : 0.84, 'Ar' : 1.00, 'Li' : 1.02, 'Be' : 0.27, 'B' : 0.88, 'Na' :
24                       1.02,
25                       'Mg' : 0.72, 'Al' : 1.30, 'Si' : 1.18, 'K' : 1.38, 'Ca' : 1.00, 'Sc' :
26                       0.75,
27                       'Ti' : 0.86, 'V' : 0.79, 'Cr' : 0.73, 'Mn' : 0.67, 'Fe' : 0.61, 'Co' :
28                       0.64,
```

```
24 'Ni': 0.55, 'Cu': 0.46, 'Zn': 0.60, 'Ga': 1.22, 'Ge': 1.22, 'As':
    1.22,
25 'Se': 1.17, 'Kr': 1.03, 'X' : 0.00}
26
27 cov_rads = { 'H' : 0.31, 'C' : 0.76, 'O' : 0.66, 'N' : 0.71 }
28
29 ## -- END OF CONSTANTS -- ##
30
31 ## -- IO FUNCTIONS -- ##
32 # convert newzmat format into gaussview reformats
33 def get_gView_format(file_name):
34     #Opens file for reading
35     try:
36         file = open(file_name, "r")
37     except IOError:
38         print('Error: file (%s) not found!\n' % (file_name))
39         sys.exit()
40     file_content = file.read()
41     file.close()
42     #Opens file for writing
43     try:
44         file_1 = open(file_name, "w")
45     except IOError:
46         print('Error: file (%s) not found!\n' % (file_name))
47         sys.exit()
48     # reformats zmatrix into correct array for
49     fstring = '\n'.join('\n\n'.join(file_content.split('\n\n')[:-1]).
split('\n')) # gets rid of extra numbers at the bottom
50     ftring_header = '\n'.join(fstring.split('\n')[:7])
51     fstring = '\n'.join([string.replace(',', '4* ' ').replace('=', '4* ' ')
.replace('      Variables:', '')
52                         for string in fstring.split('\n')[7:]]
53     fstring = ftring_header + '\n' + fstring
54     flines = fstring.split('\n')
55     flines = [item+'\n' for item in flines]
56     file_1.writelines(flines)
57     file_1.close()
58
59
60 # read file data into a 2-d array
61 def get_file_string_array(file_name):
62     #Opens file for array
63     try:
64         file = open(file_name, "r")
65     except IOError:
66         print('Error: file (%s) not found!\n' % (file_name))
67         sys.exit()
68     flines = file.readlines()
```

```
69 #Opens file for string
70 try:
71     file_1 = open(file_name, "r")
72 except IOError:
73     print('Error: file (%s) not found!\n' % (file_name))
74     sys.exit()
75 file_content = file_1.read()
76 file.close()
77 file_1.close()
78
79 array = []
80 for line in flines:
81     array.append(line.split())
82
83 return array, file_content
84
85 # read in geometry from xyz file
86 def get_geom(xyz_array):
87     # xyz_array = get_file_string_array(xyz_file_name)
88     n_atoms = int(xyz_array[0][0])
89     at_types = [''] for i in range(n_atoms)]
90     coords = [[0.0 for j in range(3)] for i in range(n_atoms)]
91     for i in range(n_atoms):
92         at_types[i] = xyz_array[i+2][0]
93         for j in range(3):
94             coords[i][j] = float(xyz_array[i+2][j+1])
95     geom = [at_types, coords]
96     return geom
97
98 # input syntax and usage warnings
99 def get_inputs():
100     if (not len(sys.argv) == 2):
101         print('Usage: torsions.py XYZ_FILE\n')
102         print('  XYZ_FILE: coordinates of target molecule\n')
103         sys.exit()
104     else:
105         xyz_file_name = sys.argv[1]
106         return xyz_file_name
107
108 # print list of torsion angles to screen
109 def print_torsions(geom, torsions):
110     at_types = geom[0]
111     n_torsions = len(torsions)
112     print('%i torsion(s) found (degrees)' % (n_torsions))
113     for q in range(n_torsions):
114         n1, n2, n3, n4 = torsions[q][0:4]
115         t1234 = torsions[q][4]
116         nstr = '%i-%i-%i-%i' % (n1+1, n2+1, n3+1, n4+1)
```

```
117     tstr = '(%s-%s-%s-%s) ' % (at_types[n1], at_types[n2], at_types
118         [n3], at_types[n4])
119     print(' %-15s %-13s %8.3f\n' % (nstr, tstr, t1234), end='')
120     print('\n', end='')
121
122 ## -- END OF IO FUNCTIONS -- ##
123
124 ## -- MATHS FUNCTIONS -- ##
125
126 # calculate distance between two 3-d cartesian coordinates
127 def get_r12(coords1, coords2):
128     r2 = 0.0
129     for p in range(3):
130         r2 += (coords2[p] - coords1[p])**2
131     r = math.sqrt(r2)
132     return r
133
134 # calculate unit vector between to 3-d cartesian coordinates
135 def get_u12(coords1, coords2):
136     r12 = get_r12(coords1, coords2)
137     u12 = [0.0 for p in range(3)]
138     for p in range(3):
139         u12[p] = (coords2[p] - coords1[p]) / r12
140     return u12
141
142 # calculate dot product between two unit vectors
143 def get_udp(uvec1, uvec2):
144     uvec1 = np.array(uvec1)
145     uvec2 = np.array(uvec2)
146     udp = np.dot(uvec1, uvec2)
147     return udp
148
149 # calculate unit cross product between two unit vectors
150 def get_ucp(uvec1, uvec2):
151     ucp = np.cross(uvec1, uvec2)
152     return ucp
153
154
155 # calculate angle between three 3-d cartesian coordinates
156 def get_a123(coords1, coords2, coords3):
157     u21 = get_u12(coords2, coords1)
158     u23 = get_u12(coords2, coords3)
159     dp2123 = get_udp(u21, u23)
160     a123 = rad2deg * math.acos(dp2123)
161     return a123
162
163 # calculate torsion angle between four 3-d cartesian coordinates
```

```
164 def get_t1234(coords1, coords2, coords3, coords4):
165     u21 = get_u12(coords2, coords1)
166     u23 = get_u12(coords2, coords3)
167     u32 = get_u12(coords3, coords2)
168     u34 = get_u12(coords3, coords4)
169     u21c23 = get_ucp(u21, u23)
170     u32c34 = get_ucp(u32, u34)
171     dp = get_udp(u21c23, u32c34)
172     sign = 2 * float(get_udp(u21c23, u34) < 0) - 1
173     t1234 = rad2deg * sign * math.acos(dp)
174     return t1234
175
176 ## -- END OF MATHS FUNCTIONS -- ##
177
178
179 ## -- TOPOLOGY FUNCTIONS -- ##
180
181 # build graph of which atoms are covalently bonded
182 def get_bond_graph(geom, bond_thresh):
183     at_types, coords = geom[0:2]
184     n_atoms = len(at_types)
185     double_bonds = []
186     bond_graph = [[] for i in range(n_atoms)]
187     for i in range(n_atoms):
188         covrad1 = cov_rads[at_types[i]]
189         for j in range(i+1, n_atoms):
190             covrad2 = cov_rads[at_types[j]]
191             thresh = bond_thresh * (covrad1 + covrad2)
192             # adjusts threshold to catch double bonds
193             if bond_thresh == 1.2:
194                 double_bond_thresh = 1.2 * (covrad1*0.73 + covrad2
195 *0.73)
196             if bond_thresh == 1.4:
197                 double_bond_thresh = 1.2 * (covrad1*0.74 + covrad2
198 *0.74)
199             r12 = get_r12(coords[i], coords[j])
200             if (r12 < thresh):
201                 bond_graph[i].append(j)
202                 bond_graph[j].append(i)
203             if (r12 < double_bond_thresh):
204                 double_bonds.append([i, j])
205     return bond_graph, double_bonds
206
207 # determine atoms which are covalently bonded from bond graph
208 def get_bonds(geom, bond_graph):
209     at_types, coords = geom[0:2]
210     n_atoms = len(at_types)
211     bonds = []
```

```
210     for i in range(n_atoms):
211         for a in range(len(bond_graph[i])):
212             j = bond_graph[i][a]
213             if (i < j):
214                 r12 = get_r12(coords[i], coords[j])
215                 bonds.append([i, j, r12])
216     return bonds
217
218 # determine atoms which form a bond angle from bond graph
219 def get_angles(geom, bond_graph):
220     at_types, coords = geom[0:2]
221     n_atoms = len(at_types)
222     angles = []
223     for j in range(n_atoms):
224         n_jbonds = len(bond_graph[j])
225         for a in range(n_jbonds):
226             i = bond_graph[j][a]
227             for b in range(a+1, n_jbonds):
228                 k = bond_graph[j][b]
229                 a123 = get_a123(coords[i], coords[j], coords[k])
230                 angles.append([i, j, k, a123])
231     return angles
232
233 # determine atoms which form torsion angles from bond graph
234 def get_torsions(geom, bond_graph):
235     at_types, coords = geom[0:2]
236     n_atoms = len(at_types)
237     torsions = []
238     for j in range(n_atoms):
239         n_jbonds = len(bond_graph[j])
240         for a in range(n_jbonds):
241             k = bond_graph[j][a]
242             if (k < j):
243                 continue
244             n_kbonds = len(bond_graph[k])
245             for b in range(n_jbonds):
246                 i = bond_graph[j][b]
247                 if (i == k):
248                     continue
249                 for c in range(n_kbonds):
250                     l = bond_graph[k][c]
251                     if (l == j or l == i):
252                         continue
253                     t1234 = get_t1234(coords[i], coords[j], coords[k],
coords[l])
254                     torsions.append([i, j, k, l, t1234])
255     return torsions
256
```

```
257 # find axis where the second atom is not bonded to anything else!  
    Extract that axis and redo!  
258 # only caveat is that heavy atoms must be the first ones in zmatrix!  
259 def include_cyclics_branched(axes):  
260     rotor_axes = []  
261     check = True  
262     counter = 0  
263     while (check == True):  
264         for axis in axes:  
265             second_atom = axis[-1]  
266             first_atom = axis[0]  
267             counter_second = 0  
268             counter_first = 0  
269             for ax in axes:  
270                 if second_atom in ax:  
271                     counter_second += 1  
272                 if first_atom in ax:  
273                     counter_first += 1  
274             if counter_second == 1 or counter_first == 1:  
275                 rotor_axes.append(axis)  
276  
277         new_axes = [axis for axis in axes if axis not in rotor_axes]  
278         if axes == new_axes:  
279             check = False  
280         axes = new_axes  
281     if len(axes) > 1:  
282         TS_ring = True  
283     else:  
284         TS_ring = False  
285  
286     return rotor_axes, TS_ring  
287  
288 def get_all_rotors(bond_graph, bond_graph_woTStresh=[]):  
289     #Fixes numbering system to match Gaussian  
290     from copy import deepcopy  
291  
292     gauss_bond_graph_woTStresh = deepcopy(bond_graph_woTStresh)  
293     for bonds in gauss_bond_graph_woTStresh:  
294         for i in range(len(bonds)):  
295             bonds[i] += 1  
296  
297     gauss_bond_graph = deepcopy(bond_graph)  
298     for bonds in gauss_bond_graph:  
299         for i in range(len(bonds)):  
300             bonds[i] += 1  
301  
302     #Heavy atoms, more than 1 bond
```



```
303     heavy_atoms = [[atom, idx+1] for idx, atom in enumerate(
gauss_bond_graph) if len(atom)>1]
304
305     #'Heavy-heavy atoms' is bond graph of heavy atom bonds alone!
306     heavy_heavy_atoms = []
307     for heavy_atom in heavy_atoms:
308         heavy_heavy_atom = [atom for atom in heavy_atom[0] if len(
gauss_bond_graph[atom-1])>1]
309         heavy_heavy_atoms.append([heavy_heavy_atom, heavy_atom[1]])
310
311     #General axes from all heavy-heavy bonds
312     general_axes = []
313     for i in range(len(heavy_heavy_atoms)):
314         for j in range(len(heavy_heavy_atoms[i][0])):
315             general_axes.append([heavy_heavy_atoms[i][-1],
heavy_heavy_atoms[i][0][j]])
316
317     #Unique list of all heavy atom bonds - rotor axes for branched
molecules included here!!!
318     axes = []
319     for axis in general_axes:
320         for element in general_axes:
321             if sorted(axis) == sorted(element):
322                 if sorted(axis) not in axes:
323                     axes.append(axis)
324
325     rotor_axes, TS_ring = include_cyclics_branched(axes)
326     # alternative approach, not used at the moment (might be useful
later on)
327     # if not TS_ring and len(bond_graph_woTSthresh)>0:
328     #     #
329     #     heavy_atoms = [[atom, idx+1] for idx, atom in enumerate(
gauss_bond_graph) if len(atom)>1]
330     #     heavy_atomswo = [[atom, idx+1] for idx, atom in enumerate(
gauss_bond_graph_woTSthresh) if len(atom)>1]
331     #
332     #     heavy_heavy_atoms = []
333     #     for heavy_atom in heavy_atoms:
334     #         heavy_heavy_atom = [atom for atom in heavy_atom[0] if len
(gauss_bond_graph_woTSthresh[atom-1])>1]
335     #         heavy_heavy_atoms.append([heavy_heavy_atom, heavy_atom
[1]])
336     #
337     #     ## If there is no TS ring, rotor axes are found using a
different approach (not based on bond elimination,
338     #     ## instead compared bond graphs at diff thresholds)
339     #     # alternative approach
340     #     general_axes = []
```

```
341 #     for i in range(len(heavy_heavy_atoms)):
342 #         for j in range(len(heavy_heavy_atoms[i][0])):
343 #             general_axes.append([heavy_heavy_atoms[i][-1],
heavy_heavy_atoms[i][0][j]])
344 #
345 #     general_axes = [sorted(ax) for ax in general_axes]
346 #     print(general_axes)
347 #     # unique axes in sorted array
348 #     unique_axes = np.unique(np.array(general_axes), axis=0)
349 #     # extracts both double bond and 1.5 bond from linear TS
350 #     axes_ofInterest = []
351 #     counted_axes = Counter([tuple(i) for i in general_axes])
352 #     for key in counted_axes.keys():
353 #         if counted_axes[key] < 2:
354 #             axes_ofInterest.append(list(key))
355 #     print(axes_ofInterest)
356 #
357 #     axes_toDelete = []
358 #     for ax in axes_ofInterest:
359 #         if ax[1] in gauss_bond_graph_woTSthresh[ax[0]-1]:
360 #             axes_toDelete.append(ax)
361 #     axes_toDelete = np.array(axes_toDelete)
362 #
363 #     axes = [ax for ax in unique_axes if ax not in axes_toDelete]
364 #     axes = [list(ax) for ax in axes]
365 #
366 #     rotor_axes = axes
367
368 for ax in rotor_axes:
369     for i in range(len(ax)):
370         ax[i] -= 1
371
372 return rotor_axes
373
374 # -- Find the rotor dihedrals given the torsions found and the original
z-matrix -- #
375 #Method 1 (original), groups axes, not accurate
376 #Not used! Need to modify print_results function to work!!
377 def get_rotor_dihedrals_method_1(torsions, zmat_array):
378     counter = 0
379     axes = {}
380     rotors = {}
381     zmat = []
382     rotor_rows = []
383
384     for torsion in torsions:
385         axes.setdefault(torsion[1], []).append(torsion)
386     for key in axes:
```

```
387     rotors[key] = axes[key][0]
388
389     for array in zmat_array:
390         if len(array)==0:
391             counter+=1
392         if counter==2:
393             zmat.append(array)
394     zmat = zmat[1:]
395     for rotor in rotors.values():
396         rotor_rows.append(zmat[max(rotor[:4]) + 1])
397     rotor_dihedrals = [row[6] for row in rotor_rows]
398
399     return rotor_dihedrals, rotors
400
401 #Method 2, works from bond elimination algorithm - cant make rotors a
402 #dict bc unallow repeated elements
403 def get_rotor_dihedrals_method_2(torsions, zmat_array, bond_graph,
404     bond_graph_woTStresh=[]):
405     counter = 0
406     axes = []
407     rotors = []
408     zmat = []
409     rotor_rows = []
410     rotor_axes = get_all_rotors(bond_graph, bond_graph_woTStresh)
411     for array in zmat_array:
412         if len(array)==0:
413             counter+=1
414         if counter==2:
415             zmat.append(array)
416     zmat = zmat[1:]
417
418     largest_atomNums = []
419     for torsion in torsions:
420         ax = sorted(torsion[1:3])
421         if (ax in rotor_axes) and (ax not in axes):
422             if max(torsion[:4]) not in largest_atomNums:
423                 rotors.append(torsion[:4])
424                 axes.append(ax)
425                 largest_atomNums.append(max(torsion[:4]))
426
427     for rotor in rotors:
428         rotor_rows.append(zmat[max(rotor) + 1])
429     #adjusts 'D#' naming from the newzmat format
430     if 'R' in ' '.join(zmat_array[10]):
431         rotor_dihedrals = [f'D{int(row[6][1:])}' for row in rotor_rows]
432     else:
433         rotor_dihedrals = [row[6] for row in rotor_rows]
```

```
433     return rotor_dihedrals, rotors
434
435 # create Rotor _Files folder and returns its path
436 def create_rotor_files_directory(zmat_file):
437     directory=os.getcwd()
438     files=os.listdir(directory)
439     new_dir = os.path.join(directory, zmat_file[:-4]+'_Rotor_Files')
440     if not os.path.exists(new_dir):
441         os.makedirs(new_dir)
442     return directory, new_dir
443
444 # creates n copies of the original gjf based on how many rotors it has
445 def create_gjf_copies(new_dir, filename, rotor_dihedrals):
446     for i in range(len(rotor_dihedrals)):
447         #File naming!
448         shutil.copy(filename, new_dir+'/' +filename.split('.')[0]+'_'+
449             str(i)+'_'+filename.split('.')[1])
450 # loops through the dihedrals and the gjf copies and parses 's 36 10.0'
451 # next to the corresponding diheral, for each copy
452 def write_new_files(rotor_dihedrals, originalFilenameLen):
453     directory=os.getcwd()
454     files=os.listdir(directory)
455     files = [file for file in files if file.endswith('gjf')]
456     for dihedral, filename in zip(rotor_dihedrals, files):
457         file = open(filename, "r")
458         file_lines = file.readlines()
459         for index, line in enumerate(file_lines):
460             if ((' '+dihedral+' ') in line) and (len(line.split())==2):
461                 value = line.split()[-1]
462                 file_lines[index] = line.replace(value, f'{value} s 36
463                 10.0')
464             break
465     try:
466         file = open(filename, "w")
467     except IOError:
468         print('Error: file (%s) not found!\n' % (filename))
469         sys.exit()
470
471     file.writelines(file_lines)
472     file.close()
473     newname=filename.split('.')[0][:originalFilenameLen]+"_"+str(
474     dihedral)+"_rotor.gjf"
475     os.rename(filename, newname)
476
477 ## -- END OF TOPOLOGY FUNCTIONS -- ##
```

```
477 ## -- UPDATE_HEADER FUNCTION -- ## (by Katie L.)
478
479 def replace_header(ts, numProc):
480     #user defined job type
481     keyword='rotor'
482
483     files=os.listdir(os.getcwd())
484     for filename in files:
485         #calls the function "replace_header" to edit the file header
486         #for the specific file type
487         f=open(filename, 'r')
488         count=0
489         for line in f:
490             if line == '\n' or line == '\r\n':
491                 f.close()
492                 break
493             else:
494                 count = count + 1
495
496         #determine which route we are using based on user specified
497         #input
498         if keyword=='m062x':
499             if ts:
500                 route="#opt=(calcall,tight,ts) freq m062x/cc-pvtz
501                 maxdisk=500GB int=ultrafine"
502             if not ts:
503                 route="#opt=(calcall,tight) freq m062x/cc-pvtz maxdisk
504                 =500GB int=ultrafine"
505             elif keyword=='b3lyp':
506                 if ts:
507                     route="#opt=(calcall,tight,ts) freq b3lyp/6-311++g*
508                     maxdisk=500GB int=ultrafine"
509                 if not ts:
510                     route="#opt=(calcall,tight) freq b3lyp/6-311++g*
511                     maxdisk=500GB int=ultrafine"
512
513             elif keyword=='E':
514                 route="# roccsd(t,t1diag)/cc-pvdz maxdisk=500GB int=
515                 ultraFine"
516
517             elif keyword=='E1':
518                 route="# roccsd(t,t1diag)/cc-pvtz maxdisk=500GB int=
519                 ultraFine"
520
521             elif keyword=='E2':
522                 route="# roccsd(t)/cc-pvqz maxdisk=500GB int=ultraFine"
523
524             elif keyword=='IRC':
```

```
517         route="# irc=(maxpoints=20,recalc=5,calcfc) m062x/cc-pvtz"
518
519     elif keyword == 'rotor':
520         if not ts:
521             route="#m062x/cc-pvtz opt=internal int=ultrafine nosym"
522         if ts:
523             route="#m062x/cc-pvtz opt=(ts,calcall,noeig,intern,
150 maxcyc=50) int=ultrafine nosym"
524
525     else:
526         print("This method is not included in this code.")
527     title=filename.split(".")[::-1]
528
529     #rewrites headers
530     lines=open(filename,'r').readlines()
531     if '\r\n' in lines:
532         text=["%nprocshared="+numProc,'\r\n',"%mem=500MW","\r\n","%
150 chk="+title[0]+".chk",'\r\n',route,'\r\n']+lines[count:]
533     else:
534         text=["%nprocshared="+numProc,'\n',"%mem=500MW","\n","%chk=
150 "+title[0]+".chk",'\n',route,'\n']+lines[count:]
535     open(filename,'w').writelines(text)
536     f.close()
537
538 ## -- END OF UPDATE_HEADER FUNCTION -- ##
539
540
541 ## -- PRINTING RESULTS -- ##
542
543 def print_results(zmat_file, zmat, rotor_dihedrals, rotors, bond_graph)
150 :
544     print("\n\n"+zmat_file)
545     print('Bond Graph:')
546     # adjusts indexing in bond graph
547     for bonds in bond_graph:
548         for i in range(len(bonds)):
549             bonds[i] += 1
550     print(bond_graph)
551     print("-----")
552     print("Found "+str(len(rotor_dihedrals))+" rotors!\n")
553     for rotor in rotors:
554         for i in range(len(rotor)):
555             rotor[i] += 1
556     for rotor, dihedral in zip(rotors, rotor_dihedrals):
557         if rotor[0]>rotor[-1]:
558             pass
559         else:
560             rotor = rotor[::-1] #reversing list
```

```
561     print(rotor, ' ----> ', dihedral)
562     print("\nZ-Matrix")
563     print("-----")
564     #     for line in zmat_array:
565     #         print(''.join(line))
566     print(zmat)
567     print("-----")
568
569     ## -- END OF PRINTING RESULTS -- ##
570
571
572     ## -- UNUSED PRINTING FUNCTIONS! -- ##
573
574     # print geometry to screen - Unused
575     def print_geom(geom, comment):
576         at_types, coords = geom[0:2]
577         n_atoms = len(at_types)
578         print('%i\n%s\n' % (n_atoms, comment), end='')
579         for i in range(n_atoms):
580             print('%-2s' % (at_types[i]), end='')
581             for j in range(3):
582                 print(' %12.6f' % (coords[i][j]), end='')
583             print('\n', end='')
584         print('\n', end='')
585
586     # print bond graph to screen - Unused
587     def print_bond_graph(geom, bond_graph, comment):
588         at_types = geom[0]
589         n_atoms = len(at_types)
590         print('%s\n' % (comment), end='')
591         for i in range(n_atoms):
592             print(' %4i %-2s -' % (i+1, at_types[i]), end='')
593             for j in range(len(bond_graph[i])):
594                 print(' %i' % (bond_graph[i][j] + 1), end='')
595             print('\n', end='')
596         print('\n', end='')
597
598     # print list of bond lengths to screen - Unused
599     def print_bonds(geom, bonds):
600         at_types = geom[0]
601         n_bonds = len(bonds)
602         print('%i bond(s) found (Angstrom)' % (n_bonds))
603         for q in range(n_bonds):
604             n1, n2 = bonds[q][0:2]
605             r12 = bonds[q][2]
606             nstr = '%i-%i' % (n1+1, n2+1)
607             tstr = '(%s-%s)' % (at_types[n1], at_types[n2])
608             print(' %-15s %-13s %6.4f\n' % (nstr, tstr, r12), end='')
```

```

609     print('\n', end='')
610
611 # print list of bond angles to screen - Unused
612 def print_angles(geom, angles):
613     at_types = geom[0]
614     n_angles = len(angles)
615     print('%i angle(s) found (degrees)' % (n_angles))
616     for q in range(n_angles):
617         n1, n2, n3 = angles[q][0:3]
618         a123 = angles[q][3]
619         nstr = '%i-%i-%i' % (n1+1, n2+1, n3+1)
620         tstr = '%s-%s-%s' % (at_types[n1], at_types[n2], at_types[n3
621 ])
622         print(' %-15s %-13s  %7.3f\n' % (nstr, tstr, a123), end='')
623     print('\n', end='')
624
625 ## -- END OF UNUSED PRINTING FUNCTIONS -- ##
626 # end of program

```

B.2 get_rotors.py

```

1 import os, shutil, re, ast
2 from get_geometry import *
3 from geometryInfo import get_xyzGeom
4
5 ## -- FUNCTION CALLS AND MAIN BLOCKS -- ##
6
7 def main(xyzGeoms=[], rotorFile=[]):
8     '''
9     Takes xyzGeoms of all log files pulled from kinbot. Default set to
10    empty list for other cases.
11    '''
12    # looping through all gjfs and finding rotors for each one
13    directory=os.getcwd()
14    files=os.listdir(directory)
15    # convert all gjfs into gaussview reformats
16    for fileName in files:
17        if fileName.endswith('gjf'):
18            file = open(fileName, 'r')
19            fstring = file.read()
20            file.close()
21            if 'Variables' in fstring:
22                get_gView_format(fileName)
23
24    for fileName in files:
25        if fileName.endswith('gjf'):
26            zmat_file = fileName

```



```
26     file = open(fileName, 'r')
27     fstring = file.read()
28     multiplicity = [item for item in re.findall(r"\s?\d\,?\s?\s
? \s?\s?\d", fstring, re.MULTILINE)[0] if item.isdigit()][1]
29     # finds if molecule is a transition state
30     if 'ts' in fstring.split('opt=')[1].split()[0]:
31         ts = 'y'
32     else:
33         ts = 'n'
34     # extracts number of processors used for m062x jobs (uses
35     3 less for rotor jobs)
36     numProc = str(int(fstring.split('nprocshared=')[1].split()
37     [0]) - 3)
38     file.close()
39
40     file_length = len(zmat_file.split(".gjf")[0])
41
42     # get original zmat array
43     zmat_array, zmat = get_file_string_array(zmat_file)
44
45     # read in z-matrix
46     # mol = zmat2xyz.molecule(zmat_file)
47     # convert to xyz-coordinates
48     # xyz_array = mol.zmat2xyz()
49
50     # extract xyz-coordinates from log file
51     if fileName[:-3]+'log' in os.listdir():
52         xyz_array = get_xyzGeom(fileName[:-3]+'log')
53     else:
54         xyz_array = xyzGeoms[fileName.split('_E')[0]+'gjf']
55     xyz_array.insert(0, fileName)
56     xyz_array.insert(0, len(xyz_array[1:]))
57     xyz_array = [[item] for item in xyz_array]
58     for i, item in enumerate(xyz_array[2:]):
59         new_element = [float(elem) for elem in item[0].split(',
60         ') if elem[-1].isdigit()]
61         new_element.insert(0, item[0].split(',') [0])
62         xyz_array[i+2] = new_element
63
64     # read in geometry, determine bond topology
65     geom = get_geom(xyz_array)
66     print(f'geom: {geom}')
67
68     if ts == 'y':
69         ts = True
70         # calculates bond graph without changing threshold.
71         Used for extracting rotors of non-ring-structured TS
72         bond_thresh = 1.2
```

```
69         bond_graph_woTStresh, double_bonds = get_bond_graph(
geom, bond_thresh)
70         bond_thresh = 1.4
71     else:
72         ts = False
73         bond_thresh = 1.2
74
75     bond_graph, double_bonds = get_bond_graph(geom, bond_thresh
)
76     # double_bonds = new_func_Pray(bond_graph, geom[0],
multiplicity)
77
78     # calculate bond lengths, angles, and torsions
79     bonds = get_bonds(geom, bond_graph)
80     angles = get_angles(geom, bond_graph)
81     torsions = get_torsions(geom, bond_graph)
82     if ts:
83         print(f'torsions: {torsions}')
84
85         print(f'BG: {bond_graph}')
86         print(f'TSBG: {bond_graph_woTStresh}')
87         rotor_dihedrals, rotors = get_rotor_dihedrals_method_2(
torsions, zmat_array, bond_graph, bond_graph_woTStresh)
88         if not isinstance(rotorFile, list):
89             rotor_dihedrals, rotors = get_rotors_from_rotorFile
(rotorFile)
90         else:
91             rotor_dihedrals, rotors = get_rotor_dihedrals_method_2(
torsions, zmat_array, bond_graph)
92             if not isinstance(rotorFile, list):
93                 rotor_dihedrals, rotors = get_rotors_from_rotorFile
(rotorFile)
94
95         print('double bonds (Py indexing):', double_bonds)
96
97         # filtering out double bonds from possible rotors
98         new_rotors = [[rotor, dihedral] for [rotor, dihedral] in
zip(rotors, rotor_dihedrals) if rotor[1:3] not in double_bonds]
99         rotors = [item[0] for item in new_rotors]
100        rotor_dihedrals = [item[1] for item in new_rotors]
101
102        current_dir, new_dir = create_rotor_files_directory(
zmat_file)
103        create_gjf_copies(new_dir, zmat_file, rotor_dihedrals)
104        os.chdir(new_dir)
105        # write new gjf file
106        write_new_files(rotor_dihedrals, file_length)
107        replace_header(ts, numProc)
```

```
108     # creates 36 one-scan-step jobs for each rotors
109     for file in os.listdir():
110         if file.endswith('.gjf'):
111             fileName = file.split('.gjf')[0]
112             for i in range(10, 370, 10):
113                 f = open(file, 'r')
114                 flines = f.readlines()
115                 f.close()
116                 scanCommand = 's 36 10.0'
117                 for j, line in enumerate(flines):
118                     if scanCommand in line:
119                         flines[j] = line.replace(scanCommand, f
's 1 {str(i)}.0')
120
121                     if '%chk' in line:
122                         flines[j] = line.replace('_rotor', f'
_rotor_{str(i)}')
123
124                 fcopy = open(f'{fileName}_{str(i)}.gjf', 'w')
125                 fcopy.writelines(flines)
126                 fcopy.close()
127                 os.remove(file)
128     # moves rotor jobs shell script into rotor their dihedral
rotor folder
129     for dihedral in rotor_dihedrals:
130         os.mkdir(f'./{dihedral}')
131         shutil.copy('./../run_all_gjfs_array.sh', f'./{dihedral
}')
132     for file in os.listdir():
133         if file.endswith('.gjf'):
134             for dihedral in rotor_dihedrals:
135                 if dihedral in file:
136                     shutil.move(f'./{file}', f'./{dihedral}')
137     os.chdir(current_dir)
138     # prints results
139     print_results(zmat_file, zmat, rotor_dihedrals, rotors,
bond_graph)
140
141     return rotor_dihedrals, rotors
142
143 def get_rotors_from_rotorFile(rotorFile):
144     rotFile = open(rotorFile, 'r')
145     flines = rotFile.readlines()
146     rotFile.close()
147
148     if int(flines[0].split()[1]) > 0:
149         rotor_dihedrals, rotors = [], []
150         for line in flines:
```

```
151         if 'D' in line[0]:
152             dihedral = line.split('--->')[0].strip()
153             rotor_dihedrals.append(dihedral)
154             rotor = line.split('--->')[1].strip()
155             rotors.append(ast.literal_eval(rotor))
156     else:
157         rotor_dihedrals, rotors = [], []
158
159     return rotor_dihedrals, rotors
160
161     ## -- END FUNCTION CALLS AND MAIN BLOCKS -- ##
162
163 if __name__ == '__main__':
164     main()
```

B.3 run_all_gjfs_array.sh

```
1 #!/bin/bash
2 #SBATCH --partition=shas
3 #SBATCH --qos=normal
4 #SBATCH --nodes=1
5 #SBATCH --ntasks-per-node=8
6 #SBATCH --time=24:00:00
7 #SBATCH --job-name=83.35_rotors
8 #SBATCH --account=ucb146_summit3
9 #SBATCH --array=1-36
10
11
12 module purge
13 module load "gaussian/16_avx2"
14
15 FILES=$(ls *.gjf | sed -n ${SLURM_ARRAY_TASK_ID}p)
16 echo "Processing $FILES ...."
17
18 g16 $FILES
19
20 echo "Finished all Jobs!"
21 date
```

Appendix C

Python scripts | MESS input file generation code

C.1 get_energies.py

```
1 import xlswriter
2 import numpy as np
3 import re
4 from scipy.signal import find_peaks
5
6 # Creates and populates energies spreadsheet from input energies
  dictionary
7 def write_energies_spreadsheet(energiesDictionary, non_repeated_non_ts,
  ts_prods, dissociations):
8     # Create a workbook and add a worksheet.
9     workbook = xlswriter.Workbook('Energies_SpreadSheet.xlsx')
10    worksheet = workbook.add_worksheet('Energetics')
11    # Some data we want to write to the worksheet.
12    column_titles = ['m062X/cc-pVTZ', 'CCSD(T)/cc-pVDZ', 'CCSD(T)/cc-
  pVTZ', 'T1 diag', 'E(hartrees)']
13    # Start from the first cell. Rows and columns are zero indexed.
14    row = 0
15    col = 0
16
17    # Iterate over the data and write it out row by row.
18    for column_title in (column_titles):
19        col += 1
20        worksheet.write(row, col, column_title)
21    col = 0
22    row += 1
23    worksheet.write(row, col, 'Reactants/Products')
24
25    row += 1
26
```

```
27 # writes all product energies into excel file
28 for prod in non_repeated_non_ts:
29     worksheet.write(row, col, prod)
30     col = 1
31     for energy in energiesDictionary[prod]:
32         worksheet.write(row, col, energy)
33         col += 1
34     # extrapolation of ground energies to inf zeta limit
35     worksheet.write(row, col, '=B'+str(row+1)+'+D'+str(row+1)+'+((D
'+str(row+1)+'-C'+str(row+1)+')*0.46286)')
36     row += 1
37     col = 0
38
39 row += 1
40 worksheet.write(row, col, 'Transition States')
41 worksheet.write(row, col+6, 'E_fwd (hartrees)')
42 worksheet.write(row, col+7, 'E_rev (hartrees)')
43 worksheet.write(row, col+8, 'E_fwd (kcal/mol)')
44 worksheet.write(row, col+9, 'E_rev (kcal/mol)')
45
46 # writes all transition state energies into excel file
47 row += 1
48 for key in energiesDictionary.keys():
49     if key.startswith('TS'):
50         temp = set(ts_prods[key])
51         prod_indices = [i for i, val in enumerate(
non_repeated_non_ts) if val in temp]
52         h_index = [i for i, val in enumerate(non_repeated_non_ts)
if val == 'H']
53         worksheet.write(row, col, key)
54         col = 1
55         for energy in energiesDictionary[key]:
56             worksheet.write(row, col, energy)
57             col += 1
58         worksheet.write(row, col, '=B'+str(row+1)+'+D'+str(row+1)+'
+((D'+str(row+1)+'-C'+str(row+1)+')*0.46286)')
59         col += 1
60         worksheet.write(row, col, '=F'+str(row+1)+'-F$3')
61         col += 1
62         if len(prod_indices)==2:
63             worksheet.write(row, col, '=F'+str(row+1)+'-(F'+str(
prod_indices[0]+3)+'+F'+str(prod_indices[1]+3)+'')')
64         else:
65             if not list(temp)[0].startswith('W'):
66                 worksheet.write(row, col, '=F'+str(row+1)+'-(F'+str
(prod_indices[0]+3)+'+F'+str(h_index[0]+3)+'')')
67             else:
```

```
68         worksheet.write(row, col, '=F'+str(row+1)+'-(F'+str
(prod_indices[0]+3)+')')
69         col += 1
70         worksheet.write(row, col, '=G'+str(row+1)+'*627.51')
71         col += 1
72         worksheet.write(row, col, '=H'+str(row+1)+'*627.51')
73
74         row += 1
75         col = 0
76     # writes all dissociation energies into excel file
77     row += 1
78     worksheet.write(row, col, 'Dissociations')
79     worksheet.write(row, col+6, 'E_fwd (hartrees)')
80     worksheet.write(row, col+7, 'E_rev (hartrees)')
81     worksheet.write(row, col+8, 'E_fwd (kcal/mol)')
82     worksheet.write(row, col+9, 'E_rev (kcal/mol)')
83
84     row += 1
85     for i in range(0, len(dissociations), 2):
86         dissoc_indices = [j for j, val in enumerate(non_repeated_non_ts
) if val in dissociations[i:i+2]]
87         worksheet.write(row, col, dissociations[i]+' + '+dissociations[
i+1])
88         col += 6
89         worksheet.write(row, col, '= (F'+str(dissoc_indices[0]+3)+'+F'+
str(dissoc_indices[1]+3)+')-F3')
90         col += 1
91         worksheet.write(row, col, '= -G'+str(row+1))
92         col += 1
93         worksheet.write(row, col, '=G'+str(row+1)+'*627.51')
94         col += 1
95         worksheet.write(row, col, '=H'+str(row+1)+'*627.51')
96
97         col = 0
98         row += 1
99
100     workbook.close()
101
102 # Takes in rotor dihedrals, navigates to corresponding rotor output and
returns peaks and valleys using SciPy's find_peaks
103 def get_peaks_valleys(dihedrals, m062xFileName):
104     moleculeName = m062xFileName.split('_m062x.log')[0]
105     # dictionary, contains dihedrals as keys and extreme energies lists
as values
106     rotorEnergies = {}
107     degrees = np.arange(0, 36, 1)
108     for dihedral in dihedrals:
109         peaks_and_valleys = []
```

```
110     rotorFileName = moleculeName + '_' + dihedral + '_rotor.log'
111     rotorFile = open(rotorFileName, 'r')
112     rotorFileString = rotorFile.read()
113     rotorFile.close()
114     rotorFileString = rotorFileString.replace('\n', '').replace(' ',
115 , '')
116     # conditional for a different command in rotor header
117     if "#scan" in rotorFileString:
118         # use regex to find scanned energies at bottom of the file
119         print(rotorFileName)
120         energies = re.findall(r'\\HF=[-?\d*\.\d*,]*',
rotorFileString)[0].split(',')
121         energies[0] = energies[0].split('=')[-1]
122     else:
123         rotorFile = open(rotorFileName, 'r')
124         rotorFileString = rotorFile.readlines()
125         rotorFile.close()
126         # use regex to find scanned energies throughout the file
127         print(rotorFileName)
128         search_optimization_line = re.compile(r'Optimization
completed')
129         search_SCF_Done_line = re.compile(r'SCF Done')
130         num_lines = len(rotorFileString)
131         curr_line_num = 0
132         energies = []
133         while curr_line_num < num_lines:
134             curr_line = str.strip(rotorFileString[curr_line_num])
135             if search_SCF_Done_line.search(curr_line):
136                 SCF_Done_Line = curr_line
137             if search_optimization_line.search(curr_line):
138                 SCF_Done_line_contents = SCF_Done_Line.split()
139                 energies.append(str(SCF_Done_line_contents[4]))
140                 curr_line_num = curr_line_num + 1
141
142         # adjusts energies with respect to initial energy and converts
to kcal/mol
143         energies = np.array([float(energy)-float(energies[0]) for
energy in energies][: -1])*627.51
144         peaks_and_valleys.append(energies[0])
145
146         # finds peaks and valleys using scipy.signal.find_peaks
147         peak_indices, _ = find_peaks(energies)
148         valley_indices, _ = find_peaks(-1*energies)
149
150         # creates list with all extreme energies
151         for i in range(len(peak_indices)):
152             try:
153                 peaks_and_valleys.append(energies[peak_indices[i]])
```



```

153         peaks_and_valleys.append(energies[valley_indices[i]])
154     except IndexError:
155         pass
156     # populates dictionary of dihedral-energies
157     rotorEnergies[dihedral] = peaks_and_valleys
158
159     return rotorEnergies

```

C.2 geometryInfo.py

```

1 # Function for extracting XYZ Geometries from m062x files
2 import os
3 import re
4 from difflib import SequenceMatcher
5 from get_geometry import get_geom, get_bond_graph, get_bonds,
6     get_angles, get_torsions, get_all_rotors
7
8 ## ----- TOPOLOGY FUNCTIONS -----##
9
10 # get xyz geometry from the m062x file
11 def get_xyzGeom(m062xFileName):
12     #open and strip \n from file, locate geom using regex and remove
13     #duplicates by using non-duplicate keys feature from dicts.
14     #Regex: \d (digit), [A-Z] (caps letter), -? (0 or more appearances
15     #of '-'), \. (.), * (0 or more appearances of preceding call)
16     m062xFile = open(m062xFileName, 'r')
17     m062xFileString = m062xFile.read().replace('\n', '').replace(' ', '
18 ')
19     xyz_geom = list(dict.fromkeys(re.findall(r'[A-Z],-?\d\.\d*,-?\d\.\d
20 *,-?\d\.\d*', m062xFileString)))
21     idxs_toDelete = []
22     for i in range(len(xyz_geom)):
23         for j in range(len(xyz_geom)):
24             # library used to compare how 2 strings match
25             # used to delete repeated coordinates that differ to
26             # themselves by a few orders of magnitude (redundant!)
27             # ratios > 0.8 are accurate by 6 decimal places!
28             if SequenceMatcher(a=xyz_geom[i], b=xyz_geom[j]).ratio() >
29             0.8 and SequenceMatcher(a=xyz_geom[i], b=xyz_geom[j]).ratio() < 1.0:
30                 if sorted([i, j]) not in idxs_toDelete:
31                     idxs_toDelete.append([i, j])
32     # deletes repeated coordinates!
33     idxs_toDelete = [max(item) for item in idxs_toDelete]
34     for index in sorted(idxs_toDelete, reverse=True):
35         del xyz_geom[index]
36
37     m062xFile.close()

```

```
31     return xyz_geom
32
33 # slightly different from rotor script, returns lists of rotors via
34 # atom numbering
35 def get_rotor_dihedrals(torsions, bond_graph, bond_graph_woTsthresh=[]):
36     :
37     axes = []
38     rotors = []
39     rotor_rows = []
40     maxAtomNumber = []
41
42     rotor_axes = get_all_rotors(bond_graph, bond_graph_woTsthresh)
43
44     for torsion in torsions:
45         ax = sorted(torsion[1:3])
46         if (ax in rotor_axes) and (ax not in axes) and (max(torsion
47 [:4]) not in maxAtomNumber):
48             rotors.append(torsion[:4])
49             axes.append(ax)
50             maxAtomNumber.append(max(torsion[:4]))
51
52     return rotors
53
54 # pulls functions from get get_geomtry to get list of molecule's rotors
55 def get_rotors(xyz_geom, m062xFileName, bond_thresh, TS=False):
56     #converts xyz_geom to xyz_array format compatible with
57     #get_rotors_gjff.py script!
58     xyz_array = []
59     xyz_array.append([len(xyz_geom)])
60     xyz_array.append([m062xFileName])
61     for i in range(len(xyz_geom)):
62         line = [float(element) if len(element)>1 else element for
63 element in xyz_geom[i].split(',')]]
64         xyz_array.append(line)
65     ## -- Using functions from get_geometry script -- ##
66     #read in geometry, determine bonded topology
67     geom = get_geom(xyz_array)
68     bond_graph, double_bonds = get_bond_graph(geom, bond_thresh)
69     if TS:
70         bond_thresh = 1.2
71         bond_graph_woTsthresh, double_bonds = get_bond_graph(geom,
72 bond_thresh)
73     #calculate bond lengths, angles, and torsions
74     bonds = get_bonds(geom, bond_graph)
75     angles = get_angles(geom, bond_graph)
76     torsions = get_torsions(geom, bond_graph)
77     if TS:
```

```
72     rotors = get_rotor_dihedrals(torsions, bond_graph,
bond_graph_woTSthresh)
73     else:
74         rotors = get_rotor_dihedrals(torsions, bond_graph)
75         # filtering out double bonds from possible rotors
76         rotors = [rotor for rotor in rotors if rotor[1:3] not in
double_bonds]
77         #readjusting indices
78         for rotor in rotors:
79             for i in range(len(rotor)):
80                 rotor[i] += 1
81
82         return rotors
83
84 #extracts frequencies as well as charge and multiplicity! - Taken from
Katie's code
85 def get_frequencies(m062xFilename):
86     m062xFile = open(m062xFilename, 'r')
87     m062xFileLines = m062xFile.readlines()
88     m062xFile.close()
89     all_frequencies = ""
90     for line in m062xFileLines:
91         # finds frequencies
92         if "Frequencies --" in line:
93             freq_line=line.strip('\n')
94             freq_line=freq_line.strip('Frequencies --')+ ' '
95             freq_line=freq_line.replace(' ', ', ')
96             #stores all frequenices in one string
97             all_frequencies += freq_line
98             # finds charge and multiplicity
99             if 'Multiplicity' in line:
100                 charge_multiplicity = [item for item in line if item.
isdigit()]
101
102         if len(all_frequencies)>0:
103             #'all_frequencies' contains repeated elements
104             all_frequencies = [float(freq) for freq in all_frequencies.
split()]
105             frequencies = []
106             #adding the imaginary (negative) frequency to the completed
list (Only for transition states!!!)
107             frequencies.append(all_frequencies[0])
108             #eliminating duplicates for a complete frequency list, starts
from second element!
109             for i in range(len(all_frequencies[1:])):
110                 # try block used for some cases were frequencies are not
repeated!
111                 try:
```

```

112         if all_frequencies[1:][i+1] < all_frequencies[1:][i]:
113             frequencies.append(all_frequencies[1:][i])
114             break
115         except IndexError:
116             frequencies.append(all_frequencies[1:][i])
117             break
118         else:
119             frequencies.append(all_frequencies[1:][i])
120     else:
121         frequencies = []
122     return frequencies, charge_multiplicity

```

C.3 messParsing.py

```

1 import os, math
2
3 # ----- MESS PARSING
4 FUNCTIONS ----- #
5 # ----- Writes MESS Input Header
6 -----#
7 def write_Header():
8     MESSFile = open('MESSFile.inp', 'w')
9     MESSFile.write('TemperatureList[K]          500. 625. 750.
10    875. 1000. 1125. 1250. 1375. 1500. 1625. 1750. 1875. 2000.\n')
11    MESSFile.write('PressureList[atm]           0.00001 0.001
12    0.01 0.1 1 10 100.\n')
13    MESSFile.write('!PressureList[bar]         1.\n')
14    MESSFile.write('EnergyStepOverTemperature   .2\n')
15    MESSFile.write('ExcessEnergyOverTemperature   30\n')
16    MESSFile.write('ModelEnergyLimit[kcal/mol]       400\n')
17    MESSFile.write('CalculationMethod                direct\n')
18    MESSFile.write('!CalculationMethod                low-eigenvalue !
19    direct\n')
20    MESSFile.write('WellCutoff                        10\n')
21    MESSFile.write('ChemicalEigenvalueMax             0.2\n')
22    MESSFile.write('Model\n EnergyRelaxation\n      Exponential\n
23    Factor[1/cm]'+ ' '*16+'200\n')
24    MESSFile.write(' '*6+'Power                        .85\n')
25    MESSFile.write(' '*6+'ExponentCutoff'+ '          15\n'+ ' '*4+'
26    End\n')
27    MESSFile.write(' CollisionFrequency\n      LennardJones\n
28    Epsilons[1/cm]      --FILL HERE-- --FILL HERE-- !N2 and parent\n')
29    MESSFile.write(' Sigmas[angstrom]      --FILL HERE-- --FILL HERE
30    --\n Masses[amu]      --FILL HERE-- --FILL HERE--\n      End\n')
31    )
32    MESSFile.close()

```

```
25 # ----- CREATES AND WRITES THE BARRIER
SECTION FOR A WELL ----- #
26 # Assumes all wells are connected to Well 1!
27 def write_Well_Barrier(TSW_xyz_geom, TSW_freqs, TSW_charge_multiplicity
, TSW_rotors, rotorEnergies, path_dir, m062xFileName):
28     MESSFile = open('MESSFile.inp', 'a')
29     # gets path folder name using os library
30     pathway = os.path.basename(os.path.normpath(path_dir))
31     # extracts the number from the pathway (ie. returns 8 for the P8
folder)
32     path_num = ''.join([item for item in pathway if item.isdigit()])
33     MESSFile.write('Barrier'+ ' '*8+'B'+str(int(path_num)-1)+' '*2+'W1'+
' '*2+pathway+' '*4+'# '+m062xFileName+'\n')
34     MESSFile.write(' '*4+'Variational\n')
35     MESSFile.write(' '*8+'RRHO\n')
36     MESSFile.write(' '*4+'Geometry [angstrom]'+ ' '*8+str(len(
TSW_xyz_geom))+'\n')
37     # writes geometry section
38     for line in TSW_xyz_geom:
39         line = line.split(',')
40         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
line[3]+\n')
41     MESSFile.write(' '*4+'Core RigidRotor\n')
42     MESSFile.write(' '*8+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
FACTOR HERE ----\n')
43     MESSFile.write(' '*4+'End\n')
44     # writes rotor section
45     for i in range(len(TSW_rotors)):
46         max_atom_number = max(TSW_rotors[i])
47         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
48         MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
49         MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
50         MESSFile.write(' '*8+'Axis'+ ' '*22+str(TSW_rotors[i][1])+' '+str(
TSW_rotors[i][2])+'\n')
51         # calculates rotor symmetry
52         truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
energy in rotEnergies]
53         rotorSymmetry = '1'
54         if len(truncated_rotEnergies) == 4:
55             if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
56                 rotorSymmetry = '2'
57         if len(truncated_rotEnergies) == 6:
58             if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
59                 rotorSymmetry = '3'
60         if len(truncated_rotEnergies) == 8:
61             if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
62                 rotorSymmetry = '4'
63         MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\n')
```

```
64     rotEnergies = [round(energy, 2) for energy in rotEnergies]
65     MESSFile.write(' '*8+'Potential[kcal/mol]'+ ' '*8+str(int(len(
rotEnergies)/int(rotorSymmetry)))+'\n')
66     MESSFile.write(' '*9)
67     if not rotorSymmetry == '1' :
68         for i in range(len(rotEnergies)):
69             MESSFile.write(str(rotEnergies[i])+ ' ')
70             if i == 1:
71                 break
72     else:
73         for rotEnergy in rotEnergies:
74             MESSFile.write(str(rotEnergy)+' ')
75     MESSFile.write('\n')
76     MESSFile.write(' '*4+'End\n')
77     # writes frequcies section subtracts number of rotors + 1
imaginary frequency!
78     MESSFile.write(' '*4+'Frequencies [1/cm]'+ ' '*4+str(len(TSW_freqs)-(
len(TSW_rotors)+1))+'\n ')
79     counter = 1
80     for freq in TSW_freqs[1:]:
81         MESSFile.write(' '*5)
82         MESSFile.write(' '+str(round(freq, 2)))
83         if counter == 10:
84             MESSFile.write('\n ')
85             counter = 0
86         counter += 1
87     MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
-----!')
88     MESSFile.write('\n'+ ' '*4+'ZeroEnergy[kcal/mol]'+ ' '*4+'--- ZERO
ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
89     # change for higher excited states / pulls charge and multiplicity
from m062x file
90     MESSFile.write('\n'+ ' '*4+'ElectronicLevels [1/cm]'+ ' '*4+str(1)+'\n
'+ ' '*8+TSW_charge_multiplicity[0]+' '*2+TSW_charge_multiplicity[1]+
'\n'+ ' '*4+'End\n')
91     MESSFile.write(' '*4+'Tunneling'+ ' '*16+'Eckart\n')
92     MESSFile.write(' '*4+'ImaginaryFrequency [1/cm]'+ ' '*4+str(TSW_freqs
[0])+'\n') # first freq is list the imaginary frequency!
93     MESSFile.write(' '*4+'WellDepth[kcal/mol]'+ ' '*4+'--- FORWARD
BARRIER OF TS ---\n')
94     MESSFile.write(' '*4+'WellDepth[kcal/mol]'+ ' '*4+'--- BACKWARD
BARRIER OF TS ---\n'+ ' '*4+'End\n'+ 'End\n')
95     MESSFile.close()
96
97 # ----- CREATES AND WRITES A WELL
SECTION ----- #
98 # Place well's m062x file inside the coresponding W# directory!
99 # this function pulls pathway, m062xFileName from script
```

```
100 def write_Well(W_xyz_geom, W_freqs, W_charge_multiplicity, W_rots,
101 rotorEnergies, path_dir, m062xFileName):
102     MESSFile = open('MESSFile.inp', 'a')
103     # gets path folder name using os library
104     pathway = os.path.basename(os.path.normpath(path_dir))
105     MESSFile.write('Well'+ ' '*8+pathway+ ' '*8+# '+m062xFileName+'\n')
106     MESSFile.write(' '*4+'Species\n')
107     MESSFile.write(' '*8+'RRHO\n')
108     MESSFile.write(' '*4+'Geometry [angstrom]'+ ' '*8+str(len(W_xyz_geom)
109 )+'\n')
110     # writes geometry section
111     for line in W_xyz_geom:
112         line = line.split(',')
113         MESSFile.write(' '*5+line[0]+ ' '*8+line[1]+ ' '*4+line[2]+ ' '*4+
114 line[3]+'\n')
115     MESSFile.write(' '*4+'Core RigidRotor\n')
116     MESSFile.write(' '*8+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
117 FACTOR HERE ----\n')
118     MESSFile.write(' '*4+'End\n')
119     # writes rotor section
120     for i in range(len(W_rots)):
121         max_atom_number = max(W_rots[i])
122         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
123         MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
124         MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
125         MESSFile.write(' '*8+'Axis'+ ' '*22+str(W_rots[i][1])+ ' '+str(
126 W_rots[i][2])+'\n')
127     # calculates rotor symmetry
128     truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
129 energy in rotEnergies]
130     rotorSymmetry = '1'
131     if len(truncated_rotEnergies) == 4:
132         if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
133             rotorSymmetry = '2'
134     if len(truncated_rotEnergies) == 6:
135         if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
136             rotorSymmetry = '3'
137     if len(truncated_rotEnergies) == 8:
138         if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
139             rotorSymmetry = '4'
140     MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\n')
141     rotEnergies = [round(energy, 2) for energy in rotEnergies]
142     MESSFile.write(' '*8+'Potential [kcal/mol]'+ ' '*8+str(int(len(
143 rotEnergies)/int(rotorSymmetry))+'\n')
144     MESSFile.write(' '*9)
145     if not rotorSymmetry == '1' :
146         for i in range(len(rotEnergies)):
147             MESSFile.write(str(rotEnergies[i])+ ' ')
```

```

141         if i == 1:
142             break
143     else:
144         for rotEnergy in rotEnergies:
145             MESSFile.write(str(rotEnergy)+' ')
146         MESSFile.write('\n')
147         MESSFile.write(' '*4+'End\n')
148     # writes frequencies section subtracts number of rotors
149     MESSFile.write(' '*4+'Frequencies [1/cm]'+ ' '*4+str(len(W_freqs)-(
150 len(W_rots)))+'\n ')
151     counter = 1
152     for freq in W_freqs:
153         MESSFile.write(' '*5)
154         MESSFile.write(' '+str(round(freq, 2)))
155         if counter == 10:
156             MESSFile.write('\n ')
157             counter = 0
158             counter += 1
159     MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
160 -----!')
161     MESSFile.write('\n'+ ' '*4+'ZeroEnergy[kcal/mol]'+ ' '*4+'--- ZERO
162 ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
163     # change for higher excited states / pulls charge and multiplicity
164     from m062x file
165     MESSFile.write('\n'+ ' '*4+'ElectronicLevels [1/cm]'+ ' '*4+str(1)+'\n
166 '+ ' '*8+W_charge_multiplicity [0]'+ ' '*2+W_charge_multiplicity [1]+'\n'
167 '+ ' '*4+'End\n'+ 'End\n')
168     MESSFile.close()
169
170 # ----- CREATES AND WRITES THE BARRIER
171 SECTION FOR A TS ----- #
172 def write_TS_Barrier(xyz_geom, rots, freqs, rotorEnergies,
173 charge_multiplicity, path_dir, m062xFileName, number_of_wells,
174 h_abstraction):
175     MESSFile = open('MESSFile.inp', 'a')
176     # gets path folder name using os library
177     pathway = os.path.basename(os.path.normpath(path_dir))
178     # extracts the number from the pathway (ie. returns 8 for the P8
179 folder)
180     path_num = ''.join([item for item in pathway if item.isdigit()])
181     # ----- Naming assumes Barrier connects W1 to
182 products!(ie. B# W1 P#) -----#
183     if h_abstraction:
184         MESSFile.write('Barrier'+ ' '*8+'B'+str(int(path_num)+
185 number_of_wells)+' '*2+'W1'+ ' '*2+'pathway'+ ' '*4+'# '+m062xFileName+'
186 + [H]'+ '\n')
187     else:

```



```
175     MESSFile.write('Barrier'+ ' '*8+'B'+str(int(path_num)+
number_of_wells)+' '*2+'W1'+ ' '*2+pathway+' '*4+'# '+m062xFileName+'
\n')
176     MESSFile.write(' '*4+'Variational\n')
177     MESSFile.write(' '*8+'RRHO\n')
178     MESSFile.write(' '*4+'Geometry [angstrom]'+ ' '*8+str(len(xyz_geom))+
\n')
179     # writes geometry section
180     for line in xyz_geom:
181         line = line.split(',')
182         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
line[3]+' \n')
183     MESSFile.write(' '*4+'Core RigidRotor\n')
184     MESSFile.write(' '*8+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
FACTOR HERE ----\n')
185     MESSFile.write(' '*4+'End\n')
186     # writes rotor section
187     for i in range(len(rots)):
188         max_atom_number = max(rots[i])
189         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
190         MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
191         MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
192         MESSFile.write(' '*8+'Axis'+ ' '*22+str(rots[i][1])+' '+str(rots
[i][2])+' \n')
193         # calculates rotor symmetry
194         truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
energy in rotEnergies]
195         rotorSymmetry = '1'
196         if len(truncated_rotEnergies) == 4:
197             if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
198                 rotorSymmetry = '2'
199         if len(truncated_rotEnergies) == 6:
200             if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
201                 rotorSymmetry = '3'
202         if len(truncated_rotEnergies) == 8:
203             if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
204                 rotorSymmetry = '4'
205         MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+' \n')
206         rotEnergies = [round(energy, 2) for energy in rotEnergies]
207         MESSFile.write(' '*8+'Potential [kcal/mol]'+ ' '*8+str(int(len(
rotEnergies)/int(rotorSymmetry))+' \n')
208         MESSFile.write(' '*9)
209         if not rotorSymmetry == '1' :
210             for i in range(len(rotEnergies)):
211                 MESSFile.write(str(rotEnergies[i])+' ')
212                 if i == 1:
213                     break
214         else:
```

```
215         for rotEnergy in rotEnergies:
216             MESSFile.write(str(rotEnergy)+' ')
217         MESSFile.write('\n')
218         MESSFile.write(' '*4+'End\n')
219         # writes frequencies section subtracts number of rotors + 1
imaginary frequency!
220         MESSFile.write(' '*4+'Frequencies [1/cm]'+ ' '*4+str(len(freqs)-(len(
rots)+1))+'\n ')
221         counter = 1
222         for freq in freqs[1:]:
223             MESSFile.write(' '*5)
224             MESSFile.write(' '+str(round(freq, 2)))
225             if counter == 10:
226                 MESSFile.write('\n ')
227                 counter = 0
228             counter += 1
229         MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
-----!')
230         MESSFile.write('\n'+ ' '*4+'ZeroEnergy [kcal/mol]'+ ' '*4+'--- ZERO
ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
231         # change for higher excited states / pulls charge and multiplicity
from m062x file
232         MESSFile.write('\n'+ ' '*4+'ElectronicLevels [1/cm]'+ ' '*4+str(1)+'\n
'+ ' '*8+charge_multiplicity[0]+' '*2+charge_multiplicity[1]+' '\n'+ '
'*4+'End\n')
233         MESSFile.write(' '*4+'Tunneling'+ ' '*16+'Eckart\n')
234         MESSFile.write(' '*4+'ImaginaryFrequency [1/cm]'+ ' '*4+str(freqs[0])
+'\n') # first freq is list the imaginary frequency!
235         MESSFile.write(' '*4+'WellDepth [kcal/mol]'+ ' '*4+'--- FORWARD
BARRIER OF TS ---\n')
236         MESSFile.write(' '*4+'WellDepth [kcal/mol]'+ ' '*4+'--- BACKWARD
BARRIER OF TS ---\n'+ ' '*4+'End\n'+ 'End\n')
237         MESSFile.close()
238 # ----- WRITES THE BIMOLECULAR SECTION FOR A
TS ----- #
239 # THIS CODE ASSUMES THE TS CONNECTS TO TWO FRAGMENTS!!! -> CHANGE IF
NOT!
240 # TS log must end with _m062x.log: (ie. TS_CH20_CCCOCCC_m062x.log)
241 # Fragment folder that stores must have the name of the TS: (ie.
TS_CH20_CCCOCCC)
242 # Fragment logs inside the folder must end with _m062x.log: (ie.
CH20_m062x.log and CCCOCCC_m062x.log)
243 # fragments folder must be named 'fragments'
244 # ----- Access each fragment's log file and extract
geometries, rotors and frequencies ----- #
245
246 # This function takes in root and fragment's directory paths from from
script
```

```
247 def write_TS_Bimolecular(iteration, fragments_naming, fragmentFile,
248 fragments_directory, path_dir, m062xFragmentFileList, fr_xyz_geom,
249 fr_freqs, fr_rots, rotorEnergies, fr_charge_multiplicity,
250 h_abstraction):
251     MESSFile = open('MESSFile.inp', 'a')
252     # gets path folder name using os library
253     pathway = os.path.basename(os.path.normpath(path_dir))
254     # makes it so Bimolecular header is written only once!
255     if iteration == 1:
256         if h_abstraction:
257             MESSFile.write('Bimolecular'+ ' '*8+pathway+' '*4+'# '+
258 fragments_naming+' + [H]'+'\n')
259         else:
260             MESSFile.write('Bimolecular'+ ' '*8+pathway+' '*4+'# '+
261 fragments_naming+'\n')
262     MESSFile.write(' '*4+'Fragment'+ ' '*2+fragmentFile.split('_m062x.
263 log')[0]+'\n')
264     MESSFile.write(' '*8+'RRHO\n')
265     MESSFile.write(' '*4+'Geometry [angstrom]'+ ' '*8+str(len(fr_xyz_geom
266 ))+'\n')
267     # writes geometry section
268     for line in fr_xyz_geom:
269         line = line.split(',')
270         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
271 line[3]+'\n')
272     MESSFile.write(' '*4+'Core RigidRotor\n')
273     MESSFile.write(' '*8+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
274 FACTOR HERE ----\n')
275     MESSFile.write(' '*4+'End\n')
276     # writes rotor section
277     for i in range(len(fr_rots)):
278         max_atom_number = max(fr_rots[i])
279         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
280         MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
281         MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
282         MESSFile.write(' '*8+'Axis'+ ' '*22+str(fr_rots[i][1])+' '+str(
283 fr_rots[i][2])+'\n')
284     # calculates rotor symmetry
285     truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
286 energy in rotEnergies]
287     rotorSymmetry = '1'
288     if len(truncated_rotEnergies) == 4:
289         if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
290             rotorSymmetry = '2'
291     if len(truncated_rotEnergies) == 6:
292         if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
293             rotorSymmetry = '3'
294     if len(truncated_rotEnergies) == 8:
```

```

284         if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
285             rotorSymmetry = '4'
286             MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\n')
287             rotEnergies = [round(energy, 2) for energy in rotEnergies]
288             MESSFile.write(' '*8+'Potential[kcal/mol]'+ ' '*8+str(int(len(
rotEnergies)/int(rotorSymmetry)))+'\n')
289             MESSFile.write(' '*9)
290             if not rotorSymmetry == '1' :
291                 for i in range(len(rotEnergies)):
292                     MESSFile.write(str(rotEnergies[i])+ ' ')
293                     if i == 1:
294                         break
295             else:
296                 for rotEnergy in rotEnergies:
297                     MESSFile.write(str(rotEnergy)+' ')
298             MESSFile.write('\n')
299             MESSFile.write(' '*4+'End\n')
300             # writes frequcies section subtracts number of rotors!
301             MESSFile.write(' '*4+'Frequencies [1/cm]'+ ' '*4+str(len(fr_freqs)-(
len(fr_rots)))+'\n ')
302             counter = 1
303             for freq in fr_freqs:
304                 MESSFile.write(' '*5)
305                 MESSFile.write(' '+str(round(freq, 2)))
306                 if counter == 10:
307                     MESSFile.write('\n ')
308                     counter = 0
309                 counter += 1
310             MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
-----!')
311             MESSFile.write('\n'+ ' '*4+'ZeroEnergy[kcal/mol]'+ ' '*4+'0')
312             # change for higher excited states / pulls charge and multiplicity
from m062x file
313             MESSFile.write('\n'+ ' '*4+'ElectronicLevels [1/cm]'+ ' '*4+str(1)+'\n
'+ ' '*8+fr_charge_multiplicity[0]+' '*2+fr_charge_multiplicity[1]+' \
n'+ ' '*4+'End\n')
314             if h_abstraction:
315                 MESSFile.write(' '*4+'Fragment H\n'+ ' '*6+'Atom\n'+ ' '*8+'
Mass[amu] 1\n'+ ' '*8+'ElectronicLevels [1/cm] 1\n'+ ' '*6+' 0
2'+ '\n End\n')
316             # writes ground energy at the end of the section
317             if iteration == len(m062xFragmentFileList):
318                 MESSFile.write(' '*4+'GroundEnergy[kcal/mol]'+ ' '*8+' ----
Ground Energy Value from High Energy Calcs -----'+ '\n'+ 'End\n')
319                 MESSFile.close()
320             # goes back to fragment directory
321             os.chdir(fragments_directory)
322

```

```
323
324 # ----- WRITES THE BARRIER SECTION FOR A BF
325 # ----- #
326 # Place two fragment m062x files in the pathway folder (ie. P3)
327 # Fragment files must begin with Bi_... and end with _m062x.log (ie.
328 # Bi_COH_E9-27_m062x.log)
329 # ----- Access each fragment's log file and extract
330 # geometries, rotors and frequencies ----- #
331 # fragment#_info contains [xyz_geom, freqs, charge/multiplicity and
332 # rotors]
333 def write_BF_Barrier(fragments_naming, fragment1_info,
334 fr1_rotorEnergies, fragment2_info, fr2_rotorEnergies, pathway,
335 number_of_wells, m062xFileName, h_abstraction):
336     MESSFile = open('MESSFile.inp', 'a')
337     # extracts the number from the pathway (ie. returns 8 for the P8
338     # folder)
339     path_num = ''.join([item for item in pathway if item.isdigit()])
340     # ----- Naming assumes Barrier connects W1 to
341     # products!(ie. B# W1 P#) -----#
342     if h_abstraction:
343         MESSFile.write('Barrier'+ ' '*8+'B'+str(int(path_num)+
344 number_of_wells)+' '*2+'W1'+ ' '*2+pathway+' '*4+'# '+m062xFileName+'
345 + [H]'+'\n')
346     else:
347         MESSFile.write('Barrier'+ ' '*8+'B'+str(int(path_num)+
348 number_of_wells)+' '*2+'W1'+ ' '*2+pathway+' '*4+'# '+
349 fragments_naming+'\n')
350     MESSFile.write(' '*4+'RRHO\n')
351     MESSFile.write(' '*8+'Stoichiometry'+ ' '*8+'-----ADD MOLECULAR
352 FORMULA -----\n')
353     MESSFile.write(' '*8+'Core'+ ' '*4+'PhaseSpaceTheory\n')
354     MESSFile.write(' '*4+'FragmentGeometry[angstrom]'+ ' '*8+str(len(
355 fragment1_info[0]))+'\n')
356     # writes geometry section for fragment 1
357     for line in fragment1_info[0]:
358         line = line.split(',')
359         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
360 line[3]+'*\n')
361     # writes geometry section for fragment 2
362     if h_abstraction:
363         MESSFile.write(' '*4+'FragmentGeometry[angstrom]          1\n'+
364 '*5+'H          0.000000    0.000000    0.000000\n')
365     else:
366         MESSFile.write(' '*4+'FragmentGeometry[angstrom]'+ ' '*8+str(len(
367 fragment2_info[0]))+'\n')
368     for line in fragment2_info[0]:
369         line = line.split(',')
370
```

```
354         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+'
'*4+line[3]+'\\n')
355     MESSFile.write(' '*4+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
FACTOR HERE ----\\n')
356     MESSFile.write(' '*8+'PotentialPrefactor[au]'+ ' '*4+' -----
ADD POTENTIAL PREFACTOR HERE! -----\\n')
357     MESSFile.write(' '*8+'PotentialPowerExponent'+ ' '*4+'6\\n')
358     MESSFile.write(' '*4+'End\\n')
359     # writes rotor section for fragment 1
360     for i in range(len(fragment1_info[3])):
361         max_atom_number = max(fragment1_info[3][i])
362         fr1_rotEnergies = fr1_rotorEnergies['D'+str(max_atom_number-3)]
363         MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\\n')
364         MESSFile.write(' '*4+'Geometry[angstrom]'+ ' '*8+str(len(
fragment1_info[0]))+'\\n')
365         for line in fragment1_info[0]:
366             line = line.split(',')
367             MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+'
'*4+line[3]+'\\n')
368             MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\\n')
369             MESSFile.write(' '*8+'Axis'+ ' '*22+str(fragment1_info[3][i][1])
+' '+str(fragment1_info[3][i][2])+'\\n')
370             # calculates rotor symmetry
371             fr1_truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
energy in fr1_rotEnergies]
372             rotorSymmetry = '1'
373             if len(fr1_truncated_rotEnergies) == 4:
374                 if fr1_truncated_rotEnergies == fr1_truncated_rotEnergies
[:2]*2:
375                     rotorSymmetry = '2'
376                 if len(fr1_truncated_rotEnergies) == 6:
377                     if fr1_truncated_rotEnergies == fr1_truncated_rotEnergies
[:2]*3:
378                         rotorSymmetry = '3'
379                     if len(fr1_truncated_rotEnergies) == 8:
380                         if fr1_truncated_rotEnergies == fr1_truncated_rotEnergies
[:2]*4:
381                             rotorSymmetry = '4'
382             MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\\n')
383             fr1_rotEnergies = [round(energy, 2) for energy in
fr1_rotEnergies]
384             MESSFile.write(' '*8+'Potential[kcal/mol]'+ ' '*8+str(int(len(
fr1_rotEnergies)/int(rotorSymmetry)))+'\\n')
385             MESSFile.write(' '*9)
386             if not rotorSymmetry == '1' :
387                 for i in range(len(fr1_rotEnergies)):
388                     MESSFile.write(str(fr1_rotEnergies[i])+' ')
389                     if i == 1:
```

```

390         break
391     else:
392         for rotEnergy in fr1_rotEnergies:
393             MESSFile.write(str(rotEnergy)+' ')
394         MESSFile.write('\n')
395         MESSFile.write(' '*4+'End\n')
396     if not h_abstraction:
397         # writes rotor section for fragment 2
398         for i in range(len(fragment2_info[3])):
399             max_atom_number = max(fragment2_info[3][i])
400             fr2_rotEnergies = fr2_rotorEnergies['D'+str(max_atom_number
401 -3)]
402             MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
403             MESSFile.write(' '*4+'Geometry[angstrom]+ ' '*8+str(len(
404 fragment2_info[0]))+'\n')
405             for line in fragment2_info[0]:
406                 line = line.split(',')
407                 MESSFile.write(' '*5+line[0]+ ' '*8+line[1]+ ' '*4+line
408 [2]+ ' '*4+line[3]+'\n')
409                 MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
410                 MESSFile.write(' '*8+'Axis'+ ' '*22+str(fragment2_info[3][i
411 ][1])+ ' '+str(fragment2_info[3][i][2])+'\n')
412                 # calculates rotor symmetry
413                 fr2_truncated_rotEnergies = [math.floor(energy*10**2)/10**2
414 for energy in fr2_rotEnergies]
415                 rotorSymmetry = '1'
416                 if len(fr2_truncated_rotEnergies) == 4:
417                     if fr2_truncated_rotEnergies ==
418 fr2_truncated_rotEnergies[:2]*2:
419                         rotorSymmetry = '2'
420                     if len(fr2_truncated_rotEnergies) == 6:
421                         if fr2_truncated_rotEnergies ==
422 fr2_truncated_rotEnergies[:2]*3:
423                             rotorSymmetry = '3'
424                         if len(fr2_truncated_rotEnergies) == 8:
425                             if fr2_truncated_rotEnergies ==
426 fr2_truncated_rotEnergies[:2]*4:
427                                 rotorSymmetry = '4'
428                 MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\n')
429                 fr2_rotEnergies = [round(energy, 2) for energy in
430 fr2_rotEnergies]
431                 MESSFile.write(' '*8+'Potential[kcal/mol]+ ' '*8+str(int(
432 len(fr2_rotEnergies)/int(rotorSymmetry))+'\n')
433                 MESSFile.write(' '*9)
434                 if not rotorSymmetry == '1' :
435                     for i in range(len(fr2_rotEnergies)):
436                         MESSFile.write(str(fr2_rotEnergies[i])+ ' ')
437                     if i == 1:

```

```
428         break
429     else:
430         for rotEnergy in fr2_rotEnergies:
431             MESSFile.write(str(rotEnergy)+' ')
432             MESSFile.write('\n')
433             MESSFile.write(' '*4+'End\n')
434     # sums total number of frequencies and extracts number of
435     # rotors for both fragments
436     total_frequencies = len(fragment1_info[1])+len(fragment2_info
437     [1])-len(fragment1_info[3])-len(fragment2_info[3])
438     else:
439         total_frequencies = len(fragment1_info[1])-len(fragment1_info
440         [3])
441     MESSFile.write(' '*4+'Frequencies [1/cm]'+ ' '*4+str(
442     total_frequencies)+'\n ')
443     counter = 1
444     for freq in fragment1_info[1]:
445         MESSFile.write(' '*5)
446         MESSFile.write(' '+str(round(freq, 2)))
447         if counter == 10:
448             MESSFile.write('\n ')
449             counter = 0
450             counter += 1
451     MESSFile.write('\n ')
452     counter = 1
453     if not h_abstraction:
454         for freq in fragment2_info[1]:
455             MESSFile.write(' '*5)
456             MESSFile.write(' '+str(round(freq, 2)))
457             if counter == 10:
458                 MESSFile.write('\n ')
459                 counter = 0
460                 counter += 1
461     MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
462     -----!')
463     MESSFile.write('\n'+ ' '*4+'ZeroEnergy[kcal/mol]'+ ' '*4+'--- ZERO
464     ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
465     # change for higher excited states / pulls charge and multiplicity
466     # from m062x file
467     # for a BF, both fragments have charge and multiplicity 0 2
468     MESSFile.write('\n'+ ' '*4+'ElectronicLevels [1/cm]'+ ' '*4+str(1)+'\n
469     '+ ' '*8+fragment1_info[2][0]+' '*2+fragment1_info[2][1)+'\n'+ ' '*4+'
470     End\n')
471     MESSFile.close()
472
473 # ----- WRITES THE BIMOLECULAR SECTION FOR A
474 # BF ----- #
475 # Place two fragment m062x files in the pathway folder (ie. P3)
```



```
466 # Fragment files must begin with Bi_... and end with _m062x.log (ie.
    Bi_COH_E9-27_m062x.log)
467 # ----- Access each fragment's log file and extract
    geometries, rotors and frequencies ----- #
468
469 # This function takes in root pathway's directory paths from from
    script
470 def write_BF_Bimolecular(iteration, root_directory, fragments_naming,
    fragmentFile, path_dir, m062xFileList, fr_xyz_geom, fr_freqs,
    fr_rots, rotorEnergies, fr_charge_multiplicity, h_abstraction):
471     MESSFile = open('MESSFile.inp', 'a')
472     # gets path folder name using os library
473     pathway = os.path.basename(os.path.normpath(path_dir))
474     # makes it so Bimolecular header is written only once!
475     if iteration == 1:
476         if h_abstraction:
477             MESSFile.write('Bimolecular'+ ' '*8+pathway+' '*4+'# '+
    fragmentFile.split('_m062x.log')[0]+' + [H]'+'\n')
478         else:
479             MESSFile.write('Bimolecular'+ ' '*8+pathway+' '*4+'# '+
    fragments_naming+'\n')
480             MESSFile.write(' '*4+'Fragment'+ ' '*2+fragmentFile.split('_m062x.
    log')[0]+''\n')
481             MESSFile.write(' '*8+'RRHO\n')
482             MESSFile.write(' '*4+'Geometry [angstrom]'+ ' '*8+str(len(fr_xyz_geom
    ))+'\n')
483             # writes geometry section
484             for line in fr_xyz_geom:
485                 line = line.split(',')
486                 MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
    line[3]+''\n')
487             MESSFile.write(' '*4+'Core RigidRotor\n')
488             MESSFile.write(' '*8+'SymmetryFactor'+ ' '*4+'--- INCLUDE SYMMETRY
    FACTOR HERE ----\n')
489             MESSFile.write(' '*4+'End\n')
490             # writes rotor section
491             for i in range(len(fr_rots)):
492                 max_atom_number = max(fr_rots[i])
493                 rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
494                 MESSFile.write(' '*4+'Rotor'+ ' '*8+'Hindered\n')
495                 MESSFile.write(' '*8+'Group'+ ' '*21+'numbers!\n')
496                 MESSFile.write(' '*8+'Axis'+ ' '*22+str(fr_rots[i][1])+' '+str(
    fr_rots[i][2])+'\n')
497             # calculates rotor symmetry
498             truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
    energy in rotEnergies]
499             rotorSymmetry = '1'
500             if len(truncated_rotEnergies) == 4:
```

```
501         if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
502             rotorSymmetry = '2'
503         if len(truncated_rotEnergies) == 6:
504             if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
505                 rotorSymmetry = '3'
506         if len(truncated_rotEnergies) == 8:
507             if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
508                 rotorSymmetry = '4'
509         MESSFile.write(' '*8+'Symmetry'+ ' '*19+rotorSymmetry+'\n')
510         rotEnergies = [round(energy, 2) for energy in rotEnergies]
511         MESSFile.write(' '*8+'Potential[kcal/mol]'+ ' '*8+str(int(len(
rotEnergies)/int(rotorSymmetry)))+'\n')
512         MESSFile.write(' '*9)
513         if not rotorSymmetry == '1':
514             for i in range(len(rotEnergies)):
515                 MESSFile.write(str(rotEnergies[i])+ ' ')
516                 if i == 1:
517                     break
518         else:
519             for rotEnergy in rotEnergies:
520                 MESSFile.write(str(rotEnergy)+' ')
521         MESSFile.write('\n')
522         MESSFile.write(' '*4+'End\n')
523         # writes frequcies section subtracts number of rotors!
524         MESSFile.write(' '*4+'Frequencies[1/cm]'+ ' '*4+str(len(fr_freqs)-(
len(fr_rots)))+'\n ')
525         counter = 1
526         for freq in fr_freqs:
527             MESSFile.write(' '*5)
528             MESSFile.write(' '+str(round(freq, 2)))
529             if counter == 10:
530                 MESSFile.write('\n ')
531                 counter = 0
532             counter += 1
533         MESSFile.write('\n'+ ' '*5+'!----- INCLUDE ROTOR FREQUENCIES HERE
-----!')
534         MESSFile.write('\n'+ ' '*4+'ZeroEnergy[kcal/mol]'+ ' '*4+'--- ZERO
ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
535         # change for higher excited states / pulls charge and multiplicity
from m062x file
536         MESSFile.write('\n'+ ' '*4+'ElectronicLevels[1/cm]'+ ' '*4+str(1)+'\n
'+ ' '*8+fr_charge_multiplicity[0]+' '*2+fr_charge_multiplicity[1]+' \
n'+ ' '*4+'End\n')
537         # Adds H atom fragment section
538         if h_abstraction:
539             MESSFile.write(' '*4+'Fragment H\n'+ ' '*6+'Atom\n'+ ' '*8+'
Mass[amu] 1\n'+ ' '*8+'ElectronicLevels[1/cm] 1\n'+ ' '*6+' 0
2'+ '\n End\n')
```

```

540 # writes ground energy at the end of the section
541 if iteration == len(m062xFileList):
542     MESSFile.write(' '*4+'GroundEnergy[kcal/mol]'+ ' '*8+ ' ----
Ground Energy Value from High Energy Calcs -----'+'\n'+ 'End\n')
543     MESSFile.close()
544 # goes back to BF pathway directory
545 os.chdir(root_directory+'\\'+pathway)

```

C.4 writeMessFile.py

```

1 from messParsing import *
2 from geometryInfo import *
3 from get_energies import *
4 from os.path import basename
5
6 # Energies Dictionary, will contain all energies for each molecule to
   be added into energies spredsheat.
7 energiesDictionary = {}
8 all_molecules = []
9
10 # Condition to write excel spreadsheet
11 writeExcel = str(input("Do you want to create an Excel spreadsheet? (y/
n): "))
12 if writeExcel == 'y':
13     createExcel = True
14 else:
15     createExcel = False
16
17 ## -- Adds energies from m062x and high energy calcs into the
   energiesDictionary -- ##
18 def add_energies(pathway, FileList, non_ts_prods, non_ts,
energiesDictionary, createExcel=False):
19     num_fragments = len([file for file in FileList if file.endswith('_
m062x.log') and not file.startswith('TS') and pathway.startswith('P
')])
20     FileList = sorted(FileList)
21     for filename in FileList:
22         file = open(filename, 'r')
23         filestring = file.read().replace('\n', '').replace(' ', '')
24         file.close()
25         if filename.endswith('E.log'):
26             # gets energy from CCSD(T)
27             E_ccsdt = filestring.split('\CCSD(T)')[1].split('\ ') [0]
28             E_ccsdt = float(re.findall(r'-?\d*\.\d*', E_ccsdt)[0])
29             # gets T1 diagnostic
30             t1diag = filestring.split('T1Diagnostic')[-1]
31             t1diag = float(re.findall(r'-?\d*\.\d*', t1diag)[0])
32         if filename.endswith('E1.log'):

```

```
33     E1_ccsdt = filestring.split('\CCSD(T)')[1].split('\')[0]
34     E1_ccsdt = float(re.findall(r'?\d*\.\d*', E1_ccsdt)[0])
35     if filename.endswith('m062x.log'):
36         zeroPoint = filestring.split('\ZeroPoint')[-1]
37         zeroPoint = float(re.findall(r'?\d*\.\d*', zeroPoint)[0])
38         molecule = filename.split('_m062x.log')[0]
39         if createExcel:
40             energiesDictionary[molecule] = [zeroPoint, E_ccsdt,
E1_ccsdt, t1diag]
41             # this condition catches single fragments (assumed to
be accompanied by H)
42             if num_fragments == 1:
43                 energiesDictionary['H'] = [0, -0.499278,
-0.499809811, 0]
44                 if not molecule.startswith('TS') and basename(os.getcwd
()) != 'fragments':
45                     non_ts_prods.append(molecule)
46                     if not molecule.startswith('TS'):
47                         non_ts.append(molecule)
48                     all_molecules.append(molecule)
49
50     return non_ts_prods, non_ts
51 ## -- Writes MESS file -- ##
52 def writeMessFile():
53     global non_ts_prods, non_ts
54     non_ts = []
55     non_ts_prods = []
56     #get current working directory (root)
57     root_directory = os.getcwd()
58     write_Header()
59
60     # list that includes all reaction pathways (W1, P1, P2 ... etc.).
Makes sure that wells (W) go first!
61     pathways = []
62     for item in os.listdir():
63         if len(item)<3 and item[0] in ['P', 'W']:
64             pathways.append(item)
65     pathways = sorted(pathways)
66     pathways.sort(key = lambda pathways: pathways[0], reverse=True)
67
68     # counts the number of wells in the mechanism, excludes parent well
number_of_wells = sum('W' in path for path in pathways) - 1
69     lastParse = False
70     for pathway in pathways:
71         print('Working on: ', pathway)
72         if pathway == pathways[-1]:
73             lastParse = True
74         path_dir = root_directory+'\'+pathway
```

```
76     #looks into the TS folder and extract xyz geom from m062x file
77     os.chdir(path_dir)
78
79     m062xFileList = [filename for filename in os.listdir() if
80 filename.endswith("m062x.log")]
81     m062xFileName = m062xFileList[0]
82
83     # writes well section
84     if pathway.startswith('W'):
85         # adds energies from all fragment files into 'energies'
86         dictionary
87         try:
88             non_ts_prods, non_ts = add_energies(pathway, os.listdir
89             ()), non_ts_prods, non_ts, energiesDictionary, createExcel)
90         except PermissionError:
91             pass
92
93     if len(m062xFileList)>1:
94         # extracts Well's filename for Well Section
95         m062xFileName = [file for file in m062xFileList if
96 file.startswith('W')]
97         m062xFileName = m062xFileName[0]
98
99     # setting bond threshold for non-TS molecules
100    bond_thresh = 1.2
101    ## -- Topology Function Calls For Wells -- ##
102    # get xyz geometry and filename
103    W_xyz_geom = get_xyzGeom(m062xFileName)
104    # get frequencies from m062x file
105    W_freqs, W_charge_multiplicity = get_frequencies(
106 m062xFileName)
107    # get rotors from geometry and get_geometry (rotors script)
108    functions
109    W_rots = get_rotors(W_xyz_geom, m062xFileName, bond_thresh)
110    # finds corresponding z-matrix dihedral for each rotor
111    W_dihedrals = ['D'+str(max(rot)-3) for rot in W_rots]
112
113    print(W_dihedrals, m062xFileName)
114    rotorEnergies = get_peaks_valleys(W_dihedrals,
115 m062xFileName)
116
117    # Change back to root directory and write in Mess input
118    there!
119    os.chdir(root_directory)
120    write_Well(W_xyz_geom, W_freqs, W_charge_multiplicity,
121 W_rots, rotorEnergies, path_dir, m062xFileName)
122
123    if len(m062xFileList)>1:
```

```
115         # extracts name of Well's TS for Well's Barrier Section
116         TSWellFileName = [file for file in m062xFileList if
file.startswith('TS')]
117         TSWellFileName = TSWellFileName[0]
118
119         #looks into the TS folder and extract xyz geom from
m062x file
120         os.chdir(path_dir)
121
122         # change threshold to 1.4 for all files here bc they
are TS!
123         bond_thresh = 1.4
124         ## -- Topology Function Calls For Well's TS -- ##
125         TSW_xyz_geom = get_xyzGeom(TSWellFileName)
126         TSW_freqs, TSW_charge_multiplicity = get_frequencies(
TSWellFileName)
127         TSW_rotors = get_rotors(TSW_xyz_geom, TSWellFileName,
bond_thresh, TS=True)
128         # finds corresponding z-matrix dihedral for each rotor
129         TSW_dihedrals = ['D'+str(max(rot)-3) for rot in
TSW_rotors]
130
131         rotorEnergies = get_peaks_valleys(TSW_dihedrals,
TSWellFileName)
132
133         # Change back to root directory and write in Mess input
there!
134         os.chdir(root_directory)
135         write_Well_Barrier(TSW_xyz_geom, TSW_freqs,
TSW_charge_multiplicity, TSW_rotors, rotorEnergies, path_dir,
m062xFileName)
136
137         continue
138         continue
139
140     if m062xFileName.startswith('TS'):
141         TS = True
142     else:
143         TS = False
144         bond_thresh = 1.2
145
146     # This section writes transition states
147     if TS:
148         # adds energies from all fragment files into 'energies'
dictionary
149         try:
150             non_ts_prods, non_ts = add_energies(pathway, os.listdir
()), non_ts_prods, non_ts, energiesDictionary, createExcel)
```

```
151         except PermissionError:
152             pass
153
154         fragments_directory = root_directory+'\\'+pathway+'\\
fragments'
155         # changes to fragments' directory to write bimolecular
section
156         os.chdir(fragments_directory)
157
158         # adds energies from all fragment files into 'energies'
dictionary
159         non_ts_prods, non_ts = add_energies(pathway, os.listdir(),
non_ts_prods, non_ts, energiesDictionary, createExcel)
160
161         m062xFragmentFileList = [filename for filename in os.
listdir() if filename.endswith("m062x.log")]
162         if len(m062xFragmentFileList)>1:
163             h_abstraction = False
164             # gets fragments' names from file for parsing
165             frag1 = m062xFragmentFileList[0].split('_m062x.log')[0]
166             frag2 = m062xFragmentFileList[1].split('_m062x.log')[0]
167             # takes into account the cases with 3 products!
168             if len(m062xFragmentFileList) > 2:
169                 frag3 = m062xFragmentFileList[2].split('_m062x.log'
) [0]
170                 fragments_naming = frag1+' '*2+'+'+' '*2+frag2+' '
*2+'+'+frag3
171             else:
172                 fragments_naming = frag1+' '*2+'+'+' '*2+frag2
173             # Accounts for cases where there is only one product m062x
file, H- abstractions!
174             else:
175                 h_abstraction = True
176                 non_ts.append('H')
177                 fragments_naming = m062xFragmentFileList[0].split('_
m062x.log')[0]
178             ## -- Topology Function Calls For Fragments -- ##
179             # change threshold to 1.2 for all fragment files here bc
they are not a TS!
180             bond_thresh = 1.2
181             iteration = 1
182             for fragmentFile in m062xFragmentFileList:
183                 fr_xyz_geom = get_xyzGeom(fragmentFile)
184                 fr_freqs, fr_charge_multiplicity = get_frequencies(
fragmentFile)
185                 fr_rotors = get_rotors(fr_xyz_geom, fragmentFile,
bond_thresh)
186                 # finds corresponding z-matrix dihedral for each rotor
```

```
187         fr_dihedrals = ['D'+str(max(rot)-3) for rot in fr_rots]
188
189         print(fr_dihedrals, m062xFragmentFileList)
190         rotorEnergies = get_peaks_valleys(fr_dihedrals,
fragmentFile)
191
192         # go back to root directory
193         os.chdir(root_directory)
194         # Writes TS Bimolecular Section from topology ooutputs!
(calling this function opens/closes the file!)
195         write_TS_Bimolecular(iteration, fragments_naming,
fragmentFile, fragments_directory, path_dir, m062xFragmentFileList,
fr_xyz_geom, fr_freqs, fr_rots, rotorEnergies,
fr_charge_multiplicity, h_abstraction)
196         iteration += 1
197         # resetting h-abstraction boolean
198         h_abstraction = False
199         #looks into the TS folder and extract xyz geom from m062x
file
200         os.chdir(path_dir)
201
202         # change threshold to 1.4 for all files here bc they are TS
!
203         bond_thresh = 1.4
204         ## -- Topology Function Calls For TS -- ##
205         TS_xyz_geom = get_xyzGeom(m062xFileName)
206         TS_freqs, TS_charge_multiplicity = get_frequencies(
m062xFileName)
207         TS_rots = get_rotors(TS_xyz_geom, m062xFileName,
bond_thresh, TS=True)
208         # finds corresponding z-matrix dihedral for each rotor
209         TS_dihedrals = ['D'+str(max(rot)-3) for rot in TS_rots]
210
211         print(TS_dihedrals, m062xFileName)
212         rotorEnergies = get_peaks_valleys(TS_dihedrals,
m062xFileName)
213
214         # Change back to root directory and write in Mess input!
215         os.chdir(root_directory)
216         # Writes TS Barrier Section from topology outputs! (calling
this function closes the file!)
217         write_TS_Barrier(TS_xyz_geom, TS_rots, TS_freqs,
rotorEnergies, TS_charge_multiplicity, path_dir, m062xFileName,
number_of_wells, h_abstraction)
218
219         # This section writes BFs
220         else:
221             # goes back into the pathway's directory
```



```
222     os.chdir(path_dir)
223     # adds energies from all files into 'energies' dictionary
224     non_ts_prods, non_ts = add_energies(pathway, os.listdir(),
non_ts_prods, non_ts, energiesDictionary, createExcel)
225
226     if len(m062xFileList)>1:
227         h_abstraction = False
228         # gets fragments' names from file for parsing
229         frag1 = m062xFileList[0].split('_m062x.log')[0]
230         frag2 = m062xFileList[1].split('_m062x.log')[0]
231         # takes into account the cases with 3 products!
232         if len(m062xFileList) > 2:
233             frag3 = m062xFileList[2].split('_m062x.log')[0]
234             fragments_naming = frag1+' '*2+'+'+' '*2+frag2+' '
*2+'+'+frag3
235         else:
236             fragments_naming = frag1+' '*2+'+'+' '*2+frag2
237         else:
238             h_abstraction = True
239             non_ts_prods.append('H')
240             non_ts.append('H')
241             fragments_naming = m062xFileList[0].split('_m062x.log')
[0]
242
243     # Function calls for Bimolecular Section of Bond Fissions
244     iteration = 1
245     for fragmentFile in m062xFileList:
246         fr_xyz_geom = get_xyzGeom(fragmentFile)
247         fr_freqs, fr_charge_multiplicity = get_frequencies(
fragmentFile)
248         fr_rotors = get_rotors(fr_xyz_geom, fragmentFile,
bond_thresh)
249         # finds corresponding z-matrix dihedral for each rotor
250         fr_dihedrals = ['D'+str(max(rot)-3) for rot in fr_rotors]
251
252         rotorEnergies = get_peaks_valleys(fr_dihedrals,
fragmentFile)
253
254         # go back to root directory
255         os.chdir(root_directory)
256         # Writes TS Bimolecular Section from topology ooutputs!
(calling this function opens/closes the file!)
257         write_BF_Bimolecular(iteration, root_directory,
fragments_naming, fragmentFile, path_dir, m062xFileList, fr_xyz_geom
, fr_freqs, fr_rotors, rotorEnergies, fr_charge_multiplicity,
h_abstraction)
258         iteration += 1
259
```

```
260         # Change back to root directory and create Mess input there
        (TS Bimolecular Sections)!
261         os.chdir(root_directory)
262         # Change back into pathway's directory
263         os.chdir(path_dir)
264
265         # gets geometry, frequency and rotor information for the
        two fragments inside the BF pathway
266         # fragment 1 information
267         fr1_xyz_geom = get_xyzGeom(m062xFileList[0])
268         fr1_freqs, fr1_charge_multiplicity = get_frequencies(
        m062xFileList[0])
269         fr1_rots = get_rotors(fr1_xyz_geom, m062xFileList[0],
        bond_thresh)
270         # finds corresponding z-matrix dihedral for each rotor
271         fr1_dihedrals = ['D'+str(max(rot)-3) for rot in fr1_rots]
272
273         fr1_rotorEnergies = get_peaks_valleys(fr1_dihedrals,
        m062xFileList[0])
274
275         fragment1_info = [fr1_xyz_geom, fr1_freqs,
        fr1_charge_multiplicity, fr1_rots]
276
277         if len(m062xFileList)>1:
278             # fragment 2 information
279             fr2_xyz_geom = get_xyzGeom(m062xFileList[1])
280             fr2_freqs, fr2_charge_multiplicity = get_frequencies(
        m062xFileList[1])
281             fr2_rots = get_rotors(fr2_xyz_geom, m062xFileList[1],
        bond_thresh)
282             # finds corresponding z-matrix dihedral for each rotor
283             fr2_dihedrals = ['D'+str(max(rot)-3) for rot in
        fr2_rots]
284
285             fr2_rotorEnergies = get_peaks_valleys(fr2_dihedrals,
        m062xFileList[1])
286
287             fragment2_info = [fr2_xyz_geom, fr2_freqs,
        fr2_charge_multiplicity, fr2_rots]
288         # Change back to root directory and create Mess input there
        (TS Bimolecular Sections)!
289         os.chdir(root_directory)
290         # Writes BF Barrier Section from topology outputs! (calling
        this function closes the file!)
291         if h_abstraction:
292             fragment2_info = []
293             fr2_rotorEnergies = []
```

```
294         write_BF_Barrier(fragments_naming, fragment1_info,
150         fr1_rotorEnergies, fragment2_info, fr2_rotorEnergies, pathway,
150         number_of_wells, m062xFileName, h_abstraction)
295
296         # change back to root dir for next pathway
297         os.chdir(root_directory)
298         if lastParse:
299             MESSFile = open('MESSFile.inp', 'a')
300             MESSFile.write('End\n')
301             MESSFile.close()
302
303 writeMessFile()
304
305 # Additional data structures needed for creating energies spreadsheet
306 ts_energies = {}
307 for key in energiesDictionary:
308     if key not in non_ts_prods:
309         ts_energies[key] = energiesDictionary[key]
310
311 dissociations = [prod for prod in non_ts_prods if not prod.startswith('
150         W')]
312 # print('dissociations: ', dissociations)
313 print(f"EnergiesDictionary {energiesDictionary}")
314
315
316 all_ts_molecules = [molecule for molecule in all_molecules if molecule
150         not in dissociations]
317 ts_prods = {}
318 for i in range(len(all_molecules)):
319     try:
320         if all_molecules[i].startswith('TS'):
321             # this logic is why it doesn't work for more than two
150             molecule products
322             if not all_molecules[i+1].startswith('TS'):
323                 if all_molecules[i+1].startswith('W'):
324                     ts_prods[all_molecules[i]] = [all_molecules[i+1]]
325             else:
326                 if not all_molecules[i+2].startswith('TS'):
327                     ts_prods[all_molecules[i]] = [all_molecules[i
150                     +1], all_molecules[i+2]]
328             else:
329                 ts_prods[all_molecules[i]] = [all_molecules[i
150                 +1]]
330
331     except IndexError:
332         ts_prods[all_molecules[i]] = [all_molecules[i+1]]
333
334 # print('all ts molecules', all_ts_molecules)
```

```
335 # print('ts_prods', ts_prods)
336 # print('ts_energies', ts_energies)
337
338 non_repeated_non_ts = sorted(set(non_ts), key=non_ts.index)
339 # print('non repeated non ts', non_repeated_non_ts)
340
341 if createExcel:
342     write_energies_spreadsheet(energiesDictionary, non_repeated_non_ts,
343                               ts_prods, dissociations)
344 else:
345     pass
346
347 print('Seems like it worked!')
348 # end of program
```

Appendix D

Python scripts | Computational pipeline automation code

D.1 run_iter.py

```
1 import os
2
3 def fireIter():
4     # finds directories ending in '_E', enters and runs the local '
5     run_all_gjfs.sh' file
6     base_dir = os.getcwd()
7     print(base_dir)
8     os.chdir(base_dir)
9     fire_m062x = 'sbatch run_all_gjfs.sh'
10    os.system(fire_m062x)
11    fire_rotors = 'nohup python start_rotor_run.py > log.out &'
12    os.system(fire_rotors)
13
14 if __name__ == '__main__':
15     fireIter()
```

D.2 searchLowConf.py

```
1 import os, re, numpy as np, shutil, get_input_gjf, run_iter,
2     startHighEnergyCalcs
3
4 from get_geometry import get_gView_format
5
6 def low_conf():
7     base_dir = os.getcwd()
8     os.chdir(base_dir)
9     # print(base_dir)
10
11     curr_dir = base_dir
12     # opens m062x log file to extract HF
```

```
11 file_name=''
12 files = os.listdir()
13 for file in files:
14     if file.endswith('.log'):
15         file_name = file
16
17 # print(file_name)
18 file = open(curr_dir + '/' + file_name)
19 flines = file.readlines()
20 file.close
21
22 HF_initial = 0
23 for line in flines:
24     if 'SCF Done' in line:
25         HF_initial = float(line.split()[4])
26
27 # print(HF_initial)
28
29 # Open Rotor Directory
30 files = os.listdir()
31 # print(files)
32 # print(curr_dir)
33 for file in files:
34     if 'Rotor' in file.split('_'):
35         rotor_path = curr_dir + '/' + file
36         # print(path)
37
38 os.chdir(rotor_path)
39
40 dihedrals = []
41
42 for root, dirs, files in os.walk('.',topdown=True):
43     # print(root)
44     # for name in files:
45     #     print(os.path.join(root, name))
46     for name in dirs:
47         dihedrals.append(os.path.join(root, name))
48
49 # print(dihedrals)
50 # os.chdir(dihedrals[0])
51 # print(os.getcwd())
52
53 normal_term_key = re.compile("Normal termination")
54 file_name = ''
55 error_files=[]
56 allEnergies = []
57 for dirs in dihedrals:
58     os.chdir(os.path.join(rotor_path, dirs))
```

```
59     files = os.listdir()
60     scanEnergies = []
61     scanAngles = []
62     # scanEnergies.append(dirs)
63     # scanEnergies.append(dirs)
64     for file in files:
65         if file.endswith('.log'):
66             f = open(file)
67             flines = f.readlines()
68             f.close()
69             optEnergies = []
70             search_line = str.strip(flines[-1])
71             if normal_term_key.search(search_line):
72                 file_name = file.split('.')[0]
73                 scanPoint = file_name.split('_')[-1]
74                 for line in flines:
75                     if 'SCF Done' in line:
76                         optEnergies.append(float(line.split()[4]))
77                         scanEnergies.append(optEnergies[-1]) # last SCF
78                         energy is the optimizes energy
79                         scanAngles.append(int(scanPoint))
80                     else:
81                         error_files.append(file)
82             scanEnergies.append(HF_initial)
83             scanAngles.append(0)
84             scanAngles, scanEnergies = zip(*sorted(zip(scanAngles,
85 scanEnergies)))
86             allEnergies.append([scanAngles, scanEnergies])
87
88
89     allEnergies = np.array(allEnergies, dtype=object)
90     # print(allEnergies[0])
91
92     os.chdir(base_dir)
93
94     lowEnergy = 0
95     lowestAngle = 0
96     minDihedral = ''
97     minEnergy = []
98     minScanAngle = []
99     # minDihedrals = []
100     for i in range(0, len(allEnergies)):
101         startEnergy = allEnergies[i][1][0]
102         endEnergy = allEnergies[i][1][-1]
103         diff = (endEnergy - startEnergy)*627.5 # Convert energy
104         difference from Hartrees to KCal/Mol
105         if diff > 0.01:
106             print("Start and End energy is not same")
107             exit()
```

```
104     else:
105         minEnergy.append(np.amin(allEnergies[i][1]))
106         minScanAngle.append(allEnergies[i][0][np.where(allEnergies[
107 i][1] == np.amin(allEnergies[i][1]))[0][0]])
108         # minDihedrals.append(dihedrals[i])
109         # print(minDihedrals)
110         # print(minEnergy)
111         # print(minScanAngle)
112
113 minEnergy = np.array(minEnergy)
114 minScanAngle = np.array(minScanAngle)
115 dihedrals = np.array(dihedrals)
116
117 lowestEnergy = np.amin(minEnergy)
118 lowestAngle = minScanAngle[np.where(minEnergy == np.amin(minEnergy)
119 )][0]
120 minDihedral = dihedrals[np.where(minEnergy == np.amin(minEnergy)
121 )][0]
122 # print(lowestEnergy)
123 # print(lowestAngle)
124 # print(minDihedral)
125
126 # it checks if the difference is within range to fire a lower
127 conformer
128
129 # print(allEnergies[np.where(minEnergy == np.amin(minEnergy))
130 [0][0]][1][0])
131
132 # os.chdir(base_dir)
133
134 diff_range = lowestEnergy - allEnergies[np.where(minEnergy == np.
135 amin(minEnergy))[0][0]][1][0]
136 # print(diff_range*627.5)
137
138 if diff_range*627.5 > -0.01:
139     # Call script to run higher energy calcs
140     print('No lower conformer found')
141     print("Starting Higher Energy calculations!")
142     startHighEnergyCalcs.runHighECalcs()
143 else:
144     print('Lower Conformer Found!')
145     print('Starting next iteration')
146     # print(minDihedral[2:])
147     low_conf_path =os.path.join(curr_dir,rotor_path,minDihedral
148 [2:])
149     print(low_conf_path)
150     files = os.listdir(low_conf_path)
151     for file in files:
```



```
145         if str(lowestAngle) + '.chk' in file.split('_'):
146             lowerConfFileCHK = file
147             print(lowerConfFileCHK)
148         if str(lowestAngle) + '.log' in file.split('_'):
149             lowerConfFileLOG = file
150             print(lowerConfFileLOG)
151
152     currDirName = os.getcwd().split(r'/')[-1]
153     fileNum = currDirName[2:]
154     nextIterPath = os.path.join(os.path.dirname(base_dir), 'it'+str(
155 int(fileNum)+1))
156     os.makedirs(nextIterPath)
157     print(os.path.dirname(base_dir))
158
159     shutil.copy(f'{low_conf_path}/{lowerConfFileCHK}', f'{
160 nextIterPath}/{lowerConfFileCHK}')
161     shutil.copy(f'{low_conf_path}/{lowerConfFileLOG}', f'{
162 nextIterPath}/{lowerConfFileLOG}')
163     shutil.copy('geometryInfo.py', f'{nextIterPath}/geometryInfo.py
164 ')
165     shutil.copy('get_geometry.py', f'{nextIterPath}/get_geometry.py
166 ')
167     shutil.copy('get_rotors.py', f'{nextIterPath}/get_rotors.py')
168     shutil.copy('search_rotors.py', f'{nextIterPath}/search_rotors.
169 py')
170     shutil.copy('start_rotor_run.py', f'{nextIterPath}/
171 start_rotor_run.py')
172     shutil.copy('get_input_gjf.py', f'{nextIterPath}/get_input_gjf.
173 py')
174     shutil.copy('newzmat.sh', f'{nextIterPath}/newzmat.sh')
175     shutil.copy('searchLowConf.py', f'{nextIterPath}/searchLowConf.
176 py')
177     shutil.copy('startSearchLowConf.py', f'{nextIterPath}/
178 startSearchLowConf.py')
179     shutil.copy('run_iter.py', f'{nextIterPath}/run_iter.py')
180     shutil.copy('startHighEnergyCalcs.py', f'{nextIterPath}/
181 startHighEnergyCalcs.py')
182     shutil.copy('run_all_gjfs.sh', f'{nextIterPath}/run_all_gjfs.sh
183 ')
184     shutil.copy('run_all_gjfs_array.sh', f'{nextIterPath}/
185 run_all_gjfs_array.sh')
186
187     os.chdir(nextIterPath)
188
189     print(os.getcwd())
190
191     files=os.listdir(nextIterPath)
192     for fileName in files:
```

```

180         if fileName.endswith('.chk'):
181             newName = '_'.join(fileName.split('_')[:-3]) + '.chk'
182             os.rename(fileName, newName)
183         if fileName.endswith('.log'):
184             newName = '_'.join(fileName.split('_')[:-3]) + '.log'
185             os.rename(fileName, newName)
186
187     get_input_gjf.main(newName,3)
188
189     files=os.listdir(nextIterPath)
190     # print(files)
191     for fileName in files:
192         if fileName.endswith('.gjf'):
193             file = open(fileName, 'r')
194             flines = file.read()
195             file.close()
196             if 'Variables' in flines:
197                 get_gView_format(fileName)
198
199     print('Firing next iteration from directory: ', os.getcwd())
200
201     run_iter.fireIter()
202
203 if __name__ == '__main__':
204     low_conf()

```

D.3 start_pipeline.py

```

1 import os
2
3 print('Relax and sit back. Automation has got it from here!')
4 def main():
5     # finds directories ending in '_E', enters and runs the local '
6     run_all_gjfs.sh' file
7     base_dir = os.getcwd()
8     for fileName in os.listdir():
9         if '_E' in fileName:
10            print(fileName)
11            os.chdir(f'{base_dir}/{fileName}/it1')
12            fire_iterations = 'nohup python run_iter.py > log.out &'
13            os.system(fire_iterations)
14            os.chdir(base_dir)
15
16 if __name__ == '__main__':
17     main()

```

D.4 start_rotor_run.py

```
1 import get_rotors, get_input_gjf, time, os, sys, startSearchLowConf,
   startHighEnergyCalcs
2
3 def wait_for_file():
4     """
5     Wait for 'Finished' keyword in slurm file to fire. Checking
6     in 10 minute intervals. First checks if job has started
7
8     This method fires the rotor code once it detects that the
9     m062x/cc-pVTZ run has completed. Script stops waiting when
10    shell script job-time has been reached.
11
12    """
13    # checks job every five minutes if job has started by checking
14    any slurm files in directory (times out after 1 day)
15    timeout = 86400/300
16    attempts = 0
17    fileFound = False
18    print('entering first loop...')
19    while attempts < timeout:
20        # print(os.listdir())
21        for file in os.listdir():
22            if file.endswith('.out') and file.startswith('slurm'):
23                slurmFile = file
24                fileFound = True
25                break
26        if fileFound:
27            break
28        # Wait 5 minutes before trying again.
29        time.sleep(300) # change to 300
30        attempts += 1
31        # time out, job still in queue after 24 hours
32        if attempts == timeout:
33            sys.exit()
34        print('rotor script is running')
35        # extracts job time from shell script
36        with open('run_all_gjfs.sh', 'r') as shellScript:
37            shellLines = shellScript.readlines()
38            shellScript.close()
39        for line in shellLines:
40            if 'time' in line:
41                jobTimeLine = line
42                break
43        hrs, mins, secs = [int(time) for time in jobTimeLine.split('=')
44                           [-1].split(':')]
45        timeout = round((hrs*3600)+(mins*60)+(secs)/600)
46
47    attempts = 0
```

```
46     print('entering second loop...')
47     while attempts < timeout:
48         # Check if the file exists.
49         with open(slurmFile, 'r') as sFile:
50             slurmFile_text = sFile.read()
51             sFile.close()
52             if 'Finished' in slurmFile_text:
53                 break
54         # Wait 10 minutes before trying again.
55         time.sleep(600) # change to 600
56         attempts += 1
57         # time out, job didn't finish in time
58         if attempts == timeout:
59             sys.exit()
60     print('script detected gaussian job finished')
61     # check if m062x job finished successfully here! (cleans up and
62     # deletes unnecessary files)
63     # call rotor code
64     for logfile in os.listdir():
65         if logfile.endswith('.log'):
66             gjfFile = get_input_gjf.main(logfile) # rename and save
67             original .gjf somewhere else
68
69     rotor_dihedrals, rotors = get_rotors.get_rotors_from_rotorFile(
70     rotorFile='rotors_found.txt')
71
72     if len(rotors) != 0:
73         print('script called rotor script')
74         get_rotors.main(rotorFile='rotors_found.txt')
75
76     # starts rotor jobs
77     # finds directories ending in '_E>>D#', enters and runs
78     the local 'run_all_gjfs_array.sh' file
79     base_dir = os.getcwd()
80     for fileName in os.listdir():
81         # print(fileName)
82         if 'Rotor' in fileName.split('_') and os.path.isdir(
83     fileName):
84
85         print('Rotor directory found!')
86         print('Starting rotor jobs')
87         os.chdir(f'{base_dir}/{fileName}')
88         # inside molecule's Rotor_Files folder
89         for file in os.listdir():
90             if file.startswith('D') and os.path.isdir(file)
91 :
92                 os.chdir(f'{file}')
93                 cmd = 'sbatch run_all_gjfs_array.sh'
94                 os.system(cmd)
```

```

88         os.chdir('../..')
89         os.chdir(base_dir)
90
91         print('Starting startSearchLowConf.py')
92         startSearchLowConf.wait_for_rotors()
93
94     else:
95         print('Starting startHighEnergyCalcs.py')
96         startHighEnergyCalcs.runHighECalcs()
97
98
99 if __name__ == '__main__':
100     wait_for_file()

```

D.5 startHighEnergyCalcs.py

```

1 import os, numpy as np, get_input_gjf,shutil, re
2 from get_geometry import get_gView_format
3
4 def runHighECalcs():
5
6     baseDir = os.getcwd()
7
8     for file in os.listdir():
9         if file.endswith('.log'):
10             m062xLogFile = file
11         if file.endswith('.chk'):
12             m062xChkFile = file
13
14
15     EFileLog = m062xLogFile.split('.')[0] + '_E.' + m062xLogFile.split(
16     '.')[-1]
17     EFileChk = m062xChkFile.split('.')[0] + '_E.' + m062xChkFile.split(
18     '.')[-1]
19     E1FileChk = m062xChkFile.split('.')[0] + '_E1.' + m062xChkFile.
20     split('.')[0] + '_E1.' + m062xChkFile.
21     split('.')[0] + '_E1.' + m062xChkFile.
22     split('.')[0] + '_E1.' + m062xChkFile.
23     split('.')[0] + '_E1.' + m062xChkFile.
24     split('.')[0] + '_E1.' + m062xChkFile.
25     split('.')[0] + '_E1.' + m062xChkFile.
26     split('.')[0] + '_E1.' + m062xChkFile.
27     split('.')[0] + '_E1.' + m062xChkFile.
28     split('.')[0] + '_E1.' + m062xChkFile.

```

```
29     shutil.copy(f'{m062xLogFile}', f'HighEnergyCalcs/{E1FileLog}')
30     shutil.copy(f'{m062xChkFile}', f'HighEnergyCalcs/{E1FileChk}')
31     shutil.copy('newzmat.sh', f'HighEnergyCalcs/newzmat.sh')
32     shutil.copy('get_input_gjf.py', f'HighEnergyCalcs/get_input_gjf.py'
33 )
34     shutil.copy('get_geometry.py', f'HighEnergyCalcs/get_geometry.py')
35
36     print(baseDir)
37
38     higherCalcsPath = baseDir + '//HighEnergyCalcs'
39
40     print(higherCalcsPath)
41
42     os.chdir(higherCalcsPath)
43
44     get_input_gjf.main(EFileLog, job='E')
45     get_input_gjf.main(E1FileLog, job='E1')
46
47     os.remove(EFileLog)
48     os.remove(EFileChk)
49     os.remove(E1FileLog)
50     os.remove(E1FileChk)
51
52     files=os.listdir(higherCalcsPath)
53     print(files)
54     for fileName in files:
55         if fileName.endswith('.gjf'):
56             file = open(fileName, 'r')
57             flines = file.read()
58             file.close()
59             if 'Variables' in flines:
60                 get_gView_format(fileName)
61
62     print(baseDir)
63     print(os.getcwd())
64
65     shutil.copy(f'{baseDir}/run_all_gjfs.sh', f'{higherCalcsPath}/
66 run_all_gjfs.sh')
67
68     # file = os.listdir(higherCalcsPath)
69
70     # with open('run_all_gjf.sh', 'r') as sfile:
71     #     slines = sfile.readlines()
72     #     sfile.close()
73
74     # keySearch = re.compile('job-name')
75     # lineNum = 0
76     # while lineNum < len(slines):
```

```
75     #     line = slines[lineNum]
76     #     strLine = str.strip(line)
77     #     if keySearch.search(strLine):
78     #         slines[lineNum] = strLine + 'E'
79     #     lineNum += 1
80
81     # with open('run_all_gjf.sh', 'w') as sfile:
82     #     sfile.write(slines)
83     #     sfile.close
84
85     cmd = 'sbatch run_all_gjfs.sh'
86     os.system(cmd)
87
88 if __name__ == '__main__':
89     runHighECalcs()
```

D.6 startSearchLowConf.py

```
1 import searchLowConf, time, os, sys, numpy as np
2
3 def wait_for_rotors():
4     """
5     Wait for 'Finished' keyword in slurm file to fire. Checking
6     in 10 minute intervals. First checks if job has started
7
8     This method fires the search for lower conformer once it
9     detects that the
10    all 36 point of every rotor of the job has completed. Script
11    stops waiting when
12    shell script job-time has been reached.
13
14    """
15    # checks job every five minutes if job has started by checking
16    any slurm files in directory (times out after 1 day)
17    baseDir = os.getcwd()
18    print(baseDir)
19    timeout = 86400/300
20    attempts = 0
21    slurmCount = False
22    print('entering first loop...')
23    while attempts < timeout:
24        # print(os.listdir())
25        for file in os.listdir():
26            # print(file)
27            # rotrDir = ''
28            # print(file.split())
29            if 'Rotor' in file.split('_'):
30                rotrDir = os.path.join(baseDir, file)
```

```
28         # os.chdir(rotrDir)
29     allSlurms = []
30     for dihedralDir in os.listdir(rotrDir):
31         # print(dihedralDir)
32         slurmFile = []
33         for file in os.listdir(os.path.join(rotrDir,
dihedralDir)):
34             # print(file)
35             if file.endswith('.out') and file.startswith('slurm
'):
36                 slurmFile.append(file)
37             allSlurms.append(slurmFile)
38     allSlurms = np.array(allSlurms)
39
40     # print(allSlurms.shape)
41     for fileCount in range(0, len(allSlurms)):
42         if len(allSlurms[fileCount]) == 36:
43             # print(len(allSlurms[fileCount]))
44             slurmCount = True
45         else:
46             slurmCount = False
47             break
48     if slurmCount:
49         # print("Logic Works!")
50         break
51
52     # Wait 5 minutes before trying again.
53     time.sleep(300) # change to 300
54     attempts += 1
55     # time out, job still in queue after 24 hours
56     if attempts == timeout:
57         sys.exit()
58     print('rotor jobs are running')
59     # extracts job time from shell script
60     with open('run_all_gjfs_array.sh', 'r') as shellScript:
61         shellLines = shellScript.readlines()
62         shellScript.close()
63     for line in shellLines:
64         if 'time' in line:
65             jobTimeLine = line
66             break
67     hrs, mins, secs = [int(time) for time in jobTimeLine.split('=')
[-1].split(':')]
68     timeout = round((hrs*3600)+(mins*60)+(secs)/600)
69
70     print('entering second loop...')
71
72     attempts = 0
```



```
73     finishFound = False
74     while attempts < timeout:
75         index = 0
76         for dihedralDir in os.listdir(rotrDir):
77             dihedralPath = os.path.join(rotrDir, dihedralDir)
78             # count = 0
79             for slurmFile in allSlurms[index]:
80                 # print(slurmFile)
81                 os.chdir(dihedralPath)
82                 # print(dihedralPath)
83                 with open(slurmFile, 'r') as sFile:
84                     slurmFile_text = sFile.read()
85                     sFile.close()
86                     if 'Finished' in slurmFile_text:
87                         finishFound = True
88                     else:
89                         finishFound = False
90                         break
91                 # count += 1
92                 # print(count)
93                 index += 1
94                 if finishFound == False:
95                     break
96         if finishFound:
97             break
98
99         os.chdir(baseDir)
100
101         # Wait 10 minutes before trying again.
102         time.sleep(600) # change to 600
103         attempts += 1
104         # time out, job didn't finish in time
105         if attempts == timeout:
106             sys.exit()
107
108         print('script detected rotor jobs are finished')
109         os.chdir(baseDir)
110         # print(os.getcwd())
111         searchLowConf.low_conf()
112
113 if __name__ == '__main__':
114     wait_for_rotors()
```

Appendix E

DPM PIMS and MESS input files | DEM, DPM, and associated radicals from pyrolysis

E.1 DPM PIMS

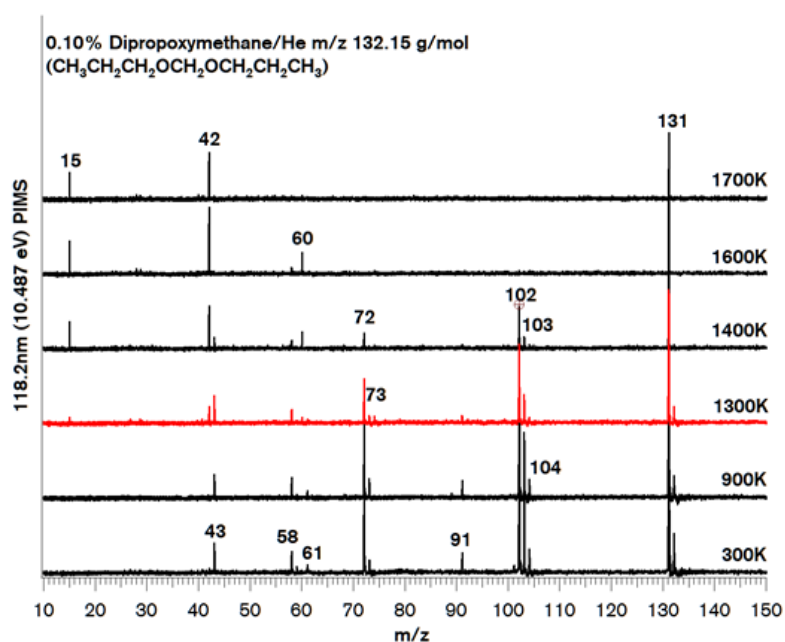


Fig. E.1 PIMS of 0.1% dipropoxymethane (P-1-P) in He in the micro reactor at 200 SCCM heated from 300 to 1700 L and ionized by 118.2 nm (10.487 eV) photons.

E.2 DEM

```
1 TemperatureList [K]          500 510 520 530 540 550 560 570
    580 590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740
```

```

750 760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910
920 930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060
1070 1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190
1200 1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320
1330 1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450
1460 1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580
1590 1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710
1720 1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840
1850 1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970
1980 1990 2000
2 PressureList[atm]                0.00001 0.001 0.01 0.1 3 10
   100.
3 !PressureList[bar]                1.
4 EnergyStepOverTemperature        .2
5 ExcessEnergyOverTemperature      30
6 ModelEnergyLimit[kcal/mol]       400
7 CalculationMethod                 direct
8 !CalculationMethod                low-eigenvalue !direct
9 WellCutoff                        10
10 ChemicalEigenvalueMax            0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor[1/cm]                200 ! He
15       Power                        .85
16       ExponentCutoff              15
17     End
18   CollisionFrequency
19     LennardJones
20       Epsilons[1/cm]              94.87 280.62 !Ar and CCOCOC
21       Sigmas[angstrom]            3.33 6.14
22       Masses[amu]                 39.88 104.15
23     End
24   Well      W1 # CCOCOC
25     Species
26     RRHO
27     Geometry[angstrom]            19
28       C                2.87151100 -0.91974300 -0.14425500
29     C                1.71189100 -0.19908400 0.50247500
30     O                1.05453600 0.56382200 -0.49541600
31     C                0.00000000 1.32951900 -0.00000200
32     O               -1.05453600 0.56382200 0.49541400
33     C               -1.71188700 -0.19909100 -0.50247400
34     C               -2.87151500 -0.91973900 0.14425600
35     H                2.51206000 -1.58102500 -0.93147800
36     H                3.40769500 -1.51629500 0.59281000
37     H                3.56341500 -0.20463800 -0.58652600
38     H                1.01048100 -0.90733200 0.95176300

```

```

39  H          2.06068700   0.47083600   1.29777000
40  H          0.33204200   1.95229600   0.83602200
41  H         -0.33204400   1.95229200  -0.83602800
42  H         -2.06067500   0.47082300  -1.29777700
43  H         -1.01047700  -0.90734600  -0.95174900
44  H         -3.56341900  -0.20462600   0.58651500
45  H         -3.40769600  -1.51629700  -0.59280600
46  H         -2.51207200  -1.58101400   0.93148900
47  Core          RigidRotor
48  SymmetryFactor                                2
49  End
50  Rotor          Hindered
51  Group                                17 18 19
52  Axis                                  7 6
53  Symmetry                                3
54  Potential[kcal/mol]  2
55  0. 3.05
56  End
57  Rotor          Hindered
58  Group                                7 15 16
59  Axis                                  6 5
60  Symmetry                                1
61  Potential[kcal/mol]  6
62  0. 1.58  1.01 4.77 0.63 1.31
63  End
64  Rotor          Hindered
65  Group                                6
66  Axis                                  5 4
67  Symmetry                                1
68  Potential[kcal/mol]  6
69  0. 7.31 3.17 3.46 2.66 3.84
70  End
71  Rotor          Hindered
72  Group                2
73  Axis                3 4
74  Symmetry            1
75  Potential[kcal/mol]  6
76  0. 7.31 3.17 3.46 2.67 3.84
77  End
78  Rotor          Hindered
79  Group 1 11 12
80  Axis  2 3
81  Symmetry  1
82  Potential[kcal/mol]  6
83  0. 1.58 1.01 4.77 0.63 1.31
84  End
85  Rotor          Hindered
86  Group 8 9 10

```

```

87     Axis 1 2
88     Symmetry 3
89     Potential[kcal/mol] 2
90     0. 3.05
91     End
92     Frequencies [1/cm] 45
93     266.6 344.74 358.88 488.95 670.57 819.87 820.13 878.81
885.99 1060.16 1064.91 1101.59 1141.04 1165.3 1186.28 1190.57
1202.45 1232.21 1306.77 1307.25 1342.26 1397.51 1400.55 1429.91
1436.33 1457.84 1488.43 1488.73 1504.87 1505.5 1516.52 1535.41
1542.15 3017.53 3018.2 3036.86 3069.45 3070.58 3071.9 3072.12
3087.71 3147.9 3147.95 3149.88 3149.98
94     !50.73 57.89 74.4 176.16 235.73 258.31! Torsions
95     ZeroEnergy[kcal/mol] 0
96     ElectronicLevels [1/cm] 1
97     0 1
98     End
99     End
100    Bimolecular P1 # CCOC[O] + [CH2]C
101    Fragment CCOC[O]
102    RRHO
103    Geometry[angstrom] 12
104    O -0.03684500 0.62337700 -0.21626000
105    C 0.83914400 -0.35064900 0.32991000
106    C 2.23651200 -0.05572200 -0.16008200
107    C -1.35876500 0.45047100 0.16929400
108    H -1.92132100 1.31885200 -0.20159800
109    H -1.45570300 0.44913100 1.27567500
110    H 0.79058300 -0.30540700 1.42548100
111    O -1.96169300 -0.67772900 -0.24643500
112    H 0.51758500 -1.34807300 0.02010500
113    H 2.54400900 0.94186600 0.14942500
114    H 2.94105400 -0.78092800 0.24486200
115    H 2.27074200 -0.10522500 -1.24712500
116    Core RigidRotor
117    SymmetryFactor 1
118    End
119    Rotor Hindered
120    Group 5 6 8
121    Axis 4 1
122    Symmetry 1
123    Potential[kcal/mol] 6
124    0. 2.32 0.0 3.36 2.24 3.36
125    End
126    Rotor Hindered
127    Group 4
128    Axis 1 2
129    Symmetry 1

```

```
130      Potential[kcal/mol]      8
131  0. 1.74 0.99 4.51 1.166 1.178 1.072 1.41
132      End
133      Rotor                    Hindered
134      Group                    10 11 12
135      Axis                      3 2
136      Symmetry                  3
137      Potential[kcal/mol] 2
138      0. 3.088
139      End
140      Frequencies [1/cm]      27
141      281.68 401.61 637.56 797.03 825.93 885.15 1048.18 1081.1
142      1134.03 1187.87 1193.87 1245.45 1310.9 1355.19 1393.15 1409.18
143      1442.46 1487.8 1505.84 1535.9 2884.66 3009.4 3011.82 3075.12
144      3078.04 3151.9 3154.27
145      !70.21 146.84 248.71! Torsions
146      ZeroEnergy[kcal/mol]      0.0
147      ElectronicLevels [1/cm]    1
148      0 2
149      End
150      Fragment [CH2]C
151      RRHO
152      Geometry[angstrom] 7
153      C -0.69222800 0.00000000 -0.00057700
154      C 0.79186100 0.00000000 -0.02396000
155      H -1.10189400 0.88331200 -0.49094000
156      H -1.08426500 0.00001300 1.02462600
157      H -1.10189400 -0.88332500 -0.49091800
158      H 1.34512800 0.92312000 0.05222700
159      H 1.34512900 -0.92312000 0.05222700
160      Core RigidRotor
161      SymmetryFactor 1
162      End
163      Rotor                    Hindered
164      Group                    3 4 5
165      Axis                      1 2
166      Symmetry                  3
167      Potential[kcal/mol] 4
168      0. 0.07 0.0 0.08
169      End
170      Frequencies [1/cm]      14
171      444.91 810.81 982.95 1081.35 1195.68 1403.91 1471.58 1487.61
172      1489.49 3004.53 3085.23 3128.72 3174.72 3276.16
173      !125.25! Torsions
174      ZeroEnergy[kcal/mol]      0
175      ElectronicLevels [1/cm]    1
176      0 2
177      End
```

```

174      GroundEnergy [kcal/mol]      84.1
175      End
176      Bimolecular      P2      # CCO[CH2] + CC[0]
177      Fragment      CCO[CH2]
178      RRHO
179      Geometry [angstrom]      11
180      O      -0.58408900      -0.46219100      0.00087000
181      C      0.44314400      0.51637400      0.04241600
182      C      1.77563600      -0.18931500      -0.02763400
183      C      -1.83740900      0.03341200      0.03858200
184      H      -2.60953400      -0.71258000      -0.05571200
185      H      -1.99460100      1.04964700      -0.30213200
186      H      0.31449400      1.20272600      -0.80109500
187      H      0.34725400      1.09386100      0.96636500
188      H      1.85215400      -0.76363100      -0.94943900
189      H      2.58809100      0.53547900      0.00078500
190      H      1.88662600      -0.87079400      0.81408600
191      Core      RigidRotor
192      SymmetryFactor      1
193      End
194      Rotor      Hindered
195      Group      5 6
196      Axis      4 1
197      Symmetry      2
198      Potential [kcal/mol]      2
199      0. 5.5
200      End
201      Rotor      Hindered
202      Group      4
203      Axis      1 2
204      Symmetry      1
205      Potential [kcal/mol]      6
206      0. 1.51 0.60 4.08 0.15 1.5
207      End
208      Rotor      Hindered
209      Group      9 10 11
210      Axis      3 2
211      Symmetry      3
212      Potential [kcal/mol]      2
213      0. 3.0
214      End
215      Frequencies [1/cm]      24
216      303.35 487.19 593.22 821.8 883.99 1073.33 1122.2 1187.61
1234.87 1308.92 1313.32 1400.08 1434.83 1488.69 1493.38 1506.22
1531.36 3029.29 3069.09 3075.45 3137.07 3152.88 3154.08 3283.45
217      !99.2 239.29 290.05! Torsions
218      ZeroEnergy [kcal/mol]      0
219      ElectronicLevels [1/cm]      1

```

```

220      0 2
221      End
222      Fragment  CC[0]
223      RRHO
224      Geometry [angstrom]  8
225      C          0.99339700   -0.58703400   0.00000000
226      C          0.00000000   0.58827100   0.00000000
227      O         -1.24967300   0.02452200   0.00000000
228      H          2.00644500   -0.18921500   0.00000000
229      H          0.84823600   -1.20028500   0.88617500
230      H          0.84823600   -1.20028500  -0.88617500
231      H          0.16704400   1.19309300   0.89813400
232      H          0.16704400   1.19309300  -0.89813400
233      Core          RigidRotor
234      SymmetryFactor          1
235      End
236      Rotor          Hindered
237      Group          4 5 6
238      Axis          1 2
239      Symmetry      3
240      Potential [kcal/mol]  2
241      0. 2.34
242      End
243      Frequencies [1/cm]      17
244      389.37  759.82  914.81  971.51  1034.8  1156.42  1266.06  1316.76
1389.99  1481.94  1503.1  1546.86  3008.76  3055.73  3081.36  3164.27
3170.31
245      !244.47! Torsions
246      ZeroEnergy [kcal/mol]    0
247      ElectronicLevels [1/cm]  1
248      0 2
249      End
250      GroundEnergy [kcal/mol]  92.7
251      End
252      Bimolecular  P3      # CCOCO [CH2] + [CH3]
253      Fragment  CCOCO [CH2]
254      RRHO
255      Geometry [angstrom]  15
256      C          2.04184100   0.97940900  -0.23650800
257      O          1.63963800  -0.06987200   0.52169000
258      C          0.81124200  -0.99413900  -0.15113800
259      O         -0.38579500  -0.43724000  -0.56930300
260      C         -1.22597700  -0.02415200   0.49942400
261      C         -2.52515300   0.46978300  -0.09104300
262      H          2.63690400   1.70068700   0.29810600
263      H          1.43218100   1.25645300  -1.08472300
264      H          1.31526500  -1.35717500  -1.04817800
265      H          0.64903100  -1.80201100   0.56648700

```



```

266      H          -1.39588500   -0.87369500    1.17114100
267      H          -0.73109200    0.76294000    1.07386200
268      H          -3.00867800   -0.32169600   -0.66138000
269      H          -3.20073300    0.79539500    0.69883400
270      H          -2.33945300    1.31059200   -0.75764600
271      Core              RigidRotor
272              SymmetryFactor                      1
273      End
274      Rotor              Hindered
275          Group              13 14 15
276          Axis              6 5
277          Symmetry          3
278          Potential [kcal/mol] 2
279      0. 3.05
280      End
281      Rotor              Hindered
282          Group              6 11 12
283          Axis              5 4
284          Symmetry          1
285          Potential [kcal/mol] 6
286      0. 1.627 1.045 4.613 0.766 1.227
287      End
288      Rotor              Hindered
289          Group              5
290          Axis              4 3
291          Symmetry          1
292          Potential [kcal/mol] 6
293      0. 6.906 2.099 4.464 3.800 4.790
294      End
295      Rotor              Hindered
296          Group              1
297          Axis              2 3
298          Symmetry          1
299          Potential [kcal/mol] 6
300      0. 4.275 2.508 3.573 3.149 3.995
301      End
302      Rotor              Hindered
303          Group              7 8
304          Axis              1 2
305          Symmetry          2
306          Potential [kcal/mol] 2
307      0. 5.2
308      End
309      Frequencies [1/cm]          34
310          302.16 359.65 462.79 573.73 649.76 821.45 881.67 991.14
          1065.83 1107.19 1161.87 1185.76 1199.09 1246.95 1269.05 1309.95
          1345.91 1400.15 1433.72 1446.61 1488.63 1491.73 1505.56 1519.45

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1536.64 3024.66 3057.19 3073.81 3076.5 3115.41 3150.44 3152.21
3161.74 3302.14
311  !57.06 80.74 172 241.97 273.48! Torsions
312     ZeroEnergy [kcal/mol]           0
313     ElectronicLevels [1/cm]       1
314     0 2
315     End
316     Fragment [CH3]
317     RRHO
318     Geometry [angstrom] 4
319     C           0.00000000  0.00000000  0.00000000
320     H           0.00000000  0.00000000  1.07652900
321     H           0.93230200  0.00000000 -0.53826500
322     H          -0.93230200 -0.00000000 -0.53826500
323     Core RigidRotor
324     SymmetryFactor 6
325     End
326     Frequencies [1/cm] 6
327     409.94 1411.49 1412.56 3141.77 3320.20 3321.01
328     !! torsion
329     ZeroEnergy [kcal/mol]           0
330     ElectronicLevels [1/cm]       1
331     0 2
332     End
333     GroundEnergy [kcal/mol]        85.3
334     End
335     Bimolecular P4 # CCO[CH]OCC + [H]
336     Fragment H
337     Atom
338     Mass [amu] 1
339     ElectronicLevels [1/cm]       1
340     0 2
341     End
342     Fragment CCO[CH]OCC
343     RRHO
344     Geometry [angstrom] 18
345     C           1.85123800  1.36692300 -0.11393900
346     C           1.96689700 -0.02829500  0.46760200
347     O           1.35369200 -1.01369700 -0.36424900
348     C           0.03415500 -0.85685700 -0.58928400
349     O          -0.69614700 -0.61826900  0.54142300
350     C          -2.06451100 -0.34257700  0.28446300
351     C          -2.27184300  1.06738700 -0.23360400
352     H           2.24378200  1.38817000 -1.12996300
353     H           2.41909800  2.06979700  0.49527800
354     H           0.81162300  1.69137600 -0.13652000
355     H           3.00777400 -0.33711600  0.53429500
356     H           1.52760000 -0.07194000  1.46460200

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357      H          -0.36385800   -1.61659300   -1.26056200
358      H          -2.45580700   -1.07882900   -0.42562200
359      H          -2.57592300   -0.48826100    1.23398200
360      H          -1.74442300    1.20754600   -1.17653400
361      H          -3.33229600    1.26016800   -0.39476900
362      H          -1.89354200    1.79191800    0.48699300
363      Core          RigidRotor
364      SymmetryFactor          2
365      End
366      Rotor          Hindered
367      Group          16 17 18
368      Axis          7 6
369      Symmetry          3
370      Potential[kcal/mol]          2
371      0. 3.025
372      End
373      Rotor          Hindered
374      Group          7 14 15
375      Axis          6 5
376      Symmetry          1
377      Potential[kcal/mol]          6
378      0. 4.23 0.926 1.612 0.0435 1.442
379      End
380      Rotor          Hindered
381      Group          6
382      Axis          5 4
383      Symmetry          1
384      Potential[kcal/mol]          4
385      0. 2.49 1.964 9.0
386      End
387      Rotor          Hindered
388      Group          2
389      Axis          3 4
390      Symmetry          1
391      Potential[kcal/mol]          4
392      0. 2.49 1.964 9.0
393      End
394      Rotor          Hindered
395      Group          1 11 12
396      Axis          2 3
397      Symmetry          1
398      Potential[kcal/mol]          6
399      0. 4.23 0.926 1.612 0.0435 1.442
400      End
401      Rotor          Hindered
402      Group          8 9 10
403      Axis          1 2
404      Symmetry          3

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405      Potential [kcal/mol]          2
406      0. 3.025
407      End
408      Frequencies [1/cm]          42
409      277.13 352.87 422.86 475.76 607.35 809.76 811.76 869.59
918.15 947.28 1039.68 1082.94 1115.36 1118.49 1175.57 1199.67
1232.05 1282.91 1333.66 1342.41 1365.73 1397.21 1401.53 1423.49
1442.81 1485.7 1486.96 1500.82 1502.41 1521.69 1527.53 3037.38
3066.85 3070.41 3086.17 3105.4 3121.98 3131.75 3143.04 3145.58
3149.98 3156.17
410      !54.18 70.62 121.24 175.73 222.29 268.03!Torsions
411      ZeroEnergy [kcal/mol]          0
412      ElectronicLevels [1/cm]      1
413      0 2
414      End
415      GroundEnergy [kcal/mol]      97.3
416      End
417      Bimolecular      P5      # CCOCO[CH]C + [H]
418      Fragment H
419      Atom
420      Mass [amu]      1
421      ElectronicLevels [1/cm]      1
422      0 2
423      End
424      Fragment CCOCO[CH]C
425      RRHO
426      Geometry [angstrom] 18
427      C      -1.75842200      -0.13403300      -0.46781200
428      O      -1.09509700      0.60904400      0.46548700
429      C      -0.01330100      1.35501300      -0.04090700
430      C      -2.85410500      -0.96514700      0.08007400
431      O      1.01893100      0.55641700      -0.51103000
432      C      1.65649100      -0.20390200      0.50439200
433      C      2.80557300      -0.95567500      -0.12445000
434      H      -2.47846600      -1.76188100      0.73417500
435      H      -3.41611000      -1.43101500      -0.72713700
436      H      -3.53683600      -0.35551300      0.67407300
437      H      -1.17785600      -0.44495900      -1.32790800
438      H      -0.34255100      1.96285200      -0.88525400
439      H      0.31673100      1.98162600      0.79154500
440      H      2.01218200      0.47292700      1.29023000
441      H      0.93781500      -0.89170300      0.95729300
442      H      3.51379600      -0.26075000      -0.57288800
443      H      3.32540300      -1.55052000      0.62546900
444      H      2.43780800      -1.62229200      -0.90303500
445      Core      RigidRotor
446      SymmetryFactor      1
447      End

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448         Rotor                               Hindered
449         Group                                16 17 18
450         Axis                                 7 6
451         Symmetry                             3
452         Potential [kcal/mol]                  2
453     0. 3.0522
454 End
455 Rotor                               Hindered
456     Group                                7 14 15
457     Axis                                 6 5
458     Symmetry                             1
459     Potential [kcal/mol]                  8
460     0. 1.627 1.032 1.115 1.063 4.677 0.586 1.190
461 End
462 Rotor                               Hindered
463     Group                                6
464     Axis                                 5 3
465     Symmetry                             1
466     Potential [kcal/mol]                  6
467     0. 6.63 2.07 3.64 2.99 4.09
468 End
469 Rotor                               Hindered
470     Group                                1
471     Axis                                 2 3
472     Symmetry                             1
473     Potential [kcal/mol]                  6
474     0. 9.97 1.65 2.70 2.29 2.93
475 End
476 Rotor                               Hindered
477     Group                                4 11
478     Axis                                 1 2
479     Symmetry                             1
480     Potential [kcal/mol]                  4
481     0. 4.573 1.338 4.174
482 End
483 Rotor                               Hindered
484     Group                                8 9 10
485     Axis                                 4 1
486     Symmetry                             3
487     Potential [kcal/mol]                  2
488     0. 1.32
489 End
490     Frequencies [1/cm]                    42
491     51.91 330.6 364.23 484.26 575.24 677.56 821.46 881.7
901.01 1022.16 1064.95 1089.77 1110.76 1148.96 1179.46 1192.1
1214.36 1257.91 1308.65 1347.01 1382.68 1400.39 1426.85 1436.73
1464.37 1469.93 1488.79 1495.37 1505.5 1520.02 1537.66 3006.46

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3021.82 3055.1 3073.03 3075.09 3088.73 3113.75 3146.3 3149.87
3151.12 3182.77
492 !62.09 81.45 159.44 197.19 241.07 261.41!Torsions
493 ZeroEnergy [kcal/mol] 0
494 ElectronicLevels [1/cm] 1
495 0 2
496 End
497 GroundEnergy [kcal/mol] 94.6
498 End
499 Bimolecular P6 # CCOCOC[CH2] + [H]
500 Fragment H
501 Atom
502 Mass [amu] 1
503 ElectronicLevels [1/cm] 1
504 0 2
505 End
506 Fragment CCOCOC[CH2]
507 RRHO
508 Geometry [angstrom] 18
509 C 2.94233500 -0.67034400 -0.14761700
510 C 1.78742600 0.14457100 0.38575300
511 O 0.80817900 0.24343000 -0.63524800
512 C -0.28223800 1.03652700 -0.28368300
513 O -1.03682300 0.49569300 0.76284600
514 C -1.71162100 -0.70408300 0.40845000
515 C -2.86279900 -0.45941400 -0.49590600
516 H 2.60356500 -1.66748400 -0.42538500
517 H 3.72126300 -0.76622200 0.60785300
518 H 3.36704400 -0.19434500 -1.03009700
519 H 1.35335100 -0.32249500 1.27350700
520 H 2.11614900 1.15201300 0.66825800
521 H 0.04724600 2.01712500 0.07145300
522 H -0.88407800 1.13637100 -1.19045600
523 H -1.00929200 -1.41413700 -0.03811800
524 H -2.04480500 -1.13149900 1.36035400
525 H -3.47587800 0.41624000 -0.34190400
526 H -3.20403400 -1.22209400 -1.17822300
527 Core RigidRotor
528 SymmetryFactor 1
529 End
530 Rotor Hindered
531 Group 8 9 10
532 Axis 1 2
533 Symmetry 3
534 Potential [kcal/mol] 2
535 0. 3.048
536 End
537 Rotor Hindered

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538      Group                1 11 12
539      Axis                  2 3
540      Symmetry              1
541      Potential [kcal/mol]  8
542      0. 1.525 0.954 1.108 1.077 4.728 0.771 1.294
543      End
544      Rotor                Hindered
545      Group                 2
546      Axis                  3 4
547      Symmetry              1
548      Potential [kcal/mol]  6
549      0. 7.39 3.02 3.07 2.66 3.95
550      End
551      Rotor                Hindered
552      Group                 6
553      Axis                  5 4
554      Symmetry              1
555      Potential [kcal/mol]  6
556      0. 7.87 3.80 3.97 3.29 4.46
557      End
558      Rotor                Hindered
559      Group                 7 15 16
560      Axis                  6 5
561      Symmetry              1
562      Potential [kcal/mol]  6
563      0. 3.2 0.26 1.347 0.319 1.836
564      End
565      Rotor                Hindered
566      Group                 17 18
567      Axis                  7 6
568      Symmetry              2
569      Potential [kcal/mol]  2
570      0. 1.67
571      End
572      Frequencies [1/cm]    42
573      47.2 325.16 438.49 468.49 529.08 646.42 821.67 848.43 882.07
      944.34 1054.46 1063.51 1101.92 1130.71 1147.54 1183.77 1195.02
      1221.39 1300.89 1309.84 1347.07 1395.04 1399.47 1433.39 1453
      1459.44 1488.57 1491.71 1505.47 1516.64 1539.3 3019.76 3025.12
      3046.83 3068.1 3072.25 3074.09 3099.48 3148.38 3150.29 3174.81
      3285.12
574      !58.76 93.4 190.21 194.44 239.52 287.32! Torsions
575      ZeroEnergy [kcal/mol]  0
576      ElectronicLevels [1/cm] 1
577      0 2
578      End
579      GroundEnergy [kcal/mol] 101.7
580      End
```

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581 Bimolecular P7 # CCOCO + C=C
582 Fragment CCOCO
583 RRHO
584 Geometry [angstrom] 13
585 O -1.92826300 -0.68196600 -0.07973400
586 O 0.01015400 0.58970200 -0.30216800
587 C 0.89304700 -0.25879500 0.41481000
588 C 2.27188600 -0.12033700 -0.18641800
589 C -1.30056300 0.54685900 0.16433400
590 H -1.97484400 -0.80731600 -1.03181800
591 H -1.81992400 1.36846600 -0.33161200
592 H -1.33439300 0.68135600 1.24941000
593 H 0.89594800 0.03666700 1.47086500
594 H 0.54134800 -1.29155700 0.35888500
595 H 2.60988900 0.91307300 -0.12640900
596 H 2.98309100 -0.75247700 0.34381200
597 H 2.25753200 -0.41646200 -1.23427500
598 Core RigidRotor
599 SymmetryFactor 1
600 End
601 Rotor Hindered
602 Group 11 12 13
603 Axis 4 3
604 Symmetry 3
605 Potential [kcal/mol] 2
606 0. 3.068
607 End
608 Rotor Hindered
609 Group 4 9 10
610 Axis 3 2
611 Symmetry 1
612 Potential [kcal/mol] 6
613 0. 1.515 0.886 4.604 0.988 1.276
614 End
615 Rotor Hindered
616 Group 1 7 8
617 Axis 5 2
618 Symmetry 1
619 Potential [kcal/mol] 6
620 0. 6.542 1.952 4.165 2.665 3.863
621 End
622 Rotor Hindered
623 Group 6
624 Axis 1 5
625 Symmetry 1
626 Potential [kcal/mol] 4
627 0. 3.883 1.92 3.614
628 End

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629      Frequencies [1/cm]      29
630      375.2 412.14 626.92 820.25 882.02 1051.0 1066.09 1101.42
1155.27 1189.13 1193.91 1303.77 1310.25 1391.35 1398.67 1432.81
1460.37 1487.52 1506.25 1529.36 1540.44 3020.25 3050.27 3073.23
3080.49 3104.68 3149.72 3151.22 3871.22
631      !61.49 158.34 250.95 289.95! Torsions
632      ZeroEnergy [kcal/mol]      0
633      ElectronicLevels [1/cm]      1
634      0 1
635      End
636      Fragment C=C
637      RRHO
638      Geometry [angstrom] 6
639      C      0.00000000      0.00000000      0.00000000
640      H      0.00000000      0.00000000      1.08216909
641      H      0.96588500      0.00000000      -0.48801240
642      C      -1.12558139      -0.00000000      -0.69239269
643      H      -1.12558139      -0.00000000      -1.77456178
644      H      -2.09146639      -0.00000000      -0.20438028
645      Core RigidRotor
646      SymmetryFactor 2
647      End
648      Frequencies [1/cm]      12
649      829.14 990.4 1002.92 1070.96 1243.08 1388.11 1473.77 1718.56
3159.71 3175.83 3235.53 3261.92
650      !!torsions
651      ZeroEnergy [kcal/mol]      0
652      ElectronicLevels [1/cm]      1
653      0 1
654      End
655      GroundEnergy [kcal/mol]      15.2
656      End
657      Bimolecular      P8      # CCOCC + CH2O
658      Fragment CCOCC
659      RRHO
660      Geometry [angstrom] 15
661      C      -2.36671500      0.40939100      0.00000000
662      C      -1.17240100      -0.51689000      0.00000000
663      O      0.00000000      0.26250200      0.00000000
664      C      1.17240100      -0.51689000      0.00000000
665      C      2.36671500      0.40939100      0.00000000
666      H      -2.34819700      1.04628100      0.88302400
667      H      -3.29422700      -0.16193900      0.00000000
668      H      -2.34819700      1.04628100      -0.88302400
669      H      -1.18641200      -1.16781900      0.88393000
670      H      -1.18641200      -1.16781900      -0.88392900
671      H      1.18641200      -1.16781900      0.88392900
672      H      1.18641200      -1.16781900      -0.88393000

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```
673 H 2.34819700 1.04628100 0.88302400
674 H 3.29422700 -0.16193900 0.00000000
675 H 2.34819700 1.04628100 -0.88302400
676 Core RigidRotor
677 SymmetryFactor 2
678 End
679 Rotor Hindered
680 Group 6 7 8
681 Axis 1 2
682 Symmetry 3
683 Potential [kcal/mol] 2
684 0. 3.0
685 End
686 Rotor Hindered
687 Group 1 9 10
688 Axis 2 3
689 Symmetry 1
690 Potential [kcal/mol] 6
691 0. 2.413 1.165 5.868 1.165 2.413
692 End
693 Rotor Hindered
694 Group 5 11 12
695 Axis 4 3
696 Symmetry 1
697 Potential [kcal/mol] 6
698 0. 2.413 1.165 5.868 1.165 2.413
699 End
700 Rotor Hindered
701 Group 13 14 15
702 Axis 5 4
703 Symmetry 3
704 Potential [kcal/mol] 2
705 0. 3.0
706 End
707 Frequencies [1/cm] 35
708 115.4 197.52 437.2 450.61 830.12 875.89 959.32 1087.06 1108.5
1177.04 1198.69 1206.46 1209.21 1305.39 1314.85 1386.88 1401.58
1416.11 1461.43 1486.74 1487.1 1503.63 1506.27 1526.83 1545.29
2994.83 3003.32 3025.73 3028.59 3072.82 3073.18 3149.47 3149.67
3150.89 3150.99
709 !98.05 247.28 254.77 815.07! Torsions
710 ZeroEnergy [kcal/mol] 0
711 ElectronicLevels [1/cm] 1
712 0 1
713 End
714 Fragment CH2O
715 RRHO
716 Geometry [angstrom] 4
```

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717      O      -0.67047700    0.00000100    0.00000200
718      C      0.52488300   -0.00000200   -0.00000900
719      H      1.10726700    0.93752700    0.00001900
720      H      1.10725400   -0.93752400    0.00001900
721      Core   RigidRotor
722      SymmetryFactor 2
723      End
724      Frequencies [1/cm] 6
725          1218.60          1279.77          1546.46
726          1877.07          2943.65          3014.58
727      !!torsions
728      ZeroEnergy [kcal/mol] 0
729      ElectronicLevels [1/cm] 1
730      0 1
731      End
732      GroundEnergy [kcal/mol] 13.7
733      End
734      Bimolecular      P9      # CCO + CCO [[C]]
735      Fragment      CCO
736      RRHO
737      Geometry [angstrom] 9
738      C      -0.0005504046   -0.0000016618   0.004356613
739      C      0.0025412193    0.0000010702    1.5158131688
740      O      1.3546236279    0.0000210282    1.9425094513
741      H      0.514830693     0.882999015    -0.3707849607
742      H      -1.0203704632   -0.0000152764   -0.3788652927
743      H      0.5148531996   -0.8829904547   -0.3707819942
744      H      -0.5219744501    0.8843981578    1.8921319904
745      H      -0.5219493386   -0.8844095541    1.8921351504
746      H      1.3800687831    0.0000207816    2.9011244281
747      Core      RigidRotor
748      SymmetryFactor 1
749      End
750      Rotor      Hindered
751      Group      4 5 6
752      Axis      1 2
753      Symmetry  3
754      Potential [kcal/mol] 2
755      0. 3.2
756      End
757      Rotor      Hindered
758      Group      9
759      Axis      3 2
760      Symmetry  3
761      Potential [kcal/mol] 2
762      0. 1.1
763      End
764      Frequencies [1/cm] 19

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765 421.7 825.29 920.25 1051.13 1139.96 1187.28 1273.09 1310.39 1403.39
1463.28 1487.29 1505.39 1539.06 3021.48 3052.31 3071.37 3148.14
3149.95 3901.97
766 !232.92 271.7! Torsions
767 ZeroEnergy[kcal/mol] 0
768 ElectronicLevels [1/cm] 1
769 0 1
770 End
771 Fragment CCO[[C]]
772 RRHO
773 Geometry[angstrom] 10
774 C 0.2962234158 0.2799519783 0.0252389473
775 O 0.1446716238 -0.1255305641 1.2720513805
776 C 1.29444481399 0.0022054547 2.1303302756
777 C 1.5788506213 1.4518618524 2.4536649072
778 H 0.5351832549 -0.3751190301 -0.8093652333
779 H 1.0437077815 -0.5660668847 3.0234590174
780 H 2.1470686136 -0.4700165085 1.6370309882
781 H 0.7134709961 1.9097143961 2.930397192
782 H 2.431190729 1.5264741833 3.128390386
783 H 1.8071838203 2.0032381221 1.5419321275
784 Core RigidRotor
785 SymmetryFactor 1
786 End
787 Rotor Hindered
788 Group 8 9 10
789 Axis 4 3
790 Symmetry 3
791 Potential[kcal/mol] 2
792 0. 3.14
793 End
794 Rotor Hindered
795 Group 4 6 7
796 Axis 3 2
797 Symmetry 1
798 Potential[kcal/mol] 6
799 0. 0.59 0. 2.41 2.11 2.42
800 End
801 Frequencies [1/cm] 22
802 126.75 239.12 287.85 369.51 505.85 814.8 869.5 1034.92 1115.84 1118.67
1189.04 1290.81 1335.21 1401.86 1426.52 1486.91 1499.3 1518.85
3064.96 3069.95 3124.2 3130.8 3148.51 3155.81
803 !99.2 239.29 290.05! Torsions
804 ZeroEnergy[kcal/mol] 0.0
805 ElectronicLevels [1/cm] 1
806 0 2
807 End
808 GroundEnergy[kcal/mol] 67.0

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809      End
810 Bimolecular          P10      # CCOH + CH2O + C=C approx as: CCOH
      + CH2O_C=C
811      Fragment  CCOH
812      RRHO
813      Geometry [angstrom]  9
814      C              0.08463800    0.54848000    0.00000000
815      H              0.13973200    1.19166300   -0.88440500
816      H              0.13973300    1.19166400    0.88440400
817      O              1.14287200   -0.39509100   -0.00000100
818      H              1.97961300    0.07336700    0.00000500
819      C             -1.21571800   -0.22196200    0.00000000
820      H             -1.27446800   -0.85670800    0.88299900
821      H             -2.06664400    0.45834700   -0.00000100
822      H             -1.27446600   -0.85671000   -0.88299700
823      Core              RigidRotor
824      SymmetryFactor                    1
825      End
826      Rotor              Hindered
827      Group              5
828      Axis              4 1
829      Symmetry          3
830      Potential [kcal/mol]  2
831      0. 1.12
832      End
833      Rotor              Hindered
834      Group              7 8 9
835      Axis              6 1
836      Symmetry          3
837      Potential [kcal/mol]  2
838      0. 3.21
839      End
840      Frequencies [1/cm]    19
841      421.70 825.30 920.25 1051.13 1139.97 1187.28 1273.09 1310.40
      1403.39 1463.29 1487.29
842      1505.39 1539.06 3021.47 3052.30 3071.36 3148.12 3149.94 3901.98
843      ! 232.91 271.69 ! Torsions
844      ZeroEnergy [kcal/mol]  0
845      ElectronicLevels [1/cm]  1
846      0 1
847      End
848      Fragment  CH2O_C=C
849      RRHO
850      Geometry [angstrom]  10
851      C              -2.22308600   -0.38804100    0.00000500
852      H              -2.60698400   -0.80604300   -0.92177300
853      H              -2.60697500   -0.80603000    0.92179200
854      C              1.76407000   -0.62797700   -0.00000300

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855 H          2.68985700   -1.22874900    0.00000400
856 H          0.80898100   -1.17966000   -0.00001600
857 C         -1.33377900    0.59096200   -0.00000600
858 H         -0.94409000    1.01086600    0.91791700
859 H         -0.94409800    1.01085300   -0.91793800
860 O          1.79501000    0.56863800    0.00000500
861   Core          RigidRotor
862     SymmetryFactor          1
863   End
864   Frequencies [1/cm]      24
865   30.31 30.38 92.69 108.25 125.25 135.20 823.54 994.94 1017.54
866   1075.60 1223.33 1238.35
867   1282.56 1384.01 1471.90 1539.71 1713.08 1867.69 2945.393023.40
868   3159.41 3177.82 3234.34 3262.56
869   ! ! Torsions
870   ZeroEnergy [kcal/mol]      0
871   ElectronicLevels [1/cm]    1
872     0 1
873   End
874   GroundEnergy [kcal/mol]    29.4
875   End
876   Barrier      B1   W1   P1   # CCOC[0] + [CH2]C = CCOC0CC
877     RRHO
878     Stoichiometry C5H12O2
879     Core      PhaseSpaceTheory
880     FragmentGeometry [angstrom] 12
881     O          -0.03684500    0.62337700   -0.21626000
882     C          0.83914400   -0.35064900    0.32991000
883     C          2.23651200   -0.05572200   -0.16008200
884     C          -1.35876500    0.45047100    0.16929400
885     H          -1.92132100    1.31885200   -0.20159800
886     H          -1.45570300    0.44913100    1.27567500
887     H          0.79058300   -0.30540700    1.42548100
888     O          -1.96169300   -0.67772900   -0.24643500
889     H          0.51758500   -1.34807300    0.02010500
890     H          2.54400900    0.94186600    0.14942500
891     H          2.94105400   -0.78092800    0.24486200
892     H          2.27074200   -0.10522500   -1.24712500
893     FragmentGeometry [angstrom] 7
894     C          -0.69222800    0.00000000   -0.00057700
895     C          0.79186100    0.00000000   -0.02396000
896     H          -1.10189400    0.88331200   -0.49094000
897     H          -1.08426500    0.00001300    1.02462600
898     H          -1.10189400   -0.88332500   -0.49091800
899     H          1.34512800    0.92312000    0.05222700
900     H          1.34512900   -0.92312000    0.05222700
901     SymmetryFactor          1
902     PotentialPrefactor [au] 2.96 #3 4 4.5 4.8 5 5.5

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901           PotentialPowerExponent           6.63
902       End
903       Rotor                               Hindered
904       Geometry [angstrom] 12
905           O           -0.03684500    0.62337700   -0.21626000
906           C           0.83914400   -0.35064900    0.32991000
907           C           2.23651200   -0.05572200   -0.16008200
908           C           -1.35876500    0.45047100    0.16929400
909           H           -1.92132100    1.31885200   -0.20159800
910           H           -1.45570300    0.44913100    1.27567500
911           H           0.79058300   -0.30540700    1.42548100
912           O           -1.96169300   -0.67772900   -0.24643500
913           H           0.51758500   -1.34807300    0.02010500
914           H           2.54400900    0.94186600    0.14942500
915           H           2.94105400   -0.78092800    0.24486200
916           H           2.27074200   -0.10522500
-1.24712500
917           Group                               5 6 8
918           Axis                               4 1
919           Symmetry                             1
920           Potential [kcal/mol] 6
921       0. 2.32 0.0 3.36 2.24 3.36
922       End
923       Rotor                               Hindered
924       Geometry [angstrom] 12
925           O           -0.03684500    0.62337700   -0.21626000
926           C           0.83914400   -0.35064900    0.32991000
927           C           2.23651200   -0.05572200   -0.16008200
928           C           -1.35876500    0.45047100    0.16929400
929           H           -1.92132100    1.31885200   -0.20159800
930           H           -1.45570300    0.44913100    1.27567500
931           H           0.79058300   -0.30540700    1.42548100
932           O           -1.96169300   -0.67772900   -0.24643500
933           H           0.51758500   -1.34807300    0.02010500
934           H           2.54400900    0.94186600    0.14942500
935           H           2.94105400   -0.78092800    0.24486200
936           H           2.27074200   -0.10522500
-1.24712500
937           Group                               4
938           Axis                               1 2
939           Symmetry                             1
940           Potential [kcal/mol] 8
941       0. 1.74 0.99 4.51 1.166 1.178 1.072 1.41
942       End
943       Rotor                               Hindered
944       Geometry [angstrom] 12
945           O           -0.03684500    0.62337700   -0.21626000
946           C           0.83914400   -0.35064900    0.32991000

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947      C      2.23651200   -0.05572200   -0.16008200
948      C      -1.35876500    0.45047100    0.16929400
949      H      -1.92132100    1.31885200   -0.20159800
950      H      -1.45570300    0.44913100    1.27567500
951      H      0.79058300   -0.30540700    1.42548100
952      O      -1.96169300   -0.67772900   -0.24643500
953      H      0.51758500   -1.34807300    0.02010500
954      H      2.54400900    0.94186600    0.14942500
955      H      2.94105400   -0.78092800    0.24486200
956      H      2.27074200
-0.10522500  -1.24712500
957      Group      10 11 12
958      Axis      3 2
959      Symmetry      3
960      Potential[kcal/mol] 2
961      0. 3.088
962      End
963      Rotor      Hindered
964      Geometry[angstrom] 7
965      C      -0.69222800    0.00000000
-0.00057700
966      C      0.79186100    0.00000000
-0.02396000
967      H      -1.10189400    0.88331200
-0.49094000
968      H      -1.08426500    0.00001300
1.02462600
969      H      -1.10189400   -0.88332500
-0.49091800
970      H      1.34512800    0.92312000
0.05222700
971      H      1.34512900   -0.92312000
0.05222700
972      Group      3 4 5
973      Axis      1 2
974      Symmetry      3
975      Potential[kcal/mol] 4
976      0. 0.07 0.0 0.08
977      End
978      Frequencies[1/cm]      41
979      444.91  810.81  982.95  1081.35  1195.68  1403.91  1471.58  1487.61
1489.49  3004.53  3085.23  3128.72  3174.72  3276.16
980      281.68  401.61  637.56  797.03  825.93  885.15  1048.18  1081.1
1134.03  1187.87  1193.87  1245.45  1310.9  1355.19  1393.15  1409.18
1442.46  1487.8  1505.84  1535.9  2884.66  3009.4  3011.82  3075.12
3078.04  3151.9  3154.27
981      !70.21  146.84  248.71  125.25!
982      ZeroEnergy[kcal/mol]      84.1

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983      ElectronicLevels [1/cm]          1
984      0      2
985      End
986      Barrier      B2      W1      P2      # CCO[CH2] + CC[O] = CCOCOC
987      RRHO
988      Stoichiometry C5H12O2
989      Core      PhaseSpaceTheory
990      FragmentGeometry [angstrom]  11
991      O          -0.58408900   -0.46219100   0.00087000
992      C          0.44314400   0.51637400   0.04241600
993      C          1.77563600   -0.18931500  -0.02763400
994      C          -1.83740900   0.03341200   0.03858200
995      H          -2.60953400   -0.71258000  -0.05571200
996      H          -1.99460100   1.04964700  -0.30213200
997      H          0.31449400   1.20272600  -0.80109500
998      H          0.34725400   1.09386100   0.96636500
999      H          1.85215400   -0.76363100  -0.94943900
1000     H          2.58809100   0.53547900   0.00078500
1001     H          1.88662600   -0.87079400
0.81408600
1002     FragmentGeometry [angstrom]  8
1003     C          0.99339700   -0.58703400   0.00000000
1004     C          0.00000000   0.58827100   0.00000000
1005     O          -1.24967300   0.02452200   0.00000000
1006     H          2.00644500   -0.18921500   0.00000000
1007     H          0.84823600   -1.20028500   0.88617500
1008     H          0.84823600   -1.20028500  -0.88617500
1009     H          0.16704400   1.19309300   0.89813400
1010     H          0.16704400   1.19309300
-0.89813400
1011     SymmetryFactor          1
1012     PotentialPrefactor [au]  3.91   #3 4 5 6
1013     PotentialPowerExponent  7.34
1014     End
1015     Rotor          Hindered
1016     Geometry [angstrom]  11
1017     O          -0.58408900   -0.46219100
0.00087000
1018     C          0.44314400   0.51637400
0.04241600
1019     C          1.77563600   -0.18931500
-0.02763400
1020     C          -1.83740900   0.03341200
0.03858200
1021     H          -2.60953400   -0.71258000
-0.05571200
1022     H          -1.99460100   1.04964700
-0.30213200

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1023          H          0.31449400   1.20272600
      -0.80109500
1024          H          0.34725400   1.09386100
      0.96636500
1025          H          1.85215400  -0.76363100
      -0.94943900
1026          H          2.58809100   0.53547900
      0.00078500
1027          H          1.88662600  -0.87079400
      0.81408600
1028          Group          5 6
1029          Axis          4 1
1030          Symmetry          2
1031          Potential[kcal/mol]          2
1032          0. 5.5
1033          End
1034          Rotor          Hindered
1035          Geometry[angstrom]  11
1036          O          -0.58408900  -0.46219100
      0.00087000
1037          C          0.44314400   0.51637400
      0.04241600
1038          C          1.77563600  -0.18931500
      -0.02763400
1039          C          -1.83740900   0.03341200
      0.03858200
1040          H          -2.60953400  -0.71258000
      -0.05571200
1041          H          -1.99460100   1.04964700
      -0.30213200
1042          H          0.31449400   1.20272600
      -0.80109500
1043          H          0.34725400   1.09386100
      0.96636500
1044          H          1.85215400  -0.76363100
      -0.94943900
1045          H          2.58809100   0.53547900
      0.00078500
1046          H          1.88662600  -0.87079400
      0.81408600
1047          Group          4
1048          Axis          1 2
1049          Symmetry          1
1050          Potential[kcal/mol]          6
1051          0. 1.51 0.60 4.08 0.15 1.5
1052          End
1053          Rotor          Hindered
1054          Geometry[angstrom]  11

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1055      0          -0.58408900   -0.46219100
0.00087000
1056      C          0.44314400    0.51637400
0.04241600
1057      C          1.77563600   -0.18931500
-0.02763400
1058      C          -1.83740900    0.03341200
0.03858200
1059      H          -2.60953400   -0.71258000
-0.05571200
1060      H          -1.99460100    1.04964700
-0.30213200
1061      H          0.31449400    1.20272600
-0.80109500
1062      H          0.34725400    1.09386100
0.96636500
1063      H          1.85215400   -0.76363100
-0.94943900
1064      H          2.58809100    0.53547900
0.00078500
1065      H          1.88662600   -0.87079400
0.81408600
1066      Group          9 10 11
1067      Axis          3 2
1068      Symmetry          3
1069      Potential[kcal/mol] 2
1070      0. 3.0
1071      End
1072      Rotor          Hindered
1073      Geometry[angstrom] 8
1074      C          0.99339700   -0.58703400
0.00000000
1075      C          0.00000000    0.58827100
0.00000000
1076      O          -1.24967300    0.02452200
0.00000000
1077      H          2.00644500   -0.18921500
0.00000000
1078      H          0.84823600   -1.20028500
0.88617500
1079      H          0.84823600   -1.20028500
-0.88617500
1080      H          0.16704400    1.19309300
0.89813400
1081      H          0.16704400    1.19309300
-0.89813400
1082      Group          4 5 6
1083      Axis          1 2

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1084          Symmetry                      3
1085          Potential[kcal/mol]          2
1086          0. 2.34
1087      End
1088      Frequencies [1/cm]                41
1089          389.37 759.82 914.81 971.51 1034.8 1156.42 1266.06 1316.76
          1389.99 1481.94 1503.1 1546.86 3008.76 3055.73 3081.36 3164.27
1090          3170.31
          303.35 487.19 593.22 821.8 883.99 1073.33 1122.2 1187.61
          1234.87 1308.92 1313.32 1400.08 1434.83 1488.69 1493.38 1506.22
          1531.36 3029.29 3069.09 3075.45 3137.07 3152.88 3154.08 3283.45
1091          !99.2 239.29 290.05 244.47!
1092      ZeroEnergy[kcal/mol]            92.7
1093          ElectronicLevels [1/cm]      1
1094          0 2
1095      End
1096      Barrier      B3  W1  P3  # CCOC0[CH2] + [CH3] = CCOC0CC
1097          RRHO
1098          Stoichiometry C5H12O2
1099          Core      PhaseSpaceTheory
1100          FragmentGeometry[angstrom] 15
1101          C          2.04184100 0.97940900 -0.23650800
1102          O          1.63963800 -0.06987200 0.52169000
1103          C          0.81124200 -0.99413900 -0.15113800
1104          O          -0.38579500 -0.43724000 -0.56930300
1105          C          -1.22597700 -0.02415200 0.49942400
1106          C          -2.52515300 0.46978300 -0.09104300
1107          H          2.63690400 1.70068700 0.29810600
1108          H          1.43218100 1.25645300 -1.08472300
1109          H          1.31526500 -1.35717500 -1.04817800
1110          H          0.64903100 -1.80201100 0.56648700
1111          H          -1.39588500 -0.87369500 1.17114100
1112          H          -0.73109200 0.76294000 1.07386200
1113          H          -3.00867800 -0.32169600 -0.66138000
1114          H          -3.20073300 0.79539500 0.69883400
1115          H          -2.33945300 1.31059200 -0.75764600
1116          FragmentGeometry[angstrom] 4
1117          C          0.00000000 0.00000000 0.00000000
1118          H          0.00000000 0.00000000 1.07652900
1119          H          0.93230200 0.00000000 -0.53826500
1120          H          -0.93230200 -0.00000000 -0.53826500
1121          SymmetryFactor                6
1122          PotentialPrefactor [au]      4.68 #0.2 0.3
1123          PotentialPowerExponent       6.31
1124      End
1125      Rotor          Hindered
1126      Geometry[angstrom] 15

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1127      C      2.04184100   0.97940900
      -0.23650800
1128      O      1.63963800  -0.06987200
      0.52169000
1129      C      0.81124200  -0.99413900
      -0.15113800
1130      O     -0.38579500  -0.43724000
      -0.56930300
1131      C     -1.22597700  -0.02415200
      0.49942400
1132      C     -2.52515300   0.46978300
      -0.09104300
1133      H      2.63690400   1.70068700
      0.29810600
1134      H      1.43218100   1.25645300
      -1.08472300
1135      H      1.31526500  -1.35717500
      -1.04817800
1136      H      0.64903100  -1.80201100
      0.56648700
1137      H     -1.39588500  -0.87369500
      1.17114100
1138      H     -0.73109200   0.76294000
      1.07386200
1139      H     -3.00867800  -0.32169600
      -0.66138000
1140      H     -3.20073300   0.79539500
      0.69883400
1141      H      -2.33945300
      1.31059200  -0.75764600
1142      Group      13 14 15
1143      Axis      6 5
1144      Symmetry      3
1145      Potential [kcal/mol]      2
1146      0. 3.05
1147      End
1148      Rotor      Hindered
1149      Geometry [angstrom] 15
1150      C      2.04184100   0.97940900  -0.23650800
1151      O      1.63963800  -0.06987200   0.52169000
1152      C      0.81124200  -0.99413900  -0.15113800
1153      O     -0.38579500  -0.43724000  -0.56930300
1154      C     -1.22597700  -0.02415200   0.49942400
1155      C     -2.52515300   0.46978300  -0.09104300
1156      H      2.63690400   1.70068700   0.29810600
1157      H      1.43218100   1.25645300  -1.08472300
1158      H      1.31526500  -1.35717500  -1.04817800
1159      H      0.64903100  -1.80201100   0.56648700

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1160      H      -1.39588500   -0.87369500    1.17114100
1161      H      -0.73109200    0.76294000    1.07386200
1162      H      -3.00867800   -0.32169600   -0.66138000
1163      H      -3.20073300    0.79539500    0.69883400
1164      H      -2.33945300
1.31059200  -0.75764600
1165      Group      6 11 12
1166      Axis      5 4
1167      Symmetry    1
1168      Potential [kcal/mol]    6
1169      0. 1.627 1.045 4.613 0.766 1.227
1170      End
1171      Rotor      Hindered
1172      Geometry [angstrom] 15
1173      C      2.04184100    0.97940900   -0.23650800
1174      O      1.63963800   -0.06987200    0.52169000
1175      C      0.81124200   -0.99413900   -0.15113800
1176      O      -0.38579500   -0.43724000   -0.56930300
1177      C      -1.22597700   -0.02415200    0.49942400
1178      C      -2.52515300    0.46978300   -0.09104300
1179      H      2.63690400    1.70068700    0.29810600
1180      H      1.43218100    1.25645300   -1.08472300
1181      H      1.31526500   -1.35717500   -1.04817800
1182      H      0.64903100   -1.80201100    0.56648700
1183      H      -1.39588500   -0.87369500    1.17114100
1184      H      -0.73109200    0.76294000    1.07386200
1185      H      -3.00867800   -0.32169600   -0.66138000
1186      H      -3.20073300    0.79539500    0.69883400
1187      H      -2.33945300
1.31059200  -0.75764600
1188      Group      5
1189      Axis      4 3
1190      Symmetry    1
1191      Potential [kcal/mol]    6
1192      0. 6.906 2.099 4.464 3.800 4.790
1193      End
1194      Rotor      Hindered
1195      Geometry [angstrom] 15
1196      C      2.04184100    0.97940900   -0.23650800
1197      O      1.63963800   -0.06987200    0.52169000
1198      C      0.81124200   -0.99413900   -0.15113800
1199      O      -0.38579500   -0.43724000   -0.56930300
1200      C      -1.22597700   -0.02415200    0.49942400
1201      C      -2.52515300    0.46978300   -0.09104300
1202      H      2.63690400    1.70068700    0.29810600
1203      H      1.43218100    1.25645300   -1.08472300
1204      H      1.31526500   -1.35717500   -1.04817800
1205      H      0.64903100   -1.80201100    0.56648700

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1206      H      -1.39588500   -0.87369500    1.17114100
1207      H      -0.73109200    0.76294000    1.07386200
1208      H      -3.00867800   -0.32169600   -0.66138000
1209      H      -3.20073300    0.79539500    0.69883400
1210      H      -2.33945300
1.31059200  -0.75764600
1211      Group      1
1212      Axis      2 3
1213      Symmetry    1
1214      Potential [kcal/mol] 6
1215      0. 4.275 2.508 3.573 3.149 3.995
1216      End
1217      Rotor      Hindered
1218      Geometry [angstrom] 15
1219      C      2.04184100    0.97940900   -0.23650800
1220      O      1.63963800   -0.06987200    0.52169000
1221      C      0.81124200   -0.99413900   -0.15113800
1222      O      -0.38579500   -0.43724000   -0.56930300
1223      C      -1.22597700   -0.02415200    0.49942400
1224      C      -2.52515300    0.46978300   -0.09104300
1225      H      2.63690400    1.70068700    0.29810600
1226      H      1.43218100    1.25645300   -1.08472300
1227      H      1.31526500   -1.35717500   -1.04817800
1228      H      0.64903100   -1.80201100    0.56648700
1229      H      -1.39588500   -0.87369500    1.17114100
1230      H      -0.73109200    0.76294000    1.07386200
1231      H      -3.00867800   -0.32169600   -0.66138000
1232      H      -3.20073300    0.79539500    0.69883400
1233      H      -2.33945300
1.31059200  -0.75764600
1234      Group      7 8
1235      Axis      1 2
1236      Symmetry    2
1237      Potential [kcal/mol] 2
1238      0. 5.2
1239      End
1240      Frequencies [1/cm]      40
1241      302.16 359.65 462.79 573.73 649.76 821.45 881.67 991.14
1242      1065.83 1107.19 1161.87 1185.76 1199.09 1246.95 1269.05 1309.95
1243      1345.91 1400.15 1433.72 1446.61 1488.63 1491.73 1505.56 1519.45
1244      1536.64 3024.66 3057.19 3073.81 3076.5 3115.41 3150.44 3152.21
1245      3161.74 3302.14
1246      409.94 1411.49 1412.56 3141.77 3320.20 3321.01
1247      !57.06 80.74 172 241.97 273.48!
1248      ZeroEnergy [kcal/mol]      85.3
1249      ElectronicLevels [1/cm]      1
1250      0 2
1251      End

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1248   Barrier      B4   W1   P4   # CCO[CH]OCC + [H] = CCOCOC
1249               RRHO
1250               Stoichiometry C5H12O2
1251               Core      PhaseSpaceTheory
1252               FragmentGeometry [angstrom]      1
1253   H                0.000000      0.000000      0.000000
1254   FragmentGeometry [angstrom]  18
1255   C                1.85123800      1.36692300      -0.11393900
1256   C                1.96689700      -0.02829500      0.46760200
1257   O                1.35369200      -1.01369700      -0.36424900
1258   C                0.03415500      -0.85685700      -0.58928400
1259   O               -0.69614700      -0.61826900      0.54142300
1260   C               -2.06451100      -0.34257700      0.28446300
1261   C               -2.27184300      1.06738700      -0.23360400
1262   H                2.24378200      1.38817000      -1.12996300
1263   H                2.41909800      2.06979700      0.49527800
1264   H                0.81162300      1.69137600      -0.13652000
1265   H                3.00777400      -0.33711600      0.53429500
1266   H                1.52760000      -0.07194000      1.46460200
1267   H               -0.36385800      -1.61659300      -1.26056200
1268   H               -2.45580700      -1.07882900      -0.42562200
1269   H               -2.57592300      -0.48826100      1.23398200
1270   H               -1.74442300      1.20754600      -1.17653400
1271   H               -3.33229600      1.26016800      -0.39476900
1272   H                -1.89354200      1.79191800      0.48699300
1273   SymmetryFactor      2
1274               PotentialPrefactor [au]      0.31 #0.01 0.007
1275               PotentialPowerExponent      2.61
1276   End
1277   Rotor              Hindered
1278   Geometry [angstrom]  18
1279   C                1.85123800      1.36692300
-0.11393900
1280   C                1.96689700      -0.02829500
0.46760200
1281   O                1.35369200      -1.01369700
-0.36424900
1282   C                0.03415500      -0.85685700
-0.58928400
1283   O               -0.69614700      -0.61826900
0.54142300
1284   C               -2.06451100      -0.34257700
0.28446300
1285   C               -2.27184300      1.06738700
-0.23360400
1286   H                2.24378200      1.38817000
-1.12996300

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1287          H          2.41909800    2.06979700
0.49527800
1288          H          0.81162300    1.69137600
-0.13652000
1289          H          3.00777400   -0.33711600
0.53429500
1290          H          1.52760000   -0.07194000
1.46460200
1291          H          -0.36385800   -1.61659300
-1.26056200
1292          H          -2.45580700   -1.07882900
-0.42562200
1293          H          -2.57592300   -0.48826100
1.23398200
1294          H          -1.74442300    1.20754600
-1.17653400
1295          H          -3.33229600    1.26016800
-0.39476900
1296          H          -1.89354200    1.79191800
0.48699300
1297          Group          16 17 18
1298          Axis          7 6
1299          Symmetry          3
1300          Potential [kcal/mol]          2
1301          0. 3.025
1302          End
1303          Rotor          Hindered
1304          Geometry [angstrom]          18
1305          C          1.85123800    1.36692300   -0.11393900
1306          C          1.96689700   -0.02829500    0.46760200
1307          O          1.35369200   -1.01369700   -0.36424900
1308          C          0.03415500   -0.85685700   -0.58928400
1309          O          -0.69614700   -0.61826900    0.54142300
1310          C          -2.06451100   -0.34257700    0.28446300
1311          C          -2.27184300    1.06738700   -0.23360400
1312          H          2.24378200    1.38817000   -1.12996300
1313          H          2.41909800    2.06979700    0.49527800
1314          H          0.81162300    1.69137600   -0.13652000
1315          H          3.00777400   -0.33711600    0.53429500
1316          H          1.52760000   -0.07194000    1.46460200
1317          H          -0.36385800   -1.61659300   -1.26056200
1318          H          -2.45580700   -1.07882900   -0.42562200
1319          H          -2.57592300   -0.48826100    1.23398200
1320          H          -1.74442300    1.20754600   -1.17653400
1321          H          -3.33229600    1.26016800   -0.39476900
1322          H          -1.89354200    1.79191800
0.48699300
1323          Group          7 14 15

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1324           Axis                6 5
1325           Symmetry            1
1326           Potential [kcal/mol] 6
1327     0. 4.23 0.926 1.612 0.0435 1.442
1328     End
1329     Rotor                      Hindered
1330     Geometry [angstrom] 18
1331     C          1.85123800    1.36692300   -0.11393900
1332     C          1.96689700   -0.02829500    0.46760200
1333     O          1.35369200   -1.01369700   -0.36424900
1334     C          0.03415500   -0.85685700   -0.58928400
1335     O         -0.69614700   -0.61826900    0.54142300
1336     C         -2.06451100   -0.34257700    0.28446300
1337     C         -2.27184300    1.06738700   -0.23360400
1338     H          2.24378200    1.38817000   -1.12996300
1339     H          2.41909800    2.06979700    0.49527800
1340     H          0.81162300    1.69137600   -0.13652000
1341     H          3.00777400   -0.33711600    0.53429500
1342     H          1.52760000   -0.07194000    1.46460200
1343     H         -0.36385800   -1.61659300   -1.26056200
1344     H         -2.45580700   -1.07882900   -0.42562200
1345     H         -2.57592300   -0.48826100    1.23398200
1346     H         -1.74442300    1.20754600   -1.17653400
1347     H         -3.33229600    1.26016800   -0.39476900
1348           H                -1.89354200    1.79191800
1349     0.48699300
1349           Group                6
1350           Axis                5 4
1351           Symmetry            1
1352           Potential [kcal/mol] 4
1353     0. 2.49 1.964 9.0
1354     End
1355     Rotor                      Hindered
1356     Geometry [angstrom] 18
1357     C          1.85123800    1.36692300   -0.11393900
1358     C          1.96689700   -0.02829500    0.46760200
1359     O          1.35369200   -1.01369700   -0.36424900
1360     C          0.03415500   -0.85685700   -0.58928400
1361     O         -0.69614700   -0.61826900    0.54142300
1362     C         -2.06451100   -0.34257700    0.28446300
1363     C         -2.27184300    1.06738700   -0.23360400
1364     H          2.24378200    1.38817000   -1.12996300
1365     H          2.41909800    2.06979700    0.49527800
1366     H          0.81162300    1.69137600   -0.13652000
1367     H          3.00777400   -0.33711600    0.53429500
1368     H          1.52760000   -0.07194000    1.46460200
1369     H         -0.36385800   -1.61659300   -1.26056200
1370     H         -2.45580700   -1.07882900   -0.42562200

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1371      H      -2.57592300   -0.48826100   1.23398200
1372      H      -1.74442300    1.20754600  -1.17653400
1373      H      -3.33229600    1.26016800  -0.39476900
1374      H      -1.89354200    1.79191800
0.48699300
1375      Group      2
1376      Axis      3 4
1377      Symmetry    1
1378      Potential [kcal/mol] 4
1379      0. 2.49 1.964 9.0
1380      End
1381      Rotor      Hindered
1382      Geometry [angstrom] 18
1383      C      1.85123800   1.36692300  -0.11393900
1384      C      1.96689700   -0.02829500  0.46760200
1385      O      1.35369200   -1.01369700  -0.36424900
1386      C      0.03415500   -0.85685700  -0.58928400
1387      O      -0.69614700   -0.61826900  0.54142300
1388      C      -2.06451100   -0.34257700  0.28446300
1389      C      -2.27184300    1.06738700  -0.23360400
1390      H      2.24378200    1.38817000  -1.12996300
1391      H      2.41909800    2.06979700  0.49527800
1392      H      0.81162300    1.69137600  -0.13652000
1393      H      3.00777400   -0.33711600  0.53429500
1394      H      1.52760000   -0.07194000  1.46460200
1395      H      -0.36385800   -1.61659300  -1.26056200
1396      H      -2.45580700   -1.07882900  -0.42562200
1397      H      -2.57592300   -0.48826100  1.23398200
1398      H      -1.74442300    1.20754600  -1.17653400
1399      H      -3.33229600    1.26016800  -0.39476900
1400      H      -1.89354200    1.79191800
0.48699300
1401      Group      1 11 12
1402      Axis      2 3
1403      Symmetry    1
1404      Potential [kcal/mol] 6
1405      0. 4.23 0.926 1.612 0.0435 1.442
1406      End
1407      Rotor      Hindered
1408      Geometry [angstrom] 18
1409      C      1.85123800   1.36692300  -0.11393900
1410      C      1.96689700   -0.02829500  0.46760200
1411      O      1.35369200   -1.01369700  -0.36424900
1412      C      0.03415500   -0.85685700  -0.58928400
1413      O      -0.69614700   -0.61826900  0.54142300
1414      C      -2.06451100   -0.34257700  0.28446300
1415      C      -2.27184300    1.06738700  -0.23360400
1416      H      2.24378200    1.38817000  -1.12996300

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1417      H          2.41909800    2.06979700    0.49527800
1418      H          0.81162300    1.69137600   -0.13652000
1419      H          3.00777400   -0.33711600    0.53429500
1420      H          1.52760000   -0.07194000    1.46460200
1421      H         -0.36385800   -1.61659300   -1.26056200
1422      H         -2.45580700   -1.07882900   -0.42562200
1423      H         -2.57592300   -0.48826100    1.23398200
1424      H         -1.74442300    1.20754600   -1.17653400
1425      H         -3.33229600    1.26016800   -0.39476900
1426      H          -1.89354200    1.79191800
0.48699300
1427      Group          8 9 10
1428      Axis          1 2
1429      Symmetry        3
1430      Potential[kcal/mol] 2
1431      0. 3.025
1432      End
1433      Frequencies [1/cm] 42
1434      277.13 352.87 422.86 475.76 607.35 809.76 811.76 869.59
      918.15 947.28 1039.68 1082.94 1115.36 1118.49 1175.57 1199.67
      1232.05 1282.91 1333.66 1342.41 1365.73 1397.21 1401.53 1423.49
      1442.81 1485.7 1486.96 1500.82 1502.41 1521.69 1527.53 3037.38
      3066.85 3070.41 3086.17 3105.4 3121.98 3131.75 3143.04 3145.58
      3149.98 3156.17
1435      !54.18 70.62 121.24 175.73 222.29 268.03!Torsions
1436      ZeroEnergy[kcal/mol] 97.3
1437      ElectronicLevels [1/cm] 1
1438      0 2
1439      End
1440      Barrier      B5 W1 P5 # CCOC0 [CH]C + [H] = CCOC0CC
1441      RRHO
1442      Stoichiometry C5H12O2
1443      Core PhaseSpaceTheory
1444      FragmentGeometry [angstrom] 1
1445      H          0.000000    0.000000    0.000000
1446      FragmentGeometry [angstrom] 18
1447      C          -1.75842200   -0.13403300   -0.46781200
1448      O          -1.09509700    0.60904400    0.46548700
1449      C          -0.01330100    1.35501300   -0.04090700
1450      C          -2.85410500   -0.96514700    0.08007400
1451      O          1.01893100    0.55641700   -0.51103000
1452      C          1.65649100   -0.20390200    0.50439200
1453      C          2.80557300   -0.95567500   -0.12445000
1454      H          -2.47846600   -1.76188100    0.73417500
1455      H          -3.41611000   -1.43101500   -0.72713700
1456      H          -3.53683600   -0.35551300    0.67407300
1457      H          -1.17785600   -0.44495900   -1.32790800
1458      H          -0.34255100    1.96285200   -0.88525400

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1459      H      0.31673100      1.98162600      0.79154500
1460      H      2.01218200      0.47292700      1.29023000
1461      H      0.93781500     -0.89170300      0.95729300
1462      H      3.51379600     -0.26075000     -0.57288800
1463      H      3.32540300     -1.55052000      0.62546900
1464      H      2.43780800     -1.62229200     -0.90303500
1465      SymmetryFactor      2
1466      PotentialPrefactor [au]      0.31      #0.07 0.06
1467      PotentialPowerExponent      2.65
1468      End
1469      Rotor      Hindered
1470      Geometry [angstrom]      18
1471      C      -1.75842200     -0.13403300
-0.46781200
1472      O      -1.09509700      0.60904400
0.46548700
1473      C      -0.01330100      1.35501300
-0.04090700
1474      C      -2.85410500     -0.96514700
0.08007400
1475      O      1.01893100      0.55641700
-0.51103000
1476      C      1.65649100     -0.20390200
0.50439200
1477      C      2.80557300     -0.95567500
-0.12445000
1478      H      -2.47846600     -1.76188100
0.73417500
1479      H      -3.41611000     -1.43101500
-0.72713700
1480      H      -3.53683600     -0.35551300
0.67407300
1481      H      -1.17785600     -0.44495900
-1.32790800
1482      H      -0.34255100      1.96285200
-0.88525400
1483      H      0.31673100      1.98162600
0.79154500
1484      H      2.01218200      0.47292700
1.29023000
1485      H      0.93781500     -0.89170300
0.95729300
1486      H      3.51379600     -0.26075000
-0.57288800
1487      H      3.32540300     -1.55052000
0.62546900
1488      H      2.43780800     -1.62229200
-0.90303500

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1489          Group                16 17 18
1490          Axis                  7  6
1491          Symmetry                3
1492          Potential[kcal/mol]     2
1493          0. 3.0522
1494          End
1495          Rotor                    Hindered
1496          Geometry[angstrom]  18
1497          C                        -1.75842200  -0.13403300
1498          O                        -1.09509700   0.60904400
1499          C                        -0.01330100   1.35501300
1500          C                        -2.85410500  -0.96514700
1501          O                        1.01893100   0.55641700
1502          C                        1.65649100  -0.20390200
1503          C                        2.80557300  -0.95567500
1504          H                        -2.47846600  -1.76188100
1505          H                        -3.41611000  -1.43101500
1506          H                        -3.53683600  -0.35551300
1507          H                        -1.17785600  -0.44495900
1508          H                        -0.34255100   1.96285200
1509          H                        0.31673100   1.98162600
1510          H                        2.01218200   0.47292700
1511          H                        0.93781500  -0.89170300
1512          H                        3.51379600  -0.26075000
1513          H                        3.32540300  -1.55052000
1514          H                        2.43780800
1515          -1.62229200  -0.90303500
1516          Group                7 14 15
1517          Axis                  6  5
1518          Symmetry                1
1519          Potential[kcal/mol]     8

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1519      0. 1.627 1.032 1.115 1.063 4.677 0.586 1.190
1520      End
1521      Rotor                      Hindered
1522      Geometry [angstrom] 18
1523      C                          -1.75842200  -0.13403300
1524      -0.46781200
1525      O                          -1.09509700  0.60904400
1526      0.46548700
1527      C                          -0.01330100  1.35501300
1528      -0.04090700
1529      C                          -2.85410500  -0.96514700
1530      0.08007400
1531      O                          1.01893100  0.55641700
1532      -0.51103000
1533      C                          1.65649100  -0.20390200
1534      0.50439200
1535      C                          2.80557300  -0.95567500
1536      -0.12445000
1537      H                          -2.47846600  -1.76188100
1538      0.73417500
1539      H                          -3.41611000  -1.43101500
1540      -0.72713700
1541      H                          -3.53683600  -0.35551300
1542      0.67407300
1543      H                          -1.17785600  -0.44495900
1544      -1.32790800
1545      H                          -0.34255100  1.96285200
1546      -0.88525400
1547      H                          0.31673100  1.98162600
1548      0.79154500
1549      H                          2.01218200  0.47292700
1550      1.29023000
1551      H                          0.93781500  -0.89170300
1552      0.95729300
1553      H                          3.51379600  -0.26075000
1554      -0.57288800
1555      H                          3.32540300  -1.55052000
1556      0.62546900
1557      H                          2.43780800
1558      -1.62229200  -0.90303500
1559      Group                      6
1560      Axis                      5 3
1561      Symmetry                  1
1562      Potential [kcal/mol]      6
1563      0. 6.63 2.07 3.64 2.99 4.09
1564      End
1565      Rotor                      Hindered
1566      Geometry [angstrom] 18

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1549          C          -1.75842200   -0.13403300
      -0.46781200
1550          O          -1.09509700    0.60904400
      0.46548700
1551          C          -0.01330100    1.35501300
      -0.04090700
1552          C          -2.85410500   -0.96514700
      0.08007400
1553          O          1.01893100    0.55641700
      -0.51103000
1554          C          1.65649100   -0.20390200
      0.50439200
1555          C          2.80557300   -0.95567500
      -0.12445000
1556          H          -2.47846600   -1.76188100
      0.73417500
1557          H          -3.41611000   -1.43101500
      -0.72713700
1558          H          -3.53683600   -0.35551300
      0.67407300
1559          H          -1.17785600   -0.44495900
      -1.32790800
1560          H          -0.34255100    1.96285200
      -0.88525400
1561          H          0.31673100    1.98162600
      0.79154500
1562          H          2.01218200    0.47292700
      1.29023000
1563          H          0.93781500   -0.89170300
      0.95729300
1564          H          3.51379600   -0.26075000
      -0.57288800
1565          H          3.32540300   -1.55052000
      0.62546900
1566          H          2.43780800
      -1.62229200   -0.90303500
1567          Group          1
1568          Axis          2 3
1569          Symmetry          1
1570          Potential [kcal/mol]          6
1571          0. 9.97 1.65 2.70 2.29 2.93
1572          End
1573          Rotor          Hindered
1574          Geometry [angstrom]          18
1575          C          -1.75842200   -0.13403300
      -0.46781200
1576          O          -1.09509700    0.60904400
      0.46548700

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1577          C          -0.01330100    1.35501300
      -0.04090700
1578          C          -2.85410500   -0.96514700
      0.08007400
1579          O          1.01893100    0.55641700
      -0.51103000
1580          C          1.65649100   -0.20390200
      0.50439200
1581          C          2.80557300   -0.95567500
      -0.12445000
1582          H          -2.47846600   -1.76188100
      0.73417500
1583          H          -3.41611000   -1.43101500
      -0.72713700
1584          H          -3.53683600   -0.35551300
      0.67407300
1585          H          -1.17785600   -0.44495900
      -1.32790800
1586          H          -0.34255100    1.96285200
      -0.88525400
1587          H          0.31673100    1.98162600
      0.79154500
1588          H          2.01218200    0.47292700
      1.29023000
1589          H          0.93781500   -0.89170300
      0.95729300
1590          H          3.51379600   -0.26075000
      -0.57288800
1591          H          3.32540300   -1.55052000
      0.62546900
1592          H          2.43780800
      -1.62229200  -0.90303500
1593          Group          4 11
1594          Axis          1 2
1595          Symmetry          1
1596          Potential [kcal/mol] 4
1597          0. 4.573 1.338 4.174
1598          End
1599          Rotor          Hindered
1600          Geometry [angstrom] 18
1601          C          -1.75842200   -0.13403300
      -0.46781200
1602          O          -1.09509700    0.60904400
      0.46548700
1603          C          -0.01330100    1.35501300
      -0.04090700
1604          C          -2.85410500   -0.96514700
      0.08007400

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1605          O          1.01893100    0.55641700
      -0.51103000
1606          C          1.65649100   -0.20390200
      0.50439200
1607          C          2.80557300   -0.95567500
      -0.12445000
1608          H          -2.47846600   -1.76188100
      0.73417500
1609          H          -3.41611000   -1.43101500
      -0.72713700
1610          H          -3.53683600   -0.35551300
      0.67407300
1611          H          -1.17785600   -0.44495900
      -1.32790800
1612          H          -0.34255100    1.96285200
      -0.88525400
1613          H          0.31673100    1.98162600
      0.79154500
1614          H          2.01218200    0.47292700
      1.29023000
1615          H          0.93781500   -0.89170300
      0.95729300
1616          H          3.51379600   -0.26075000
      -0.57288800
1617          H          3.32540300   -1.55052000
      0.62546900
1618                                H          2.43780800
      -1.62229200   -0.90303500
1619          Group          8 9 10
1620          Axis          4 1
1621          Symmetry          3
1622          Potential [kcal/mol]          2
1623          0. 1.32
1624          End
1625          Frequencies [1/cm] 42
1626          51.91   330.6 364.23 484.26 575.24 677.56 821.46 881.7
901.01 1022.16 1064.95 1089.77 1110.76 1148.96 1179.46 1192.1
1214.36 1257.91 1308.65 1347.01 1382.68 1400.39 1426.85 1436.73
1464.37 1469.93 1488.79 1495.37 1505.5 1520.02 1537.66 3006.46
3021.82 3055.1 3073.03 3075.09 3088.73 3113.75 3146.3 3149.87
3151.12 3182.77
1627          !62.09 81.45 159.44 197.19 241.07 261.41!Torsions
1628          ZeroEnergy [kcal/mol]          94.6
1629          ElectronicLevels [1/cm]          1
1630          0 2
1631          End
1632          Barrier          B6 W1 P6 # CCOCOC [CH2] + [H] = CCOCOC
1633          RRHO

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1634                               Stoichiometry C5H12O2
1635                               Core      PhaseSpaceTheory
1636                               FragmentGeometry [angstrom]      1
1637                               H          0.000000      0.000000      0.000000
1638                               FragmentGeometry [angstrom]      18
1639                               C          2.94233500     -0.67034400     -0.14761700
1640                               C          1.78742600      0.14457100      0.38575300
1641                               O          0.80817900      0.24343000     -0.63524800
1642                               C         -0.28223800      1.03652700     -0.28368300
1643                               O         -1.03682300      0.49569300      0.76284600
1644                               C         -1.71162100     -0.70408300      0.40845000
1645                               C         -2.86279900     -0.45941400     -0.49590600
1646                               H          2.60356500     -1.66748400     -0.42538500
1647                               H          3.72126300     -0.76622200      0.60785300
1648                               H          3.36704400     -0.19434500     -1.03009700
1649                               H          1.35335100     -0.32249500      1.27350700
1650                               H          2.11614900      1.15201300      0.66825800
1651                               H          0.04724600      2.01712500      0.07145300
1652                               H         -0.88407800      1.13637100     -1.19045600
1653                               H         -1.00929200     -1.41413700     -0.03811800
1654                               H         -2.04480500     -1.13149900      1.36035400
1655                               H         -3.47587800      0.41624000     -0.34190400
1656                               H          -3.20403400     -1.22209400     -1.17822300
1657                               SymmetryFactor                                2
1658                               PotentialPrefactor [au]                0.32      #0.07
1659                               PotentialPowerExponent                2.58
1660                               End
1661                               Rotor                                Hindered
1662                               Geometry [angstrom]      18
1663                               C          2.94233500     -0.67034400
1664                               C          1.78742600      0.14457100
1665                               O          0.80817900      0.24343000
1666                               C         -0.28223800      1.03652700
1667                               O         -1.03682300      0.49569300
1668                               C         -1.71162100     -0.70408300
1669                               C         -2.86279900     -0.45941400
1670                               H          2.60356500     -1.66748400
1671                               H          3.72126300     -0.76622200
0.60785300

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```

1672      H      3.36704400  -0.19434500
-1.03009700
1673      H      1.35335100  -0.32249500
1.27350700
1674      H      2.11614900   1.15201300
0.66825800
1675      H      0.04724600   2.01712500
0.07145300
1676      H     -0.88407800   1.13637100
-1.19045600
1677      H     -1.00929200  -1.41413700
-0.03811800
1678      H     -2.04480500  -1.13149900
1.36035400
1679      H     -3.47587800   0.41624000
-0.34190400
1680      H     -3.20403400  -1.22209400
-1.17822300
1681      Group      8 9 10
1682      Axis      1 2
1683      Symmetry    3
1684      Potential[kcal/mol] 2
1685      0. 3.048
1686      End
1687      Rotor      Hindered
1688      Geometry[angstrom] 18
1689      C      2.94233500  -0.67034400
-0.14761700
1690      C      1.78742600   0.14457100
0.38575300
1691      O      0.80817900   0.24343000
-0.63524800
1692      C     -0.28223800   1.03652700
-0.28368300
1693      O     -1.03682300   0.49569300
0.76284600
1694      C     -1.71162100  -0.70408300
0.40845000
1695      C     -2.86279900  -0.45941400
-0.49590600
1696      H      2.60356500  -1.66748400
-0.42538500
1697      H      3.72126300  -0.76622200
0.60785300
1698      H      3.36704400  -0.19434500
-1.03009700
1699      H      1.35335100  -0.32249500
1.27350700

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1700          H          2.11614900    1.15201300
0.66825800
1701          H          0.04724600    2.01712500
0.07145300
1702          H         -0.88407800    1.13637100
-1.19045600
1703          H         -1.00929200   -1.41413700
-0.03811800
1704          H         -2.04480500   -1.13149900
1.36035400
1705          H         -3.47587800    0.41624000
-0.34190400
1706          H          -3.20403400   -1.22209400   -1.17822300
1707          Group          1 11 12
1708          Axis          2 3
1709          Symmetry          1
1710          Potential[kcal/mol]          8
1711          0. 1.525 0.954 1.108 1.077 4.728 0.771 1.294
1712          End
1713          Rotor          Hindered
1714          Geometry[angstrom] 18
1715          C          2.94233500   -0.67034400
-0.14761700
1716          C          1.78742600    0.14457100
0.38575300
1717          O          0.80817900    0.24343000
-0.63524800
1718          C         -0.28223800    1.03652700
-0.28368300
1719          O         -1.03682300    0.49569300
0.76284600
1720          C         -1.71162100   -0.70408300
0.40845000
1721          C         -2.86279900   -0.45941400
-0.49590600
1722          H          2.60356500   -1.66748400
-0.42538500
1723          H          3.72126300   -0.76622200
0.60785300
1724          H          3.36704400   -0.19434500
-1.03009700
1725          H          1.35335100   -0.32249500
1.27350700
1726          H          2.11614900    1.15201300
0.66825800
1727          H          0.04724600    2.01712500
0.07145300

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1728		H	-0.88407800	1.13637100
	-1.19045600			
1729		H	-1.00929200	-1.41413700
	-0.03811800			
1730		H	-2.04480500	-1.13149900
	1.36035400			
1731		H	-3.47587800	0.41624000
	-0.34190400			
1732	H		-3.20403400	-1.22209400
				-1.17822300
1733		Group	2	
1734		Axis	3 4	
1735		Symmetry	1	
1736		Potential [kcal/mol]	6	
1737	0. 7.39 3.02 3.07 2.66 3.95			
1738	End			
1739	Rotor		Hindered	
1740	Geometry [angstrom]	18		
1741		C	2.94233500	-0.67034400
	-0.14761700			
1742		C	1.78742600	0.14457100
	0.38575300			
1743		O	0.80817900	0.24343000
	-0.63524800			
1744		C	-0.28223800	1.03652700
	-0.28368300			
1745		O	-1.03682300	0.49569300
	0.76284600			
1746		C	-1.71162100	-0.70408300
	0.40845000			
1747		C	-2.86279900	-0.45941400
	-0.49590600			
1748		H	2.60356500	-1.66748400
	-0.42538500			
1749		H	3.72126300	-0.76622200
	0.60785300			
1750		H	3.36704400	-0.19434500
	-1.03009700			
1751		H	1.35335100	-0.32249500
	1.27350700			
1752		H	2.11614900	1.15201300
	0.66825800			
1753		H	0.04724600	2.01712500
	0.07145300			
1754		H	-0.88407800	1.13637100
	-1.19045600			
1755		H	-1.00929200	-1.41413700
	-0.03811800			

```

1756          H          -2.04480500   -1.13149900
      1.36035400
1757          H          -3.47587800    0.41624000
      -0.34190400
1758          H          -3.20403400   -1.22209400   -1.17822300
1759          Group              6
1760          Axis              5 4
1761          Symmetry          1
1762          Potential[kcal/mol]  6
1763          0. 7.87 3.80 3.97 3.29 4.46
1764          End
1765          Rotor              Hindered
1766          Geometry[angstrom]  18
1767          C          2.94233500   -0.67034400
      -0.14761700
1768          C          1.78742600    0.14457100
      0.38575300
1769          O          0.80817900    0.24343000
      -0.63524800
1770          C          -0.28223800    1.03652700
      -0.28368300
1771          O          -1.03682300    0.49569300
      0.76284600
1772          C          -1.71162100   -0.70408300
      0.40845000
1773          C          -2.86279900   -0.45941400
      -0.49590600
1774          H          2.60356500   -1.66748400
      -0.42538500
1775          H          3.72126300   -0.76622200
      0.60785300
1776          H          3.36704400   -0.19434500
      -1.03009700
1777          H          1.35335100   -0.32249500
      1.27350700
1778          H          2.11614900    1.15201300
      0.66825800
1779          H          0.04724600    2.01712500
      0.07145300
1780          H          -0.88407800    1.13637100
      -1.19045600
1781          H          -1.00929200   -1.41413700
      -0.03811800
1782          H          -2.04480500   -1.13149900
      1.36035400
1783          H          -3.47587800    0.41624000
      -0.34190400
1784          H          -3.20403400   -1.22209400   -1.17822300

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1785      Group          7 15 16
1786      Axis          6 5
1787      Symmetry      1
1788      Potential [kcal/mol] 6
1789      0. 3.2 0.26 1.347 0.319 1.836
1790      End
1791      Rotor          Hindered
1792      Geometry [angstrom] 18
1793      C              2.94233500   -0.67034400
1794      C              1.78742600   0.14457100
1795      O              0.80817900   0.24343000
1796      C              -0.28223800   1.03652700
1797      O              -1.03682300   0.49569300
1798      C              -1.71162100  -0.70408300
1799      C              -2.86279900  -0.45941400
1800      H              2.60356500  -1.66748400
1801      H              3.72126300  -0.76622200
1802      H              3.36704400  -0.19434500
1803      H              1.35335100  -0.32249500
1804      H              2.11614900   1.15201300
1805      H              0.04724600   2.01712500
1806      H              -0.88407800   1.13637100
1807      H              -1.00929200  -1.41413700
1808      H              -2.04480500  -1.13149900
1809      H              -3.47587800   0.41624000
1810      H              -3.20403400  -1.22209400  -1.17822300
1811      Group          17 18
1812      Axis          7 6
1813      Symmetry      2
1814      Potential [kcal/mol] 2
1815      0. 1.67

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```
1816 End
1817 Frequencies [1/cm] 42
1818 47.2 325.16 438.49 468.49 529.08 646.42 821.67 848.43
882.07 944.34 1054.46 1063.51 1101.92 1130.71 1147.54 1183.77
1195.02 1221.39 1300.89 1309.84 1347.07 1395.04 1399.47 1433.39 1453
1459.44 1488.57 1491.71 1505.47 1516.64 1539.3 3019.76 3025.12
3046.83 3068.1 3072.25 3074.09 3099.48 3148.38 3150.29 3174.81
3285.12
1819 !58.76 93.4 190.21 194.44 239.52 287.32! Torsions
1820 ZeroEnergy [kcal/mol] 101.7
1821 ElectronicLevels [1/cm] 1
1822 0 2
1823 End
1824 Barrier B7 W1 P7 # CCOC0 + C=C
1825 Variational
1826 RRHO
1827 Geometry [angstrom] 19
1828 C 1.86865600 -1.45276400 -0.31453300
1829 C 1.99044900 -0.44756700 0.66581100
1830 O 1.26508200 0.87588900 -0.40719600
1831 C 0.09293600 1.53443100 -0.03245800
1832 O -0.88100900 0.67601300 0.48752700
1833 C -1.56221900 -0.08691000 -0.49360500
1834 C -2.57078700 -0.96542100 0.20899600
1835 H 1.29830200 -0.26031300 -0.88156200
1836 H 1.10214500 -2.20418100 -0.18020400
1837 H 2.75208400 -1.75617600 -0.85770000
1838 H 1.27823100 -0.38784500 1.47887900
1839 H 2.93441700 0.05024500 0.83885600
1840 H 0.32416900 2.24814600 0.75878600
1841 H -0.29968900 2.06766900 -0.90719200
1842 H -2.05815100 0.59095600 -1.19789500
1843 H -0.85226800 -0.69772800 -1.06030800
1844 H -3.26842100 -0.35617500 0.78153600
1845 H -3.13188900 -1.55490100 -0.51496800
1846 H -2.06572800 -1.64552100 0.89385000
1847 Core RigidRotor
1848 SymmetryFactor 1
1849 End
1850 Rotor Hindered
1851 Group 17 18 19
1852 Axis 7 6
1853 Symmetry 3
1854 Potential [kcal/mol] 2
1855 0. 3.058
1856 End
1857 Rotor Hindered
1858 Group 7 15 16
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1859   Axis                6 5
1860   Symmetry            1
1861   Potential[kcal/mol] 6
1862     0. 1.35 1.04 4.81 1.58 2.55
1863   End
1864   Rotor              Hindered
1865   Group                6
1866   Axis                5 4
1867   Symmetry            1
1868   Potential[kcal/mol] 6
1869     0. 6.72 2.04 3.04 1.23 2.59
1870   End
1871   Rotor              Hindered
1872   Group                5 13 14
1873   Axis                4 3
1874   Symmetry            1
1875   Potential[kcal/mol] 6
1876     0. 7.64 2.448 3.104 2.498 3.552
1877   End
1878   Frequencies [1/cm]  46
1879     156.89 232.28 306.77 392.59 430.39 523.33 561.46 644.79
      806.42 823.21 829.09 882.54 992.11 1052.68 1062.67 1110.28
      1161.62 1174.7 1190.47 1200.37 1238.95 1263.79 1302.66 1325.48
      1333.35 1400.42 1424.26 1447.03 1458.78 1488.27 1504.62 1512.63
      1534.68 1538.77 1637.35 3015.51 3023.81 3061.59 3071.64 3105.62
      3146.8 3151.38 3160.92 3167.52 3242.6 3263.78
1880     !33.09 57.13 115.63 257.80!
1881   ZeroEnergy[kcal/mol]                69.1
1882     ElectronicLevels [1/cm]            1
1883       0 1
1884   End
1885     Tunneling                Eckart
1886     ImaginaryFrequency [1/cm]          1895.98
1887     WellDepth[kcal/mol]                69.1
1888     WellDepth[kcal/mol]                54.0
1889   End
1890   End
1891   Barrier      B8   W1  P8   # CCOCOC = CCOCC + CH2O
1892   Variational
1893     RRHO
1894     Geometry [angstrom]                19
1895     C                -2.39520700  -0.82724900  -0.51891400
1896   C                -1.39093000  -0.66063200  0.56249100
1897   O                -1.19657700  1.38141600  0.12043300
1898   C                0.09893800  1.32827100  -0.02911100
1899   O                0.35643600  -0.13510600  -0.17294400
1900   C                1.53267100  -0.65605400  0.42368400
1901   C                2.76857500  -0.25975500  -0.36094600

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1902 H -3.07922600 0.01142000 -0.56095300
1903 H -2.93786300 -1.76214600 -0.34070600
1904 H -1.89178900 -0.92075700 -1.47998200
1905 H -1.70306900 -0.17697700 1.47390300
1906 H -0.81910900 -1.56486500 0.75466800
1907 H 0.49912000 1.78379300 -0.94929300
1908 H 0.71847700 1.64278600 0.83753600
1909 H 1.59917600 -0.30773100 1.46004800
1910 H 1.41783700 -1.74124200 0.43160200
1911 H 2.90422800 0.82086700 -0.34377600
1912 H 3.65513800 -0.72317000 0.07117700
1913 H 2.67392600 -0.57993700 -1.39737100
1914 Core RigidRotor
1915 SymmetryFactor 1
1916 End
1917 Rotor Hindered
1918 Group 17 18 19
1919 Axis 7 6
1920 Symmetry 3
1921 Potential[kcal/mol] 2
1922 0. 3.35
1923 End
1924 Rotor Hindered
1925 Group 7 15 16
1926 Axis 6 5
1927 Symmetry 1
1928 Potential[kcal/mol] 6
1929 0. 4.19 0.06 2.95 0.66 1.12
1930 End
1931 Rotor Hindered
1932 Group 8 9 10
1933 Axis 1 2
1934 Symmetry 3
1935 Potential[kcal/mol] 2
1936 0. 2.13
1937 End
1938 Frequencies [1/cm] 47
1939 96.3 105.71 145.29 330.96 340.83 369.02 516.1 582.62 761.54
808.19 826.21 906.79 931.22 1016.47 1093.12 1111.39 1132.85 1165.18
1202.86 1220.68 1225.4 1293.97 1326.72 1337.29 1395.31 1397.14
1405.6 1425.28 1462.44 1491.18 1495.1 1498.05 1514.33 1520.86
1559.22 2865.6 2964.17 3035.16 3040.27 3070.34 3097.37 3111.69
3129.46 3145.89 3152.73 3200.93 3251.72
1940 !61.84 206.8 244.8! Torsions
1941 ZeroEnergy[kcal/mol] 77.3
1942 ElectronicLevels [1/cm] 1
1943 0 1
1944 End

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1945           Tunneling           Eckart
1946           ImaginaryFrequency [1/cm]           652.47
1947           WellDepth [kcal/mol]           77.4
1948           WellDepth [kcal/mol]           63.6
1949           End
1950           End
1951           Barrier           B9           W1           P9           # CC0 + CC0 [[C]]
1952           Variational
1953           RRHO
1954           Geometry [angstrom]           19
1955           C           0.0038259251           -0.0042530719           -0.0001336264
1956           O           0.0017347903           -0.010888302           1.3998440961
1957           C           1.9805950929           0.0071986858           2.0367355204
1958           O           2.1150633304           -0.644072419           3.1420379586
1959           C           1.5115774353           -0.0615116068           4.3182969376
1960           H           0.8771096948           0.5513356318           -0.381102682
1961           H           -0.8779935791           0.5380113494           -0.3595213374
1962           H           0.9726964839           0.6786413733           1.7934304765
1963           H           2.4340106877           -0.560885994           1.2226801616
1964           H           2.2018398687           -0.2733256747           5.1319615639
1965           H           1.4491435901           1.015395797           4.1612833391
1966           C           0.0099014939           -1.4151833681           -0.5630102247
1967           H           -0.8644159281           -1.9598265483           -0.2087409289
1968           H           -0.0008499521           -1.4070883509           -1.653667084
1969           H           0.8986331154           -1.9548624097           -0.2315695773
1970           C           0.1532008337           -0.6830784574           4.5474241493
1971           H           -0.2888191848           -0.2649151568           5.4513723677
1972           H           -0.4972758232           -0.4825290689           3.6978352197
1973           H           0.2467171625           -1.760558391           4.6735926872
1974           Core RigidRotor
1975           SymmetryFactor           1
1976           End
1977           Rotor           Hindered
1978           Group           17 18 19
1979           Axis           5 16
1980           Symmetry           3
1981           Potential [kcal/mol]           2
1982           0. 3.25
1983           End
1984           Rotor           Hindered
1985           Group           13 14 15
1986           Axis           12 1
1987           Symmetry           3
1988           Potential [kcal/mol]           2
1989           0. 3.06
1990           End
1991           Rotor           Hindered
1992           Group           10 11 16

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1993      Axis                    5 4
1994      Symmetry                    1
1995      Potential[kcal/mol]        6
1996      0. 1.43 1.00 1.51 1.14 2.39
1997      End
1998      Rotor      Hindered
1999      Group                    6 7 12
2000      Axis                    1 2
2001      Symmetry                    1
2002      Potential[kcal/mol]        6
2003      0. 1.63 0.26 1.83 1.79 2.27
2004      End
2005      Frequencies [1/cm]         46
2006      57.68 115.65 173.41 204.81 412.24 436.0 518.05 583.09 806.28
      825.98 866.59 906.5 1001.4 1040.22 1092.44 1132.2 1144.14 1174.41
      1196.28 1300.57 1314.14 1357.33 1373.13 1391.73 1409.96 1422.91
      1446.59 1486.27 1488.23 1496.09 1502.8 1512.75 1521.62 1539.0
      2078.49 2949.78 3027.16 3057.33 3072.27 3088.35 3120.0 3125.87
      3141.14 3141.62 3151.3 3166.49
2007      ! 243.49 274.69 96.67 70.72! Torsions
2008      ZeroEnergy[kcal/mol]        68.2
2009      ElectronicLevels [1/cm]     1
2010      0      1
2011      End
2012      Tunneling      Eckart
2013      ImaginaryFrequency [1/cm]   1511.79
2014      WellDepth[kcal/mol]         68.16
2015      WellDepth[kcal/mol]         1.16
2016      End
2017      End
2018      Barrier      B10      W1      P10      # CCOH CH2O C=C
2019      Variational
2020      RRHO
2021      Geometry [angstrom]          19
2022      C              1.09177900      1.60943000      0.14754200
2023      C              -1.75265200     -0.31317700      0.43254800
2024      H              -1.48855400      0.10686500      1.40821200
2025      H              -2.09281100     -1.33910800      0.58451200
2026      O              -0.58553800     -0.37529200     -0.38189600
2027      H              0.00309600      0.55017000     -0.25221400
2028      H              0.90385400      2.29978100     -0.66527500
2029      H              0.76921900      1.92764000      1.13099700
2030      C              0.63260000     -1.31249400      0.25698700
2031      H              0.20851400     -2.31508200      0.13578800
2032      H              0.56578400     -0.95256000      1.30060800
2033      C              2.18120200      0.75032100      0.04848500
2034      H              2.67436300      0.40555900      0.94922100
2035      H              2.81620200      0.77532800     -0.82543400

```

```

2036 O          1.68231100   -1.02848400   -0.40355700
2037 C          -2.80708300    0.52572300   -0.25385800
2038 H          -3.71065400    0.56748400    0.35316500
2039 H          -2.44337000    1.54240400   -0.40061900
2040 H          -3.05490500    0.10290000   -1.22555700
2041   Core RigidRotor
2042       SymmetryFactor          1
2043   End
2044   Rotor      Hindered
2045       Group          17 18 19
2046       Axis          16 2
2047           Symmetry          3
2048           Potential[kcal/mol]  2
2049   0. 3.26
2050   End
2051   Rotor      Hindered
2052       Group          13 14 15
2053       Axis          12 1
2054           Symmetry          6
2055           Potential[kcal/mol]  1
2056   0. 0.95 0.74 3.71 1.64 1.80
2057   End
2058       Frequencies [1/cm]      47
2059   107.03 142.06 196.62 244.83 289.90 396.15 457.92 515.76 584.59
2060   614.63 712.31 816.19 822.61
2061   917.22 1001.43 1065.57 1093.25 1100.82 1152.91 1166.80 1199.68
2062   1242.41 1249.24 1276.75 1327.38
2063   1357.11 1399.12 1407.76 1428.58 1457.49 1481.81 1493.80 1502.11
2064   1525.07 1536.95 1587.71 1774.83 2927.04
2065   3044.60 3048.35 3072.77 3096.84 3143.38 3147.90 3155.78 3157.36
2066   3221.79 3247.73
2067   ! 53.45 264.84 ! Torsions
2068   ZeroEnergy[kcal/mol]          67.9
2069       ElectronicLevels [1/cm]  1
2070   0 1
2071   End
2072       Tunneling      Eckart
2073       ImaginaryFrequency [1/cm]  945.04
2074       WellDepth[kcal/mol]      67.87
2075       WellDepth[kcal/mol]      38.52
2076   End
2077   End
2078 End

```

E.3 DPM

```

1 TemperatureList [K]          500 510 520 530 540 550 560 570
   580 590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740

```

```

750 760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910
920 930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060
1070 1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190
1200 1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320
1330 1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450
1460 1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580
1590 1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710
1720 1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840
1850 1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970
1980 1990 2000
2 PressureList[atm]                0.00001 0.001 0.01 0.1 1 10
  100.
3 !PressureList[bar]                1.
4 EnergyStepOverTemperature        .2
5 ExcessEnergyOverTemperature      30
6 ModelEnergyLimit[kcal/mol]       400
7 CalculationMethod                direct
8 !CalculationMethod                low-eigenvalue !direct
9 WellCutoff                        10
10 ChemicalEigenvalueMax            0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor[1/cm]                200 ! He
15       Power                        .85
16       ExponentCutoff              15
17     End
18   CollisionFrequency
19     LennardJones
20       Epsilons[1/cm]              94.87 304.8 !Ar and CCCOC0CCC
21       Sigmas[angstrom]            3.33 6.77
22       Masses[amu]                 39.88 132.23
23     End
24 !-----
25 !-----WELLS-----
26 !-----
27 Well      W1 # CCCOC0CCC
28 Species
29 RRHO
30   Geometry[angstrom] 25
31 C          2.32970600 1.53569100 0.76573700
32 C          2.73755600 0.55860200 -0.32975100
33 C          1.57284100 -0.28798700 -0.79697800
34 O          1.12566800 -1.07437300 0.29510000
35 C          -0.00000500 -1.84236700 -0.00000200
36 O          -1.12567500 -1.07436900 -0.29510400
37 C          -1.57285800 -0.28799400 0.79697900
38 C          -2.73755700 0.55861400 0.32974400

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39 C          -2.32967800    1.53571000   -0.76572800
40 H          1.54040800    2.20205300    0.41193500
41 H          3.17062500    2.15032600    1.08404300
42 H          1.95159400    0.99742400    1.63357200
43 H          3.13487700    1.09857800   -1.19132900
44 H          3.52869200   -0.10177100    0.02980500
45 H          0.75697300    0.35090900   -1.15184600
46 H          1.86833500   -0.94812000   -1.62125300
47 H          0.17313100   -2.46526300   -0.88268300
48 H          -0.17314300   -2.46526500    0.88267700
49 H          -1.86837200   -0.94813600    1.62124000
50 H          -0.75699000    0.35089000    1.15187000
51 H          -3.52869600   -0.10174600   -0.02983000
52 H          -3.13488400    1.09858600    1.19132100
53 H          -1.95156500    0.99744700   -1.63356500
54 H          -3.17058200    2.15036300   -1.08403600
55 H          -1.54037200    2.20205300   -0.41190800
56      Core          RigidRotor
57      SymmetryFactor          2
58      End
59      Rotor          Hindered
60      Group          10 11 12
61      Axis          1 2
62      Symmetry          3
63      Potential[kcal/mol]          2
64      0.00 2.90
65      End
66      Rotor          Hindered
67      Group          1 13 14
68      Axis          2 3
69      Symmetry          1
70      Potential[kcal/mol]          6
71      0.00 5.12 0.31 3.88 0.64 3.73
72      End
73      Rotor          Hindered
74      Group          2 15 16
75      Axis          3 4
76      Symmetry          1
77      Potential[kcal/mol]          6
78      0.00 1.93 1.21 7.68 2.64 3.41
79      End
80      Rotor          Hindered
81      Group          6 17 18
82      Axis          5 4
83      Symmetry          1
84      Potential[kcal/mol]          6
85      0.00 7.57 3.33 4.00 3.16 4.33
86      End

```



```

87 Rotor                      Hindered
88     Group                      4 17 18
89     Axis                        5 6
90     Symmetry                     1
91     Potential[kcal/mol]          6
92 0.00 7.57 3.29 4.00 3.15 4.32
93 End
94 Rotor                      Hindered
95     Group                      8 19 20
96     Axis                        7 6
97     Symmetry                     1
98     Potential[kcal/mol]          6
99 0.00 1.93 1.21 7.68 2.64 3.41
100 End
101 Rotor                      Hindered
102     Group                      9 21 22
103     Axis                        8 7
104     Symmetry                     1
105     Potential[kcal/mol]          6
106 0.00 5.12 0.31 3.89 0.64 3.74
107 End
108 Rotor                      Hindered
109     Group                      23 24 25
110     Axis                        9 8
111     Symmetry                     3
112     Potential[kcal/mol]          2
113 0.00 2.90
114 End
115 Frequencies [1/cm] 61
116 233.78 303.58 315.41 386.45
117 444.32 515.04 672.04 768.66 770.64 900.46
118 904.25 926.39 927.68 960.72 966.67 1085.49
119 1088.04 1112.78 1133.11 1147.57 1179.54 1183.97
120 1199.45 1221.82 1281.24 1283.9 1305.64 1313.55
121 1344.72 1377.74 1378.51 1411.46 1411.69 1423.08
122 1431.9 1458.37 1482.6 1484.77 1498.9 1499.35
123 1512.28 1513.28 1515.67 1525.69 1534.92 3004.29
124 3016.11 3036.47 3055.95 3059.11 3060.22 3064.04
125 3070.79 3073.45 3087.11 3103.2 3104.93 3130.5
126 3132.54 3147.43 3150.73
127 !30.0 38.88 58.9 109.75 138.41 186.7 204.83 276.38!Torsions
128     ZeroEnergy[kcal/mol]          0
129     ElectronicLevels [1/cm]       1
130 0 1
131 End
132 End
133 !-----
134 !-----FISSION PRODUCTS-----

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135 !-----
136 Bimolecular P1 # [H] + CCCOCOCC[CH2]
137 Fragment H
138 Atom
139 Mass [amu] 1
140 ElectronicLevels [1/cm] 1
141 0 2
142 End
143 Fragment CCCOCOCC[CH2]
144 RRHO
145 Geometry [angstrom] 24
146 C -0.0062476859 -0.02126965 -0.0163303857
147 C -0.0046988522 0.0014011342 1.4704960807
148 C 1.4041056014 0.0136759017 2.0462213335
149 O 2.060696304 -1.1706363361 1.6295849883
150 C 3.4383611706 -1.1484599061 1.8579422363
151 O 4.0951878338 -0.1699438712 1.1141734754
152 C 4.0489889675 -0.3986242016 -0.2861167205
153 C 4.4812144319 0.867036039 -0.9952777783
154 C 3.5401618107 2.0291906974 -0.7020461274
155 H -0.6261609568 0.6500802134 -0.5891455735
156 H 0.5056191706 -0.8166945049 -0.5349501258
157 H -0.5403403289 0.8736463849 1.8460697671
158 H -0.5159089877 -0.8847071884 1.8665583753
159 H 1.9476627341 0.8886559429 1.6808343383
160 H 1.3758863213 0.050086519 3.1416401568
161 H 3.6571391054 -0.9233885893 2.905845261
162 H 3.7969874586 -2.1486946742 1.598074315
163 H 4.705459439 -1.2400328027 -0.5363514022
164 H 3.0278640037 -0.6582734506 -0.5815536658
165 H 5.4984206731 1.1171482707 -0.6882601899
166 H 4.5097186941 0.6618989089 -2.0672042196
167 H 3.5691956753 2.2831478998 0.3565701398
168 H 3.8122455928 2.9160652485 -1.2728612302
169 H 2.5104868528 1.7629559594 -0.9537030583
170 Core RigidRotor
171 SymmetryFactor 1
172 End
173 Rotor Hindered
174 Group 10 11
175 Axis 1 2
176 Symmetry 1
177 Potential [kcal/mol] 4
178 0.00 0.81 0.00 0.80
179 End
180 Rotor Hindered
181 Group 1 12 13
182 Axis 2 3
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183           Symmetry                1
184           Potential [kcal/mol]     6
185 0.00 5.63 0.87 4.34 1.16 4.08
186   End
187   Rotor                          Hindered
188           Group                    5
189           Axis                      4 3
190           Symmetry                1
191           Potential [kcal/mol]     6
192 0.00 2.28 0.91 5.36 1.89 2.44
193   End
194   Rotor                          Hindered
195           Group                    6 16 17
196           Axis                      5 4
197           Symmetry                1
198           Potential [kcal/mol]     6
199 0.00 8.05 3.64 4.70 3.74 4.70
200   End
201   Rotor                          Hindered
202           Group                    7
203           Axis                      6 5
204           Symmetry                1
205           Potential [kcal/mol]     6
206 0.00 7.90 3.42 4.59 3.70 4.70
207   End
208   Rotor                          Hindered
209           Group                    8 18 19
210           Axis                      7 6
211           Symmetry                1
212           Potential [kcal/mol]     6
213 0.00 2.24 1.37 7.84 2.73 3.54
214   End
215   Rotor                          Hindered
216           Group                    9 20 21
217           Axis                      8 7
218           Symmetry                1
219           Potential [kcal/mol]     6
220 0.00 5.32 0.85 4.20 1.06 4.29
221   End
222   Rotor                          Hindered
223           Group                    22 23 24
224           Axis                      9 8
225           Symmetry                3
226           Potential [kcal/mol]     2
227 0.00 2.79
228   End
229   Frequencies [1/cm] 58
230 41.37 237.47 318.42 373.23
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231 443.87 488.4 532.66 670.51 755.06 771.66
232 900.01 917.39 928.04 954.97 965.94 1067.61
233 1085.12 1088.44 1112.25 1131.49 1149.18 1184.65
234 1194.56 1219.39 1249.07 1287.29 1298.87 1309.31
235 1343.03 1360.57 1377.17 1411.46 1415.86 1430.01
236 1452.39 1462.74 1475.89 1483.54 1497.04 1511.03
237 1519.85 1525.76 1528.06 3012.83 3021.14 3022.77
238 3040.32 3055.78 3063.68 3076.35 3086.22 3091.2
239 3104.47 3108.24 3127.85 3145.69 3180.95 3286.5
240 !49.7 63.84 96.04 120.38 162.38 213.89 260.19 301.91!Torsions
241 ZeroEnergy [kcal/mol] 0
242 ElectronicLevels [1/cm] 1
243 0 2
244 End
245 GroundEnergy [kcal/mol] 100.8
246 End
247 ! -----
248 Barrier B1 W1 P1 # [H] + CCCOCCC [CH2]
249 RRHO
250 Stoichiometry C7H16O2
251 Core PhaseSpaceTheory
252 FragmentGeometry [angstrom] 1
253 H 0.000000 0.000000 0.000000
254 FragmentGeometry [angstrom] 24
255 C -0.0062476859 -0.02126965 -0.0163303857
256 C -0.0046988522 0.0014011342 1.4704960807
257 C 1.4041056014 0.0136759017 2.0462213335
258 O 2.060696304 -1.1706363361 1.6295849883
259 C 3.4383611706 -1.1484599061 1.8579422363
260 O 4.0951878338 -0.1699438712 1.1141734754
261 C 4.0489889675 -0.3986242016 -0.2861167205
262 C 4.4812144319 0.867036039 -0.9952777783
263 C 3.5401618107 2.0291906974 -0.7020461274
264 H -0.6261609568 0.6500802134 -0.5891455735
265 H 0.5056191706 -0.8166945049 -0.5349501258
266 H -0.5403403289 0.8736463849 1.8460697671
267 H -0.5159089877 -0.8847071884 1.8665583753
268 H 1.9476627341 0.8886559429 1.6808343383
269 H 1.3758863213 0.050086519 3.1416401568
270 H 3.6571391054 -0.9233885893 2.905845261
271 H 3.7969874586 -2.1486946742 1.598074315
272 H 4.705459439 -1.2400328027 -0.5363514022
273 H 3.0278640037 -0.6582734506 -0.5815536658
274 H 5.4984206731 1.1171482707 -0.6882601899
275 H 4.5097186941 0.6618989089 -2.0672042196
276 H 3.5691956753 2.2831478998 0.3565701398
277 H 3.8122455928 2.9160652485 -1.2728612302
278 H 2.5104868528 1.7629559594 -0.9537030583

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```

279      SymmetryFactor                2
280      PotentialPrefactor [au]       0.32 #0.07 0.05
281      PotentialPowerExponent        2.6
282      End
283      Rotor                          Hindered
284      Geometry [angstrom]           24
285 C   -0.0062476859  -0.02126965  -0.0163303857
286 C   -0.0046988522  0.0014011342  1.4704960807
287 C   1.4041056014  0.0136759017  2.0462213335
288 O   2.060696304  -1.1706363361  1.6295849883
289 C   3.4383611706  -1.1484599061  1.8579422363
290 O   4.0951878338  -0.1699438712  1.1141734754
291 C   4.0489889675  -0.3986242016  -0.2861167205
292 C   4.4812144319  0.867036039   -0.9952777783
293 C   3.5401618107  2.0291906974  -0.7020461274
294 H   -0.6261609568  0.6500802134  -0.5891455735
295 H   0.5056191706  -0.8166945049  -0.5349501258
296 H   -0.5403403289  0.8736463849  1.8460697671
297 H   -0.5159089877  -0.8847071884  1.8665583753
298 H   1.9476627341  0.8886559429  1.6808343383
299 H   1.3758863213  0.050086519   3.1416401568
300 H   3.6571391054  -0.9233885893  2.905845261
301 H   3.7969874586  -2.1486946742  1.598074315
302 H   4.705459439   -1.2400328027  -0.5363514022
303 H   3.0278640037  -0.6582734506  -0.5815536658
304 H   5.4984206731  1.1171482707  -0.6882601899
305 H   4.5097186941  0.6618989089  -2.0672042196
306 H   3.5691956753  2.2831478998  0.3565701398
307 H   3.81224455928  2.9160652485  -1.2728612302
308 H   2.5104868528  1.7629559594  -0.9537030583
309      Group                          10 11
310      Axis                            1 2
311      Symmetry                        1
312      Potential [kcal/mol]           4
313 0.00 0.81 0.00 0.80
314      End
315      Rotor                          Hindered
316      Geometry [angstrom]           24
317 C   -0.0062476859  -0.02126965  -0.0163303857
318 C   -0.0046988522  0.0014011342  1.4704960807
319 C   1.4041056014  0.0136759017  2.0462213335
320 O   2.060696304  -1.1706363361  1.6295849883
321 C   3.4383611706  -1.1484599061  1.8579422363
322 O   4.0951878338  -0.1699438712  1.1141734754
323 C   4.0489889675  -0.3986242016  -0.2861167205
324 C   4.4812144319  0.867036039   -0.9952777783
325 C   3.5401618107  2.0291906974  -0.7020461274
326 H   -0.6261609568  0.6500802134  -0.5891455735

```

```

327 H 0.5056191706 -0.8166945049 -0.5349501258
328 H -0.5403403289 0.8736463849 1.8460697671
329 H -0.5159089877 -0.8847071884 1.8665583753
330 H 1.9476627341 0.8886559429 1.6808343383
331 H 1.3758863213 0.050086519 3.1416401568
332 H 3.6571391054 -0.9233885893 2.905845261
333 H 3.7969874586 -2.1486946742 1.598074315
334 H 4.705459439 -1.2400328027 -0.5363514022
335 H 3.0278640037 -0.6582734506 -0.5815536658
336 H 5.4984206731 1.1171482707 -0.6882601899
337 H 4.5097186941 0.6618989089 -2.0672042196
338 H 3.5691956753 2.2831478998 0.3565701398
339 H 3.8122455928 2.9160652485 -1.2728612302
340 H 2.5104868528 1.7629559594 -0.9537030583
341      Group                1 12 13
342      Axis                  2 3
343      Symmetry              1
344      Potential [kcal/mol]   6
345 0.00 5.63 0.87 4.34 1.16 4.08
346 End
347 Rotor                      Hindered
348      Geometry [angstrom]    24
349 C -0.0062476859 -0.02126965 -0.0163303857
350 C -0.0046988522 0.0014011342 1.4704960807
351 C 1.4041056014 0.0136759017 2.0462213335
352 O 2.060696304 -1.1706363361 1.6295849883
353 C 3.4383611706 -1.1484599061 1.8579422363
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362 H 1.9476627341 0.8886559429 1.6808343383
363 H 1.3758863213 0.050086519 3.1416401568
364 H 3.6571391054 -0.9233885893 2.905845261
365 H 3.7969874586 -2.1486946742 1.598074315
366 H 4.705459439 -1.2400328027 -0.5363514022
367 H 3.0278640037 -0.6582734506 -0.5815536658
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369 H 4.5097186941 0.6618989089 -2.0672042196
370 H 3.5691956753 2.2831478998 0.3565701398
371 H 3.8122455928 2.9160652485 -1.2728612302
372 H 2.5104868528 1.7629559594 -0.9537030583
373      Group                5
374      Axis                  4 3

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375 Symmetry 1
376 Potential [kcal/mol] 6
377 0.00 2.28 0.91 5.36 1.89 2.44
378 End
379 Rotor Hindered
380 Geometry [angstrom] 24
381 C -0.0062476859 -0.02126965 -0.0163303857
382 C -0.0046988522 0.0014011342 1.4704960807
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384 O 2.060696304 -1.1706363361 1.6295849883
385 C 3.4383611706 -1.1484599061 1.8579422363
386 O 4.0951878338 -0.1699438712 1.1141734754
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395 H 1.3758863213 0.050086519 3.1416401568
396 H 3.6571391054 -0.9233885893 2.905845261
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403 H 3.81224455928 2.9160652485 -1.2728612302
404 H 2.5104868528 1.7629559594 -0.9537030583
405 Group 6 16 17
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407 Symmetry 1
408 Potential [kcal/mol] 6
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410 End
411 Rotor Hindered
412 Geometry [angstrom] 24
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414 C -0.0046988522 0.0014011342 1.4704960807
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416 O 2.060696304 -1.1706363361 1.6295849883
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436 H 2.5104868528 1.7629559594 -0.9537030583
437      Group                7
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449 C 3.4383611706 -1.1484599061 1.8579422363
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461 H 3.7969874586 -2.1486946742 1.598074315
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467 H 3.8122455928 2.9160652485 -1.2728612302
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469      Group                8 18 19
470      Axis                  7 6

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482 O 4.0951878338 -0.1699438712 1.1141734754
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500 H 2.5104868528 1.7629559594 -0.9537030583
501 Group 9 20 21
502 Axis 8 7
503 Symmetry 1
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508 Geometry [angstrom] 24
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526 H 4.705459439 -1.2400328027 -0.5363514022
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532 H 2.5104868528 1.7629559594 -0.9537030583
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534      Axis                  9 8
535      Symmetry                3
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541 443.87 488.4 532.66 670.51 755.06 771.66
542 900.01 917.39 928.04 954.97 965.94 1067.61
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544 1194.56 1219.39 1249.07 1287.29 1298.87 1309.31
545 1343.03 1360.57 1377.17 1411.46 1415.86 1430.01
546 1452.39 1462.74 1475.89 1483.54 1497.04 1511.03
547 1519.85 1525.76 1528.06 3012.83 3021.14 3022.77
548 3040.32 3055.78 3063.68 3076.35 3086.22 3091.2
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550 !49.7 63.84 96.04 120.38 162.38 213.89 260.19 301.91!Torsions
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555 !-----
556 !-----
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561 Mass [amu] 1
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571 O 2.1921274451 -1.0002392887 1.7946641173
572 C 1.7687409483 -2.30684524 2.0582618428
573 O 1.6444406178 -2.575977837 3.4198554709
574 C 2.8757189889 -2.5286225567 4.1216760662
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576 C 1.7034666186 -1.7215015966 6.2007485082
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583 H 0.7821534067 -2.4962738099 1.6276553872
584 H 2.5222182054 -2.9530710846 1.5983871464
585 H 3.5565064933 -3.2822796728 3.7082972904
586 H 3.340682038 -1.5462983146 3.9891569651
587 H 2.1346569793 -3.7724325656 5.6853591049
588 H 3.555532423 -2.8314433237 6.112775321
589 H 0.7422166319 -1.6928402958 5.6898518498
590 H 1.5234064585 -1.9129674615 7.2577232161
591 H 2.1631571936 -0.7353835483 6.1109080277
592 Core RigidRotor
593 SymmetryFactor 1
594 End
595 Rotor Hindered
596 Group 10 11 12
597 Axis 1 2
598 Symmetry 3
599 Potential [kcal/mol] 2
600 0.00 0.25
601 End
602 Rotor Hindered
603 Group 1 13
604 Axis 2 3
605 Symmetry 1
606 Potential [kcal/mol] 4
607 0.00 4.80 0.49 2.53
608 End
609 Rotor Hindered
610 Group 2 14 15
611 Axis 3 4
612 Symmetry 1
613 Potential [kcal/mol] 4
614 0.00 5.88 0.62 2.23

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615 End
616 Rotor                      Hindered
617     Group                    6 16 17
618     Axis                     5 4
619     Symmetry                  1
620     Potential [kcal/mol]      6
621 0.00 7.77 2.30 4.03 2.83 3.68
622 End
623 Rotor                      Hindered
624     Group                    7
625     Axis                     6 5
626     Symmetry                  1
627     Potential [kcal/mol]      6
628 0.00 7.57 3.14 3.53 2.97 4.16
629 End
630 Rotor                      Hindered
631     Group                    8 18 19
632     Axis                     7 6
633     Symmetry                  1
634     Potential [kcal/mol]      6
635 0.00 1.71 1.13 7.53 3.02 3.40
636 End
637 Rotor                      Hindered
638     Group                    9 20 21
639     Axis                     8 7
640     Symmetry                  1
641     Potential [kcal/mol]      6
642 0.00 5.03 0.22 3.79 0.54 3.73
643 End
644 Rotor                      Hindered
645     Group                    22 23 24
646     Axis                     9 8
647     Symmetry                  3
648     Potential [kcal/mol]      2
649 0.00 2.91
650 End
651 Frequencies [1/cm] 58
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653 395.1 478.22 605.07 653.6 771.5 885.42
654 902.25 923.94 931.35 953.92 966.19 995.33
655 1087.27 1104.36 1112.34 1136.3 1158.69 1181.11
656 1189.53 1212.98 1284.04 1301.89 1315.95 1346.1
657 1377.09 1378.89 1394.61 1410.91 1417.38 1428.94
658 1454.92 1480.78 1484.24 1488.38 1493.96 1499.43
659 1513.27 1515.11 1531.56 3001.21 3018.12 3022.75
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673   Core      PhaseSpaceTheory
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678 C  -0.009071703   -0.0175444756  1.4870498268
679 C  1.274613024   -0.003526504  2.241472572
680 O  2.1921274451  -1.0002392887  1.7946641173
681 C  1.7687409483  -2.30684524  2.0582618428
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687 H  0.1303127427  1.0042713586  -0.3942202372
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697 H  3.555532423  -2.8314433237  6.112775321
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700 H  2.1631571936  -0.7353835483  6.1109080277
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703   PotentialPowerExponent         2.6
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708 C  -0.009071703   -0.0175444756  1.4870498268
709 C  1.274613024   -0.003526504  2.241472572
710 O  2.1921274451  -1.0002392887  1.7946641173

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716 H  0.8211932724  -0.6105888564  -0.3865122561
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764      Axis                        2 3
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773 C 1.274613024 -0.003526504 2.241472572
774 O 2.1921274451 -1.0002392887 1.7946641173
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1189 0.00 2.36 0.37 1.85 0.49 1.62
1190 End

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1191 Rotor                      Hindered
1192 Geometry [angstrom]      24
1193 C  -0.0170347954  -0.042787223  -0.0096479289
1194 C  -0.0103493905  -0.00574936   1.5254452795
1195 C  1.3609626603   0.0134329938  2.0910962383
1196 O  2.0717771554   -1.1296747497  1.8665190464
1197 C  3.424495751    -1.0712574673  2.2548318118
1198 O  4.1386275867   -0.105293047   1.5617498313
1199 C  4.2288852372   -0.3546645325  0.1665566211
1200 C  4.9296949737   0.820108021    -0.4808277032
1201 C  4.1394862671   2.1130109891   -0.3224175239
1202 H  0.4738905145   0.8419861727   -0.4168027131
1203 H  -1.0338721144   -0.0807139299  -0.4001200724
1204 H  0.5196748539   -0.9224174817  -0.3638284901
1205 H  -0.5464190356   0.8748536578   1.8803139529
1206 H  -0.5400203646   -0.8828377721  1.9061604744
1207 H  1.9372196587    0.9288054062   2.1626848698
1208 H  3.4992399408    -0.810304153   3.3118909895
1209 H  3.8188275083    -2.0731744067  2.0670764988
1210 H  4.7803217317    -1.2876011437  0.002034374
1211 H  3.2238435373    -0.4733227786  -0.2517504526
1212 H  5.9208529181    0.9258975795   -0.036222829
1213 H  5.0736048782    0.5900423737   -1.5381794198
1214 H  4.0168531139    2.357841837    0.731459885
1215 H  4.640589712     2.9472041973   -0.8114061524
1216 H  3.1450686243     2.0117248472   -0.7614365875
1217 Group                      2 15
1218 Axis                        3 4
1219 Symmetry                     1
1220 Potential [kcal/mol]        6
1221 0.00 4.99 1.51 4.63 3.19 5.89
1222 End
1223 Rotor                      Hindered
1224 Geometry [angstrom]      24
1225 C  -0.0170347954  -0.042787223  -0.0096479289
1226 C  -0.0103493905  -0.00574936   1.5254452795
1227 C  1.3609626603   0.0134329938  2.0910962383
1228 O  2.0717771554   -1.1296747497  1.8665190464
1229 C  3.424495751    -1.0712574673  2.2548318118
1230 O  4.1386275867   -0.105293047   1.5617498313
1231 C  4.2288852372   -0.3546645325  0.1665566211
1232 C  4.9296949737   0.820108021    -0.4808277032
1233 C  4.1394862671   2.1130109891   -0.3224175239
1234 H  0.4738905145   0.8419861727   -0.4168027131
1235 H  -1.0338721144   -0.0807139299  -0.4001200724
1236 H  0.5196748539   -0.9224174817  -0.3638284901
1237 H  -0.5464190356   0.8748536578   1.8803139529
1238 H  -0.5400203646   -0.8828377721  1.9061604744

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1240 H 3.4992399408 -0.810304153 3.3118909895
1241 H 3.8188275083 -2.0731744067 2.0670764988
1242 H 4.7803217317 -1.2876011437 0.002034374
1243 H 3.2238435373 -0.4733227786 -0.2517504526
1244 H 5.9208529181 0.9258975795 -0.036222829
1245 H 5.0736048782 0.5900423737 -1.5381794198
1246 H 4.0168531139 2.357841837 0.731459885
1247 H 4.640589712 2.9472041973 -0.8114061524
1248 H 3.1450686243 2.0117248472 -0.7614365875
1249 Group 3
1250 Axis 4 5
1251 Symmetry 1
1252 Potential [kcal/mol] 6
1253 0.00 12.0 2.41 3.32 2.98 3.55
1254 End
1255 Rotor Hindered
1256 Geometry [angstrom] 24
1257 C -0.0170347954 -0.042787223 -0.0096479289
1258 C -0.0103493905 -0.00574936 1.5254452795
1259 C 1.3609626603 0.0134329938 2.0910962383
1260 O 2.0717771554 -1.1296747497 1.8665190464
1261 C 3.424495751 -1.0712574673 2.2548318118
1262 O 4.1386275867 -0.105293047 1.5617498313
1263 C 4.2288852372 -0.3546645325 0.1665566211
1264 C 4.9296949737 0.820108021 -0.4808277032
1265 C 4.1394862671 2.1130109891 -0.3224175239
1266 H 0.4738905145 0.8419861727 -0.4168027131
1267 H -1.0338721144 -0.0807139299 -0.4001200724
1268 H 0.5196748539 -0.9224174817 -0.3638284901
1269 H -0.5464190356 0.8748536578 1.8803139529
1270 H -0.5400203646 -0.8828377721 1.9061604744
1271 H 1.9372196587 0.9288054062 2.1626848698
1272 H 3.4992399408 -0.810304153 3.3118909895
1273 H 3.8188275083 -2.0731744067 2.0670764988
1274 H 4.7803217317 -1.2876011437 0.002034374
1275 H 3.2238435373 -0.4733227786 -0.2517504526
1276 H 5.9208529181 0.9258975795 -0.036222829
1277 H 5.0736048782 0.5900423737 -1.5381794198
1278 H 4.0168531139 2.357841837 0.731459885
1279 H 4.640589712 2.9472041973 -0.8114061524
1280 H 3.1450686243 2.0117248472 -0.7614365875
1281 Group 7
1282 Axis 6 5
1283 Symmetry 1
1284 Potential [kcal/mol] 6
1285 0.00 6.99 2.23 4.18 3.47 4.48
1286 End
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1287 Rotor                      Hindered
1288           Geometry [angstrom]      24
1289 C   -0.0170347954  -0.042787223  -0.0096479289
1290 C   -0.0103493905  -0.00574936   1.5254452795
1291 C   1.3609626603   0.0134329938   2.0910962383
1292 O   2.0717771554  -1.1296747497   1.8665190464
1293 C   3.424495751   -1.0712574673   2.2548318118
1294 O   4.1386275867  -0.105293047   1.5617498313
1295 C   4.2288852372  -0.3546645325   0.1665566211
1296 C   4.9296949737   0.820108021   -0.4808277032
1297 C   4.1394862671   2.1130109891   -0.3224175239
1298 H   0.4738905145   0.8419861727   -0.4168027131
1299 H  -1.0338721144   -0.0807139299   -0.4001200724
1300 H   0.5196748539  -0.9224174817   -0.3638284901
1301 H  -0.5464190356   0.8748536578   1.8803139529
1302 H  -0.5400203646  -0.8828377721   1.9061604744
1303 H   1.9372196587   0.9288054062   2.1626848698
1304 H   3.4992399408  -0.810304153   3.3118909895
1305 H   3.8188275083  -2.0731744067   2.0670764988
1306 H   4.7803217317  -1.2876011437   0.002034374
1307 H   3.2238435373  -0.4733227786  -0.2517504526
1308 H   5.9208529181   0.9258975795  -0.036222829
1309 H   5.0736048782   0.5900423737  -1.5381794198
1310 H   4.0168531139   2.357841837   0.731459885
1311 H   4.640589712   2.9472041973  -0.8114061524
1312 H   3.1450686243   2.0117248472  -0.7614365875
1313           Group                      8 18 19
1314           Axis                        7 6
1315           Symmetry                    1
1316           Potential [kcal/mol]        6
1317 0.00 2.02 1.24 7.74 2.66 3.57
1318 End
1319 Rotor                      Hindered
1320           Geometry [angstrom]      24
1321 C   -0.0170347954  -0.042787223  -0.0096479289
1322 C   -0.0103493905  -0.00574936   1.5254452795
1323 C   1.3609626603   0.0134329938   2.0910962383
1324 O   2.0717771554  -1.1296747497   1.8665190464
1325 C   3.424495751   -1.0712574673   2.2548318118
1326 O   4.1386275867  -0.105293047   1.5617498313
1327 C   4.2288852372  -0.3546645325   0.1665566211
1328 C   4.9296949737   0.820108021   -0.4808277032
1329 C   4.1394862671   2.1130109891   -0.3224175239
1330 H   0.4738905145   0.8419861727   -0.4168027131
1331 H  -1.0338721144   -0.0807139299   -0.4001200724
1332 H   0.5196748539  -0.9224174817   -0.3638284901
1333 H  -0.5464190356   0.8748536578   1.8803139529
1334 H  -0.5400203646  -0.8828377721   1.9061604744

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1335 H 1.9372196587 0.9288054062 2.1626848698
1336 H 3.4992399408 -0.810304153 3.3118909895
1337 H 3.8188275083 -2.0731744067 2.0670764988
1338 H 4.7803217317 -1.2876011437 0.002034374
1339 H 3.2238435373 -0.4733227786 -0.2517504526
1340 H 5.9208529181 0.9258975795 -0.036222829
1341 H 5.0736048782 0.5900423737 -1.5381794198
1342 H 4.0168531139 2.357841837 0.731459885
1343 H 4.640589712 2.9472041973 -0.8114061524
1344 H 3.1450686243 2.0117248472 -0.7614365875
1345          Group                      9 20 21
1346          Axis                       8 7
1347          Symmetry                    1
1348          Potential [kcal/mol]        6
1349 0.00 5.15 0.35 3.91 0.66 3.72
1350 End
1351 Rotor                               Hindered
1352          Geometry [angstrom]         24
1353 C -0.0170347954 -0.042787223 -0.0096479289
1354 C -0.0103493905 -0.00574936 1.5254452795
1355 C 1.3609626603 0.0134329938 2.0910962383
1356 O 2.0717771554 -1.1296747497 1.8665190464
1357 C 3.424495751 -1.0712574673 2.2548318118
1358 O 4.1386275867 -0.105293047 1.5617498313
1359 C 4.2288852372 -0.3546645325 0.1665566211
1360 C 4.9296949737 0.820108021 -0.4808277032
1361 C 4.1394862671 2.1130109891 -0.3224175239
1362 H 0.4738905145 0.8419861727 -0.4168027131
1363 H -1.0338721144 -0.0807139299 -0.4001200724
1364 H 0.5196748539 -0.9224174817 -0.3638284901
1365 H -0.5464190356 0.8748536578 1.8803139529
1366 H -0.5400203646 -0.8828377721 1.9061604744
1367 H 1.9372196587 0.9288054062 2.1626848698
1368 H 3.4992399408 -0.810304153 3.3118909895
1369 H 3.8188275083 -2.0731744067 2.0670764988
1370 H 4.7803217317 -1.2876011437 0.002034374
1371 H 3.2238435373 -0.4733227786 -0.2517504526
1372 H 5.9208529181 0.9258975795 -0.036222829
1373 H 5.0736048782 0.5900423737 -1.5381794198
1374 H 4.0168531139 2.357841837 0.731459885
1375 H 4.640589712 2.9472041973 -0.8114061524
1376 H 3.1450686243 2.0117248472 -0.7614365875
1377          Group                      22 23 24
1378          Axis                       9 8
1379          Symmetry                    3
1380          Potential [kcal/mol]        2
1381 0.00 2.64
1382 End

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1385 436.0 508.65 600.36 675.99 770.37 779.5
1386 902.17 911.37 925.92 963.07 972.59 1058.48
1387 1088.4 1099.05 1118.58 1145.5 1171.55 1188.38
1388 1210.08 1247.04 1285.29 1296.06 1309.92 1334.78
1389 1350.45 1377.37 1392.11 1411.87 1418.4 1432.69
1390 1469.48 1475.81 1483.67 1495.88 1498.28 1507.02
1391 1510.3 1520.54 1529.1 3020.3 3054.67 3056.25
1392 3059.33 3060.08 3061.84 3073.08 3105.99 3107.05
1393 3113.36 3131.1 3132.03 3140.91 3148.29 3175.15
1394 !32.79 51.77 53.63 138.98 193.1 212.95 223.84 273.48!Torsions
1395   ZeroEnergy [kcal/mol]          94.8
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1399 !-----
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1401 !-----
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1404   Atom
1405   Mass [amu]      1
1406   ElectronicLevels [1/cm]      1
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1410   RRHO
1411   Geometry [angstrom]  24
1412 C   0.1272836176   -0.0980909414   0.0670793598
1413 C   0.0279854388   0.0213509486   1.5821135859
1414 C   1.3835889491   0.0984857464   2.2500008907
1415 O   2.0269096879   1.2916311462   1.8039833799
1416 C   3.3337453847   1.3952720573   2.1124981028
1417 O   3.6166046274   1.1274510121   3.4189133337
1418 C   4.9980333045   1.2117165474   3.7299873392
1419 C   5.1817389474   0.8741978383   5.1936050221
1420 C   4.7454822632   -0.5486370162   5.5184559671
1421 H   0.6529940289   0.759264736   -0.34960684
1422 H   -0.8595000208   -0.1501063095   -0.390892139
1423 H   0.6769159573   -0.9978869925   -0.2138784206
1424 H   -0.5423450774   0.9113322552   1.8545255462
1425 H   -0.5030175413   -0.8373060581   1.9976095994
1426 H   1.2897134088   0.1217870336   3.3364092777
1427 H   2.007070188   -0.7597531465   1.976608288
1428 H   3.7899351263   2.2930571471   1.6975225622
1429 H   5.5518159502   0.5108555694   3.0962923662
1430 H   5.3562597864   2.2239785098   3.5130684671

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1431 H 6.2351251895 1.0149296251 5.4429878715
1432 H 4.6126339337 1.5896450659 5.7897467152
1433 H 5.3203591415 -1.2709566824 4.9367779445
1434 H 4.8905822352 -0.7744307183 6.57384944
1435 H 3.6923498108 -0.689415 5.2803319621
1436 Core RigidRotor
1437 SymmetryFactor 2
1438 End
1439 Rotor Hindered
1440 Group 10 11 12
1441 Axis 1 2
1442 Symmetry 3
1443 Potential [kcal/mol] 2
1444 0.00 2.69
1445 End
1446 Rotor Hindered
1447 Group 1 13 14
1448 Axis 2 3
1449 Symmetry 1
1450 Potential [kcal/mol] 6
1451 0.00 3.61 0.32 3.59 0.04 4.68
1452 End
1453 Rotor Hindered
1454 Group 2 15 16
1455 Axis 3 4
1456 Symmetry 1
1457 Potential [kcal/mol] 6
1458 0.00 0.75 0.44 6.06 0.74 1.48
1459 End
1460 Rotor Hindered
1461 Group 3
1462 Axis 4 5
1463 Symmetry 1
1464 Potential [kcal/mol] 4
1465 0.00 1.96 1.51 8.93
1466 End
1467 Rotor Hindered
1468 Group 7
1469 Axis 6 5
1470 Symmetry 1
1471 Potential [kcal/mol] 4
1472 0.00 1.96 1.51 8.93
1473 End
1474 Rotor Hindered
1475 Group 8 18 19
1476 Axis 7 6
1477 Symmetry 1
1478 Potential [kcal/mol] 6

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1480 End
1481 Rotor                      Hindered
1482      Group                    9 20 21
1483      Axis                      8 7
1484      Symmetry                   1
1485      Potential [kcal/mol]       6
1486 0.00 3.61 0.32 3.59 0.04 4.68
1487 End
1488 Rotor                      Hindered
1489      Group                    22 23 24
1490      Axis                      9 8
1491      Symmetry                   3
1492      Potential [kcal/mol]       2
1493 0.00 2.69
1494 End
1495      Frequencies [1/cm] 58
1496 185.29 296.31 326.5 334.78
1497 437.29 506.85 634.41 768.03 783.95 889.91
1498 907.31 920.0 928.19 940.92 970.58 1013.01 1091.4
1499 1104.51 1134.75 1160.39 1178.64 1181.03 1230.14
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1502 1481.74 1484.33 1499.48 1500.22 1512.21 1512.42
1503 1524.13 1526.13 3022.11 3034.86 3056.98 3064.67
1504 3065.22 3067.43 3073.44 3101.05 3106.31 3107.2
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1508 ElectronicLevels [1/cm]       1
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1510 End
1511 GroundEnergy [kcal/mol]       97.0
1512 End
1513 ! -----
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1515      RRHO
1516      Stoichiometry C7H16O2
1517      Core      PhaseSpaceTheory
1518      FragmentGeometry [angstrom]      1
1519      H                      0.000000      0.000000      0.000000
1520      FragmentGeometry [angstrom]      24
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1522 C 0.0279854388      0.0213509486      1.5821135859
1523 C 1.3835889491      0.0984857464      2.2500008907
1524 O 2.0269096879      1.2916311462      1.8039833799
1525 C 3.3337453847      1.3952720573      2.1124981028
1526 O 3.6166046274      1.1274510121      3.4189133337

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1527 C 4.9980333045 1.2117165474 3.7299873392
1528 C 5.1817389474 0.8741978383 5.1936050221
1529 C 4.7454822632 -0.5486370162 5.5184559671
1530 H 0.6529940289 0.759264736 -0.34960684
1531 H -0.8595000208 -0.1501063095 -0.390892139
1532 H 0.6769159573 -0.9978869925 -0.2138784206
1533 H -0.5423450774 0.9113322552 1.8545255462
1534 H -0.5030175413 -0.8373060581 1.9976095994
1535 H 1.2897134088 0.1217870336 3.3364092777
1536 H 2.007070188 -0.7597531465 1.976608288
1537 H 3.7899351263 2.2930571471 1.6975225622
1538 H 5.5518159502 0.5108555694 3.0962923662
1539 H 5.3562597864 2.2239785098 3.5130684671
1540 H 6.2351251895 1.0149296251 5.4429878715
1541 H 4.6126339337 1.5896450659 5.7897467152
1542 H 5.3203591415 -1.2709566824 4.9367779445
1543 H 4.8905822352 -0.7744307183 6.57384944
1544 H 3.6923498108 -0.689415 5.2803319621
1545 SymmetryFactor 2
1546 PotentialPrefactor [au] 0.31 #0.009 0.0007
1547 PotentialPowerExponent 2.62
1548 End
1549 Rotor Hindered
1550 Geometry [angstrom] 24
1551 C 0.1272836176 -0.0980909414 0.0670793598
1552 C 0.0279854388 0.0213509486 1.5821135859
1553 C 1.3835889491 0.0984857464 2.2500008907
1554 O 2.0269096879 1.2916311462 1.8039833799
1555 C 3.3337453847 1.3952720573 2.1124981028
1556 O 3.6166046274 1.1274510121 3.4189133337
1557 C 4.9980333045 1.2117165474 3.7299873392
1558 C 5.1817389474 0.8741978383 5.1936050221
1559 C 4.7454822632 -0.5486370162 5.5184559671
1560 H 0.6529940289 0.759264736 -0.34960684
1561 H -0.8595000208 -0.1501063095 -0.390892139
1562 H 0.6769159573 -0.9978869925 -0.2138784206
1563 H -0.5423450774 0.9113322552 1.8545255462
1564 H -0.5030175413 -0.8373060581 1.9976095994
1565 H 1.2897134088 0.1217870336 3.3364092777
1566 H 2.007070188 -0.7597531465 1.976608288
1567 H 3.7899351263 2.2930571471 1.6975225622
1568 H 5.5518159502 0.5108555694 3.0962923662
1569 H 5.3562597864 2.2239785098 3.5130684671
1570 H 6.2351251895 1.0149296251 5.4429878715
1571 H 4.6126339337 1.5896450659 5.7897467152
1572 H 5.3203591415 -1.2709566824 4.9367779445
1573 H 4.8905822352 -0.7744307183 6.57384944
1574 H 3.6923498108 -0.689415 5.2803319621

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1575          Group                10 11 12
1576          Axis                 1 2
1577          Symmetry              3
1578          Potential [kcal/mol]   2
1579 0.00 2.69
1580  End
1581  Rotor                        Hindered
1582          Geometry [angstrom]   24
1583 C  0.1272836176  -0.0980909414  0.0670793598
1584 C  0.0279854388  0.0213509486  1.5821135859
1585 C  1.3835889491  0.0984857464  2.2500008907
1586 O  2.0269096879  1.2916311462  1.8039833799
1587 C  3.3337453847  1.3952720573  2.1124981028
1588 O  3.6166046274  1.1274510121  3.4189133337
1589 C  4.9980333045  1.2117165474  3.7299873392
1590 C  5.1817389474  0.8741978383  5.1936050221
1591 C  4.7454822632  -0.5486370162  5.5184559671
1592 H  0.6529940289  0.759264736  -0.34960684
1593 H  -0.8595000208  -0.1501063095  -0.390892139
1594 H  0.6769159573  -0.9978869925  -0.2138784206
1595 H  -0.5423450774  0.9113322552  1.8545255462
1596 H  -0.5030175413  -0.8373060581  1.9976095994
1597 H  1.2897134088  0.1217870336  3.3364092777
1598 H  2.007070188  -0.7597531465  1.976608288
1599 H  3.7899351263  2.2930571471  1.6975225622
1600 H  5.5518159502  0.5108555694  3.0962923662
1601 H  5.3562597864  2.2239785098  3.5130684671
1602 H  6.2351251895  1.0149296251  5.4429878715
1603 H  4.6126339337  1.5896450659  5.7897467152
1604 H  5.3203591415  -1.2709566824  4.9367779445
1605 H  4.8905822352  -0.7744307183  6.57384944
1606 H  3.6923498108  -0.689415  5.2803319621
1607          Group                1 13 14
1608          Axis                 2 3
1609          Symmetry              1
1610          Potential [kcal/mol]   6
1611 0.00 3.61 0.32 3.59 0.04 4.68
1612  End
1613  Rotor                        Hindered
1614          Geometry [angstrom]   24
1615 C  0.1272836176  -0.0980909414  0.0670793598
1616 C  0.0279854388  0.0213509486  1.5821135859
1617 C  1.3835889491  0.0984857464  2.2500008907
1618 O  2.0269096879  1.2916311462  1.8039833799
1619 C  3.3337453847  1.3952720573  2.1124981028
1620 O  3.6166046274  1.1274510121  3.4189133337
1621 C  4.9980333045  1.2117165474  3.7299873392
1622 C  5.1817389474  0.8741978383  5.1936050221
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1623 C 4.7454822632 -0.5486370162 5.5184559671
1624 H 0.6529940289 0.759264736 -0.34960684
1625 H -0.8595000208 -0.1501063095 -0.390892139
1626 H 0.6769159573 -0.9978869925 -0.2138784206
1627 H -0.5423450774 0.9113322552 1.8545255462
1628 H -0.5030175413 -0.8373060581 1.9976095994
1629 H 1.2897134088 0.1217870336 3.3364092777
1630 H 2.007070188 -0.7597531465 1.976608288
1631 H 3.7899351263 2.2930571471 1.6975225622
1632 H 5.5518159502 0.5108555694 3.0962923662
1633 H 5.3562597864 2.2239785098 3.5130684671
1634 H 6.2351251895 1.0149296251 5.4429878715
1635 H 4.6126339337 1.5896450659 5.7897467152
1636 H 5.3203591415 -1.2709566824 4.9367779445
1637 H 4.8905822352 -0.7744307183 6.57384944
1638 H 3.6923498108 -0.689415 5.2803319621
1639 Group 2 15 16
1640 Axis 3 4
1641 Symmetry 1
1642 Potential [kcal/mol] 6
1643 0.00 0.75 0.44 6.06 0.74 1.48
1644 End
1645 Rotor Hindered
1646 Geometry [angstrom] 24
1647 C 0.1272836176 -0.0980909414 0.0670793598
1648 C 0.0279854388 0.0213509486 1.5821135859
1649 C 1.3835889491 0.0984857464 2.2500008907
1650 O 2.0269096879 1.2916311462 1.8039833799
1651 C 3.3337453847 1.3952720573 2.1124981028
1652 O 3.6166046274 1.1274510121 3.4189133337
1653 C 4.9980333045 1.2117165474 3.7299873392
1654 C 5.1817389474 0.8741978383 5.1936050221
1655 C 4.7454822632 -0.5486370162 5.5184559671
1656 H 0.6529940289 0.759264736 -0.34960684
1657 H -0.8595000208 -0.1501063095 -0.390892139
1658 H 0.6769159573 -0.9978869925 -0.2138784206
1659 H -0.5423450774 0.9113322552 1.8545255462
1660 H -0.5030175413 -0.8373060581 1.9976095994
1661 H 1.2897134088 0.1217870336 3.3364092777
1662 H 2.007070188 -0.7597531465 1.976608288
1663 H 3.7899351263 2.2930571471 1.6975225622
1664 H 5.5518159502 0.5108555694 3.0962923662
1665 H 5.3562597864 2.2239785098 3.5130684671
1666 H 6.2351251895 1.0149296251 5.4429878715
1667 H 4.6126339337 1.5896450659 5.7897467152
1668 H 5.3203591415 -1.2709566824 4.9367779445
1669 H 4.8905822352 -0.7744307183 6.57384944
1670 H 3.6923498108 -0.689415 5.2803319621

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1671          Group                      3
1672          Axis                      4 5
1673          Symmetry                  1
1674          Potential [kcal/mol]      4
1675 0.00 1.96 1.51 8.93
1676  End
1677  Rotor                            Hindered
1678          Geometry [angstrom]      24
1679 C  0.1272836176  -0.0980909414  0.0670793598
1680 C  0.0279854388  0.0213509486  1.5821135859
1681 C  1.3835889491  0.0984857464  2.2500008907
1682 O  2.0269096879  1.2916311462  1.8039833799
1683 C  3.3337453847  1.3952720573  2.1124981028
1684 O  3.6166046274  1.1274510121  3.4189133337
1685 C  4.9980333045  1.2117165474  3.7299873392
1686 C  5.1817389474  0.8741978383  5.1936050221
1687 C  4.7454822632  -0.5486370162  5.5184559671
1688 H  0.6529940289  0.759264736  -0.34960684
1689 H  -0.8595000208  -0.1501063095  -0.390892139
1690 H  0.6769159573  -0.9978869925  -0.2138784206
1691 H  -0.5423450774  0.9113322552  1.8545255462
1692 H  -0.5030175413  -0.8373060581  1.9976095994
1693 H  1.2897134088  0.1217870336  3.3364092777
1694 H  2.007070188  -0.7597531465  1.976608288
1695 H  3.7899351263  2.2930571471  1.6975225622
1696 H  5.5518159502  0.5108555694  3.0962923662
1697 H  5.3562597864  2.2239785098  3.5130684671
1698 H  6.2351251895  1.0149296251  5.4429878715
1699 H  4.6126339337  1.5896450659  5.7897467152
1700 H  5.3203591415  -1.2709566824  4.9367779445
1701 H  4.8905822352  -0.7744307183  6.57384944
1702 H  3.6923498108  -0.689415  5.2803319621
1703          Group                      7
1704          Axis                      6 5
1705          Symmetry                  1
1706          Potential [kcal/mol]      4
1707 0.00 1.96 1.51 8.93
1708  End
1709  Rotor                            Hindered
1710          Geometry [angstrom]      24
1711 C  0.1272836176  -0.0980909414  0.0670793598
1712 C  0.0279854388  0.0213509486  1.5821135859
1713 C  1.3835889491  0.0984857464  2.2500008907
1714 O  2.0269096879  1.2916311462  1.8039833799
1715 C  3.3337453847  1.3952720573  2.1124981028
1716 O  3.6166046274  1.1274510121  3.4189133337
1717 C  4.9980333045  1.2117165474  3.7299873392
1718 C  5.1817389474  0.8741978383  5.1936050221

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1719 C  4.7454822632  -0.5486370162  5.5184559671
1720 H  0.6529940289  0.759264736  -0.34960684
1721 H  -0.8595000208  -0.1501063095  -0.390892139
1722 H  0.6769159573  -0.9978869925  -0.2138784206
1723 H  -0.5423450774  0.9113322552  1.8545255462
1724 H  -0.5030175413  -0.8373060581  1.9976095994
1725 H  1.2897134088  0.1217870336  3.3364092777
1726 H  2.007070188  -0.7597531465  1.976608288
1727 H  3.7899351263  2.2930571471  1.6975225622
1728 H  5.5518159502  0.5108555694  3.0962923662
1729 H  5.3562597864  2.2239785098  3.5130684671
1730 H  6.2351251895  1.0149296251  5.4429878715
1731 H  4.6126339337  1.5896450659  5.7897467152
1732 H  5.3203591415  -1.2709566824  4.9367779445
1733 H  4.8905822352  -0.7744307183  6.57384944
1734 H  3.6923498108  -0.689415  5.2803319621
1735      Group                      8 18 19
1736      Axis                        7 6
1737      Symmetry                      1
1738      Potential [kcal/mol]         6
1739 0.00 0.75 0.44 6.06 0.74 1.48
1740 End
1741 Rotor                      Hindered
1742      Geometry [angstrom]          24
1743 C  0.1272836176  -0.0980909414  0.0670793598
1744 C  0.0279854388  0.0213509486  1.5821135859
1745 C  1.3835889491  0.0984857464  2.2500008907
1746 O  2.0269096879  1.2916311462  1.8039833799
1747 C  3.3337453847  1.3952720573  2.1124981028
1748 O  3.6166046274  1.1274510121  3.4189133337
1749 C  4.9980333045  1.2117165474  3.7299873392
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1751 C  4.7454822632  -0.5486370162  5.5184559671
1752 H  0.6529940289  0.759264736  -0.34960684
1753 H  -0.8595000208  -0.1501063095  -0.390892139
1754 H  0.6769159573  -0.9978869925  -0.2138784206
1755 H  -0.5423450774  0.9113322552  1.8545255462
1756 H  -0.5030175413  -0.8373060581  1.9976095994
1757 H  1.2897134088  0.1217870336  3.3364092777
1758 H  2.007070188  -0.7597531465  1.976608288
1759 H  3.7899351263  2.2930571471  1.6975225622
1760 H  5.5518159502  0.5108555694  3.0962923662
1761 H  5.3562597864  2.2239785098  3.5130684671
1762 H  6.2351251895  1.0149296251  5.4429878715
1763 H  4.6126339337  1.5896450659  5.7897467152
1764 H  5.3203591415  -1.2709566824  4.9367779445
1765 H  4.8905822352  -0.7744307183  6.57384944
1766 H  3.6923498108  -0.689415  5.2803319621

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1767          Group                9 20 21
1768          Axis                 8 7
1769          Symmetry              1
1770          Potential [kcal/mol]   6
1771 0.00 3.61 0.32 3.59 0.04 4.68
1772      End
1773      Rotor                      Hindered
1774          Geometry [angstrom]    24
1775 C   0.1272836176  -0.0980909414  0.0670793598
1776 C   0.0279854388  0.0213509486  1.5821135859
1777 C   1.3835889491  0.0984857464  2.2500008907
1778 O   2.0269096879  1.2916311462  1.8039833799
1779 C   3.3337453847  1.3952720573  2.1124981028
1780 O   3.6166046274  1.1274510121  3.4189133337
1781 C   4.9980333045  1.2117165474  3.7299873392
1782 C   5.1817389474  0.8741978383  5.1936050221
1783 C   4.7454822632  -0.5486370162  5.5184559671
1784 H   0.6529940289  0.759264736  -0.34960684
1785 H  -0.8595000208  -0.1501063095  -0.390892139
1786 H   0.6769159573  -0.9978869925  -0.2138784206
1787 H  -0.5423450774  0.9113322552  1.8545255462
1788 H  -0.5030175413  -0.8373060581  1.9976095994
1789 H   1.2897134088  0.1217870336  3.3364092777
1790 H   2.007070188  -0.7597531465  1.976608288
1791 H   3.7899351263  2.2930571471  1.6975225622
1792 H   5.5518159502  0.5108555694  3.0962923662
1793 H   5.3562597864  2.2239785098  3.5130684671
1794 H   6.2351251895  1.0149296251  5.4429878715
1795 H   4.6126339337  1.5896450659  5.7897467152
1796 H   5.3203591415  -1.2709566824  4.9367779445
1797 H   4.8905822352  -0.7744307183  6.57384944
1798 H   3.6923498108  -0.689415  5.2803319621
1799          Group                22 23 24
1800          Axis                 9 8
1801          Symmetry              3
1802          Potential [kcal/mol]   2
1803 0.00 2.69
1804      End
1805          Frequencies [1/cm] 58
1806 185.29 296.31 326.5 334.78
1807 437.29 506.85 634.41 768.03 783.95 889.91
1808 907.31 920.0 928.19 940.92 970.58 1013.01 1091.4
1809 1104.51 1134.75 1160.39 1178.64 1181.03 1230.14
1810 1279.62 1284.11 1291.42 1311.01 1315.82 1368.48
1811 1381.21 1390.65 1412.81 1414.18 1426.27 1450.29
1812 1481.74 1484.33 1499.48 1500.22 1512.21 1512.42
1813 1524.13 1526.13 3022.11 3034.86 3056.98 3064.67
1814 3065.22 3067.43 3073.44 3101.05 3106.31 3107.2
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1815 3108.57 3134.29 3135.48 3148.14 3150.9
1816 !26.47 42.12 54.62 112.86 131.44 149.62 214.02 257.6!Torsions
1817      ZeroEnergy[kcal/mol]          97.0
1818      ElectronicLevels[1/cm]       1
1819      0      2
1820      End
1821 !-----
1822 !-----
1823 !-----
1824 Bimolecular      P5 # CCCOCOC[CH2] + [CH3]
1825      Fragment          CCCOCOC[CH2]
1826      RRHO
1827      Geometry[angstrom]      21
1828      C      2.94549700      0.92678700      -0.45160800
1829      C      1.84415100      0.74209600      0.52595900
1830      O      1.48912200      -0.62395300      0.69534100
1831      C      0.83562100      -1.17091700      -0.41422000
1832      O      -0.40255000      -0.58162700      -0.66138000
1833      C      -1.35570300      -0.81254900      0.36315700
1834      C      -2.63212200      -0.08378500      0.00049200
1835      C      -2.42929700      1.42415200      -0.07699400
1836      H      3.75871800      0.21627200      -0.46940300
1837      H      3.04011300      1.84184700      -1.01486800
1838      H      2.14619600      1.07740400      1.52396900
1839      H      0.96565900      1.32775900      0.23851900
1840      H      1.42091700      -1.02695200      -1.32577100
1841      H      0.72509500      -2.23564300      -0.18974000
1842      H      -1.53063000      -1.89090300      0.45706800
1843      H      -0.96662600      -0.44966600      1.31991300
1844      H      -2.99193000      -0.46443100      -0.95708400
1845      H      -3.38866300      -0.32715600      0.74897400
1846      H      -1.69080500      1.66948600      -0.83872700
1847      H      -3.35763300      1.93776800      -0.32321700
1848      H      -2.07187800      1.81413800      0.87795600
1849      Core      RigidRotor
1850      SymmetryFactor          1
1851      End
1852      Rotor          Hindered
1853      Group          4
1854      Axis          3 2
1855      Symmetry          1
1856      Potential[kcal/mol]      6
1857      0. 3.31 0.06 0.83 0.25 1.81
1858      End
1859      Rotor          Hindered
1860      Group          6
1861      Axis          5 4
1862      Symmetry          1

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1863           Potential [kcal/mol]           6
1864           0. 7.54 2.92 3.22 2.77 4.12
1865       End
1866       Rotor                               Hindered
1867           Group                           7 15 16
1868           Axis                             6 5
1869           Symmetry                         1
1870           Potential [kcal/mol]           6
1871           0. 1.67 1.19 7.50 2.97 3.36
1872       End
1873       Rotor                               Hindered
1874           Group                           8 17 18
1875           Axis                             7 6
1876           Symmetry                         1
1877           Potential [kcal/mol]           6
1878           0. 5.03 0.19 3.76 0.51 3.71
1879       End
1880       Rotor                               Hindered
1881           Group                           9 10
1882           Axis                             1 2
1883           Symmetry                         2
1884           Potential [kcal/mol]           2
1885           0. 1.69
1886       End
1887       Rotor                               Hindered
1888           Group                           5 13 14
1889           Axis                             4 3
1890           Symmetry                         1
1891           Potential [kcal/mol]           4
1892           0. 7.29 3.13 3.82
1893       End
1894       Rotor                               Hindered
1895           Group                           19 20 21
1896           Axis                             8 7
1897           Symmetry                         3
1898           Potential [kcal/mol]           2
1899           0. 2.87
1900       End
1901       Frequencies [1/cm]           50
1902       278.78 308.42 375.02 459.15 480.48 529.6
1903       648.93 771.32 846.58 902.96 925.37 944.09
1904       966.31 1054.92 1087.42 1108.79 1130.11 1136.96
1905       1181.66 1188.74 1215.53 1284.17 1298.07 1313.96
1906       1347.09 1378.07 1395.43 1410.8 1429.02 1453.06
1907       1459.3 1484.43 1490.62 1498.77 1513.23 1516.66
1908       1531.62 3018.96 3026.97 3046.37 3058.66 3060.81
1909       3066.33 3071.69 3098.75 3104.93 3130.69 3146.68
1910       3173.51 3283.61
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1911 !37.25 169.21 224.22 84.79 44.83 144.36 196.42! Torsions
1912 ZeroEnergy[kcal/mol] 0
1913 ElectronicLevels[1/cm] 1
1914 0 2
1915 End
1916 Fragment [CH3]
1917 RRHO
1918 Geometry[angstrom] 4
1919 C 0.00000000 0.00000000 0.00000000
1920 H 0.00000000 0.00000000 1.07652900
1921 H 0.93230200 0.00000000 -0.53826500
1922 H -0.93230200 -0.00000000 -0.53826500
1923 Core RigidRotor
1924 SymmetryFactor 6
1925 End
1926 Frequencies[1/cm] 6
1927 409.94 1411.49 1412.56 3141.77 3320.20 3321.01
1928 ! ! torsion
1929 ZeroEnergy[kcal/mol] 0
1930 ElectronicLevels[1/cm] 1
1931 0 2
1932 End
1933 GroundEnergy[kcal/mol] 88.0
1934 End
1935 !-----
1936 Barrier B5 W1 P5 # CCCOCOC[CH2] + [CH3]
1937 RRHO
1938 Stoichiometry C7H16O2
1939 Core PhaseSpaceTheory
1940 FragmentGeometry[angstrom] 21
1941 C 2.94549700 0.92678700 -0.45160800
1942 C 1.84415100 0.74209600 0.52595900
1943 O 1.48912200 -0.62395300 0.69534100
1944 C 0.83562100 -1.17091700 -0.41422000
1945 O -0.40255000 -0.58162700 -0.66138000
1946 C -1.35570300 -0.81254900 0.36315700
1947 C -2.63212200 -0.08378500 0.00049200
1948 C -2.42929700 1.42415200 -0.07699400
1949 H 3.75871800 0.21627200 -0.46940300
1950 H 3.04011300 1.84184700 -1.01486800
1951 H 2.14619600 1.07740400 1.52396900
1952 H 0.96565900 1.32775900 0.23851900
1953 H 1.42091700 -1.02695200 -1.32577100
1954 H 0.72509500 -2.23564300 -0.18974000
1955 H -1.53063000 -1.89090300 0.45706800
1956 H -0.96662600 -0.44966600 1.31991300
1957 H -2.99193000 -0.46443100 -0.95708400
1958 H -3.38866300 -0.32715600 0.74897400

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1959 H -1.69080500 1.66948600 -0.83872700
1960 H -3.35763300 1.93776800 -0.32321700
1961 H -2.07187800 1.81413800 0.87795600
1962 FragmentGeometry [angstrom] 4
1963 C 0.000000 0.000000 0.000000
1964 H 0.000000 0.000000 1.076529
1965 H 0.932302 0.000000 -0.538265
1966 H -0.932302 -0.000000 -0.538265
1967 SymmetryFactor 6
1968 PotentialPrefactor [au] 5.96 #0.3 0.5
1969 PotentialPowerExponent 6.64
1970 End
1971 Rotor Hindered
1972 Geometry [angstrom] 21
1973 C 2.94549700 0.92678700 -0.45160800
1974 C 1.84415100 0.74209600 0.52595900
1975 O 1.48912200 -0.62395300 0.69534100
1976 C 0.83562100 -1.17091700 -0.41422000
1977 O -0.40255000 -0.58162700 -0.66138000
1978 C -1.35570300 -0.81254900 0.36315700
1979 C -2.63212200 -0.08378500 0.00049200
1980 C -2.42929700 1.42415200 -0.07699400
1981 H 3.75871800 0.21627200 -0.46940300
1982 H 3.04011300 1.84184700 -1.01486800
1983 H 2.14619600 1.07740400 1.52396900
1984 H 0.96565900 1.32775900 0.23851900
1985 H 1.42091700 -1.02695200 -1.32577100
1986 H 0.72509500 -2.23564300 -0.18974000
1987 H -1.53063000 -1.89090300 0.45706800
1988 H -0.96662600 -0.44966600 1.31991300
1989 H -2.99193000 -0.46443100 -0.95708400
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1992 H -3.35763300 1.93776800 -0.32321700
1993 H -2.07187800 1.81413800 0.87795600
1994 Group 4
1995 Axis 3 2
1996 Symmetry 1
1997 Potential [kcal/mol] 6
1998 0. 3.31 0.06 0.83 0.25 1.81
1999 End
2000 Rotor Hindered
2001 Geometry [angstrom] 21
2002 C 2.94549700 0.92678700 -0.45160800
2003 C 1.84415100 0.74209600 0.52595900
2004 O 1.48912200 -0.62395300 0.69534100
2005 C 0.83562100 -1.17091700 -0.41422000
2006 O -0.40255000 -0.58162700 -0.66138000

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2007      C      -1.35570300   -0.81254900    0.36315700
2008      C      -2.63212200   -0.08378500    0.00049200
2009      C      -2.42929700    1.42415200   -0.07699400
2010      H       3.75871800    0.21627200   -0.46940300
2011      H       3.04011300    1.84184700   -1.01486800
2012      H       2.14619600    1.07740400    1.52396900
2013      H       0.96565900    1.32775900    0.23851900
2014      H       1.42091700   -1.02695200   -1.32577100
2015      H       0.72509500   -2.23564300   -0.18974000
2016      H      -1.53063000   -1.89090300    0.45706800
2017      H      -0.96662600   -0.44966600    1.31991300
2018      H      -2.99193000   -0.46443100   -0.95708400
2019      H      -3.38866300   -0.32715600    0.74897400
2020      H      -1.69080500    1.66948600   -0.83872700
2021      H      -3.35763300    1.93776800   -0.32321700
2022      H      -2.07187800    1.81413800    0.87795600
2023      Group                6
2024      Axis                  5 4
2025      Symmetry                1
2026      Potential [kcal/mol]    6
2027      0. 7.54 2.92 3.22 2.77 4.12
2028      End
2029      Rotor Hindered
2030      Geometry [angstrom]    21
2031      C       2.94549700    0.92678700   -0.45160800
2032      C       1.84415100    0.74209600    0.52595900
2033      O       1.48912200   -0.62395300    0.69534100
2034      C       0.83562100   -1.17091700   -0.41422000
2035      O      -0.40255000   -0.58162700   -0.66138000
2036      C      -1.35570300   -0.81254900    0.36315700
2037      C      -2.63212200   -0.08378500    0.00049200
2038      C      -2.42929700    1.42415200   -0.07699400
2039      H       3.75871800    0.21627200   -0.46940300
2040      H       3.04011300    1.84184700   -1.01486800
2041      H       2.14619600    1.07740400    1.52396900
2042      H       0.96565900    1.32775900    0.23851900
2043      H       1.42091700   -1.02695200   -1.32577100
2044      H       0.72509500   -2.23564300   -0.18974000
2045      H      -1.53063000   -1.89090300    0.45706800
2046      H      -0.96662600   -0.44966600    1.31991300
2047      H      -2.99193000   -0.46443100   -0.95708400
2048      H      -3.38866300   -0.32715600    0.74897400
2049      H      -1.69080500    1.66948600   -0.83872700
2050      H      -3.35763300    1.93776800   -0.32321700
2051      H      -2.07187800    1.81413800    0.87795600
2052      Group                7 15 16
2053      Axis                  6 5
2054      Symmetry                1

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2055     Potential [kcal/mol]           6
2056     0. 1.67 1.19 7.50 2.97 3.36
2057     End
2058     Rotor Hindered
2059     Geometry [angstrom]           21
2060     C           2.94549700      0.92678700      -0.45160800
2061     C           1.84415100      0.74209600      0.52595900
2062     O           1.48912200     -0.62395300      0.69534100
2063     C           0.83562100     -1.17091700     -0.41422000
2064     O          -0.40255000     -0.58162700     -0.66138000
2065     C          -1.35570300     -0.81254900      0.36315700
2066     C          -2.63212200     -0.08378500      0.00049200
2067     C          -2.42929700      1.42415200     -0.07699400
2068     H           3.75871800      0.21627200     -0.46940300
2069     H           3.04011300      1.84184700     -1.01486800
2070     H           2.14619600      1.07740400      1.52396900
2071     H           0.96565900      1.32775900      0.23851900
2072     H           1.42091700     -1.02695200     -1.32577100
2073     H           0.72509500     -2.23564300     -0.18974000
2074     H          -1.53063000     -1.89090300      0.45706800
2075     H          -0.96662600     -0.44966600      1.31991300
2076     H          -2.99193000     -0.46443100     -0.95708400
2077     H          -3.38866300     -0.32715600      0.74897400
2078     H          -1.69080500      1.66948600     -0.83872700
2079     H          -3.35763300      1.93776800     -0.32321700
2080     H          -2.07187800      1.81413800      0.87795600
2081     Group                8 17 18
2082     Axis                   7 6
2083     Symmetry                1
2084     Potential [kcal/mol]           6
2085     0. 5.03 0.19 3.76 0.51 3.71
2086     End
2087     Rotor Hindered
2088     Geometry [angstrom]           21
2089     C           2.94549700      0.92678700      -0.45160800
2090     C           1.84415100      0.74209600      0.52595900
2091     O           1.48912200     -0.62395300      0.69534100
2092     C           0.83562100     -1.17091700     -0.41422000
2093     O          -0.40255000     -0.58162700     -0.66138000
2094     C          -1.35570300     -0.81254900      0.36315700
2095     C          -2.63212200     -0.08378500      0.00049200
2096     C          -2.42929700      1.42415200     -0.07699400
2097     H           3.75871800      0.21627200     -0.46940300
2098     H           3.04011300      1.84184700     -1.01486800
2099     H           2.14619600      1.07740400      1.52396900
2100     H           0.96565900      1.32775900      0.23851900
2101     H           1.42091700     -1.02695200     -1.32577100
2102     H           0.72509500     -2.23564300     -0.18974000
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2103      H      -1.53063000   -1.89090300    0.45706800
2104      H      -0.96662600   -0.44966600    1.31991300
2105      H      -2.99193000   -0.46443100   -0.95708400
2106      H      -3.38866300   -0.32715600    0.74897400
2107      H      -1.69080500    1.66948600   -0.83872700
2108      H      -3.35763300    1.93776800   -0.32321700
2109      H      -2.07187800    1.81413800    0.87795600
2110      Group                9 10
2111      Axis                  1 2
2112      Symmetry              2
2113      Potential [kcal/mol]   2
2114      0. 1.69
2115      End
2116      Rotor Hindered
2117      Geometry [angstrom]    21
2118      C      2.94549700    0.92678700   -0.45160800
2119      C      1.84415100    0.74209600    0.52595900
2120      O      1.48912200   -0.62395300    0.69534100
2121      C      0.83562100   -1.17091700   -0.41422000
2122      O      -0.40255000   -0.58162700   -0.66138000
2123      C      -1.35570300   -0.81254900    0.36315700
2124      C      -2.63212200   -0.08378500    0.00049200
2125      C      -2.42929700    1.42415200   -0.07699400
2126      H      3.75871800    0.21627200   -0.46940300
2127      H      3.04011300    1.84184700   -1.01486800
2128      H      2.14619600    1.07740400    1.52396900
2129      H      0.96565900    1.32775900    0.23851900
2130      H      1.42091700   -1.02695200   -1.32577100
2131      H      0.72509500   -2.23564300   -0.18974000
2132      H      -1.53063000   -1.89090300    0.45706800
2133      H      -0.96662600   -0.44966600    1.31991300
2134      H      -2.99193000   -0.46443100   -0.95708400
2135      H      -3.38866300   -0.32715600    0.74897400
2136      H      -1.69080500    1.66948600   -0.83872700
2137      H      -3.35763300    1.93776800   -0.32321700
2138      H      -2.07187800    1.81413800    0.87795600
2139      Group                5 13 14
2140      Axis                  4 3
2141      Symmetry              1
2142      Potential [kcal/mol]   4
2143      0. 7.29 3.13 3.82
2144      End
2145      Rotor Hindered
2146      Geometry [angstrom]    21
2147      C      2.94549700    0.92678700   -0.45160800
2148      C      1.84415100    0.74209600    0.52595900
2149      O      1.48912200   -0.62395300    0.69534100
2150      C      0.83562100   -1.17091700   -0.41422000

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2151      O          -0.40255000   -0.58162700   -0.66138000
2152      C          -1.35570300   -0.81254900    0.36315700
2153      C          -2.63212200   -0.08378500    0.00049200
2154      C          -2.42929700    1.42415200   -0.07699400
2155      H           3.75871800    0.21627200   -0.46940300
2156      H           3.04011300    1.84184700   -1.01486800
2157      H           2.14619600    1.07740400    1.52396900
2158      H           0.96565900    1.32775900    0.23851900
2159      H           1.42091700   -1.02695200   -1.32577100
2160      H           0.72509500   -2.23564300   -0.18974000
2161      H          -1.53063000   -1.89090300    0.45706800
2162      H          -0.96662600   -0.44966600    1.31991300
2163      H          -2.99193000   -0.46443100   -0.95708400
2164      H          -3.38866300   -0.32715600    0.74897400
2165      H          -1.69080500    1.66948600   -0.83872700
2166      H          -3.35763300    1.93776800   -0.32321700
2167      H          -2.07187800    1.81413800    0.87795600
2168      Group                19 20 21
2169      Axis                  8 7
2170      Symmetry              3
2171      Potential [kcal/mol]   2
2172      0. 2.87
2173      End
2174      Frequencies [1/cm]     56
2175      278.78 308.42 375.02 459.15 480.48 529.6 648.93 771.32 846.58
902.96 925.37 944.09 966.31 1054.92 1087.42 1108.79 1130.11 1136.96
1181.66 1188.74 1215.53 1284.17 1298.07 1313.96 1347.09 1378.07
1395.43 1410.8 1429.02 1453.06 1459.3 1484.43 1490.62 1498.77
1513.23 1516.66 1531.62 3018.96 3026.97 3046.37 3058.66 3060.81
3066.33 3071.69 3098.75 3104.93 3130.69 3146.68 3173.51 3283.61
2176      436.03 1412.64 1412.73 3144.41 3323.11 3323.14
2177      ! 37.25 169.21 224.22 84.79 44.83 144.36 196.42 ! Torsions
2178      ZeroEnergy [kcal/mol]   88.0
2179      ElectronicLevels [1/cm] 1
2180      0 2
2181      End
2182      !-----
2183      !-----
2184      !-----
2185      Bimolecular      P6 # CCCOCO [CH2] + [CH2]C
2186      Fragment      CCCOCO [CH2]
2187      RRHO
2188      Geometry [angstrom]    18
2189      C          -1.94844600    1.34603200   -0.02364300
2190      O          -1.99833800    0.06676400   -0.46784100
2191      C          -1.41208600   -0.87943300    0.40124300
2192      O          -0.06725200   -0.63706500    0.62513000
2193      C           0.73962300   -0.78301800   -0.53591100

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2194      C          2.14983100   -0.35591100   -0.19139900
2195      C          2.21952600    1.11138500    0.21269100
2196      H          -2.35406300    2.06443900   -0.71594300
2197      H          -1.18632700    1.60835200    0.69589600
2198      H          -1.90151500   -0.83911200    1.37566500
2199      H          -1.57359700   -1.84552000   -0.08305400
2200      H           0.70918100   -1.82783200   -0.86507900
2201      H           0.34005100   -0.15831600   -1.34085300
2202      H           2.52131800   -0.98859100    0.61666900
2203      H           2.78217300   -0.54090700   -1.06178200
2204      H           1.62193200    1.28976200    1.10520000
2205      H           3.24385200    1.41700900    0.42091500
2206      H           1.83102700    1.74879000   -0.58383900
2207      Core      RigidRotor
2208          SymmetryFactor          1
2209      End
2210      Rotor          Hindered
2211          Group          8 9
2212          Axis          1 2
2213          Symmetry          1
2214          Potential[kcal/mol]          4
2215          0. 4.95 0. 4.58
2216      End
2217      Rotor          Hindered
2218          Group          1
2219          Axis          2 3
2220          Symmetry          1
2221          Potential[kcal/mol]          6
2222          0. 4.27 2.05 2.88 2.49 3.23
2223      End
2224      Rotor          Hindered
2225          Group          5
2226          Axis          4 3
2227          Symmetry          1
2228          Potential[kcal/mol]          6
2229          0. 7.10 2.12 4.66 3.93 4.87
2230      End
2231      Rotor          Hindered
2232          Group          6 12 13
2233          Axis          5 4
2234          Symmetry          1
2235          Potential[kcal/mol]          6
2236          0. 1.83 1.19 7.28 2.94 3.12
2237      End
2238      Rotor          Hindered
2239          Group          7 14 15
2240          Axis          6 5
2241          Symmetry          1
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2242     Potential [kcal/mol]           6
2243     0. 5.06 0.26 3.81 0.55 3.72
2244     End
2245     Rotor                          Hindered
2246     Group                          16 17 18
2247     Axis                            7 6
2248     Symmetry                        3
2249     Potential [kcal/mol]           6
2250     0. 2.65 0. 2.65 0. 2.65
2251     End
2252     Frequencies [1/cm]             42
2253     302.98 320.40 403.53 484.76 547.99 651.91
2254     771.94 901.65 924.85 964.05 992.83 1089.89
2255     1113.29 1146.62 1185.12 1193.40 1241.81 1269.08
2256     1286.98 1309.09 1347.55 1378.42 1412.76 1430.59
2257     1447.63 1484.95 1492.60 1497.44 1511.48 1521.44
2258     1528.95 3024.07 3057.90 3061.28 3063.87 3075.38
2259     3106.52 3116.50 3132.47 3148.95 3164.17 3304.07
2260     !   38.26 72.94 136.42 190.27 212.06 270.86   ! Torsions
2261     ZeroEnergy [kcal/mol]          0
2262     ElectronicLevels [1/cm]         1
2263     0   2
2264     End
2265     Fragment   [CH2]C
2266             RRHO
2267     Geometry [angstrom]             7
2268     C           0.00000000    0.00000000    0.00000000
2269     H           0.00000000    0.00000000    1.07891861
2270     H           0.95569277    0.00000000   -0.50071618
2271     C          -1.25516714    0.22579375   -0.75938703
2272     H          -2.11691855   -0.20402144   -0.24834925
2273     H          -1.46763143    1.29494164   -0.88792976
2274     H          -1.20242708   -0.20402144   -1.75988369
2275     Core                          RigidRotor
2276     SymmetryFactor                  1
2277     End
2278     Rotor                          Hindered
2279     Group                          5 6 7
2280     Axis                            4 1
2281     Symmetry                        3
2282     Potential [kcal/mol]           2
2283     0. 0.08
2284     End
2285     Frequencies [1/cm]             14
2286     445.30 810.67 983.05 1081.37 1195.61 1403.88 1471.54
1487.47
2287     1489.48 3004.42 3085.31 3128.78 3174.30 3275.74
2288     !126.44! Torsions

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2289     ZeroEnergy [kcal/mol]          0
2290     ElectronicLevels [1/cm]       1
2291         0 2
2292     End
2293     GroundEnergy [kcal/mol]       85.2
2294 End
2295 !-----
2296 Barrier      B6  W1  P6  # CCCOCO[CH2] + [CH2]C
2297 RRHO
2298 Stoichiometry C7H16O2
2299 Core          PhaseSpaceTheory
2300     FragmentGeometry [angstrom]  18
2301     C             -1.94844600     1.34603200     -0.02364300
2302     O             -1.99833800     0.06676400     -0.46784100
2303     C             -1.41208600     -0.87943300     0.40124300
2304     O             -0.06725200     -0.63706500     0.62513000
2305     C             0.73962300     -0.78301800     -0.53591100
2306     C             2.14983100     -0.35591100     -0.19139900
2307     C             2.21952600     1.11138500     0.21269100
2308     H             -2.35406300     2.06443900     -0.71594300
2309     H             -1.18632700     1.60835200     0.69589600
2310     H             -1.90151500     -0.83911200     1.37566500
2311     H             -1.57359700     -1.84552000     -0.08305400
2312     H             0.70918100     -1.82783200     -0.86507900
2313     H             0.34005100     -0.15831600     -1.34085300
2314     H             2.52131800     -0.98859100     0.61666900
2315     H             2.78217300     -0.54090700     -1.06178200
2316     H             1.62193200     1.28976200     1.10520000
2317     H             3.24385200     1.41700900     0.42091500
2318     H             1.83102700     1.74879000     -0.58383900
2319     FragmentGeometry [angstrom]  7
2320     C             0.000000     0.000000     0.000000
2321     H             0.000000     0.000000     1.078919
2322     H             0.955693     0.000000     -0.500716
2323     C             -1.255167     0.225794     -0.759387
2324     H             -2.116919     -0.204021     -0.248349
2325     H             -1.467631     1.294942     -0.887930
2326     H             -1.202427     -0.204021     -1.759884
2327     SymmetryFactor          1
2328     PotentialPrefactor [au]  26.33 #5.5 6.3
2329     PotentialPowerExponent  9.67
2330     End
2331     Rotor Hindered
2332     Geometry [angstrom]      18
2333     C             -1.94844600     1.34603200     -0.02364300
2334     O             -1.99833800     0.06676400     -0.46784100
2335     C             -1.41208600     -0.87943300     0.40124300
2336     O             -0.06725200     -0.63706500     0.62513000

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2337      C          0.73962300   -0.78301800   -0.53591100
2338      C          2.14983100   -0.35591100   -0.19139900
2339      C          2.21952600   1.11138500    0.21269100
2340      H         -2.35406300    2.06443900   -0.71594300
2341      H         -1.18632700    1.60835200    0.69589600
2342      H         -1.90151500   -0.83911200    1.37566500
2343      H         -1.57359700   -1.84552000   -0.08305400
2344      H          0.70918100   -1.82783200   -0.86507900
2345      H          0.34005100   -0.15831600   -1.34085300
2346      H          2.52131800   -0.98859100    0.61666900
2347      H          2.78217300   -0.54090700   -1.06178200
2348      H          1.62193200    1.28976200    1.10520000
2349      H          3.24385200    1.41700900    0.42091500
2350      H          1.83102700    1.74879000   -0.58383900
2351      Group                8 9
2352      Axis                  1 2
2353      Symmetry              1
2354      Potential [kcal/mol]   4
2355      0. 4.95 0. 4.58
2356      End
2357      Rotor Hindered
2358      Geometry [angstrom]   18
2359      C         -1.94844600    1.34603200   -0.02364300
2360      O         -1.99833800    0.06676400   -0.46784100
2361      C         -1.41208600   -0.87943300    0.40124300
2362      O         -0.06725200   -0.63706500    0.62513000
2363      C          0.73962300   -0.78301800   -0.53591100
2364      C          2.14983100   -0.35591100   -0.19139900
2365      C          2.21952600    1.11138500    0.21269100
2366      H         -2.35406300    2.06443900   -0.71594300
2367      H         -1.18632700    1.60835200    0.69589600
2368      H         -1.90151500   -0.83911200    1.37566500
2369      H         -1.57359700   -1.84552000   -0.08305400
2370      H          0.70918100   -1.82783200   -0.86507900
2371      H          0.34005100   -0.15831600   -1.34085300
2372      H          2.52131800   -0.98859100    0.61666900
2373      H          2.78217300   -0.54090700   -1.06178200
2374      H          1.62193200    1.28976200    1.10520000
2375      H          3.24385200    1.41700900    0.42091500
2376      H          1.83102700    1.74879000   -0.58383900
2377      Group                1
2378      Axis                  2 3
2379      Symmetry              1
2380      Potential [kcal/mol]   6
2381      0. 4.27 2.05 2.88 2.49 3.23
2382      End
2383      Rotor Hindered
2384      Geometry [angstrom]   18

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2385      C      -1.94844600      1.34603200      -0.02364300
2386      O      -1.99833800      0.06676400      -0.46784100
2387      C      -1.41208600      -0.87943300      0.40124300
2388      O      -0.06725200      -0.63706500      0.62513000
2389      C      0.73962300      -0.78301800      -0.53591100
2390      C      2.14983100      -0.35591100      -0.19139900
2391      C      2.21952600      1.11138500      0.21269100
2392      H      -2.35406300      2.06443900      -0.71594300
2393      H      -1.18632700      1.60835200      0.69589600
2394      H      -1.90151500      -0.83911200      1.37566500
2395      H      -1.57359700      -1.84552000      -0.08305400
2396      H      0.70918100      -1.82783200      -0.86507900
2397      H      0.34005100      -0.15831600      -1.34085300
2398      H      2.52131800      -0.98859100      0.61666900
2399      H      2.78217300      -0.54090700      -1.06178200
2400      H      1.62193200      1.28976200      1.10520000
2401      H      3.24385200      1.41700900      0.42091500
2402      H      1.83102700      1.74879000      -0.58383900
2403      Group                5
2404      Axis                  4 3
2405      Symmetry              1
2406      Potential [kcal/mol]   6
2407      0. 7.10 2.12 4.66 3.93 4.87
2408      End
2409      Rotor Hindered
2410      Geometry [angstrom]    18
2411      C      -1.94844600      1.34603200      -0.02364300
2412      O      -1.99833800      0.06676400      -0.46784100
2413      C      -1.41208600      -0.87943300      0.40124300
2414      O      -0.06725200      -0.63706500      0.62513000
2415      C      0.73962300      -0.78301800      -0.53591100
2416      C      2.14983100      -0.35591100      -0.19139900
2417      C      2.21952600      1.11138500      0.21269100
2418      H      -2.35406300      2.06443900      -0.71594300
2419      H      -1.18632700      1.60835200      0.69589600
2420      H      -1.90151500      -0.83911200      1.37566500
2421      H      -1.57359700      -1.84552000      -0.08305400
2422      H      0.70918100      -1.82783200      -0.86507900
2423      H      0.34005100      -0.15831600      -1.34085300
2424      H      2.52131800      -0.98859100      0.61666900
2425      H      2.78217300      -0.54090700      -1.06178200
2426      H      1.62193200      1.28976200      1.10520000
2427      H      3.24385200      1.41700900      0.42091500
2428      H      1.83102700      1.74879000      -0.58383900
2429      Group                6 12 13
2430      Axis                  5 4
2431      Symmetry              1
2432      Potential [kcal/mol]   6

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```
2433      0. 1.83 1.19 7.28 2.94 3.12
2434 End
2435 Rotor Hindered
2436 Geometry [angstrom]      18
2437 C      -1.94844600      1.34603200      -0.02364300
2438 O      -1.99833800      0.06676400      -0.46784100
2439 C      -1.41208600     -0.87943300      0.40124300
2440 O      -0.06725200     -0.63706500      0.62513000
2441 C       0.73962300     -0.78301800     -0.53591100
2442 C       2.14983100     -0.35591100     -0.19139900
2443 C       2.21952600      1.11138500      0.21269100
2444 H      -2.35406300      2.06443900     -0.71594300
2445 H      -1.18632700      1.60835200      0.69589600
2446 H      -1.90151500     -0.83911200      1.37566500
2447 H      -1.57359700     -1.84552000     -0.08305400
2448 H       0.70918100     -1.82783200     -0.86507900
2449 H       0.34005100     -0.15831600     -1.34085300
2450 H       2.52131800     -0.98859100      0.61666900
2451 H       2.78217300     -0.54090700     -1.06178200
2452 H       1.62193200      1.28976200      1.10520000
2453 H       3.24385200      1.41700900      0.42091500
2454 H       1.83102700      1.74879000     -0.58383900
2455 Group              7 14 15
2456 Axis                6 5
2457 Symmetry            1
2458 Potential [kcal/mol] 6
2459      0. 5.06 0.26 3.81 0.55 3.72
2460 End
2461 Rotor Hindered
2462 Geometry [angstrom]      18
2463 C      -1.94844600      1.34603200      -0.02364300
2464 O      -1.99833800      0.06676400      -0.46784100
2465 C      -1.41208600     -0.87943300      0.40124300
2466 O      -0.06725200     -0.63706500      0.62513000
2467 C       0.73962300     -0.78301800     -0.53591100
2468 C       2.14983100     -0.35591100     -0.19139900
2469 C       2.21952600      1.11138500      0.21269100
2470 H      -2.35406300      2.06443900     -0.71594300
2471 H      -1.18632700      1.60835200      0.69589600
2472 H      -1.90151500     -0.83911200      1.37566500
2473 H      -1.57359700     -1.84552000     -0.08305400
2474 H       0.70918100     -1.82783200     -0.86507900
2475 H       0.34005100     -0.15831600     -1.34085300
2476 H       2.52131800     -0.98859100      0.61666900
2477 H       2.78217300     -0.54090700     -1.06178200
2478 H       1.62193200      1.28976200      1.10520000
2479 H       3.24385200      1.41700900      0.42091500
2480 H       1.83102700      1.74879000     -0.58383900
```



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2522      H           -2.49993900   -1.32000100    0.10195800
2523      H           -1.96045200    0.05427900    1.26775200
2524      H            0.21562100    1.37685500   -1.18381500
2525      H           -0.66451900    1.73033500    0.31502500
2526      H            1.70201500    1.22640500    0.78328400
2527      H            0.65353000    0.02475100    1.51629800
2528      H            2.14744800   -0.35155400   -1.13523500
2529      H            2.60297800   -1.08342900    0.40445300
2530      H            1.09113200   -1.54406600   -0.38180700
2531      Core      RigidRotor
2532          SymmetryFactor          1
2533      End
2534      Rotor              Hindered
2535          Group              6 7
2536          Axis                1 2
2537          Symmetry            1
2538          Potential [kcal/mol]  4
2539              0. 5.10 0. 5.37
2540      End
2541      Rotor              Hindered
2542          Group              1
2543          Axis                2 3
2544          Symmetry            1
2545          Potential [kcal/mol]  6
2546              0. 1.60 0.12 1.17 1.10 5.99
2547      End
2548      Rotor              Hindered
2549          Group              5 10 11
2550          Axis                4 3
2551          Symmetry            1
2552          Potential [kcal/mol]  6
2553              0. 3.74 0.47 3.46 0.73 4.79
2554      End
2555      Rotor              Hindered
2556          Group              12 13 14
2557          Axis                5 4
2558          Symmetry            3
2559          Potential [kcal/mol]  2
2560              0. 2.78
2561      End
2562      Frequencies [1/cm]    32
2563      282.38 440.57 525.81 631.81 771.33 880.55
2564      921.94 967.17 1074.67 1120.36 1156.41 1221.23
2565      1279.48 1307.55 1338.15 1379.84 1410.34 1423.03
2566      1481.32 1485.96 1500.86 1509.25 1520.27 3037.27
2567      3063.03 3066.28 3097.68 3120.11 3127.22 3134.42
2568      3146.23 3276.88
2569      !      70.31 168.24 232.84 307.28      ! Torsions

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```
2570 ZeroEnergy [kcal/mol]      0
2571 ElectronicLevels [1/cm]   1
2572 0      2
2573 End
2574 Fragment CCC [0]
2575 RRHO
2576 Geometry [angstrom]      11
2577 C      -1.49590800    -0.48329300    0.10802900
2578 C      -0.568831200    0.66534600    -0.26144700
2579 C      0.84087600     0.44659000    0.27076000
2580 O      1.45814100     -0.68198500   -0.19676600
2581 H      -1.08741200    -1.42684200   -0.25185400
2582 H      -2.48614800    -0.35213400   -0.32501100
2583 H      -1.60940000    -0.55763200    1.19092100
2584 H      -0.51218700    0.77212100    -1.34631700
2585 H      -0.94736500    1.61106700    0.13180500
2586 H      1.49493800     1.31421200    0.10098500
2587 H      0.82251400     0.32322800    1.36955000
2588 Core RigidRotor
2589 SymmetryFactor            1
2590 End
2591 Rotor                      Hindered
2592 Group                      4 10 11
2593 Axis                        3 2
2594 Symmetry                    1
2595 Potential [kcal/mol]       6
2596 0. 3.15 0.44 3.15 0. 3.29
2597 End
2598 Rotor                      Hindered
2599 Group                      5 6 7
2600 Axis                        1 2
2601 Symmetry                    3
2602 Potential [kcal/mol]       2
2603 0. 2.78
2604 End
2605 Frequencies [1/cm]        25
2606 312.26 474.66 506.23 792.85 885.51 984.56
2607 1001.42 1097.32 1115.56 1223.19 1291.87 1361.37
2608 1373.72 1386.87 1421.11 1486.1 1502.31 1511.67
2609 2936.28 2996.28 3062.53 3066.56 3102.81 3133.89 3147.38
2610 ! 141.59 231.1 ! Torsions
2611 ZeroEnergy [kcal/mol]      0
2612 ElectronicLevels [1/cm]   1
2613 0      2
2614 End
2615 GroundEnergy [kcal/mol]    89.1
2616 End
2617 !-----
```

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2618 Barrier      B7  W1  P7  # CCCO[CH2] + CCC[O]
2619 RRHO
2620 Stoichiometry  C7H16O2
2621 Core          PhaseSpaceTheory
2622   FragmentGeometry [angstrom]  14
2623     C              -1.78045700   -0.57633100   0.40428300
2624     O              -1.06456400   -0.06010800  -0.61593800
2625     C              -0.13758000   0.95064700   -0.24518600
2626     C              1.02666700   0.39769000   0.56030500
2627     C              1.76281900   -0.71079000  -0.17947000
2628     H              -2.49993900   -1.32000100   0.10195800
2629     H              -1.96045200   0.05427900   1.26775200
2630     H              0.21562100   1.37685500   -1.18381500
2631     H              -0.66451900   1.73033500   0.31502500
2632     H              1.70201500   1.22640500   0.78328400
2633     H              0.65353000   0.02475100   1.51629800
2634     H              2.14744800   -0.35155400  -1.13523500
2635     H              2.60297800   -1.08342900   0.40445300
2636     H              1.09113200   -1.54406600  -0.38180700
2637   FragmentGeometry [angstrom]  11
2638     C              -1.49590800   -0.48329300   0.10802900
2639     C              -0.56831200   0.66534600   -0.26144700
2640     C              0.84087600   0.44659000   0.27076000
2641     O              1.45814100   -0.68198500  -0.19676600
2642     H              -1.08741200   -1.42684200  -0.25185400
2643     H              -2.48614800   -0.35213400  -0.32501100
2644     H              -1.60940000   -0.55763200   1.19092100
2645     H              -0.51218700   0.77212100   -1.34631700
2646     H              -0.94736500   1.61106700   0.13180500
2647     H              1.49493800   1.31421200   0.10098500
2648     H              0.82251400   0.32322800   1.36955000
2649     SymmetryFactor          1
2650     PotentialPrefactor [au]  10.07 #0.5 0.75
2651     PotentialPowerExponent  9.18
2652 End
2653 Rotor Hindered
2654   Geometry [angstrom]  14
2655     C              -1.78045700   -0.57633100   0.40428300
2656     O              -1.06456400   -0.06010800  -0.61593800
2657     C              -0.13758000   0.95064700   -0.24518600
2658     C              1.02666700   0.39769000   0.56030500
2659     C              1.76281900   -0.71079000  -0.17947000
2660     H              -2.49993900   -1.32000100   0.10195800
2661     H              -1.96045200   0.05427900   1.26775200
2662     H              0.21562100   1.37685500   -1.18381500
2663     H              -0.66451900   1.73033500   0.31502500
2664     H              1.70201500   1.22640500   0.78328400
2665     H              0.65353000   0.02475100   1.51629800
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2666      H          2.14744800   -0.35155400   -1.13523500
2667      H          2.60297800   -1.08342900    0.40445300
2668      H          1.09113200   -1.54406600   -0.38180700
2669      Group                6 7
2670      Axis                  1 2
2671      Symmetry              1
2672      Potential [kcal/mol]    4
2673      0. 5.10 0. 5.37
2674      End
2675      Rotor Hindered
2676      Geometry [angstrom]    14
2677      C          -1.78045700   -0.57633100    0.40428300
2678      O          -1.06456400   -0.06010800   -0.61593800
2679      C          -0.13758000    0.95064700   -0.24518600
2680      C          1.02666700    0.39769000    0.56030500
2681      C          1.76281900   -0.71079000   -0.17947000
2682      H          -2.49993900   -1.32000100    0.10195800
2683      H          -1.96045200    0.05427900    1.26775200
2684      H          0.21562100    1.37685500   -1.18381500
2685      H          -0.66451900    1.73033500    0.31502500
2686      H          1.70201500    1.22640500    0.78328400
2687      H          0.65353000    0.02475100    1.51629800
2688      H          2.14744800   -0.35155400   -1.13523500
2689      H          2.60297800   -1.08342900    0.40445300
2690      H          1.09113200   -1.54406600   -0.38180700
2691      Group                1
2692      Axis                  2 3
2693      Symmetry              1
2694      Potential [kcal/mol]    6
2695      0. 1.60 0.12 1.17 1.10 5.99
2696      End
2697      Rotor Hindered
2698      Geometry [angstrom]    14
2699      C          -1.78045700   -0.57633100    0.40428300
2700      O          -1.06456400   -0.06010800   -0.61593800
2701      C          -0.13758000    0.95064700   -0.24518600
2702      C          1.02666700    0.39769000    0.56030500
2703      C          1.76281900   -0.71079000   -0.17947000
2704      H          -2.49993900   -1.32000100    0.10195800
2705      H          -1.96045200    0.05427900    1.26775200
2706      H          0.21562100    1.37685500   -1.18381500
2707      H          -0.66451900    1.73033500    0.31502500
2708      H          1.70201500    1.22640500    0.78328400
2709      H          0.65353000    0.02475100    1.51629800
2710      H          2.14744800   -0.35155400   -1.13523500
2711      H          2.60297800   -1.08342900    0.40445300
2712      H          1.09113200   -1.54406600   -0.38180700
2713      Group                5 10 11
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2714     Axis                4 3
2715     Symmetry            1
2716     Potential [kcal/mol] 6
2717         0. 3.74 0.47 3.46 0.73 4.79
2718     End
2719     Rotor Hindered
2720     Geometry [angstrom]  14
2721     C                    -1.78045700   -0.57633100   0.40428300
2722     O                    -1.06456400   -0.06010800  -0.61593800
2723     C                    -0.13758000   0.95064700  -0.24518600
2724     C                    1.02666700   0.39769000   0.56030500
2725     C                    1.76281900  -0.71079000  -0.17947000
2726     H                    -2.49993900  -1.32000100   0.10195800
2727     H                    -1.96045200   0.05427900   1.26775200
2728     H                    0.21562100   1.37685500  -1.18381500
2729     H                    -0.66451900   1.73033500   0.31502500
2730     H                    1.70201500   1.22640500   0.78328400
2731     H                    0.65353000   0.02475100   1.51629800
2732     H                    2.14744800  -0.35155400  -1.13523500
2733     H                    2.60297800  -1.08342900   0.40445300
2734     H                    1.09113200  -1.54406600  -0.38180700
2735     Group                12 13 14
2736     Axis                5 4
2737     Symmetry            3
2738     Potential [kcal/mol] 2
2739         0. 2.78
2740     End
2741     Rotor Hindered
2742     Geometry [angstrom]  11
2743     C                    -1.49590800  -0.48329300   0.10802900
2744     C                    -0.56831200   0.66534600  -0.26144700
2745     C                    0.84087600   0.44659000   0.27076000
2746     O                    1.45814100  -0.68198500  -0.19676600
2747     H                    -1.08741200  -1.42684200  -0.25185400
2748     H                    -2.48614800  -0.35213400  -0.32501100
2749     H                    -1.60940000  -0.55763200   1.19092100
2750     H                    -0.51218700   0.77212100  -1.34631700
2751     H                    -0.94736500   1.61106700   0.13180500
2752     H                    1.49493800   1.31421200   0.10098500
2753     H                    0.82251400   0.32322800   1.36955000
2754     Group                4 10 11
2755     Axis                3 2
2756     Symmetry            1
2757     Potential [kcal/mol] 6
2758         0. 3.15 0.44 3.15 0. 3.29
2759     End
2760     Rotor Hindered
2761     Geometry [angstrom]  11

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2762      C          -1.49590800   -0.48329300    0.10802900
2763      C          -0.56831200    0.66534600   -0.26144700
2764      C           0.84087600    0.44659000    0.27076000
2765      O           1.45814100   -0.68198500   -0.19676600
2766      H          -1.08741200   -1.42684200   -0.25185400
2767      H          -2.48614800   -0.35213400   -0.32501100
2768      H          -1.60940000   -0.55763200    1.19092100
2769      H          -0.51218700    0.77212100   -1.34631700
2770      H          -0.94736500    1.61106700    0.13180500
2771      H           1.49493800    1.31421200    0.10098500
2772      H           0.82251400    0.32322800    1.36955000
2773      Group                5 6 7
2774      Axis                  1 2
2775      Symmetry                3
2776      Potential [kcal/mol]    2
2777      0. 2.78
2778      End
2779      Frequencies [1/cm]      57
2780      282.38 440.57 525.81 631.81 771.33 880.55 921.94 967.17 1074.67
1120.36 1156.41 1221.23 1279.48 1307.55 1338.15 1379.84 1410.34
1423.03 1481.32 1485.96 1500.86 1509.25 1520.27 3037.27 3063.03
3066.28 3097.68 3120.11 3127.22 3134.42 3146.23 3276.88
2781      312.26 474.66 506.23 792.85 885.51 984.56 1001.42 1097.32 1115.56
1223.19 1291.87 1361.37 1373.72 1386.87 1421.11 1486.1 1502.31
1511.67 2936.28 2996.28 3062.53 3066.56 3102.81 3133.89 3147.38
2782      !    70.31 168.24 232.84 307.28 141.59 231.1 ! Torsions
2783      ZeroEnergy [kcal/mol]    89.1
2784      ElectronicLevels [1/cm]  1
2785      0    2
2786      End
2787      !-----
2788      !-----
2789      !-----
2790      Bimolecular      P8      # CCCOC [0] + CC [CH2]
2791      Fragment      CCCOC [0]
2792      RRHO
2793      Geometry [angstrom]      15
2794      O              2.57240700    0.43032500   -0.10693800
2795      C              1.72881400   -0.59369500    0.11318800
2796      O              0.42531800   -0.42837200   -0.33341500
2797      C             -0.26608100    0.62485100    0.32084700
2798      C             -1.68092200    0.67656700   -0.21398300
2799      C             -2.45912000   -0.60124900    0.07111200
2800      H              2.12524600   -1.49827000   -0.36931500
2801      H              1.75566100   -0.77135500    1.20909800
2802      H             -0.27299600    0.43272400    1.40317600
2803      H              0.25430800    1.56959100    0.14634100
2804      H             -2.18189500    1.53591200    0.23563800

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2805      H          -1.63463300    0.85888200   -1.28891600
2806      H          -2.52631100   -0.78110400    1.14548000
2807      H          -3.47263500   -0.54255300   -0.32298300
2808      H          -1.96468300   -1.45829900   -0.38268200
2809      Core      RigidRotor
2810          SymmetryFactor          1
2811      End
2812          Rotor                      Hindered
2813          Group                        1 7 8
2814          Axis                          2 3
2815          Symmetry                       1
2816          Potential [kcal/mol]          6
2817          0. 2.35 0.05 3.26 2.17 3.36
2818      End
2819          Rotor                      Hindered
2820          Group                        2
2821          Axis                          3 4
2822          Symmetry                       1
2823          Potential [kcal/mol]          4
2824          0. 7.19 0.78 1.44
2825      End
2826          Rotor                      Hindered
2827          Group                        6 11 12
2828          Axis                          5 4
2829          Symmetry                       1
2830          Potential [kcal/mol]          6
2831          0. 3.64 0.35 3.58 0.10 4.82
2832      End
2833          Rotor                      Hindered
2834          Group                        13 14 15
2835          Axis                          6 5
2836          Symmetry                       3
2837          Potential [kcal/mol]          2
2838          0. 2.74
2839      End
2840          Frequencies [1/cm]          35
2841          294.3 322.94 469.02 636.93 769.87 806.52
2842          907.93 929.04 963.69 1059.99 1095.67 1133.72
2843          1169.32 1196.54 1240.41 1284.46 1314.35 1354.75
2844          1379.33 1400.27 1413.51 1439.76 1483.62 1500.31
2845          1513.05 1527.32 2886.01 2995.25 3008.58 3063.95
2846          3066.97 3081.76 3107.34 3134.25 3151.03
2847          ! 49.19 109.4 212.14 164.27 ! Torsions
2848          ZeroEnergy [kcal/mol]          0
2849          ElectronicLevels [1/cm]          1
2850          0 2
2851      End
2852          Fragment CC[CH2]
```

```
2853 RRHO
2854 Geometry [angstrom] 10
2855 C -1.21576400 -0.24393400 -0.03513100
2856 C 0.07906700 0.55925200 0.04786100
2857 C 1.29106100 -0.29615900 -0.03188100
2858 H -1.27316400 -0.78426700 -0.98002700
2859 H -2.09049500 0.40029700 0.04349600
2860 H -1.26327100 -0.97710700 0.77093600
2861 H 0.10443800 1.31177800 -0.74483100
2862 H 0.08395300 1.13114900 0.98641300
2863 H 2.25628600 0.12468300 -0.26877100
2864 H 1.25606300 -1.32148700 0.30769100
2865 Core RigidRotor
2866 SymmetryFactor 1
2867 End
2868 Rotor Hindered
2869 Group 4 5 6
2870 Axis 1 2
2871 Symmetry 3
2872 Potential [kcal/mol] 6
2873 0. 3.0 0. 3.0 0. 3.0
2874 End
2875 Rotor Hindered
2876 Group 9 10
2877 Axis 3 2
2878 Symmetry 2
2879 Potential [kcal/mol] 2
2880 0. 0.26
2881 End
2882 Frequencies [1/cm] 22
2883 373.58 453.53 756.21 896.17 928.95 1053.02
2884 1101.17 1178.18 1271.23 1363.51 1410.57 1469.66
2885 1474.78 1502.4 1508.75 2984.28 3059.08 3062.57
2886 3130.39 3139.2 3166.94 3270.35
2887 ! 93.61 253.67 ! Torsions
2888 ZeroEnergy [kcal/mol] 0
2889 ElectronicLevels [1/cm] 1
2890 0 2
2891 End
2892 GroundEnergy [kcal/mol] 85.7
2893 End
2894 !-----
2895 Barrier B8 W1 P8 # CCCOC [0] + CC [CH2]
2896 RRHO
2897 Stoichiometry C7H16O2
2898 Core PhaseSpaceTheory
2899 FragmentGeometry [angstrom] 15
2900 0 2.57240700 0.43032500 -0.10693800
```

```
2901      C      1.72881400   -0.59369500    0.11318800
2902      O      0.42531800   -0.42837200   -0.33341500
2903      C     -0.26608100    0.62485100    0.32084700
2904      C     -1.68092200    0.67656700   -0.21398300
2905      C     -2.45912000   -0.60124900    0.07111200
2906      H      2.12524600   -1.49827000   -0.36931500
2907      H      1.75566100   -0.77135500    1.20909800
2908      H     -0.27299600    0.43272400    1.40317600
2909      H      0.25430800    1.56959100    0.14634100
2910      H     -2.18189500    1.53591200    0.23563800
2911      H     -1.63463300    0.85888200   -1.28891600
2912      H     -2.52631100   -0.78110400    1.14548000
2913      H     -3.47263500   -0.54255300   -0.32298300
2914      H     -1.96468300   -1.45829900   -0.38268200
2915      FragmentGeometry [angstrom]  10
2916      C     -1.21576400   -0.24393400   -0.03513100
2917      C      0.07906700    0.55925200    0.04786100
2918      C      1.29106100   -0.29615900   -0.03188100
2919      H     -1.27316400   -0.78426700   -0.98002700
2920      H     -2.09049500    0.40029700    0.04349600
2921      H     -1.26327100   -0.97710700    0.77093600
2922      H      0.10443800    1.31177800   -0.74483100
2923      H      0.08395300    1.13114900    0.98641300
2924      H      2.25628600    0.12468300   -0.26877100
2925      H      1.25606300   -1.32148700    0.30769100
2926      SymmetryFactor                1
2927      PotentialPrefactor [au]       11.02 #1
2928      PotentialPowerExponent        9.12
2929      End
2930      Rotor Hindered
2931      Geometry [angstrom]           15
2932      O      2.57240700    0.43032500   -0.10693800
2933      C      1.72881400   -0.59369500    0.11318800
2934      O      0.42531800   -0.42837200   -0.33341500
2935      C     -0.26608100    0.62485100    0.32084700
2936      C     -1.68092200    0.67656700   -0.21398300
2937      C     -2.45912000   -0.60124900    0.07111200
2938      H      2.12524600   -1.49827000   -0.36931500
2939      H      1.75566100   -0.77135500    1.20909800
2940      H     -0.27299600    0.43272400    1.40317600
2941      H      0.25430800    1.56959100    0.14634100
2942      H     -2.18189500    1.53591200    0.23563800
2943      H     -1.63463300    0.85888200   -1.28891600
2944      H     -2.52631100   -0.78110400    1.14548000
2945      H     -3.47263500   -0.54255300   -0.32298300
2946      H     -1.96468300   -1.45829900   -0.38268200
2947      Group                1 7 8
2948      Axis                  2 3
```

```

2949     Symmetry                1
2950     Potential [kcal/mol]     6
2951         0. 2.35 0.05 3.26 2.17 3.36
2952     End
2953     Rotor Hindered
2954         Geometry [angstrom]  15
2955         O                    2.57240700    0.43032500   -0.10693800
2956         C                    1.72881400   -0.59369500    0.11318800
2957         O                    0.42531800   -0.42837200   -0.33341500
2958         C                   -0.26608100    0.62485100    0.32084700
2959         C                   -1.68092200    0.67656700   -0.21398300
2960         C                   -2.45912000   -0.60124900    0.07111200
2961         H                    2.12524600   -1.49827000   -0.36931500
2962         H                    1.75566100   -0.77135500    1.20909800
2963         H                   -0.27299600    0.43272400    1.40317600
2964         H                    0.25430800    1.56959100    0.14634100
2965         H                   -2.18189500    1.53591200    0.23563800
2966         H                   -1.63463300    0.85888200   -1.28891600
2967         H                   -2.52631100   -0.78110400    1.14548000
2968         H                   -3.47263500   -0.54255300   -0.32298300
2969         H                   -1.96468300   -1.45829900   -0.38268200
2970     Group                    2
2971     Axis                      3 4
2972     Symmetry                1
2973     Potential [kcal/mol]     4
2974         0. 7.19 0.78 1.44
2975     End
2976     Rotor Hindered
2977         Geometry [angstrom]  15
2978         O                    2.57240700    0.43032500   -0.10693800
2979         C                    1.72881400   -0.59369500    0.11318800
2980         O                    0.42531800   -0.42837200   -0.33341500
2981         C                   -0.26608100    0.62485100    0.32084700
2982         C                   -1.68092200    0.67656700   -0.21398300
2983         C                   -2.45912000   -0.60124900    0.07111200
2984         H                    2.12524600   -1.49827000   -0.36931500
2985         H                    1.75566100   -0.77135500    1.20909800
2986         H                   -0.27299600    0.43272400    1.40317600
2987         H                    0.25430800    1.56959100    0.14634100
2988         H                   -2.18189500    1.53591200    0.23563800
2989         H                   -1.63463300    0.85888200   -1.28891600
2990         H                   -2.52631100   -0.78110400    1.14548000
2991         H                   -3.47263500   -0.54255300   -0.32298300
2992         H                   -1.96468300   -1.45829900   -0.38268200
2993     Group                    6 11 12
2994     Axis                      5 4
2995     Symmetry                1
2996     Potential [kcal/mol]     6

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2997      0. 3.64 0.35 3.58 0.10 4.82
2998      End
2999      Rotor Hindered
3000      Geometry [angstrom]          15
3001      O                2.57240700    0.43032500    -0.10693800
3002      C                1.72881400    -0.59369500    0.11318800
3003      O                0.42531800    -0.42837200    -0.33341500
3004      C               -0.26608100    0.62485100    0.32084700
3005      C               -1.68092200    0.67656700    -0.21398300
3006      C               -2.45912000    -0.60124900    0.07111200
3007      H                2.12524600    -1.49827000    -0.36931500
3008      H                1.75566100    -0.77135500    1.20909800
3009      H               -0.27299600    0.43272400    1.40317600
3010      H                0.25430800    1.56959100    0.14634100
3011      H               -2.18189500    1.53591200    0.23563800
3012      H               -1.63463300    0.85888200    -1.28891600
3013      H               -2.52631100    -0.78110400    1.14548000
3014      H               -3.47263500    -0.54255300    -0.32298300
3015      H               -1.96468300    -1.45829900    -0.38268200
3016      Group                13 14 15
3017      Axis                  6 5
3018      Symmetry                3
3019      Potential [kcal/mol]      2
3020      0. 2.74
3021      End
3022      Rotor Hindered
3023      Geometry [angstrom]          10
3024      C               -1.21576400    -0.24393400    -0.03513100
3025      C                0.07906700    0.55925200    0.04786100
3026      C                1.29106100    -0.29615900    -0.03188100
3027      H               -1.27316400    -0.78426700    -0.98002700
3028      H               -2.09049500    0.40029700    0.04349600
3029      H               -1.26327100    -0.97710700    0.77093600
3030      H                0.10443800    1.31177800    -0.74483100
3031      H                0.08395300    1.13114900    0.98641300
3032      H                2.25628600    0.12468300    -0.26877100
3033      H                1.25606300    -1.32148700    0.30769100
3034      Group                4 5 6
3035      Axis                  1 2
3036      Symmetry                3
3037      Potential [kcal/mol]      6
3038      0. 3.0 0. 3.0 0. 3.0
3039      End
3040      Rotor Hindered
3041      Geometry [angstrom]          10
3042      C               -1.21576400    -0.24393400    -0.03513100
3043      C                0.07906700    0.55925200    0.04786100
3044      C                1.29106100    -0.29615900    -0.03188100

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```

3045      H          -1.27316400   -0.78426700   -0.98002700
3046      H          -2.09049500    0.40029700    0.04349600
3047      H          -1.26327100   -0.97710700    0.77093600
3048      H           0.10443800    1.31177800   -0.74483100
3049      H           0.08395300    1.13114900    0.98641300
3050      H           2.25628600    0.12468300   -0.26877100
3051      H           1.25606300   -1.32148700    0.30769100
3052      Group                9 10
3053      Axis                  3 2
3054      Symmetry                2
3055      Potential [kcal/mol]      2
3056      0. 0.26
3057      End
3058      Frequencies [1/cm]       57
3059      294.3 322.94 469.02 636.93 769.87 806.52 907.93 929.04 963.69
1059.99 1095.67 1133.72 1169.32 1196.54 1240.41 1284.46 1314.35
1354.75 1379.33 1400.27 1413.51 1439.76 1483.62 1500.31 1513.05
1527.32 2886.01 2995.25 3008.58 3063.95 3066.97 3081.76 3107.34
3134.25 3151.03
3060      373.58 453.53 756.21 896.17 928.95 1053.02 1101.17 1178.18
1271.23 1363.51 1410.57 1469.66 1474.78 1502.4 1508.75 2984.28
3059.08 3062.57 3130.39 3139.2 3166.94 3270.35
3061      !    93.61 253.67 49.19 109.4 212.14 164.27      ! Torsions
3062      ZeroEnergy [kcal/mol]    85.7
3063      ElectronicLevels [1/cm]  1
3064      0    2
3065      End
3066      !-----
3067      !-----TS PRODUCTS-----
3068      !-----
3069      Bimolecular    P9 # CC=C + CCCOCO
3070      Fragment      CC=C
3071      RRHO
3072      Geometry [angstrom]  9
3073      C    0.0036214937   -0.0000114327   0.0051615123
3074      C   -0.0039889758   -0.0000394546   1.500892564
3075      C    1.07912644    0.0000345476   2.2615817567
3076      H   -0.5150658471   -0.8766640488   -0.3868397296
3077      H    1.0214524858    0.0000723263   -0.3822168897
3078      H   -0.515197614    0.876577764    -0.3868072993
3079      H   -0.9797651506   -0.0001270642   1.9768345388
3080      H    1.0142061682    0.0000099149   3.34096794
3081      H    2.0713279302    0.0001224921   1.8258035873
3082      Core                RigidRotor
3083      SymmetryFactor        1
3084      End
3085      Rotor                Hindered
3086      Group                4 5 6

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```
3087      Axis                      1 2
3088      Symmetry                    3
3089      Potential[kcal/mol]         2
3090 0.00 2.01
3091      End
3092      Frequencies[1/cm] 21
3093 206.03 430.51 596.0 938.41 947.42 967.29
3094 1036.32 1079.5 1195.46 1330.57 1407.13 1454.25
3095 1484.54 1497.22 1742.34 3056.62 3111.88 3138.7
3096 3159.03 3168.59 3248.77
3097 !206.03!Torsions
3098      ZeroEnergy[kcal/mol]        0
3099      ElectronicLevels[1/cm]      1
3100      0 2
3101      End
3102      Fragment CCCOCO
3103      RRHO
3104      Geometry[angstrom] 16
3105 O -0.0070840343 0.0074935394 0.002485829
3106 C -0.0052295361 -0.0011633336 1.4035402734
3107 O 1.2769173339 -0.0001760102 1.9450189173
3108 C 1.994960368 -1.2008949833 1.7067639473
3109 C 3.3454734353 -1.0953810921 2.3828006609
3110 C 3.2308461484 -0.9453409113 3.8941177227
3111 H 0.4089591955 0.8234248166 -0.289985711
3112 H -0.5011758121 0.8812907321 1.8112104507
3113 H -0.5498680154 -0.9051527654 1.6908158425
3114 H 1.4266005788 -2.0458507992 2.1184037593
3115 H 2.1043805809 -1.3603307372 0.6317282107
3116 H 3.9219367639 -1.987850797 2.131735042
3117 H 3.8776483113 -0.2417971891 1.9587696541
3118 H 2.7189686338 -1.8054470792 4.3291377946
3119 H 4.212257742 -0.8680061494 4.360045638
3120 H 2.6601503483 -0.0533242743 4.1461459727
3121      Core                      RigidRotor
3122      SymmetryFactor             1
3123      End
3124      Rotor                      Hindered
3125      Group                      7
3126      Axis                      1 2
3127      Symmetry                    1
3128      Potential[kcal/mol]         4
3129 0.00 3.88 1.85 3.60
3130      End
3131      Rotor                      Hindered
3132      Group                      4
3133      Axis                      3 2
3134      Symmetry                    1
```



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3135      Potential [kcal/mol]      6
3136 0.00 6.53 1.96 3.99 2.66 3.89
3137   End
3138   Rotor                      Hindered
3139      Group                      2
3140      Axis                      3 4
3141      Symmetry                   1
3142      Potential [kcal/mol]      4
3143 0.00 6.72 0.96 1.31
3144   End
3145   Rotor                      Hindered
3146      Group                      6 12 13
3147      Axis                      5 4
3148      Symmetry                   1
3149      Potential [kcal/mol]      6
3150 0.00 3.61 0.36 3.58 0.07 4.86
3151   End
3152   Rotor                      Hindered
3153      Group                      14 15 16
3154      Axis                      6 5
3155      Symmetry                   3
3156      Potential [kcal/mol]      2
3157 0.00 2.73
3158   End
3159      Frequencies [1/cm] 37
3160 293.77 334.78 469.42 626.34 768.17 900.63 928.85
3161 963.33 1055.02 1088.72 1106.95 1143.48 1178.74
3162 1194.09 1279.38 1297.37 1321.49 1379.31 1391.74
3163 1412.62 1427.11 1460.64 1482.68 1499.38 1512.17
3164 1527.51 1535.37 3005.84 3050.91 3063.51 3066.07
3165 3086.26 3104.39 3104.79 3133.09 3151.04 3871.0
3166 !42.97 107.33 170.94 209.45 367.96!Torsions
3167   ZeroEnergy [kcal/mol]      0
3168   ElectronicLevels [1/cm]    1
3169     0 2
3170   End
3171   GroundEnergy [kcal/mol]    13.1
3172   End
3173 !-----
3174   Barrier      B9      W1      P9      # TS: CC=C + CCCOC
3175   Variational
3176   RRHO
3177   Geometry [angstrom] 25
3178 C 0.0167726852 -0.0011656826 -0.0035102651
3179 C 0.0050199859 -0.0005832888 1.5082116449
3180 C 1.2058640161 0.0031095776 2.2370221966
3181 O 1.1111527393 1.8707111927 2.5899211208
3182 C 1.1863728083 2.4302655822 3.8585419819

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3183 O  0.5849188541  1.6409484035  4.8504368591
3184 C  -0.8275027078  1.6204621347  4.7898140631
3185 C  -1.342595167  0.6898593028  5.8679389065
3186 C  -0.8622466294  -0.741321895  5.6625784546
3187 H  0.0752455206  -1.0102750682  -0.416901552
3188 H  0.8719190593  0.5629254617  -0.3783498515
3189 H  -0.881532865  0.4645912054  -0.4071348115
3190 H  0.1324629328  1.2927113328  2.0239015209
3191 H  -0.8468723042  -0.4635136453  1.9944328146
3192 H  1.22596035  -0.3252898892  3.2682721279
3193 H  2.1647934139  0.0489156797  1.7374416323
3194 H  2.2312749378  2.5301979991  4.1560727257
3195 H  0.7152573048  3.4221665032  3.8339527379
3196 H  -1.2148365536  2.6367321713  4.929587707
3197 H  -1.1606494527  1.2666009614  3.8064688709
3198 H  -1.0118845242  1.061919829  6.839153618
3199 H  -2.4335519639  0.7287619893  5.8613338879
3200 H  0.2243675556  -0.7886870892  5.716390056
3201 H  -1.270022524  -1.4110766954  6.4184127455
3202 H  -1.1692604021  -1.1142360472  4.6827847884
3203      Core RigidRotor
3204      SymmetryFactor          0.5
3205      End
3206      Rotor                    Hindered
3207      Group                      10 11 12
3208      Axis                        1 2
3209      Symmetry                    3
3210      Potential[kcal/mol]        2
3211 0.00 1.55
3212      End
3213      Rotor                    Hindered
3214      Group                      6 17 18
3215      Axis                        5 4
3216      Symmetry                    1
3217      Potential[kcal/mol]        6
3218 0.00 7.51 2.82 3.28 3.24 3.91
3219      End
3220      Rotor                    Hindered
3221      Group                      7
3222      Axis                        6 5
3223      Symmetry                    1
3224      Potential[kcal/mol]        6
3225 0.00 6.67 2.40 3.28 1.29 2.66
3226      End
3227      Rotor                    Hindered
3228      Group                      8 19 20
3229      Axis                        7 6
3230      Symmetry                    1

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3231      Potential [kcal/mol]          6
3232 0.00 1.70 1.58 9.16 8.41 13.97
3233      End
3234      Rotor                          Hindered
3235      Group                            9 21 22
3236      Axis                             8 7
3237      Symmetry                         1
3238      Potential [kcal/mol]          6
3239 0.00 5.25 0.37 3.94 0.71 3.75
3240      End
3241      Rotor                          Hindered
3242      Group                            23 24 25
3243      Axis                             9 8
3244      Symmetry                         3
3245      Potential [kcal/mol]          2
3246 0.00 2.80
3247      End
3248      Frequencies [1/cm]            62
3249 117.89 166.0 205.77 308.01 350.84
3250 387.2 426.71 463.37 529.01 637.25 755.43
3251 771.58 897.19 904.66 926.24 929.31 962.19
3252 984.85 1025.75 1078.29 1083.07 1114.62 1143.68
3253 1156.61 1180.53 1185.64 1200.42 1258.67 1284.35
3254 1295.17 1315.26 1328.51 1377.35 1408.82 1410.08
3255 1422.36 1435.99 1444.9 1484.45 1492.03 1499.11
3256 1508.48 1511.17 1513.6 1527.96 1549.25 1601.1
3257 3002.19 3013.38 3045.91 3050.17 3057.33 3070.77
3258 3096.41 3106.08 3108.47 3128.7 3128.99 3146.59
3259 3160.97 3167.5 3252.96
3260 !47.77 59.97 85.73 151.33 184.1 235.42!Torsions
3261      ZeroEnergy [kcal/mol]        67.1
3262      ElectronicLevels [1/cm]      1
3263      0      1
3264      End
3265      Tunneling                      Eckart
3266      ImaginaryFrequency [1/cm]    1858.51
3267      WellDepth [kcal/mol]         67.1
3268      WellDepth [kcal/mol]         54.0
3269      End
3270      End
3271 !-----
3272 !-----
3273 !-----
3274 Bimolecular      P10 # CH2O + CCCOCCC
3275      Fragment    CH2O
3276      RRHO
3277      Geometry [angstrom] 4
3278      0              -0.67047700      0.00000100      0.00000200

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3279          C          0.52488300   -0.00000200   -0.00000900
3280          H          1.10726700    0.93752700    0.00001900
3281          H          1.10725400   -0.93752400    0.00001900
3282      Core  RigidRotor
3283      SymmetryFactor  2
3284      End
3285      Frequencies [1/cm]  6
3286          1218.60          1279.77          1546.46
3287          1877.07          2943.65          3014.58
3288      !!torsions
3289          ZeroEnergy [kcal/mol]      0
3290          ElectronicLevels [1/cm]    1
3291          0 1
3292      End
3293      Fragment  CCCOCCC
3294      RRHO
3295      Geometry [angstrom]  21
3296  C -0.0091120319  0.0318976555  0.0140270155
3297  C  0.0076480544  0.003019928  1.5368771873
3298  C  1.4151072597 -0.0090342913  2.0966049439
3299  O  2.068631021  1.1789261673  1.7166217725
3300  C  3.4018293127  1.23950968  2.1656681858
3301  C  4.0037317542  2.563633421  1.7428293813
3302  C  3.2867148829  3.7518655262  2.3706660009
3303  H  0.5084579275  0.9154998431  -0.3549639519
3304  H -1.0279584179  0.0441753618  -0.3709015659
3305  H  0.4939225903 -0.846615849  -0.3937450685
3306  H -0.5143122593  0.8746125952  1.936064385
3307  H -0.5152872461 -0.8813245007  1.9063228173
3308  H  1.3969864114 -0.0890275817  3.1910289633
3309  H  1.9690435532 -0.8767794906  1.7103091638
3310  H  3.4289443256  1.1434600255  3.2606981916
3311  H  3.9732870959  0.4016860188  1.7461700967
3312  H  5.0590355738  2.5649384134  2.0227372361
3313  H  3.9604134115  2.6296732015  0.6541471454
3314  H  3.3421192777  3.7040928395  3.45959027
3315  H  3.729606735  4.6949223832  2.0530826932
3316  H  2.2354096682  3.7535686208  2.0886371151
3317      Core  RigidRotor
3318      SymmetryFactor  2.0
3319      End
3320      Rotor          Hindered
3321          Group          19 20 21
3322          Axis          7 6
3323          Symmetry      3
3324          Potential [kcal/mol]  2
3325      0.00 2.73
3326      End

```

```

3327 Rotor                      Hindered
3328      Group                      7 17 18
3329      Axis                       6 5
3330      Symmetry                    1
3331      Potential [kcal/mol]        6
3332 0.00 3.54 0.36 3.54 0.07 4.74
3333 End
3334 Rotor                      Hindered
3335      Group                      6 15 16
3336      Axis                       5 4
3337      Symmetry                    1
3338      Potential [kcal/mol]        6
3339 0.00 3.42 3.37 7.91 0.74 2.34
3340 End
3341      Frequencies [1/cm] 54
3342 115.58 163.28 228.07
3343 272.32 326.16 338.86 488.35 504.21 757.79
3344 789.06 895.97 916.73 926.55 939.76 971.08
3345 1037.51 1103.93 1116.99 1156.21 1185.33 1190.88
3346 1207.0 1278.86 1288.61 1309.22 1316.9 1376.06
3347 1379.61 1401.47 1412.08 1414.32 1457.87 1482.7
3348 1482.76 1498.57 1499.34 1511.95 1513.54 1518.02
3349 1536.54 2984.22 2992.11 3022.48 3025.59 3062.71
3350 3062.89 3067.72 3067.86 3103.4 3103.59 3131.32
3351 3131.32 3150.44 3150.56
3352 !43.43 79.47 161.64!Torsions
3353      ZeroEnergy [kcal/mol]      0
3354      ElectronicLevels [1/cm]    1
3355      0 2
3356      End
3357      GroundEnergy [kcal/mol]    14.6
3358 End
3359 !-----
3360 Barrier      B10  W1  P10      # CH20 + CCCOCCC
3361 Variational
3362 RRHO
3363 Geometry [angstrom] 25
3364 C              -1.78945300    1.71595700    -0.46761900
3365 C              -2.48127800    0.63506400    0.35516100
3366 C              -1.52914000    -0.31559200    0.99265800
3367 O              -1.37808000    -1.40439300    -0.79603800
3368 C              -0.07342300    -1.35704300    -0.84946000
3369 O              0.25556500    -0.31485000    0.16080800
3370 C              1.43294100    -0.46536600    0.93495800
3371 C              2.67383700    -0.11636300    0.12793200
3372 C              2.61632800    1.29790700    -0.43307200
3373 H              3.51485000    1.53307800    -1.00114300
3374 H              1.75495900    1.41532400    -1.08961700

```

```

3375      H           2.52461900    2.03008900    0.37102600
3376      H           2.78191700   -0.84059200   -0.68216400
3377      H           3.54392600   -0.23744200    0.77662400
3378      H           1.33100400    0.22155100    1.77941100
3379      H           1.48885000   -1.48837800    1.32103800
3380      H           0.35743700   -0.98816900   -1.79691500
3381      H           0.47752100   -2.26327400   -0.52220200
3382      H          -0.93734500    0.15270900    1.77679500
3383      H          -1.89957800   -1.28630900    1.28060200
3384      H          -3.19190100    0.08967900   -0.25711500
3385      H          -3.01885500    1.10714000    1.18930300
3386      H          -2.51283900    2.44918300   -0.82013200
3387      H          -1.03007500    2.23356000    0.12020700
3388      H          -1.30324000    1.25842400   -1.32722000
3389      Core      RigidRotor
3390          SymmetryFactor          1
3391      End
3392      Rotor      Hindered
3393          Group          23 24 25
3394          Axis           1 2
3395          Symmetry       3
3396          Potential[kcal/mol] 2
3397          0. 3.64
3398      End
3399      Rotor      Hindered
3400          Group          1 21 22
3401          Axis           2 3
3402          Symmetry       1
3403          Potential[kcal/mol] 6
3404          0. 4.12 0.95 2.99 1.45 2.84
3405      End
3406      Rotor      Hindered
3407          Group          9 13 14
3408          Axis           8 7
3409          Symmetry       1
3410          Potential[kcal/mol] 6
3411          0. 4.15 0.59 4.02 0.67 4.74
3412      End
3413      Rotor      Hindered
3414          Group          10 11 12
3415          Axis           9 8
3416          Symmetry       3
3417          Potential[kcal/mol] 2
3418          0. 2.78
3419      End
3420      Rotor      Hindered
3421          Group          8 15 16
3422          Axis           7 6

```

```

3423 Symmetry 1
3424 Potential [kcal/mol] 4
3425 0. 2.29 0.84 5.12
3426 End
3427 Frequencies [1/cm] 63
3428 102.04 138.6 152.24 270.81 301.52 350.69 400.94 447.57 549.93
592.12 757.78 791.51 798.37 889.13 890.07 906.07 931.56 972.91
1007.41 1051.36 1104.13 1115.42 1127.25 1165.43 1191.01 1207.59
1220.08 1263.42 1293.99 1302.71 1318.03 1332.48 1376.14 1377.49
1397.64 1404.17 1407.69 1425.63 1467.73 1489.1 1491.07 1494.1
1503.27 1507.78 1510.07 1514.23 1558.12 2875.6 2939.96 3006.89
3034.21 3061.68 3064.93 3065.04 3082.97 3097.82 3103.16 3132.95
3133.65 3147.18 3154.25 3166.03 3253.38
3429 ! 41.87 52.66 105.97 229.73 259.97 ! Torsions
3430 ZeroEnergy [kcal/mol] 75.2
3431 ElectronicLevels [1/cm] 1
3432 0 1
3433 End
3434 Tunneling Eckart
3435 ImaginaryFrequency [1/cm] 623.59
3436 WellDepth [kcal/mol] 75.2 #forward
3437 WellDepth [kcal/mol] 60.6 #reverse
3438 End
3439 End
3440 !-----
3441 !-----
3442 !-----
3443 Bimolecular P11 # CCCOH + CH2O + CC=C
3444 Fragment CCCOH
3445 RRHO
3446 Geometry [angstrom] 12
3447 C -0.76638800 0.54197400 0.30744200
3448 H -0.68989900 0.51309800 1.39542400
3449 H -1.36276700 1.42058700 0.04122900
3450 C 0.62135600 0.64084800 -0.30584300
3451 H 1.05982000 1.60005700 -0.02116000
3452 H 0.52455700 0.65729100 -1.39608100
3453 O -1.44103100 -0.64976500 -0.05727000
3454 H -1.55616700 -0.65245600 -1.01069500
3455 C 1.52716500 -0.50623100 0.12172300
3456 H 2.50265700 -0.44583100 -0.35880500
3457 H 1.68152400 -0.49044800 1.20162500
3458 H 1.07572600 -1.46372900 -0.13330500
3459 Core RigidRotor
3460 SymmetryFactor 1
3461 End
3462 Rotor Hindered
3463 Group 5 6 9

```

```
3464      Axis                4 1
3465      Symmetry             1
3466      Potential[kcal/mol]  6
3467      0.00 4.73 0.12 3.99 0.27 3.93
3468      End
3469      Rotor                 Hindered
3470      Group                 8
3471      Axis                 7 1
3472      Symmetry             1
3473      Potential[kcal/mol]  6
3474      0.00 1.47 0.08 0.81 0.03 1.09
3475      End
3476      Rotor                 Hindered
3477      Group                 10 11 12
3478      Axis                 9 4
3479      Symmetry             3
3480      Potential[kcal/mol]  2
3481      0.00 2.66
3482      End
3483      Frequencies [1/cm]  27
3484      1329.10 495.74 779.30 883.17 912.08 999.97 1093.35 1110.10 1148.02
3485      1245.92 1305.74 1373.34 1385.96 1411.18 1428.30 1486.33 1499.45
3486      1511.53 1520.86 3032.45
3487      3043.64 3065.99 3085.67 3103.59 3133.63 3148.78 3878.55
3487      ! 47.01 229.69 284.50 !torsions
3488      ZeroEnergy[kcal/mol]  0
3489      ElectronicLevels [1/cm]  1
3490      0 1
3491      End
3492      Fragment  CH2O_CC=C # modeled as CH2O + CC=C
3493      RRHO
3494      Geometry[angstrom]  13
3495      C                1.70393900   -0.12689800   0.23836200
3496      H                2.57483300   -0.15398600   0.88629100
3497      C                -1.98376900    0.00019000   0.58412100
3498      H                -2.90175000    0.08135500   1.19082100
3499      H                -1.02704000   -0.07059400   1.12848700
3500      C                1.16542700   -1.26763200  -0.16706300
3501      H                1.57530000   -2.22323800   0.13102200
3502      H                0.29691800   -1.27299300  -0.81623300
3503      O                -2.02562200   -0.01450500  -0.61272400
3504      C                1.19425200    1.22791100  -0.14115700
3505      H                0.32159800    1.14774400  -0.78804000
3506      H                0.92205600    1.80586300   0.74551600
3507      H                1.96396200    1.80045800  -0.66165800
3508      Core  RigidRotor
3509      SymmetryFactor  1
3510      End
```



```

3511 Rotor                      Hindered
3512 Group                      11 12 13
3513 Axis                        10 1
3514 Symmetry                    3
3515 Potential [kcal/mol]        2
3516 0.00 2.01
3517 End
3518 Frequencies [1/cm] 32
3519 61.05 78.27 95.02 123.94 133.22 155.46 436.53 603.91 937.86
3520 952.87 983.07 1042.88
3521 1080.88 1200.43 1224.88 1284.84 1333.58 1406.81 1452.74 1491.58
3522 1497.85 1541.85 1736.70
3523 1864.43 2951.87 3031.61 3049.39 3102.84 3140.69 3154.12 3165.17
3524 3246.78
3525 ! 232.59 !Torsions
3526 ZeroEnergy [kcal/mol]        0
3527 ElectronicLevels [1/cm]      1
3528 0 1
3529 End
3530 GroundEnergy [kcal/mol]      27.6
3531 End
3532 !-----
3533 Barrier B11 W1 P11 # CCCOH + CH2O + CC=C
3534 Variational
3535 RRHO
3536 Geometry [angstrom] 25
3537 C -1.15807200 1.29059800 -0.38172200
3538 H -0.78736100 1.73132700 -1.30274100
3539 C 1.39742900 -0.83047300 0.68158000
3540 H 1.50068200 -1.82065100 1.13227300
3541 H 1.15649800 -0.11662100 1.47664100
3542 C 2.66408000 -0.42827900 -0.04587800
3543 H 2.86197200 -1.16543800 -0.82532900
3544 H 3.49196100 -0.47897000 0.66399800
3545 C -0.85269300 2.05336000 0.89384300
3546 H 0.21912300 2.14833500 1.08012500
3547 H -1.28684300 1.54888200 1.75941800
3548 H -0.20094700 0.09411200 -0.38166300
3549 H -1.25734600 3.06862800 0.87423500
3550 C -2.30967600 0.52112300 -0.49959900
3551 H -2.76941400 0.36952100 -1.46500300
3552 H -2.98852900 0.44265700 0.34272100
3553 O -1.98261700 -1.37267600 -0.43165500
3554 C -1.04554700 -1.57175000 0.41036100
3555 H -1.07440800 -1.00109600 1.35839800
3556 H -0.71689600 -2.60588000 0.57152900
3557 O 0.30876900 -0.90274100 -0.23533700
3558 C 2.57138700 0.96739600 -0.64870700

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```
3556 H 3.48765400 1.22849200 -1.17557100
3557 H 1.74739100 1.03183000 -1.35957900
3558 H 2.40579800 1.71636100 0.12721500
3559 Core RigidRotor
3560 SymmetryFactor 0.5
3561 End
3562 Rotor Hindered
3563 Group 23 24 25
3564 Axis 22 6
3565 Symmetry 3
3566 Potential[kcal/mol] 2
3567 0. 2.89
3568 End
3569 Rotor Hindered
3570 Group 10 11 13
3571 Axis 9 1
3572 Symmetry 3
3573 Potential[kcal/mol] 2
3574 0. 1.17
3575 End
3576 Rotor Hindered
3577 Group 7 8 22
3578 Axis 6 3
3579 Symmetry 1
3580 Potential[kcal/mol] 6
3581 0. 4.11 0.38 3.84 0.24 4.37
3582 End
3583 Rotor Hindered
3584 Group 4 5 6
3585 Axis 3 21
3586 Symmetry 1
3587 Potential[kcal/mol] 8
3588 0. 4.94 3.27 5.02 4.41 5.63 0.87 1.42
3589 End
3590 Frequencies[1/cm] 63
3591 91.98 150.04 161.68 205.78 248.33 289.90 383.54 439.86 493.91
3592 519.38 591.21
3593 716.18 778.73 846.60 894.86 903.59 922.90 958.99 1008.28 1041.82
3594 1079.35 1106.40 1110.76 1146.64 1160.20
3595 1180.17 1186.74 1244.10 1270.02 1285.45 1310.77 1360.34 1378.65
3596 1390.55 1403.97 1411.75 1417.79 1425.30
3597 1462.26 1481.42 1487.09 1501.37 1507.80 1513.25 1520.71 1541.09
3598 1581.48 1697.82 2916.52 3027.19 3036.79
3599 3038.53 3063.77 3068.92 3085.13 3088.73 3107.70 3109.32 3136.16
3600 3143.67 3145.57 3146.38 3244.05
3601 ! 49.10 82.08 175.57 262.15 ! Torsions
3602 ZeroEnergy[kcal/mol] 69.3
3603 ElectronicLevels[1/cm] 1
```

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3599     0     1
3600     End
3601     Tunneling           Eckart
3602     ImaginaryFrequency [1/cm]      945.04
3603     WellDepth[kcal/mol]           69.3 #forward
3604     WellDepth[kcal/mol]           41.7 #reverse
3605     End
3606     End
3607     End

```

E.4 CCOCO[CH]C

```

1 TemperatureList [K]           500 510 520 530 540 550 560 570 580
   590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750
   760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920
   930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060 1070
   1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200
   1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320 1330
   1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460
   1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580 1590
   1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710 1720
   1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840 1850
   1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980
   1990 2000
2 PressureList [atm]           0.00001 0.001 0.01 0.1 1 10 100.
3 !PressureList [bar]         1.
4 EnergyStepOverTemperature    .2
5 ExcessEnergyOverTemperature  30
6 ModelEnergyLimit [kcal/mol]  400
7 CalculationMethod            direct
8 !CalculationMethod          low-eigenvalue !direct
9 WellCutoff                   10
10 ChemicalEigenvalueMax       0.2
11 Model
12   EnergyRelaxation
13     Exponential
14     Factor [1/cm]           200
15     Power                    .85
16     ExponentCutoff          15
17   End
18   CollisionFrequency
19     LennardJones
20     Epsilons [1/cm]         94.87 280.62 !Ar and parent
21     Sigmas [angstrom]       3.33 6.14
22     Masses [amu]            39.88 103.14
23   End
24 !-----
25 !-----WELL 1 to Products -----

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```
26 !-----
27 Well          W1          # W_CCOCO[CH]C_m062x.log
28 Species
29   RRHO
30 Geometry[angstrom]      18
31   C          0.0018769997  0.0094064935  0.0012941865
32   O          0.0039309591  0.0072602134  1.3662849761
33   C          1.2855525506  0.0024860843  1.9499037665
34   C          -1.346396422  -0.0499286474  -0.6070549333
35   O          1.9906696984  -1.1640472244  1.6924437196
36   C          1.4124285819  -2.3190617661  2.2817038138
37   C          2.3182091531  -3.4937477233  1.997679624
38   H          -1.8440152607  -1.0080384834  -0.411761856
39   H          -1.2813663239  0.0804784422  -1.68558997
40   H          -1.9856104581  0.7344173299  -0.1986214421
41   H          0.8664421701  -0.4358868633  -0.4759230566
42   H          1.8829927666  0.82040967    1.5438726681
43   H          1.1126468079  0.1339867918  3.0210491031
44   H          1.3053534229  -2.1566238159  3.3607326044
45   H          0.4138671779  -2.4839512655  1.8689428887
46   H          3.3095168826  -3.3177320862  2.4123189612
47   H          1.910371308   -4.4025224742  2.438405425
48   H          2.4160899446  -3.6421806901  0.9233374842
49 Core RigidRotor
50   SymmetryFactor      1
51 End
52 Rotor      Hindered
53   Group          4 11
54   Axis           1 2
55   Symmetry       1
56   Potential[kcal/mol]  4
57   0.0  4.57  1.34  4.17
58 End
59 Rotor      Hindered
60   Group          8 9 10
61   Axis           4 1
62   Symmetry       3
63   Potential[kcal/mol]  2
64   0.0  1.32
65 End
66 Rotor      Hindered
67   Group          1
68   Axis           2 3
69   Symmetry       1
70   Potential[kcal/mol]  6
71   0.0  9.97  1.65  2.7  2.29  2.93
72 End
73 Rotor      Hindered
```

```

74      Group                6
75      Axis                 5 3
76      Symmetry             1
77      Potential [kcal/mol]  6
78      0.0  6.63  2.07  3.63  2.99  4.09
79      End
80      Rotor      Hindered
81      Group                7 14 15
82      Axis                 6 5
83      Symmetry             1
84      Potential [kcal/mol]  8
85      0.0  1.63  1.03  1.11  1.06  4.68  0.59  1.19
86      End
87      Rotor      Hindered
88      Group                16 17 18
89      Axis                 7 6
90      Symmetry             3
91      Potential [kcal/mol]  2
92      0.0  3.05
93      End
94      Frequencies [1/cm]   42
95      261.41      330.6      364.23      484.26
96      575.24      677.56      821.46      881.7      901.01
1022.16      1064.95      1089.77      1110.76      1148.96
97      1179.46      1192.1      1214.36      1257.91      1308.65
1347.01      1382.68      1400.39      1426.85      1436.73
98      1464.37      1469.93      1488.79      1495.37      1505.5
1520.02      1537.66      3006.46      3021.82      3055.1
99      3073.03      3075.09      3088.73      3113.75      3146.3
3149.87      3151.12      3182.77
100      !51.91      62.09      81.45      159.44      197.19      241.07!
Torsions
101      ZeroEnergy [kcal/mol]  0
102      ElectronicLevels [1/cm]  1
103      0  2
104      End
105      End
106      Well      W2      # W_CCOCOC [CH2] _m062x.log
107      Species
108      RRHO
109      Geometry [angstrom]    18
110      C      0.0178514596      0.001513644      0.0015050088
111      C      0.0061733634      0.0060023634      1.5122092312
112      O      1.3503838993      -0.000462482      1.9640903547
113      C      1.4695606045      -0.0679502667      3.350760128
114      O      0.9724288929      1.0682112413      3.9981565554
115      C      1.7359894587      2.2399023396      3.7441343836
116      C      3.0431599872      2.2264259073      4.4470251509

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117 H 0.5328050795 0.884658872 -0.3741076412
118 H -0.9999152244 0.0016478828 -0.3868338208
119 H 0.5348524908 -0.8813260579 -0.3713600265
120 H -0.5120122208 0.887265821 1.898910857
121 H -0.5093275874 -0.8797487016 1.9027366081
122 H 0.8932370681 -0.9068222381 3.7512582343
123 H 2.5353928321 -0.1999953512 3.5532013909
124 H 1.8739990233 2.3741461536 2.6671959717
125 H 1.1095824236 3.0662606886 4.0970698107
126 H 3.1000482125 1.8153779981 5.4440992415
127 H 3.886509222 2.7768942041 4.0604685335
128 Core RigidRotor
129 SymmetryFactor 1
130 End
131 Rotor Hindered
132 Group 8 9 10
133 Axis 1 2
134 Symmetry 1
135 Potential[kcal/mol] 6
136 0.0 3.05 0.0 3.05 0.0 3.05
137 End
138 Rotor Hindered
139 Group 4
140 Axis 3 2
141 Symmetry 1
142 Potential[kcal/mol] 8
143 0.0 1.53 0.95 1.11 1.08 4.73 0.77 1.29
144 End
145 Rotor Hindered
146 Group 5 13 14
147 Axis 4 3
148 Symmetry 1
149 Potential[kcal/mol] 6
150 0.0 7.38 2.68 3.06 2.66 3.95
151 End
152 Rotor Hindered
153 Group 6
154 Axis 5 4
155 Symmetry 1
156 Potential[kcal/mol] 6
157 0.0 7.87 2.85 4.21 2.88 3.57
158 End
159 Rotor Hindered
160 Group 7 15 16
161 Axis 6 5
162 Symmetry 1
163 Potential[kcal/mol] 6
164 0.0 3.2 0.26 1.35 0.32 1.84
```

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165 End
166 Rotor      Hindered
167   Group          17 18
168   Axis           7 6
169   Symmetry       1
170   Potential [kcal/mol] 4
171   0.0  1.66  0.0  1.68
172 End
173 Frequencies [1/cm] 42
174   287.32   325.16   438.49   468.49
175   529.08   646.42   821.67   848.43   882.07
176  944.34   1054.46   1063.51   1101.92   1130.71
177   1147.54   1183.77   1195.02   1221.39   1300.89
178   1309.84   1347.07   1395.04   1399.47   1433.39
179   1453.0    1459.44   1488.57   1491.71   1505.47
180   1516.64   1539.3    3019.76   3025.12   3046.83
181   3068.1    3072.25   3074.09   3099.48   3148.38
182   3150.29   3174.81   3285.12
183   !47.2     58.76     93.4      190.21    194.44    239.52!
184 Torsions
185 ZeroEnergy [kcal/mol] 7.1
186 ElectronicLevels [1/cm] 1
187   0 2
188 End
189 End
190 Barrier      B1  W1  W2  # W_CCOCOC[CH2]_m062x.log
191 Variational
192   RRHO
193 Geometry [angstrom] 18
194   C      0.0291534613   0.0291135435   0.0022248553
195   C      0.038909059   -0.0467305797   1.5024767004
196   O      1.3550074629   -0.0195272448   2.0368748677
197   C      2.0689992934   -1.211207772    1.9703022812
198   O      2.6482348505   -1.4726275816   0.7200596194
199   C      1.7666050564   -1.966393255    -0.2376049469
200   H      1.2435806975   -2.86345737     0.1138572717
201   C      2.4498442264   -2.1153028938   -1.5628419875
202   H      0.8353289444   -1.0703216507   -0.3428760312
203   H      0.5690676587   0.8767044645    -0.4094115617
204   H      -0.9333338235    -0.1523638473    -0.4666688809
205   H      -0.4752898278    0.8051347715    1.9524766809
206   H      -0.473912245    -0.9560926026    1.8419010164
207   H      2.8958259828    -1.114174801     2.6685115874
208   H      1.4205179652    -2.0541464319    2.2538600376
209   H      1.7518555396    -2.4892115905    -2.3104466087
210   H      2.8380420199    -1.1526416087    -1.894097549
211   H      3.2881549995    -2.8112755004    -1.4894884615
212 Core RigidRotor

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208     SymmetryFactor      0.5
209   End
210   Rotor      Hindered
211     Group              16 17 18
212     Axis              8 6
213     Symmetry          1
214     Potential[kcal/mol] 6
215     0.0  2.37  0.0  2.37  0.0  2.37
216   End
217   Frequencies [1/cm]  46
218     89.45      142.21      181.39      282.88      382.76
416.56      443.98      548.41      563.69
219     654.2      845.13      871.55      897.26      911.27
1021.65      1079.68      1100.39      1119.97      1135.27
220     1163.4      1177.85      1188.43      1257.09      1314.52
     1351.23      1365.47      1400.73      1410.19      1438.87
221     1441.94      1457.12      1478.95      1489.43      1498.62
     1510.27      1518.36      2986.4      3012.57      3031.02
222     3057.06      3078.69      3117.27      3124.59      3150.17
     3153.01      3205.56
223   !220.24! Torsions
224   ZeroEnergy [kcal/mol]  21.3
225   ElectronicLevels [1/cm]  1
226     0  2
227   End
228   Tunneling      Eckart
229   ImaginaryFrequency [1/cm]  1713.1882
230   WellDepth[kcal/mol]  21.3
231   WellDepth[kcal/mol]  14.2
232   End
233 End
234 Well      W3      # W_CCO[CH]OCC_m062x.log
235   Species
236     RRHO
237   Geometry [angstrom]  18
238   C      0.0416232376      -0.37750273      0.1259507271
239   C      0.064858533      0.0468264808      1.5811502014
240   O      1.3885661895      0.0727441412      2.1160722767
241   C      2.0530796439      -1.0997084414      2.1021605902
242   O      1.3283383836      -2.1530229094      2.585939944
243   C      1.9923620462      -3.4014452666      2.4635967907
244   C      1.9486900981      -3.9307345213      1.0432721483
245   H      0.7082422586      0.2512444402      -0.4632387071
246   H      -0.9691159014      -0.2836520477      -0.2705842106
247   H      0.3588097986      -1.4142493039      0.0204649586
248   H      -0.2952907809      1.0669209536      1.6949190779
249   H      -0.5581205202      -0.6106713951      2.1881833486
250   H      3.0676123132      -1.004417402      2.4866981573

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251 H 3.0268268166 -3.2974090352 2.8077760606
252 H 1.4781808821 -4.074807134 3.1466442951
253 H 2.4530598175 -3.2429740763 0.36538534
254 H 2.4402670067 -4.9016395637 0.985008223
255 H 0.9155186867 -4.0452846885 0.7165437614
256 Core RigidRotor
257 SymmetryFactor 1
258 End
259 Rotor Hindered
260 Group 8 9 10
261 Axis 1 2
262 Symmetry 1
263 Potential[kcal/mol] 6
264 0.0 3.02 0.0 3.02 0.0 3.03
265 End
266 Rotor Hindered
267 Group 1 11 12
268 Axis 2 3
269 Symmetry 1
270 Potential[kcal/mol] 6
271 0.0 4.23 0.93 1.61 0.04 1.44
272 End
273 Rotor Hindered
274 Group 2
275 Axis 3 4
276 Symmetry 1
277 Potential[kcal/mol] 4
278 0.0 2.5 1.96 9.0
279 End
280 Rotor Hindered
281 Group 6
282 Axis 5 4
283 Symmetry 1
284 Potential[kcal/mol] 4
285 0.0 2.5 1.96 9.0
286 End
287 Rotor Hindered
288 Group 7 14 15
289 Axis 6 5
290 Symmetry 1
291 Potential[kcal/mol] 6
292 0.0 4.23 0.93 1.61 0.04 1.44
293 End
294 Rotor Hindered
295 Group 16 17 18
296 Axis 7 6
297 Symmetry 1
298 Potential[kcal/mol] 6
```

```

299      0.0  3.02  0.0  3.02  0.0  3.03
300      End
301      Frequencies [1/cm]      42
302          277.13      352.87      422.86      475.76
303          607.35      809.76      811.76      869.59      918.15
          947.28      1039.68      1082.94      1115.36      1118.49
304          1175.57      1199.67      1232.05      1282.91      1333.66
          1342.41      1365.73      1397.21      1401.53      1423.49
305          1442.81      1485.7      1486.96      1500.82      1502.41
          1521.69      1527.53      3037.38      3066.85      3070.41
306          3086.17      3105.4      3121.98      3131.75      3143.04
          3145.58      3149.98      3156.17
307      !54.18      70.62      121.24      175.73      222.29      268.03!
      Torsions
308      ZeroEnergy [kcal/mol]      2.7
309      ElectronicLevels [1/cm]      1
310          0  2
311      End
312      End
313      Barrier      B2  W1  W3      # W_CC0[CH]OCC_m062x.log
314      Variational
315          RRHO
316      Geometry [angstrom]      18
317      C      -0.0001323234      0.0040976776      0.0000333068
318      C      -0.0003628155      -0.009351158      1.509667851
319      O      1.3551114327      -0.0090822941      1.945193012
320      C      1.543344293      -0.0426376655      3.2851818521
321      O      0.8775227636      0.9447772638      4.0265274903
322      C      0.2360601518      0.0517182754      4.9264202216
323      H      0.6994755055      0.0506549958      5.9117511448
324      C      -1.2574101633      0.1052606438      4.8932331708
325      H      0.5025521372      0.8969743284      -0.36801236
326      H      -1.0221607345      -0.0001680744      -0.3764885573
327      H      0.5195807861      -0.8699718527      -0.3887851191
328      H      -0.5127909119      0.8638706009      1.9160624459
329      H      -0.4910694374      -0.9085554011      1.8989031303
330      H      0.8407830213      -0.9318754718      4.1040192214
331      H      2.6082196165      -0.1105900382      3.5036621271
332      H      -1.6053474201      1.1071095764      5.1617779016
333      H      -1.6420003491      -0.1238584055      3.8995075006
334      H      -1.6776505615      -0.6054570187      5.6032856661
335      Core RigidRotor
336          SymmetryFactor      0.25
337      End
338      Rotor      Hindered
339          Group      9 10 11
340          Axis      1 2
341          Symmetry      3

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342     Potential [kcal/mol]          2
343     0.0  3.07
344 End
345 Rotor      Hindered
346     Group          4
347     Axis           3 2
348     Symmetry      1
349     Potential [kcal/mol]          6
350     0.0  2.26  0.35  6.59  0.96  1.86
351 End
352 Rotor      Hindered
353     Group          2
354     Axis           3 4
355     Symmetry      1
356     Potential [kcal/mol]          6
357     0.0  3.61  2.03  3.43  1.39  4.57
358 End
359 Rotor      Hindered
360     Group          16 17 18
361     Axis           8 6
362     Symmetry      3
363     Potential [kcal/mol]          2
364     0.0  2.18
365 End
366 Frequencies [1/cm]      43
367     94.89      187.93      316.31      394.98      408.77
368     563.9
369     640.54      831.94      836.82      879.62      901.05
370     989.32      1062.74      1104.36      1121.92      1137.78
371     1143.97      1172.89      1192.35      1251.41      1304.64
372     1325.1      1351.42      1394.99      1399.15      1421.29
373     1434.74      1476.98      1488.76      1490.12      1506.59
374     1536.24      1886.48      3027.53      3042.39      3075.08
375     3098.21      3108.59      3114.0      3117.46      3148.95
376     3152.18      3154.33
377     !83.35  134.62  207.6      255.72! Torsions
378 ZeroEnergy [kcal/mol]      39.0
379 ElectronicLevels [1/cm]    1
380     0  2
381 End
382 Tunneling      Eckart
383 ImaginaryFrequency [1/cm]  1969.1996
384 WellDepth [kcal/mol]      39.0
385 WellDepth [kcal/mol]      36.3
386 End
387 End
388 Bimolecular      P1      # CC=0  +  [CH2]OCC
389 Fragment      CC=0

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385      RRHO
386      Geometry [angstrom]      7
387      O      -0.0087358454      0.0000127436      0.0277268521
388      C      -0.0047280904      -0.0000001382      1.2269625046
389      H      0.9544802472      -0.0000142081      1.780404527
390      C      -1.2396838276      0.0000000246      2.0771909663
391      H      -1.2332835064      0.8770130299      2.7268240198
392      H      -2.128706571      0.0000295926      1.4528082197
393      H      -1.2333121081      -0.8770468713      2.7267788357
394      Core RigidRotor
395          SymmetryFactor      1
396      End
397      Rotor      Hindered
398          Group      5 6 7
399          Axis      4 2
400          Symmetry      1
401          Potential [kcal/mol]      6
402          0.0 1.2 0.0 1.2 0.01 1.2
403      End
404      Frequencies [1/cm]      14
405          513.29      776.08      900.41      1138.06      1146.18
406          1379.69      1433.6      1464.85      1474.9
407          1874.29      2942.78      3063.51      3127.31      3180.67
408          !157.82! Torsions
409      ZeroEnergy [kcal/mol]      0
410      ElectronicLevels [1/cm]      1
411          0 1
412      End
413      Fragment [CH2]OCC
414      RRHO
415      Geometry [angstrom]      11
416      C      -0.000713851      -0.00468289      -0.0013813868
417      C      0.0020061486      0.0195391378      1.5078714749
418      O      1.3497803524      0.0331924413      1.9526669773
419      C      1.5016858874      0.0729897102      3.2917698434
420      H      0.6942750287      0.4852982544      3.8847448002
421      H      2.5265617388      0.1454538458      3.6172715885
422      H      0.5074620339      0.8739651182      -0.3952754403
423      H      -1.0231776684      -0.0142928625      -0.3764715017
424      H      0.5127457376      -0.8928926347      -0.3656189069
425      H      -0.5073568477      0.910485179      1.8898447205
426      H      -0.4999305632      -0.8603473004      1.9204598359
427      Core RigidRotor
428          SymmetryFactor      1
429      End
430      Rotor      Hindered
431          Group      7 8 9
432          Axis      1 2

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432     Symmetry                3
433     Potential [kcal/mol]    2
434     0.0  3.0
435     End
436     Rotor      Hindered
437     Group                4
438     Axis                3 2
439     Symmetry             1
440     Potential [kcal/mol]  6
441     0.0  1.5  0.15  4.08  0.6  1.51
442     End
443     Rotor      Hindered
444     Group                5 6
445     Axis                4 3
446     Symmetry             1
447     Potential [kcal/mol]  5
448     0.0  0.28  5.33  0.00  5.24
449     End
450     Frequencies [1/cm]    24
451     303.35      487.19      593.21      821.8      883.99
1073.33      1122.2
452     1187.61      1234.87      1308.92      1313.32      1400.08
1434.83      1488.69      1493.38      1506.22      1531.36
453     3029.29      3069.09      3075.45      3137.07      3152.88
3154.08      3283.45
454     !99.2      239.29      290.05!
455     ZeroEnergy [kcal/mol]  0
456     ElectronicLevels [1/cm] 1
457     0  2
458     End
459     GroundEnergy [kcal/mol] 9.1
460     End
461     Barrier      B3  W1  P1  # TS_[CH2]OCC+CC=O_m062x.log
462     Variational
463     RRHO
464     Geometry [angstrom]    18
465     C      0.2892651787    0.4355725263    0.2088041375
466     C      0.1927708311    0.0615880561    1.6670646364
467     O      1.5121356891    0.0411313718    2.2109818852
468     C      1.5520378285    -0.0884728634    3.5405629387
469     O      1.097182838     1.7193582988    4.1683940128
470     C      1.3822917157    2.5869799751    3.3121857974
471     H      0.6097213073    2.9416751252    2.6191935408
472     C      2.7854760811    3.059080859     3.1116660598
473     H      0.7292004905    1.4264507089    0.1036484217
474     H      -0.7011420089    0.4429844687    -0.2439589688
475     H      0.912116916     -0.2789594862    -0.3269247623
476     H      -0.4058473849    0.780817811     2.231058101

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477 H -0.2502652182 -0.9307453884 1.7970468517
478 H 0.7325102793 -0.60065802 4.0284541651
479 H 2.5504559704 -0.1935493182 3.9347167594
480 H 2.8204439178 4.0121763144 2.5863925539
481 H 3.2940050949 3.1499929659 4.0714878507
482 H 3.3341790788 2.3234148975 2.5121615096
483 Core RigidRotor
484 SymmetryFactor 1
485 End
486 Rotor Hindered
487 Group 9 10 11
488 Axis 1 2
489 Symmetry 3
490 Potential [kcal/mol] 2
491 0.0 3.03
492 End
493 Rotor Hindered
494 Group 4
495 Axis 3 2
496 Symmetry 1
497 Potential [kcal/mol] 6
498 0.0 2.19 0.89 3.73 1.29 2.84
499 End
500 Rotor Hindered
501 Group 2
502 Axis 3 4
503 Symmetry 1
504 Potential [kcal/mol] 4
505 0.0 10.72 3.5 7.05
506 End
507 Rotor Hindered
508 Group 6
509 Axis 5 4
510 Symmetry 1
511 Potential [kcal/mol] 4
512 0.0 5.1 3.58 4.11
513 End
514 Rotor Hindered
515 Group 16 17 18
516 Axis 8 6
517 Symmetry 3
518 Potential [kcal/mol] 2
519 0.0 0.45
520 End
521 Frequencies [1/cm] 42
522 105.64 266.0 310.86 406.84 493.11
523 522.02 659.92 700.12 822.89 881.23
908.17 940.1 1024.19 1073.45 1121.51
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524      1124.1      1186.28      1247.34      1257.1      1308.18
      1352.76      1389.27      1400.27      1436.73      1464.75
525      1475.55      1487.53      1503.43      1509.23      1523.01
      1532.74      3024.03      3028.46      3040.3      3073.77
526      3088.22      3102.98      3145.2      3150.32      3151.06
      3153.66      3280.87
527      !50.87      82.89      94.79      148.6      223.25! Torsions
528      ZeroEnergy [kcal/mol]      22.9
529      ElectronicLevels [1/cm]      1
530      0 2
531      End
532      Tunneling      Eckart
533      ImaginaryFrequency [1/cm]      650.5068
534      WellDepth [kcal/mol]      22.9
535      WellDepth [kcal/mol]      13.8
536      End
537      End
538      Bimolecular      P2      # CCOCOC=C + [H]
539      Fragment      CCOCOC=C
540      RRHO
541      Geometry [angstrom]      17
542      C      0.003704926      0.011003447      0.0030123498
543      C      -0.0001753209      -0.0111612222      1.5130392284
544      O      1.3488412493      -0.0083458226      1.955267626
545      C      1.4878789917      -0.1344914621      3.3275401745
546      O      0.9230283265      0.9327964379      4.0527734254
547      C      1.5431702152      2.1388556198      3.9627766339
548      H      1.1098293717      2.831767739      4.671955592
549      C      2.5376446081      2.4852391641      3.1576906268
550      H      0.5090017066      0.9058488399      -0.3570470834
551      H      -1.0164850284      0.0106347429      -0.3785648335
552      H      0.5246846344      -0.8610772423      -0.3890182473
553      H      -0.5216245523      0.860217875      1.9161358018
554      H      -0.5017897138      -0.9090694755      1.893455498
555      H      0.967953537      -1.022596122      3.6958681857
556      H      2.5587067785      -0.1923572933      3.5305549059
557      H      2.9360332044      3.4847561322      3.2368289234
558      H      2.9503070969      1.823094593      2.4125811985
559      Core RigidRotor
560      SymmetryFactor      1
561      End
562      Rotor      Hindered
563      Group      9 10 11
564      Axis      1 2
565      Symmetry      1
566      Potential [kcal/mol]      6
567      0.0 3.09 0.0 3.09 0.0 3.09
568      End

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```

569 Rotor      Hindered
570   Group                4
571   Axis                 3 2
572   Symmetry             1
573   Potential [kcal/mol] 8
574   0.0  1.64  1.12  1.16  1.02  4.7  0.84  1.26
575 End
576 Rotor      Hindered
577   Group                5 14 15
578   Axis                 4 3
579   Symmetry             1
580   Potential [kcal/mol] 6
581   0.0  6.87  3.44  5.47  3.25  4.03
582 End
583 Rotor      Hindered
584   Group                6
585   Axis                 5 4
586   Symmetry             1
587   Potential [kcal/mol] 6
588   0.0  23.03  3.72  4.13  1.66  4.79
589 End
590 Rotor      Hindered
591   Group                7 8
592   Axis                 6 5
593   Symmetry             1
594   Potential [kcal/mol] 4
595   0.0  4.7  1.02  4.96
596 End
597 Frequencies [1/cm]    40
598   273.28    348.3    410.48    552.88    688.35
599   737.64    822.64    883.78    892.23    925.25
600 1017.82    1043.59    1066.7    1127.76    1179.8
601   1197.15    1218.88    1249.45    1310.9    1347.59
602   1364.99    1401.33    1429.33    1437.29    1470.8
603   1488.78    1505.54    1517.99    1536.78    1724.01
604   3021.8    3056.71    3073.83    3079.92    3116.01
605   3151.19    3152.23    3198.53    3215.5    3293.31
606   !56.52    65.51    143.41    204.74    250.54!
607 ZeroEnergy [kcal/mol] 0
608 ElectronicLevels [1/cm] 1
609   0 1
610 End
611 Fragment      H
612   Atom
613   Mass [amu]    1
614   ElectronicLevels [1/cm] 1
615   0 2
616 End

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614   GroundEnergy [kcal/mol]           36.55
615 End
616 Barrier      B4   W1   P2      # TS_C=COCOCC_m062x.log
617   Variational
618     RRHO
619   Geometry [angstrom]           18
620     C      -0.003339935    -0.0115834043    -0.0019916556
621     C      0.000670349     0.0145241132     1.5073403092
622     O      1.3550375237    0.009660827     1.9372520714
623     C      1.5166431385    -0.0500381398    3.3085996248
624     O      0.9145734104    1.0267276745    3.9986818365
625     C      1.3926716581    2.2683265972    3.7611522479
626     H      0.9087287007    2.9889856141    4.4061700562
627     C      2.2797242445    2.6375093145    2.8276780537
628     H      0.5083370338    0.8708380929    -0.3855730689
629     H      -1.0257037015   -0.0124343291   -0.3777330978
630     H      0.5076460713    -0.8997097623   -0.370581228
631     H      -0.4980362421    0.9135898245    1.8785066299
632     H      -0.5138139625   -0.8585438393    1.9261117955
633     H      1.0406638583    -0.9384704813    3.7307823632
634     H      2.5917871545    -0.0520820292    3.4978769955
635     H      1.162346159     2.8131745513    1.2162993637
636     H      2.5929135647    3.6697659297    2.8059041199
637     H      2.8036329387    1.9310264618    2.2039335003
638   Core RigidRotor
639     SymmetryFactor      1
640 End
641 Rotor      Hindered
642   Group           9 10 11
643   Axis            1 2
644   Symmetry        1
645   Potential [kcal/mol]      6
646     0.0  3.14  0.0  3.14  0.0  3.14
647 End
648 Rotor      Hindered
649   Group           4
650   Axis            3 2
651   Symmetry        1
652   Potential [kcal/mol]      6
653     0.0  2.22  1.58  5.28  1.56  1.99
654 End
655 Rotor      Hindered
656   Group           5 14 15
657   Axis            4 3
658   Symmetry        1
659   Potential [kcal/mol]      6
660     0.0  8.15  3.98  5.58  4.05  5.24
661 End

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662 Rotor      Hindered
663   Group                6
664   Axis                 5 4
665   Symmetry             1
666   Potential [kcal/mol] 6
667     0.0 24.63 5.03 5.6 3.04 6.12
668 End
669 Rotor      Hindered
670   Group                7 8
671   Axis                 6 5
672   Symmetry             1
673   Potential [kcal/mol] 4
674     0.0 6.38 2.14 6.12
675 End
676 Frequencies [1/cm]    42
677     276.98      330.53      353.86      398.78      422.7
678     543.97      692.59      783.27      818.61      881.51
679  920.98      933.1      997.88      1035.27      1065.48
680     1126.75      1179.1      1197.59      1211.35      1250.88
681     1310.07      1339.63      1351.08      1397.93      1423.17
682     1435.51      1467.77      1486.38      1501.79      1516.52
683     1532.3      1667.4      3021.67      3056.12      3070.8
684     3077.62      3112.22      3147.36      3151.59      3200.07
685     3218.32      3295.43
686     !89.02      98.37      144.96      213.47      251.97!
687 ZeroEnergy [kcal/mol] 38.9
688 ElectronicLevels [1/cm] 1
689     0 2
690 End
691 Tunneling              Eckart
692 ImaginaryFrequency [1/cm] 629.6205
693 WellDepth [kcal/mol]    38.9
694 WellDepth [kcal/mol]    2.4
695 End
696 End
697 !-----
698 !-----WELL 2 to Products -----
699 !-----
700 Bimolecular      P3      # CCOC[0] + C=C
701 Fragment CCOC[0]
702 RRHO
703 Geometry [angstrom] 12
704   O      -0.0000136479      -0.0158947662      0.0001300488
705   C      0.0003804679      -0.0116558615      1.4194515571
706   C      1.4348826083      0.0041591029      1.8907607535
707   C      -1.2747334222      -0.0278957055      -0.5487163989
708   H      -1.1614851697      0.0929277806      -1.6352880151
709   H      -1.8740917079      0.8342817878      -0.1867784254

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706   H      -0.5391724883    0.8746145099    1.7772187915
707   O      -2.0241910818   -1.1168828411   -0.3006299029
708   H      -0.5240324399   -0.896234416    1.7892024768
709   H      1.948419974     0.8871976315    1.5138163786
710   H      1.4763606257     0.0127262847    2.9791096444
711   H      1.9577182949   -0.8794154994    1.528544097
712   Core RigidRotor
713       SymmetryFactor      1
714   End
715   Rotor      Hindered
716       Group              4
717       Axis                1 2
718       Symmetry            1
719       Potential [kcal/mol] 8
720           0.0  1.74  0.99  4.51  1.17  1.18  1.07  1.41
721   End
722   Rotor      Hindered
723       Group              5 6 8
724       Axis                4 1
725       Symmetry            1
726       Potential [kcal/mol] 6
727           0.0  2.32  0.0  3.36  2.24  3.36
728   End
729   Rotor      Hindered
730       Group              10 11 12
731       Axis                3 2
732       Symmetry            3
733       Potential [kcal/mol] 2
734           0.0  3.09
735   End
736   Frequencies [1/cm]      27
737       281.68    401.61    637.56    797.03    825.93
885.15    1048.18
738       1081.1    1134.03    1187.87    1193.87    1245.45
       1310.9    1355.19    1393.15    1409.18    1442.46
739       1487.8    1505.84    1535.9    2884.66    3009.4
       3011.82    3075.12    3078.04    3151.9    3154.27
740
741       !70.21    146.84    248.71!
742   ZeroEnergy [kcal/mol]    0
743   ElectronicLevels [1/cm]  1
744       0  2
745   End
746   Fragment      C=C
747               RRHO
748       Geometry [angstrom]  6
749       C              0.00000000    0.00000000    0.00000000
750       H              0.00000000    0.00000000    1.08216909

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```

751      H          0.96588500    0.00000000   -0.48801240
752      C         -1.12558139   -0.00000000   -0.69239269
753      H         -1.12558139   -0.00000000   -1.77456178
754      H         -2.09146639   -0.00000000   -0.20438028
755      Core      RigidRotor
756      SymmetryFactor  2
757      End
758      Frequencies [1/cm]      12
759      829.14  990.4   1002.92  1070.96  1243.08  1388.11  1473.77  1718.56
3159.71  3175.83  3235.53  3261.92
760      !!torsions
761      ZeroEnergy [kcal/mol]          0
762      ElectronicLevels [1/cm]       1
763      0    1
764      End
765      GroundEnergy [kcal/mol]       25.2
766      End
767 Barrier      B5  W2  P3    # TS_CCOC [0]+C=C_m062x.log
768 Variational
769 RRHO
770 Geometry [angstrom]      18
771 C          -0.0073123889    -0.0302621407    -0.0078844496
772 C          0.0005488715     0.0225318002     1.5023133777
773 O          1.348941257      0.0170118014     1.935096638
774 C          1.491899933      0.0219483243     3.3280351973
775 O          0.8860257444     1.0520845257     3.9770747869
776 C          2.0409439939      2.7471700546     3.8090802456
777 C          2.2165894427      2.8163648032     2.4716049713
778 H          1.4855413698      3.2969019275     1.8362148364
779 H          3.05031334       2.3331991554     1.9827784067
780 H          0.5089778769      0.8376145917     -0.4168184983
781 H          -1.0297527764     -0.0347115072     -0.3838587099
782 H          0.4993728256     -0.9272962032     -0.3606648767
783 H          -0.5020848279      0.9209208093     1.8674264457
784 H          -0.5205370102     -0.8451304746     1.9267945836
785 H          1.0215908685     -0.8847870873     3.7552307628
786 H          2.5703793195     -0.02762034      3.5113635956
787 H          1.2538517349      3.3029048116     4.2953202826
788 H          2.8122924374      2.3429500946     4.4492114061
789      Core RigidRotor
790      SymmetryFactor  1
791      End
792      Rotor          Hindered
793      Group          10 11 12
794      Axis           1 2
795      Symmetry       3
796      Potential [kcal/mol]  2
797      0.0  3.12

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798 End
799 Rotor          Hindered
800   Group                4
801   Axis                 3 2
802   Symmetry             1
803   Potential [kcal/mol] 6
804   0.0  1.63  0.8  5.06  0.8  1.35
805 End
806 Rotor          Hindered
807   Group                5 15 16
808   Axis                 4 3
809   Symmetry             1
810   Potential [kcal/mol] 6
811   0.0  6.35  3.0  5.25  2.67  4.22
812 End
813 Rotor          Hindered
814   Group                3 15 16
815   Axis                 4 5
816   Symmetry             1
817   Potential [kcal/mol] 4
818   0.0  16.44  3.51  8.29
819 End
820 Rotor          Hindered
821   Group                7 17 18
822   Axis                 6 5
823   Symmetry             1
824   Potential [kcal/mol] 4
825   0.0  2.94  0.38  1.27
826 End
827 Frequencies [1/cm]    41
828   214.09      228.48      318.68      393.07      428.54
829   650.27      819.15      825.8      878.14      941.23
972.79      1018.36      1046.09      1057.11      1115.82
830   1160.6      1185.05      1190.48      1242.04      1274.31
   1307.79      1327.36      1395.24      1405.95      1432.51
831   1454.84      1475.57      1487.87      1504.68      1536.22
   1602.5      2922.05      3012.29      3044.71      3071.06
832   3080.18      3145.55      3150.05      3171.2      3183.07
   3255.7      3281.22
833   !49.16      61.81      68.6      257.07      150.33! Torsions
834 ZeroEnergy [kcal/mol] 29.9
835 ElectronicLevels [1/cm] 1
836   0  2
837 End
838 Tunneling          Eckart
839 ImaginaryFrequency [1/cm] 495.1418
840 WellDepth [kcal/mol] 22.84
841 WellDepth [kcal/mol] 4.77

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842 End
843 End
844 !-----
845 !-----WELL 3 to Products -----
846 !-----
847 Barrier      B6  W3  W2      # W_CCOCOC[CH2]_m062x.log
848 Variational
849 RRHO
850 Geometry[angstrom]      18
851 C      -0.0025244205      0.0056905039      0.0052114419
852 C      0.0030527174      -0.0070677518      1.5090603793
853 O      1.3796096603      -0.0095103862      1.9572710314
854 C      2.2339392713      0.4519195532      0.9790537239
855 H      3.0789473393      -0.2099321694      0.8103696197
856 O      2.7018876774      1.7263190923      1.1428348699
857 C      1.7096452024      2.7048316387      1.416327854
858 C      2.3853118982      4.0548511916      1.4577190352
859 H      1.3606983305      0.3816927582      -0.020673918
860 H      -0.6003474534      0.7580464504      -0.4941259996
861 H      -0.0107417894      -0.9585264976      -0.4908480508
862 H      -0.4981074459      0.8727012819      1.9187671598
863 H      -0.456862618      -0.8969717152      1.9355598297
864 H      0.9458016159      2.6706793556      0.6303318064
865 H      1.2278545449      2.4762966345      2.3696364095
866 H      2.858895726      4.2727578019      0.5019572329
867 H      1.6576047964      4.8357324475      1.6745821379
868 H      3.150385874      4.0667948224      2.2322734199
869 Core RigidRotor
870 SymmetryFactor      0.5
871 End
872 Rotor      Hindered
873 Group      7
874 Axis      6 4
875 Symmetry      1
876 Potential[kcal/mol]      6
877 0.0 3.69 1.28 2.58 0.82 3.77
878 End
879 Rotor      Hindered
880 Group      4
881 Axis      6 7
882 Symmetry      1
883 Potential[kcal/mol]      6
884 0.0 2.42 1.08 7.13 0.91 2.2
885 End
886 Rotor      Hindered
887 Group      16 17 18
888 Axis      8 7
889 Symmetry      3

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890      Potential [kcal/mol]          2
891      0.0  3.07
892      End
893      Frequencies [1/cm]          44
894      111.53  175.99  274.74  378.86  473.57
602.13  661.31
895      696.85  831.34  846.41  875.2  900.46
994.2  1033.52  1068.27  1089.15  1126.45
896      1170.31  1186.51  1197.56  1233.26  1265.54
      1309.85  1362.5  1388.19  1398.34  1420.17
897      1436.48  1465.32  1488.71  1506.19  1526.38
      1538.53  1706.91  3022.82  3062.76  3074.46
898      3083.48  3118.64  3140.66  3146.84  3151.4
      3153.67  3226.26
899      !84.26  139.63  245.26!
900      ZeroEnergy [kcal/mol]        26.5
901      ElectronicLevels [1/cm]      1
902      0  2
903      End
904      Tunneling                      Eckart
905      ImaginaryFrequency [1/cm]    1761.9442
906      WellDepth [kcal/mol]         23.8
907      WellDepth [kcal/mol]         19.4
908      End
909      End
910      Bimolecular      P4      # CCOC=0 + [CH2]C
911      Fragment      CCOC=0
912      RRHO
913      Geometry [angstrom]          11
914      O      0.0003751914  0.0195019996  0.0000937786
915      C      0.0001265563  -0.004345369  1.1953307137
916      H      0.9004012035  -0.0400753727  1.8192029238
917      O      -1.0829367177  0.0082212829  1.9688922103
918      C      -2.3404949867  0.0546247319  1.2732313729
919      C      -3.4329185306  0.0620891264  2.3131654086
920      H      -2.3591827021  0.9480385077  0.6494872714
921      H      -2.4046538937  -0.8110246448  0.6143470667
922      H      -3.3385498744  0.9308923884  2.9624082139
923      H      -4.406482661  0.0969837863  1.8264015124
924      H      -3.3842195937  -0.835651434  2.9271125409
925      Core RigidRotor
926      SymmetryFactor      1.0
927      End
928      Rotor      Hindered
929      Group          1 3
930      Axis           2 4
931      Symmetry       1
932      Potential [kcal/mol] 4

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933      0.0  12.99  5.27  12.99
934  End
935  Rotor      Hindered
936      Group                2
937      Axis                  4 5
938      Symmetry              1
939      Potential[kcal/mol]    6
940      0.0  1.12  0.01  6.55  0.01  1.12
941  End
942  Rotor      Hindered
943      Group                4 7 8
944      Axis                  5 6
945      Symmetry              1
946      Potential[kcal/mol]    6
947      0.0  3.12  0.0  3.12  0.0  3.12
948  End
949  Frequencies [1/cm]      24
950      237.16      389.93      806.77      814.71      883.19
1062.71      1063.87
951      1145.7      1187.56      1261.98      1310.78      1399.55
      1413.17      1434.43      1490.84      1503.7      1528.65
952      1852.53      3076.3      3081.04      3086.08      3124.94
      3153.11      3158.28
953      !77.65      236.19      344.76!
954  ZeroEnergy[kcal/mol]    0
955  ElectronicLevels [1/cm]  1
956      0  1
957  End
958  Fragment  [CH2]C
959      RRHO
960  Geometry[angstrom]      7
961      C      0.0002983383  -0.0005389889  0.0004031088
962      C      0.0047388604  -0.0084680438  1.4846485597
963      H      1.0125028336  -0.0004449026  -0.404522378
964      H      -0.4985399523  0.8907396606  -0.4014899118
965      H      -0.5291032253  -0.8632636678  -0.4045194797
966      H      0.770457535  0.5135203684  2.0371553306
967      H      -0.8406008348  -0.3881967978  2.037158663
968  Core RigidRotor
969      SymmetryFactor      1.0
970  End
971  Rotor      Hindered
972      Group                3 4 5
973      Axis                  1 2
974      Symmetry              1
975      Potential[kcal/mol]    12
976      0.0  0.07  0.0  0.08  0.0  0.07  0.0  0.08  0.0  0.07  0.0
0.08

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977 End
978 Frequencies [1/cm]      14
979      444.91      810.81      982.95      1081.35      1195.68
      1403.91      1471.58      1487.61      1489.49
980      3004.53      3085.23      3128.72      3174.72      3276.16
981 !125.25!
982 ZeroEnergy [kcal/mol]    0
983 ElectronicLevels [1/cm]  1
984      0  2
985 End
986 GroundEnergy [kcal/mol] -8.5
987 End
988 Barrier      B7  W3  P4  # TS_C[CH2]+CCOC=O_m062x.log
989 Variational
990 RRHO
991 Geometry [angstrom]      18
992 C      0.0000195605      -0.0472638199      0.0287198103
993 C      0.0253434927      0.0201317747      1.5145228557
994 O      1.8045050035      0.0142911779      1.97451411
995 C      2.6013087674      -0.5546067834      1.1882554509
996 H      3.0243833619      -0.0810173971      0.3075481595
997 O      2.8037819939      -1.8908717469      1.1832014256
998 C      2.4403675918      -2.5917469208      2.3744674322
999 C      3.4092207332      -2.3034915987      3.5033852905
1000 H      0.4692349885      0.8336524478      -0.4098914219
1001 H      -1.0218082174      -0.1096374114      -0.3521629558
1002 H      0.5343335661      -0.9315341625      -0.3271200146
1003 H      -0.2441638626      0.9599688676      1.9745973978
1004 H      -0.3393537      -0.8484228916      2.0483515014
1005 H      1.4228411211      -2.3267702314      2.6604706734
1006 H      2.4614024225      -3.6424383173      2.0941214856
1007 H      3.3684133116      -1.2508251925      3.7778586308
1008 H      3.1517304806      -2.9001370543      4.378179816
1009 H      4.4258033717      -2.5507087124      3.2005793676
1010 Core RigidRotor
1011 SymmetryFactor      1.0
1012 End
1013 Rotor      Hindered
1014 Group      9 10 11
1015 Axis      1 2
1016 Symmetry      1
1017 Potential [kcal/mol]      6
1018      0.0  1.11  0.0  1.1  0.0  1.12
1019 End
1020 Rotor      Hindered
1021 Group      1 12 13
1022 Axis      2 3
1023 Symmetry      1

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1024     Potential [kcal/mol]           4
1025     0.0  2.09  0.85  1.59
1026   End
1027   Rotor           Hindered
1028     Group           7
1029     Axis            6 4
1030     Symmetry        1
1031     Potential [kcal/mol]           4
1032     0.0  8.86  2.26  7.04
1033   End
1034   Rotor           Hindered
1035     Group           4
1036     Axis            6 7
1037     Symmetry        1
1038     Potential [kcal/mol]           6
1039     0.0  5.78  0.7  0.9  0.0  0.98
1040   End
1041   Rotor           Hindered
1042     Group           6 14 15
1043     Axis            7 8
1044     Symmetry        1
1045     Potential [kcal/mol]           6
1046     0.0  2.94  0.05  2.94  0.05  2.94
1047   End
1048   Frequencies [1/cm]           42
1049     144.97           282.94           325.2           413.68           467.65
1050     696.67           723.0           771.55           816.7           856.27
1051     874.57           917.8           1028.03           1065.06           1103.71
1052     1121.54           1186.7           1203.7           1226.51           1329.54
1053     1353.19           1388.78           1400.19           1416.66           1475.84
1054     1486.32           1488.27           1490.43           1495.06           1503.39
1055     1525.26           3045.62           3072.17           3092.69           3102.55
1056     3126.25           3136.2           3147.05           3152.95           3161.51
1057     3164.69           3244.26
1058     !27.96           67.63           106.01           173.43           221.36!
1059   ZeroEnergy [kcal/mol]           16.5
1060   ElectronicLevels [1/cm]           1
1061     0  2
1062   End
1063   Tunneling           Eckart
1064   ImaginaryFrequency [1/cm]           791.7485
1065   WellDepth [kcal/mol]           13.8
1066   WellDepth [kcal/mol]           25.0
1067   End
1068 End
1069 End

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E.5 CCCOCO[CH]CC

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1 TemperatureList [K]                500 510 520 530 540 550 560 570 580
   590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750
   760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920
   930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060 1070
   1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200
   1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320 1330
   1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460
   1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580 1590
   1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710 1720
   1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840 1850
   1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980
   1990 2000
2 PressureList [atm]                0.00001 0.001 0.01 0.1 1 10 100.
3 !PressureList [bar]                1.
4 EnergyStepOverTemperature          .2
5 ExcessEnergyOverTemperature        30
6 ModelEnergyLimit [kcal/mol]        400
7 CalculationMethod                  direct
8 !CalculationMethod                 low-eigenvalue !direct
9 WellCutoff                          10
10 ChemicalEigenvalueMax              0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor [1/cm]                200
15       Power                        .85
16       ExponentCutoff               15
17   End
18   CollisionFrequency
19     LennardJones
20       Epsilons [1/cm]              94.87 304.79 !Ar and parent
21       Sigmas [angstrom]            3.33 6.77
22       Masses [amu]                 39.88 131.19
23   End
24 !-----
25 !-----WELL 1 to Products -----
26 !-----
27 Well          W1          # W_CCCOCO [CH] CC_m062x.log
28   Species
29     RRHO
30   Geometry [angstrom]              24
31     C          -0.0170347954        -0.042787223        -0.0096479289
32     C          -0.0103493905        -0.00574936         1.5254452795
33     C          1.3609626603         0.0134329938         2.0910962383
34     O          2.0717771554         -1.1296747497         1.8665190464
35     C          3.424495751          -1.0712574673         2.2548318118

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```
36 O 4.1386275867 -0.105293047 1.5617498313
37 C 4.2288852372 -0.3546645325 0.1665566211
38 C 4.9296949737 0.820108021 -0.4808277032
39 C 4.1394862671 2.1130109891 -0.3224175239
40 H 0.4738905145 0.8419861727 -0.4168027131
41 H -1.0338721144 -0.0807139299 -0.4001200724
42 H 0.5196748539 -0.9224174817 -0.3638284901
43 H -0.5464190356 0.8748536578 1.8803139529
44 H -0.5400203646 -0.8828377721 1.9061604744
45 H 1.9372196587 0.9288054062 2.1626848698
46 H 3.4992399408 -0.810304153 3.3118909895
47 H 3.8188275083 -2.0731744067 2.0670764988
48 H 4.7803217317 -1.2876011437 0.002034374
49 H 3.2238435373 -0.4733227786 -0.2517504526
50 H 5.9208529181 0.9258975795 -0.036222829
51 H 5.0736048782 0.5900423737 -1.5381794198
52 H 4.0168531139 2.357841837 0.731459885
53 H 4.640589712 2.9472041973 -0.8114061524
54 H 3.1450686243 2.0117248472 -0.7614365875
55 Core RigidRotor
56 SymmetryFactor 1.0
57 End
58 Rotor Hindered
59 Group 10 11 12
60 Axis 1 2
61 Symmetry 3
62 Potential [kcal/mol] 2
63 0.0 3.11
64 End
65 Rotor Hindered
66 Group 1 13 14
67 Axis 2 3
68 Symmetry 1
69 Potential [kcal/mol] 6
70 0.0 2.36 0.37 1.85 0.49 1.62
71 End
72 Rotor Hindered
73 Group 2 15
74 Axis 3 4
75 Symmetry 1
76 Potential [kcal/mol] 6
77 0.0 4.88 2.4 3.2 2.81 3.46
78 End
79 Rotor Hindered
80 Group 3
81 Axis 4 5
82 Symmetry 1
83 Potential [kcal/mol] 6
```

```

84      0.0  6.99  2.23  4.18  3.47  4.48
85  End
86  Rotor      Hindered
87      Group          4 16 17
88      Axis           5 6
89      Symmetry       1
90      Potential[kcal/mol] 6
91      0.0  6.99  2.23  4.18  3.47  4.48
92  End
93  Rotor      Hindered
94      Group          5
95      Axis           6 7
96      Symmetry       1
97      Potential[kcal/mol] 6
98      0.0  2.02  1.24  7.62  2.66  3.57
99  End
100 Rotor      Hindered
101      Group          6 18 19
102      Axis           7 8
103      Symmetry       1
104      Potential[kcal/mol] 6
105      0.0  5.15  0.35  3.91  0.66  3.72
106 End
107 Rotor      Hindered
108      Group          7 20 21
109      Axis           8 9
110      Symmetry       3
111      Potential[kcal/mol] 2
112      0.0  2.64
113 End
114 Frequencies [1/cm] 58
115      223.84      302.11
116      309.99      366.51      436.0      508.65      600.36
117 675.99      770.37      779.5      902.17      911.37
118      925.92      963.07      972.59      1058.48      1088.4
119 1099.05      1118.58      1145.5      1171.55      1188.38
120      1210.08      1247.04      1285.29      1296.06      1309.92
121      1334.78      1350.45      1377.37      1392.11      1411.87
122      1418.4      1432.69      1469.48      1475.81      1483.67
123      1495.88      1498.28      1507.02      1510.3      1520.54
124      1529.1      3020.3      3054.67      3056.25      3059.33
      3060.08      3061.84      3073.08      3105.99      3107.05
      3113.36      3131.1      3132.03      3140.91      3148.29
      3175.15
      !32.79      51.77      53.63      103.35      138.98      193.1
      212.95      273.48!
123 ZeroEnergy[kcal/mol] 0
124 ElectronicLevels [1/cm] 1

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```
125      0  2
126      End
127      End
128      Well      W2      # W_CCCOCOC[CH]C_m062x.log
129      Species
130      RRHO
131      Geometry[angstrom]      24
132      C      -0.0036417969      -0.0113165538      0.0009621034
133      C      -0.009071703      -0.0175444756      1.4870498268
134      C      1.274613024      -0.003526504      2.241472572
135      O      2.1921274451      -1.0002392887      1.7946641173
136      C      1.7687409483      -2.30684524      2.0582618428
137      O      1.6444406178      -2.575977837      3.4198554709
138      C      2.8757189889      -2.5286225567      4.1216760662
139      C      2.5996301779      -2.7898591305      5.5871006631
140      C      1.7034666186      -1.7215015966      6.2007485082
141      H      0.8211932724      -0.6105888564      -0.3865122561
142      H      0.1303127427      1.0042713586      -0.3942202372
143      H      -0.9380836718      -0.3922607998      -0.4093885349
144      H      -0.9241205215      0.196415055      2.0203125821
145      H      1.8095489902      0.9403769374      2.0876089519
146      H      1.0940579811      -0.1149164068      3.3134731075
147      H      0.7821534067      -2.4962738099      1.6276553872
148      H      2.5222182054      -2.9530710846      1.5983871464
149      H      3.5565064933      -3.2822796728      3.7082972904
150      H      3.340682038      -1.5462983146      3.9891569651
151      H      2.1346569793      -3.7724325656      5.6853591049
152      H      3.555532423      -2.8314433237      6.112775321
153      H      0.7422166319      -1.6928402958      5.6898518498
154      H      1.5234064585      -1.9129674615      7.2577232161
155      H      2.1631571936      -0.7353835483      6.1109080277
156      Core RigidRotor
157      SymmetryFactor      1.0
158      End
159      Rotor      Hindered
160      Group      10 11 12
161      Axis      1 2
162      Symmetry      3
163      Potential[kcal/mol]      2
164      0.0  0.25
165      End
166      Rotor      Hindered
167      Group      1 13
168      Axis      2 3
169      Symmetry      1
170      Potential[kcal/mol]      4
171      0.0  4.8  0.5  2.64
172      End
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173 Rotor      Hindered
174   Group                2 14 15
175   Axis                  3 4
176   Symmetry              1
177   Potential [kcal/mol]  4
178     0.0  2.23  0.62  5.88
179 End
180 Rotor      Hindered
181   Group                3
182   Axis                  4 5
183   Symmetry              1
184   Potential [kcal/mol]  6
185     0.0  7.77  2.3  4.03  2.83  3.68
186 End
187 Rotor      Hindered
188   Group                4 16 17
189   Axis                  5 6
190   Symmetry              1
191   Potential [kcal/mol]  8
192     0.0  7.57  3.14  3.54  2.98  4.7  2.8  4.17
193 End
194 Rotor      Hindered
195   Group                5
196   Axis                  6 7
197   Symmetry              1
198   Potential [kcal/mol]  8
199     0.0  1.71  1.2  1.24  1.13  7.43  3.02  3.4
200 End
201 Rotor      Hindered
202   Group                6 18 19
203   Axis                  7 8
204   Symmetry              1
205   Potential [kcal/mol]  6
206     0.0  5.03  0.22  3.79  0.54  3.73
207 End
208 Rotor      Hindered
209   Group                7 20 21
210   Axis                  8 9
211   Symmetry              3
212   Potential [kcal/mol]  2
213     0.0  2.91
214 End
215 Frequencies [1/cm]    58
216     224.5      308.22
217     327.06     362.73     395.1      478.22     605.07
653.6      771.5      885.42     902.25     923.94
218     931.35     953.92     966.19     995.33     1087.27
1104.36     1112.34     1136.3      1158.69     1181.11

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219      1189.53      1212.98      1284.04      1301.89      1315.95
      1346.1      1377.09      1378.89      1394.61      1410.91
220      1417.38      1428.94      1454.92      1480.78      1484.24
      1488.38      1493.96      1499.43      1513.27      1515.11
221      1531.56      3001.21      3018.12      3022.75      3043.63
      3058.1      3060.67      3071.72      3081.17      3090.51
222      3095.81      3105.5      3130.5      3136.87      3146.79
      3209.61
223      !30.02      38.37      54.99      70.59      100.17      148.23
      181.99      247.59!
224      ZeroEnergy [kcal/mol]      3.9
225      ElectronicLevels [1/cm]      1
226      0 2
227      End
228      End
229      Barrier      B1  W1  W2      # W_CCCOCO[CH]C_m062x.log
230      Variational
231      RRHO
232      Geometry [angstrom]      24
233      C      -0.0207083008      -0.0126520428      0.019198108
234      C      -0.0074282377      0.0010512106      1.5228137321
235      C      1.3558663108      0.0012382675      2.1588911755
236      O      1.3067359434      0.1896964903      3.5640914783
237      C      1.1325606473      1.4997075837      3.9995119502
238      O      -0.1882225199      1.9646510375      3.9344602013
239      C      -0.6163406432      2.3310787694      2.6599928303
240      C      -2.062896585      2.735256129      2.6714114145
241      C      -2.9845391525      1.5902964936      3.0796994587
242      H      -0.4827063908      1.2307723528      1.9361611207
243      H      0.5379803445      0.8347916488      -0.3846354525
244      H      -1.0363412701      0.0381124971      -0.3715570058
245      H      0.4394084244      -0.9219860005      -0.3822158264
246      H      -0.6893352468      -0.6978220382      2.0034616972
247      H      1.8668438114      -0.9529185809      2.0027343545
248      H      1.979241558      0.7837762186      1.702322423
249      H      1.4033606154      1.5130072446      5.0516481238
250      H      1.7833517417      2.175135642      3.4236772201
251      H      0.061967466      3.0563936602      2.196023778
252      H      -2.1871468137      3.5756453356      3.3623757707
253      H      -2.3244713636      3.0997923496      1.6765070001
254      H      -2.6970677475      1.201684531      4.05518868
255      H      -4.0212292066      1.9196629426      3.1311730144
256      H      -2.9235804145      0.7726032529      2.3604327746
257      Core RigidRotor
258      SymmetryFactor      0.25
259      End
260      Rotor      Hindered
261      Group      11 12 13

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262     Axis                1 2
263     Symmetry           3
264     Potential [kcal/mol] 2
265     0.0  1.87
266     End
267     Rotor              Hindered
268     Group              9 20 21
269     Axis               8 7
270     Symmetry          1
271     Potential [kcal/mol] 6
272     0.0  3.81  0.27  2.96  0.16  2.66
273     End
274     Rotor              Hindered
275     Group              22 23 24
276     Axis               9 8
277     Symmetry          3
278     Potential [kcal/mol] 2
279     0.0  2.69
280     End
281     Frequencies [1/cm] 62
282     71.33      128.93      137.84      202.02      290.37
283     295.32      338.54
284     413.49      447.92      510.42      560.9       637.61
285     774.04      844.63      903.02      908.9       936.16
286     955.42      982.37      997.35      1089.16     1102.07
287     1119.57     1135.34     1146.03     1150.12     1179.69
288     1188.45     1247.85     1293.5      1306.76     1332.36
289     1348.7      1366.8      1371.44     1409.71     1412.48
290     1416.34     1441.05     1456.87     1474.2      1487.92
291     1494.61     1495.37     1502.37     1509.11     1513.08
292     1515.58     2984.03     2994.53     3026.77     3027.99
293     3039.77     3064.72     3067.63     3084.6      3095.15
294     3121.84     3133.56     3136.05     3151.07     3153.07
295     !56.02      166.58      217.62!
296     ZeroEnergy [kcal/mol] 19.1
297     ElectronicLevels [1/cm] 1
298     0  2
299     End
300     Tunneling              Eckart
301     ImaginaryFrequency [1/cm] 1671.6942
302     WellDepth [kcal/mol] 19.1
303     WellDepth [kcal/mol] 15.2
304     End
305     End
306     Well      W3      # W_CCCOCOCC[CH2]_m062x.log
307     Species
308     RRHO
309     Geometry [angstrom] 24

```

```
304 C -0.0062476859 -0.02126965 -0.0163303857
305 C -0.0046988522 0.0014011342 1.4704960807
306 C 1.4041056014 0.0136759017 2.0462213335
307 O 2.060696304 -1.1706363361 1.6295849883
308 C 3.4383611706 -1.1484599061 1.8579422363
309 O 4.0951878338 -0.1699438712 1.1141734754
310 C 4.0489889675 -0.3986242016 -0.2861167205
311 C 4.4812144319 0.867036039 -0.9952777783
312 C 3.5401618107 2.0291906974 -0.7020461274
313 H -0.6261609568 0.6500802134 -0.5891455735
314 H 0.5056191706 -0.8166945049 -0.5349501258
315 H -0.5403403289 0.8736463849 1.8460697671
316 H -0.5159089877 -0.8847071884 1.8665583753
317 H 1.9476627341 0.8886559429 1.6808343383
318 H 1.3758863213 0.050086519 3.1416401568
319 H 3.6571391054 -0.9233885893 2.905845261
320 H 3.7969874586 -2.1486946742 1.598074315
321 H 4.705459439 -1.2400328027 -0.5363514022
322 H 3.0278640037 -0.6582734506 -0.5815536658
323 H 5.4984206731 1.1171482707 -0.6882601899
324 H 4.5097186941 0.6618989089 -2.0672042196
325 H 3.5691956753 2.2831478998 0.3565701398
326 H 3.8122455928 2.9160652485 -1.2728612302
327 H 2.5104868528 1.7629559594 -0.9537030583
328 Core RigidRotor
329 SymmetryFactor 1.0
330 End
331 Rotor Hindered
332 Group 10 11
333 Axis 1 2
334 Symmetry 1
335 Potential[kcal/mol] 4
336 0.0 0.81 -0.0 0.8
337 End
338 Rotor Hindered
339 Group 1 12 13
340 Axis 2 3
341 Symmetry 1
342 Potential[kcal/mol] 6
343 0.0 5.63 0.87 4.34 1.16 4.08
344 End
345 Rotor Hindered
346 Group 2 14 15
347 Axis 3 4
348 Symmetry 1
349 Potential[kcal/mol] 6
350 0.0 2.28 0.91 5.36 1.89 2.44
351 End
```

```

352 Rotor      Hindered
353   Group                3
354   Axis                 4 5
355   Symmetry             1
356   Potential [kcal/mol] 6
357     0.0  8.05  3.64  5.32  3.75  4.7
358 End
359 Rotor      Hindered
360   Group                4 16 17
361   Axis                 5 6
362   Symmetry             1
363   Potential [kcal/mol] 6
364     0.0  7.93  3.43  5.11  3.78  4.75
365 End
366 Rotor      Hindered
367   Group                5
368   Axis                 6 7
369   Symmetry             1
370   Potential [kcal/mol] 6
371     0.0  3.57  2.73  7.84  1.37  2.24
372 End
373 Rotor      Hindered
374   Group                6 18 19
375   Axis                 7 8
376   Symmetry             1
377   Potential [kcal/mol] 6
378     0.0  5.32  0.85  4.2  1.06  4.33
379 End
380 Rotor      Hindered
381   Group                22 23 24
382   Axis                 9 8
383   Symmetry             1
384   Potential [kcal/mol] 6
385     0.0  2.79  -0.0  2.79  0.0  2.79
386 End
387 Frequencies [1/cm]    58
388     237.47     301.91
389     318.42     373.23     443.87     488.4     532.66
390 670.51     755.06     771.66     900.01     917.39
391     928.04     954.97     965.94     1067.61     1085.12
392 1088.44     1112.25     1131.49     1149.18     1184.65
393     1194.56     1219.39     1249.07     1287.29     1298.87
394     1309.31     1343.03     1360.57     1377.17     1411.46
395     1415.86     1430.01     1452.39     1462.74     1475.89
396     1483.54     1497.04     1511.03     1519.85     1525.76
397     1528.06     3012.83     3021.14     3022.77     3040.32
398     3055.78     3063.68     3076.35     3086.22     3091.2

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394          3104.47      3108.24      3127.85      3145.69      3180.95
          3286.5
395      !41.37      49.7      63.84      96.04      120.38      162.38
          213.89      260.19!
396      ZeroEnergy [kcal/mol]      6.0
397      ElectronicLevels [1/cm]      1
398          0  2
399      End
400      End
401      Barrier      B2  W1  W3      # W_CCCOCOCC [CH2] _m062x.log
402      Variational
403          RRHO
404      Geometry [angstrom]      24
405      C      0.0063543956      -0.0023067813      -0.009240457
406      C      0.0019448391      -0.0070882557      1.4963992392
407      C      1.4170199035      -0.0032029093      2.071907247
408      O      2.3112648134      0.8716905792      1.4015546517
409      C      2.1603037574      2.2224258141      1.6812036117
410      O      0.9695016282      2.7748629251      1.1862883584
411      C      0.7696687124      2.5676685475      -0.1787911088
412      C      -0.3606511164      3.4194843895      -0.687755721
413      C      -1.6598632965      3.1829504735      0.0756986393
414      H      0.4137232661      1.3078419703      -0.2986678061
415      H      -0.9676179331      -0.1004014325      -0.4799890318
416      H      0.7686806983      -0.6189372635      -0.4789970045
417      H      -0.556333731      0.8573084462      1.8634481656
418      H      -0.5064125715      -0.894146489      1.8912520574
419      H      1.3983244014      0.2383454879      3.1406205333
420      H      1.8596756828      -0.9923469733      1.9547119308
421      H      2.1396039138      2.407035973      2.7590983958
422      H      3.0206622184      2.7150156725      1.2195074101
423      H      1.7013924987      2.6506777982      -0.7468202552
424      H      -0.07821961      4.4745760147      -0.6154430797
425      H      -0.4977984812      3.1990619833      -1.7481004931
426      H      -1.5299686282      3.416884835      1.1311029482
427      H      -2.4632037121      3.8049527895      -0.316393649
428      H      -1.9698077205      2.1400664509      -0.0024515451
429      Core RigidRotor
430          SymmetryFactor      0.5
431      End
432      Rotor      Hindered
433          Group      9 20 21
434          Axis      8 7
435          Symmetry      1
436          Potential [kcal/mol]      6
437          0.0  3.94  0.19  3.09  0.19  3.27
438      End
439      Rotor      Hindered

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```

440      Group                22 23 24
441      Axis                 9 8
442      Symmetry             3
443      Potential [kcal/mol] 2
444      0.0 2.89
445      End
446      Frequencies [1/cm]   63
447      72.39      138.46      228.26      250.15      273.61
448      291.36      308.78      418.13
449      474.22      480.12      525.85      632.22      678.42
450      778.26      803.87      888.13      904.72      920.43
451      953.59      965.69      979.37      1059.49     1090.35
452      1113.25     1117.62     1138.29     1163.36     1174.06
453      1202.93     1213.79     1257.9      1294.38     1321.95
454      1345.28     1366.27     1368.89     1384.02     1408.54
455      1415.09     1427.63     1450.78     1461.77     1477.33
456      1480.21     1491.54     1501.28     1503.47     1512.11
457      1520.68     3023.9      3034.68     3036.91     3039.37
458      3057.04     3069.18     3075.81     3090.86     3093.29
459      3107.34     3112.93     3136.91     3148.75     3188.9
460      !100.09      209.83!
461      ZeroEnergy [kcal/mol] 20.2
462      ElectronicLevels [1/cm] 1
463      0 2
464      End
465      Tunneling            Eckart
466      ImaginaryFrequency [1/cm] 1721.6105
467      WellDepth [kcal/mol] 20.2
468      WellDepth [kcal/mol] 14.2
469      End
470      End
471      Bimolecular          P1 # CCC=O + CCCO[CH2]
472      Fragment            CCC=O
473      RRHO
474      Geometry [angstrom] 10
475      O      -0.0016887113      0.0713256657      0.0025329724
476      C      -0.0002866444      -0.0006238542      1.2003000648
477      C      1.2414214573      0.0044649469      2.0474156978
478      C      2.5200956405      0.1108944722      1.2367087341
479      H      -0.9548921268      -0.0771166876      1.7562509656
480      H      1.1389672739      0.8283859718      2.7607751845
481      H      1.2171547154      -0.9046876655      2.6565767532
482      H      2.5240120839      1.0254852172      0.6465567594
483      H      3.3931207594      0.1112190273      1.8863927315
484      H      2.6028715485      -0.7225020952      0.5414611314
485      Core RigidRotor
486      SymmetryFactor      1.0
487      End

```

```

482 Rotor      Hindered
483   Group                1 5
484   Axis                 2 3
485   Symmetry             1
486   Potential [kcal/mol] 6
487     0.0  2.34  1.42  2.11  1.42  2.34
488 End
489 Rotor      Hindered
490   Group                2 6 7
491   Axis                 3 4
492   Symmetry             3
493   Potential [kcal/mol] 2
494     0.0  2.12
495 End
496 Frequencies [1/cm]    22
497     266.82     673.44     677.86     873.63     908.86
1008.52     1121.87     1156.86
498     1283.92     1372.83     1414.21     1430.39     1457.55
     1497.45     1504.72     1866.92     2945.02     3050.32
499     3077.74     3081.28     3153.86     3156.87
500   !148.66     238.11!
501 ZeroEnergy [kcal/mol] 0
502 ElectronicLevels [1/cm] 1
503     0  1
504 End
505 Fragment CCCO [CH2]
506   RRHO
507 Geometry [angstrom] 14
508   C      -0.0002301642    0.000779469    0.0007852634
509   O      -0.0001081683    0.0004484355    1.3498002998
510   C      1.2885083909    -0.0002312539    1.9480065736
511   C      2.0188320424    1.317189872     1.7453369611
512   C      1.2223868513    2.5031840503    2.2716522358
513   H      -0.9849359431    -0.0292074563    -0.4368838879
514   H      0.8486696718    -0.4436878423    -0.5066231056
515   H      1.1144973047    -0.1812898889    3.008368478
516   H      1.8698582902    -0.8352511245    1.5428034104
517   H      2.9835329869    1.2456869418    2.2521128773
518   H      2.2268062162    1.4495464457    0.6816326348
519   H      1.0116874266    2.3884900839    3.3360426458
520   H      1.7671144817    3.4358545839    2.1334849946
521   H      0.2698405869    2.5833486777    1.7494626238
522 Core RigidRotor
523   SymmetryFactor      1.0
524 End
525 Rotor      Hindered
526   Group                6 7
527   Axis                 1 2

```

```
528 Symmetry 1
529 Potential [kcal/mol] 6
530 0.0 5.1 0.6 0.64 0.0 5.38
531 End
532 Rotor Hindered
533 Group 1
534 Axis 2 3
535 Symmetry 1
536 Potential [kcal/mol] 6
537 0.0 1.6 0.12 1.17 1.1 6.0
538 End
539 Rotor Hindered
540 Group 2 8 9
541 Axis 3 4
542 Symmetry 1
543 Potential [kcal/mol] 6
544 0.0 3.74 0.47 3.46 0.73 4.79
545 End
546 Rotor Hindered
547 Group 3 10 11
548 Axis 4 5
549 Symmetry 3
550 Potential [kcal/mol] 2
551 0.0 2.78
552 End
553 Frequencies [1/cm] 32
554 307.28 440.57 525.81 631.81 771.33
880.55
555 921.94 967.17 1074.67 1120.36 1156.41
1221.23 1279.48 1307.55 1338.15 1379.84
556 1410.34 1423.03 1481.32 1485.96 1500.86
1509.25 1520.27 3037.27 3063.03 3066.28
557 3097.68 3120.11 3127.22 3134.42 3146.23
3276.88
558 !70.31 168.24 232.84 282.38!
559 ZeroEnergy [kcal/mol] 0
560 ElectronicLevels [1/cm] 1
561 0 2
562 End
563 GroundEnergy [kcal/mol] 9.5
564 End
565 Barrier B3 W1 P1 # TS_CCCO [CH2]+CCC=0_m062x.log
566 Variational
567 RRHO
568 Geometry [angstrom] 24
569 C -0.2977681986 0.94025752 0.8446553582
570 C 0.1345516785 0.4902163595 2.2341817319
571 C 1.612520992 0.1805370586 2.3106014925
```

```

572 O 2.3467930225 1.3534164845 1.9556663001
573 C 3.6540944494 1.2804246792 2.2207925747
574 O 3.723757381 1.6164224058 4.1452532961
575 C 2.6981502122 2.2131502993 4.5471971612
576 C 2.4881515167 3.6868660087 4.3764743717
577 C 1.0882137659 4.0202016809 3.8639592068
578 H 1.8780524693 1.6403748438 5.0029426516
579 H 0.2294018983 1.8473883809 0.5533276482
580 H -1.3673587317 1.1417114752 0.8123393733
581 H -0.0768059314 0.1716479838 0.1023175605
582 H -0.0961881588 1.2616417561 2.9716031475
583 H -0.410020693 -0.4085226587 2.5297545558
584 H 1.9078903675 -0.1257763242 3.3168831347
585 H 1.8825529155 -0.6174235008 1.6095127526
586 H 4.1165552432 0.3016821579 2.2380222626
587 H 4.2174383309 2.1227981881 1.8515345924
588 H 2.6502498328 4.1850174504 5.3389556655
589 H 3.2576868637 4.0585191799 3.698005871
590 H 0.3271514924 3.5993325677 4.5234840544
591 H 0.9288440207 5.0968689204 3.817686415
592 H 0.9381220209 3.6029894988 2.8682926818
593 Core RigidRotor
594 SymmetryFactor 1.0
595 End
596 Rotor Hindered
597 Group 11 12 13
598 Axis 1 2
599 Symmetry 1
600 Potential [kcal/mol] 6
601 0.0 2.69 0.0 2.69 0.0 2.69
602 End
603 Rotor Hindered
604 Group 1 14 15
605 Axis 2 3
606 Symmetry 1
607 Potential [kcal/mol] 6
608 0.0 3.66 0.38 3.03 0.02 4.88
609 End
610 Rotor Hindered
611 Group 2 16 17
612 Axis 3 4
613 Symmetry 1
614 Potential [kcal/mol] 8
615 0.0 1.98 1.46 5.18 4.64 4.98 1.61 2.59
616 End
617 Rotor Hindered
618 Group 3
619 Axis 4 5

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620      Symmetry                1
621      Potential[kcal/mol]     6
622      0.0  11.39  4.1  9.46  4.95  6.37
623      End
624      Rotor      Hindered
625      Group                4 18 19
626      Axis                 5 6
627      Symmetry            1
628      Potential[kcal/mol]  4
629      0.0  5.97  4.14  5.0
630      End
631      Rotor      Hindered
632      Group                9 20 21
633      Axis                 8 7
634      Symmetry            1
635      Potential[kcal/mol]  6
636      0.0  1.15  0.13  0.29  0.1  0.65
637      End
638      Rotor      Hindered
639      Group                22 23 24
640      Axis                 9 8
641      Symmetry            1
642      Potential[kcal/mol]  6
643      0.0  2.6  0.0  2.58  0.0  2.59
644      End
645      Frequencies [1/cm]     58
646      152.94      233.67      313.2
647      345.69      360.72      434.28      507.08      541.99
648      679.16      704.22      768.89      810.18      899.99
649      900.65      925.81      927.53      967.0      1036.16
650      1075.67     1095.3     1124.28     1151.33     1176.49
651      1237.97     1247.27     1269.82     1287.81     1315.15
652      1324.19     1357.34     1381.27     1405.59     1414.59
653      1430.78     1469.12     1481.39     1498.45     1500.33
654      1505.73     1510.43     1512.28     1522.18     1525.34
655      3005.76     3025.5     3028.73     3058.13     3064.35
656      3068.22     3088.05     3098.49     3105.82     3127.58
657      3135.33     3139.66     3145.03     3149.89     3280.03
658      !210.4     259.02     32.87     48.26     71.65     95.18
659      108.25!
660      ZeroEnergy[kcal/mol]    23.6
661      ElectronicLevels [1/cm] 1
662      0 2
663      End
664      Tunneling      Eckart
665      ImaginaryFrequency [1/cm] 647.1787
666      WellDepth[kcal/mol]    23.6
667      WellDepth[kcal/mol]    14.1

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```
662 End
663 End
664 Bimolecular P2 # CCCOCOC=C + [CH3]
665 Fragment CCCOCOC=C
666 RRHO
667 Geometry[angstrom] 20
668 C 0.0001382433 -0.0042677269 0.0055963329
669 C 0.0018443352 0.0017509637 1.528540548
670 C 1.400333565 0.0063919074 2.1076951505
671 O 2.0475617435 1.2037105878 1.7031038956
672 C 3.3910291673 1.2560592444 2.0352317372
673 O 3.6310626296 1.2176727007 3.4224893201
674 C 3.2690818581 2.310765694 4.1444291626
675 C 2.5790248539 3.3658213201 3.7348073567
676 H 3.6345993458 2.2217755539 5.1589825489
677 H 0.5163644521 0.8731188284 -0.3800549883
678 H -1.0150749421 -0.0046672329 -0.3886280278
679 H 0.5095981989 -0.8900693394 -0.3777073386
680 H -0.5277834175 0.8791114413 1.9041948029
681 H -0.5211061595 -0.8757819161 1.9134154853
682 H 1.3730271055 -0.0464079383 3.1985401456
683 H 1.973598099 -0.8547461925 1.738816927
684 H 3.927533483 0.3900420857 1.6394459287
685 H 3.7817614552 2.1861815387 1.61863812
686 H 2.1669871371 3.4514358534 2.7414719831
687 H 2.4024308441 4.1659116531 4.4367228655
688 Core RigidRotor
689 SymmetryFactor 1.0
690 End
691 Rotor Hindered
692 Group 10 11 12
693 Axis 1 2
694 Symmetry 3
695 Potential[kcal/mol] 2
696 0.0 2.71
697 End
698 Rotor Hindered
699 Group 1 13 14
700 Axis 2 3
701 Symmetry 1
702 Potential[kcal/mol] 6
703 0.0 3.65 0.35 3.49 0.0 4.81
704 End
705 Rotor Hindered
706 Group 2 15 16
707 Axis 3 4
708 Symmetry 1
709 Potential[kcal/mol] 8
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710      0.0  3.52  3.03  6.97  0.59  0.7  0.58  1.19
711  End
712  Rotor      Hindered
713      Group                3
714      Axis                  4 5
715      Symmetry              1
716      Potential[kcal/mol]   6
717      0.0  6.85  3.41  5.08  2.8  4.0
718  End
719  Rotor      Hindered
720      Group                4 17 18
721      Axis                  5 6
722      Symmetry              1
723      Potential[kcal/mol]   6
724      0.0  4.76  1.58  4.01  3.56  11.44
725  End
726  Rotor      Hindered
727      Group                5
728      Axis                  6 7
729      Symmetry              1
730      Potential[kcal/mol]   4
731      0.0  4.69  1.02  4.94
732  End
733  Frequencies [1/cm]      48
734      276.08      307.46      387.49      452.62
735      560.19      689.39      738.11      772.27      892.16
736      901.6      924.56      930.59      965.2      1020.18
737      1047.31      1090.63      1128.87      1162.0      1198.88
738      1214.23      1250.34      1283.71      1313.25      1347.86
739      1365.54      1381.67      1414.26      1428.86      1433.66
740      1471.77      1484.62      1500.81      1513.37      1517.23
741      1531.15      1724.3      3007.79      3057.25      3063.12
742      3066.36      3084.36      3105.76      3115.98      3132.8
743      3150.14      3199.42      3216.04      3294.21
744      !37.64      63.89      113.28      150.74      203.16      237.51!
745  ZeroEnergy[kcal/mol]    0
746  ElectronicLevels [1/cm]  1
747      0  1
748  End
749  Fragment  [CH3]
750      RRHO
751  Geometry[angstrom]      3
752      C      0.      0.      0.
753      H      0.      0.      1.0765291468
754      H      0.9323015891      0.      -0.5382645734
755  Core RigidRotor
756      SymmetryFactor      6.0
757  End

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754   Frequencies [1/cm]      6
755       436.03      1412.64      1412.73      3144.41      3323.11
756       3323.14
757   !   !
757   ZeroEnergy [kcal/mol]      0
758   ElectronicLevels [1/cm]      1
759       0   2
760   End
761   GroundEnergy [kcal/mol]      22.9
762   End
763   Barrier      B4   W1   P2      # TS_CCCOCOC=C+[CH3]_m062x.log
764   Variational
765       RRHO
766   Geometry [angstrom]      24
767   C      -0.0040543148      -0.0386425229      0.0073857711
768   C      -0.0048900436      0.0061823278      1.5300622428
769   C      1.3972642581      -0.0005551268      2.0992571791
770   O      2.0019545826      -1.2476422451      1.7814371128
771   C      3.3405752059      -1.3215358129      2.1296132728
772   O      4.1497648813      -0.4681681052      1.3544114536
773   C      4.1970245146      -0.7790732066      0.0295259382
774   C      4.8053156527      0.0419774673      -0.8476695298
775   H      3.6418436109      -1.6607272095      -0.2683773973
776   C      3.30287806      1.6405400101      -1.4838550463
777   H      0.5014610447      0.8374302655      -0.4020192743
778   H      -1.0180307632      -0.0594446642      -0.3895728613
779   H      0.5209480037      -0.9246238244      -0.3475336323
780   H      -0.5120967721      0.9062976302      1.8823791475
781   H      -0.5479161416      -0.849017135      1.9363981832
782   H      1.9879766946      0.8139750743      1.6685141958
783   H      1.3846335149      0.1222871611      3.1881314955
784   H      3.5073948986      -1.010131902      3.1635375573
785   H      3.6410234428      -2.3609769182      1.9844596142
786   H      5.4455036203      0.8321233846      -0.4835767967
787   H      4.9409763173      -0.293059714      -1.8635607
788   H      3.9212887789      2.2751443976      -2.1030833855
789   H      2.5615966951      1.0390754015      -1.9884097552
790   H      3.0386283274      2.0213352419      -0.5080937686
791   Core RigidRotor
792       SymmetryFactor      1.0
793   End
794   Rotor      Hindered
795       Group      11 12 13
796       Axis      1 2
797       Symmetry      3
798       Potential [kcal/mol]      2
799       0.0  2.52
800   End

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801 Rotor      Hindered
802   Group                1 14 15
803   Axis                  2 3
804   Symmetry              1
805   Potential [kcal/mol]   6
806   0.0  4.82  0.31  3.82  0.54  3.57
807 End
808 Rotor      Hindered
809   Group                2 16 17
810   Axis                  3 4
811   Symmetry              1
812   Potential [kcal/mol]   8
813   0.0  3.16  2.62  7.24  1.21  1.46  1.43  1.93
814 End
815 Rotor      Hindered
816   Group                3
817   Axis                  4 5
818   Symmetry              1
819   Potential [kcal/mol]   6
820   0.0  6.49  1.74  4.07  3.43  4.38
821 End
822 Rotor      Hindered
823   Group                4 18 19
824   Axis                  5 6
825   Symmetry              1
826   Potential [kcal/mol]   6
827   0.0 13.23  3.02  3.38  3.29  3.87
828 End
829 Rotor      Hindered
830   Group                5
831   Axis                  6 7
832   Symmetry              1
833   Potential [kcal/mol]   4
834   0.0  4.1  -0.04  3.2
835 End
836 Rotor      Hindered
837   Group                22 23 24
838   Axis                  10 8
839   Symmetry              3
840   Potential [kcal/mol]   2
841   0.0  2.52
842 End
843 Frequencies [1/cm]      58
844   194.66      260.63      285.58
845   316.67      363.32      422.86      473.51      514.17
846   521.71      674.69      743.54      771.03      782.35
847   886.53      902.56      911.83      927.61      958.77
848   964.71      1088.46      1113.65      1123.94      1143.86

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847      1185.27      1202.85      1242.57      1284.17      1309.25
      1313.56      1349.05      1378.21      1412.87      1416.53
848      1422.86      1425.36      1433.42      1460.04      1483.77
      1499.09      1510.98      1521.47      1527.85      1621.17
849      3023.61      3055.62      3061.41      3064.01      3074.88
      3105.83      3108.44      3111.05      3134.06      3145.59
850      3184.98      3192.37      3266.32      3276.08      3286.21
851      !33.53      34.63      50.72      84.92      116.06      134.24
      199.9!
852      ZeroEnergy [kcal/mol]      30.2
853      ElectronicLevels [1/cm]      1
854      0 2
855      End
856      Tunneling      Eckart
857      ImaginaryFrequency [1/cm]      589.1433
858      WellDepth [kcal/mol]      30.2
859      WellDepth [kcal/mol]      7.3
860      End
861      End
862      !-----
863      !-----WELL 2 to Products -----
864      !-----
865      Well      W4      # W_CCCO [CH] OCCC_m062x.log
866      Species
867      RRHO
868      Geometry [angstrom]      24
869      C      0.1272836176      -0.0980909414      0.0670793598
870      C      0.0279854388      0.0213509486      1.5821135859
871      C      1.3835889491      0.0984857464      2.2500008907
872      O      2.0269096879      1.2916311462      1.8039833799
873      C      3.3337453847      1.3952720573      2.1124981028
874      O      3.6166046274      1.1274510121      3.4189133337
875      C      4.9980333045      1.2117165474      3.7299873392
876      C      5.1817389474      0.8741978383      5.1936050221
877      C      4.7454822632      -0.5486370162      5.5184559671
878      H      0.6529940289      0.759264736      -0.34960684
879      H      -0.8595000208      -0.1501063095      -0.390892139
880      H      0.6769159573      -0.9978869925      -0.2138784206
881      H      -0.5423450774      0.9113322552      1.8545255462
882      H      -0.5030175413      -0.8373060581      1.9976095994
883      H      1.2897134088      0.1217870336      3.3364092777
884      H      2.007070188      -0.7597531465      1.976608288
885      H      3.7899351263      2.2930571471      1.6975225622
886      H      5.5518159502      0.5108555694      3.0962923662
887      H      5.3562597864      2.2239785098      3.5130684671
888      H      6.2351251895      1.0149296251      5.4429878715
889      H      4.6126339337      1.5896450659      5.7897467152
890      H      5.3203591415      -1.2709566824      4.9367779445

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```
891 H 4.8905822352 -0.7744307183 6.57384944
892 H 3.6923498108 -0.689415 5.2803319621
893 Core RigidRotor
894 SymmetryFactor 1.0
895 End
896 Rotor Hindered
897 Group 10 11 12
898 Axis 1 2
899 Symmetry 3
900 Potential[kcal/mol] 2
901 0.0 2.69
902 End
903 Rotor Hindered
904 Group 1 13 14
905 Axis 2 3
906 Symmetry 1
907 Potential[kcal/mol] 6
908 0.0 3.61 0.32 3.59 0.04 4.68
909 End
910 Rotor Hindered
911 Group 2 15 16
912 Axis 3 4
913 Symmetry 1
914 Potential[kcal/mol] 6
915 0.0 0.75 0.44 6.06 0.74 1.48
916 End
917 Rotor Hindered
918 Group 3
919 Axis 4 5
920 Symmetry 1
921 Potential[kcal/mol] 6
922 0.0 1.96 1.51 8.93 8.18 8.19
923 End
924 Rotor Hindered
925 Group 4 17
926 Axis 5 6
927 Symmetry 1
928 Potential[kcal/mol] 6
929 0.0 1.96 1.51 8.93 8.18 8.19
930 End
931 Rotor Hindered
932 Group 5
933 Axis 6 7
934 Symmetry 1
935 Potential[kcal/mol] 6
936 0.0 0.75 0.44 6.06 0.74 1.48
937 End
938 Rotor Hindered
```

```

939      Group          6 18 19
940      Axis           7 8
941      Symmetry       1
942      Potential [kcal/mol] 6
943      0.0  3.61  0.32  3.59  0.04  4.68
944      End
945      Rotor          Hindered
946      Group          22 23 24
947      Axis           9 8
948      Symmetry       3
949      Potential [kcal/mol] 2
950      0.0  2.69
951      End
952      Frequencies [1/cm] 58
953      257.6      296.31
954      326.5      334.78      437.29      506.85      634.41
955      768.03      783.95      889.91      907.31      920.0
956      928.19      940.92      970.58      1013.01      1091.44
957      1104.51      1134.75      1160.39      1178.64      1181.03
958      1230.14      1279.62      1284.11      1291.42      1311.01
959      1315.82      1368.48      1381.21      1390.65      1412.81
960      1414.18      1426.27      1450.29      1481.74      1484.33
961      1499.48      1500.22      1512.21      1512.42      1524.13
962      1526.13      3022.11      3034.86      3056.98      3064.67
963      3065.22      3067.43      3073.44      3101.05      3106.31
964      3107.2      3108.57      3134.29      3135.48      3148.14
965      3150.9
966      !26.47      42.12      54.62      112.86      131.44      149.62
967      185.29      214.02!
968      ZeroEnergy [kcal/mol] 2.2
969      ElectronicLevels [1/cm] 1
970      0 2
971      End
972      End
973      Barrier          B5  W2  W4      # W_CCCO[CH]OCCC_m062x.log
974      Variational
975      RRHO
976      Geometry [angstrom] 24
977      C      0.0016775365      0.0477152333      -0.0034631646
978      C      0.0026649258      -0.0256681971      1.5178652057
979      C      1.403121516      -0.005228173      2.0924647062
980      O      2.099587898      -1.1462140199      1.6274264448
981      C      3.3846321181      -1.2348630967      2.1268126407
982      O      4.0806145508      -2.254386116      1.5556922408
983      C      4.5252960266      -1.8223027733      0.2491909212
984      C      4.7809132083      -0.33349828      0.3225025926
985      H      5.7987233467      -0.0532500445      0.5794113327
986      C      4.1012534193      0.5488097629      -0.6849562218

```



```
980 H 0.4797604706 0.967547668 -0.3456305395
981 H -1.0126640121 0.0298785788 -0.3994240787
982 H 0.5479655371 -0.7944303945 -0.4261361282
983 H -0.5503421534 0.8158802524 1.9392453926
984 H -0.4948325043 -0.9376159465 1.8519324494
985 H 1.9371939708 0.9000023164 1.7735328143
986 H 1.3759178398 -0.0110981967 3.1881151352
987 H 4.0759551745 -0.2463853519 1.532564733
988 H 3.4321593742 -1.2498734644 3.217168969
989 H 5.4089388495 -2.4132423448 0.0180552664
990 H 3.7437988297 -2.0437864837 -0.4819741207
991 H 4.5019642315 0.4025597862 -1.6934805311
992 H 3.0329682556 0.3240354192 -0.7251056543
993 H 4.2219536079 1.6039159716 -0.4391453916
994 Core RigidRotor
995 SymmetryFactor 0.25
996 End
997 Rotor Hindered
998 Group 11 12 13
999 Axis 1 2
1000 Symmetry 3
1001 Potential[kcal/mol] 2
1002 0.0 3.09
1003 End
1004 Rotor Hindered
1005 Group 1 14 15
1006 Axis 2 3
1007 Symmetry 1
1008 Potential[kcal/mol] 6
1009 0.0 4.9 0.26 3.83 0.6 3.73
1010 End
1011 Rotor Hindered
1012 Group 2 16 17
1013 Axis 3 4
1014 Symmetry 1
1015 Potential[kcal/mol] 6
1016 0.0 2.18 1.27 7.3 1.76 2.22
1017 End
1018 Rotor Hindered
1019 Group 3
1020 Axis 4 5
1021 Symmetry 1
1022 Potential[kcal/mol] 6
1023 0.0 3.65 0.32 3.23 0.7 2.19
1024 End
1025 Rotor Hindered
1026 Group 22 23 24
1027 Axis 10 8
```

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1028      Symmetry                3
1029      Potential [kcal/mol]    2
1030      0.0  2.12
1031      End
1032      Frequencies [1/cm]      60
1033      137.68    147.89    252.32    288.74    339.3
1034      389.72    478.33    541.11    564.44    698.93
1035      778.63    815.57    906.93    913.28    928.84
1036      932.87    957.4    1004.99    1081.56    1091.81
1037      1110.75    1128.19    1154.1    1167.76    1181.89
1038      1183.17    1191.33    1265.51    1286.29    1313.15
1039      1334.27    1352.75    1379.64    1401.23    1409.22
1040      1412.48    1426.78    1453.29    1482.98    1488.42
1041      1497.31    1499.67    1511.9    1519.99    1526.03
1042      1706.99    3000.88    3027.45    3041.46    3059.87
1043      3060.49    3071.73    3086.46    3088.99    3106.76
1044      3122.01    3131.53    3131.6    3146.11    3149.38
1045      !49.56    61.62    79.17    203.38    208.68!
1046      ZeroEnergy [kcal/mol]  24.5
1047      ElectronicLevels [1/cm] 1
1048      0  2
1049      End
1050      Tunneling                Eckart
1051      ImaginaryFrequency [1/cm] 1778.2786
1052      WellDepth [kcal/mol]    20.6
1053      WellDepth [kcal/mol]    22.3
1054      End
1055      Bimolecular              P3    # CC=C_E_11-7  +  CCCOC [0]
1056      Fragment    CC=C_E_11-7
1057      RRHO
1058      Geometry [angstrom]      9
1059      C    -0.0044412043    -0.0000110914    0.0103255099
1060      C    0.0031104224    0.0000305649    1.3338548948
1061      H    0.9563842389    0.0000683216    1.853401758
1062      C    -1.2203917251    0.0000297128    2.1942686299
1063      H    0.9129247895    -0.0000084902    -0.5621505225
1064      H    -0.9344963126    -0.0000493071    -0.5458794081
1065      H    -2.1258482562    -0.0000066241    1.589131927
1066      H    -1.2392978378    -0.8765730159    2.8442160417
1067      H    -1.2393345334    0.8766687931    2.8441658868
1068      Core RigidRotor
1069      SymmetryFactor    1.0
1070      End
1071      Rotor                Hindered
1072      Group                1 3
1073      Axis                2 4
1074      Symmetry            3

```

```
1071 Potential [kcal/mol] 2
1072 0.0 2.01
1073 End
1074 Frequencies [1/cm] 20
1075 430.51 596.0 938.41 947.42 967.29
1076 1036.32 1079.5 1195.46 1330.57
1077 1407.13 1454.25 1484.54 1497.22 1742.34
1078 3056.62 3111.88 3138.7 3159.03 3168.59
1079 3248.77
1080 !206.03!
1081 ZeroEnergy [kcal/mol] 0
1082 ElectronicLevels [1/cm] 1
1083 0 1
1084 End
1085 Fragment CCCOC [0]
1086 RRHO
1087 Geometry [angstrom] 15
1088 O 0.0533340676 0.0524975625 0.0276926138
1089 C 0.0247111721 -0.0115849308 1.3707476695
1090 O 1.2527276949 0.0015027426 2.0170390537
1091 C 2.059460825 -1.1279289307 1.7188172707
1092 C 3.3438158934 -1.0246840295 2.5127091364
1093 C 3.1029266468 -1.0437506459 4.0164691369
1094 H -0.5565050223 0.83610001 1.7604186659
1095 H -0.5438276209 -0.9343351991 1.6128169707
1096 H 1.5133966609 -2.0420950005 1.9917873502
1097 H 2.2628029419 -1.1606993273 0.6457993422
1098 H 3.9906011024 -1.8539256038 2.220074996
1099 H 3.8526904915 -0.1037539302 2.2232315106
1100 H 2.6109166569 -1.9703669905 4.3171943809
1101 H 4.039235916 -0.9672944128 4.567330343
1102 H 2.4638926709 -0.2131978417 4.3110017184
1103 Core RigidRotor
1104 SymmetryFactor 1.0
1105 End
1106 Rotor Hindered
1107 Group 1 7 8
1108 Axis 2 3
1109 Symmetry 1
1110 Potential [kcal/mol] 6
1111 0.0 2.35 0.05 3.26 2.17 3.36
1112 End
1113 Rotor Hindered
1114 Group 2
1115 Axis 3 4
1116 Symmetry 1
1117 Potential [kcal/mol] 4
1118 0.0 7.19 0.78 1.44
```

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1117 End
1118 Rotor          Hindered
1119   Group          3 9 10
1120   Axis           4 5
1121   Symmetry       1
1122   Potential [kcal/mol] 6
1123   0.0  3.64  0.35  3.58  0.1  4.82
1124 End
1125 Rotor          Hindered
1126   Group          4 11 12
1127   Axis           5 6
1128   Symmetry       1
1129   Potential [kcal/mol] 6
1130   0.0  2.74  -0.0  2.74  0.0  2.74
1131 End
1132 Frequencies [1/cm] 35
1133   294.3      322.94      469.02      636.93      769.87
1134   806.52
1135   907.93      929.04      963.69      1059.99      1095.67
1136   1133.72     1169.32     1196.54     1240.41     1284.46
1137   1314.35     1354.75     1379.33     1400.27     1413.51
1138   1439.76     1483.62     1500.31     1513.05     1527.32
1139   2886.01     2995.25     3008.58     3063.95     3066.97
1140   3081.76     3107.34     3134.25     3151.03
1141   !49.19      109.4       164.27      212.14!
1142 ZeroEnergy [kcal/mol] 0
1143 ElectronicLevels [1/cm] 1
1144   0 2
1145 End
1146 GroundEnergy [kcal/mol] 23.3
1147 End
1148 Barrier          B6 W2 P3 # TS_CCCOC[0]_CC=C_E13-7_m062x.log
1149 Variational
1150 RRHO
1151 Geometry [angstrom] 24
1152 C 0.0082367959 -0.0441869379 0.0059753787
1153 C 0.0012877635 0.0306977027 1.5276564619
1154 C 1.3995290604 0.0035233363 2.1090445907
1155 O 2.000275203 -1.2316015084 1.7680579448
1156 C 3.2993977733 -1.3895120171 2.2797726508
1157 O 4.1804097252 -0.4146294666 1.9419627494
1158 C 4.8200580787 -0.6441453994 -0.0147294509
1159 C 3.7072363984 -1.0766386767 -0.6515460266
1160 H 2.9919662703 -0.3432056057 -1.0065766931
1161 C 3.3410784044 -2.5088225406 -0.8185420501
1162 H 0.566036095 0.7934312755 -0.4174054118
1163 H -1.0024653667 -0.0129944282 -0.3989466214
1164 H 0.4809803916 -0.9671891022 -0.3284430408

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1161 H -0.488657736 0.9489828608 1.8571969313
1162 H -0.5671407972 -0.8040723505 1.9416660668
1163 H 1.9978045 0.828587059 1.7110081865
1164 H 1.3703792048 0.1059840066 3.201199007
1165 H 3.2651149706 -1.3719602705 3.3857032028
1166 H 3.6150581184 -2.3895680606 1.9606427061
1167 H 5.0838060522 0.401660595 -0.0052685865
1168 H 5.5896713594 -1.3458815357 0.2781676554
1169 H 4.1483605596 -3.1665604552 -0.4986618142
1170 H 2.4483879763 -2.7334815374 -0.2279657349
1171 H 3.1024872558 -2.7323448973 -1.8602750799
1172 Core RigidRotor
1173 SymmetryFactor 1.0
1174 End
1175 Rotor Hindered
1176 Group 11 12 13
1177 Axis 1 2
1178 Symmetry 3
1179 Potential [kcal/mol] 2
1180 0.0 2.99
1181 End
1182 Rotor Hindered
1183 Group 1 14 15
1184 Axis 2 3
1185 Symmetry 1
1186 Potential [kcal/mol] 6
1187 0.0 4.99 0.42 4.06 0.69 3.95
1188 End
1189 Rotor Hindered
1190 Group 2 16 17
1191 Axis 3 4
1192 Symmetry 1
1193 Potential [kcal/mol] 8
1194 0.0 1.98 0.94 7.86 3.59 3.82 1.83 1.86
1195 End
1196 Rotor Hindered
1197 Group 3
1198 Axis 4 5
1199 Symmetry 1
1200 Potential [kcal/mol] 6
1201 0.0 6.47 4.42 6.47 3.72 4.46
1202 End
1203 Rotor Hindered
1204 Group 4 18 19
1205 Axis 5 6
1206 Symmetry 1
1207 Potential [kcal/mol] 4
1208 0.0 16.0 5.47 9.75
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1209 End
1210 Rotor      Hindered
1211   Group          5
1212   Axis           6 7
1213   Symmetry       1
1214   Potential [kcal/mol] 6
1215     0.0  3.34  1.47  1.47  1.37  1.74
1216 End
1217 Rotor      Hindered
1218   Group          22 23 24
1219   Axis           10 8
1220   Symmetry       3
1221   Potential [kcal/mol] 2
1222     0.0  1.93
1223 End
1224 Frequencies [1/cm] 57
1225     211.42     245.7     265.01
1226     311.54     363.73     435.34     463.02     652.32
1227 705.05     769.87     900.58     924.49     931.81
1228     944.29     955.93     968.47     998.52     1048.93
1229 1050.97     1080.33     1121.56     1147.49     1174.74
1230     1186.75     1200.64     1269.22     1283.75     1305.03
1231     1314.91     1375.91     1391.16     1402.91     1408.47
1232     1427.94     1443.65     1461.93     1480.35     1484.63
1233     1496.43     1498.46     1510.64     1529.65     1615.23
1234     2924.46     3011.69     3036.8     3045.37     3058.69
1235     3061.69     3072.12     3102.14     3104.4     3129.94
1236     3136.02     3142.1     3176.1     3180.81     3273.09
1237 !44.32     60.31     72.75     125.79     168.04     181.92
1238 191.09!
1239 ZeroEnergy [kcal/mol] 25.0
1240 ElectronicLevels [1/cm] 1
1241   0 2
1242 End
1243 Tunneling      Eckart
1244 ImaginaryFrequency [1/cm] 434.7994
1245 WellDepth [kcal/mol] 21.1
1246 WellDepth [kcal/mol] 1.7
1247 End
1248 End
1249 !-----
1250 !-----WELL 3 to Products -----
1251 !-----
1252 Barrier      B7  W3  W4  # W_CCCO [CH] OCCC_m062x.log
1253 Variational
1254   RRHO
1255 Geometry [angstrom] 24
1256   C      0.1780002918  -0.0671964137  0.0377491709

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1251  C      0.0625996808   -0.026879569   1.5558361128
1252  C      1.4092024243   0.0720476868   2.2393226673
1253  O      2.0116446525   1.3042283496   1.8553917044
1254  C      3.3205628785   1.4315392093   2.2084321593
1255  O      3.5022032271   1.3118379731   3.5821058089
1256  C      4.8375183462   0.9928689799   3.9300034208
1257  C      5.2085701788   -0.4082407631   3.4415165854
1258  C      5.1217751399   -0.4808865627   1.9389899405
1259  H      4.8035600824   -1.4238844924   1.5077075823
1260  H      5.9535672543   -0.0296245513   1.4040602193
1261  H      0.6693493058   0.8313782968   -0.3312629133
1262  H      -0.8021099066   -0.1384305458   -0.4318238069
1263  H      0.7676303094   -0.9281026129   -0.281967393
1264  H      -0.5439021771   0.825959277    1.866015847
1265  H      -0.4375275206   -0.9248458084   1.9238112198
1266  H      1.3067483951    0.0390699892    3.3247048039
1267  H      2.0626795425   -0.7535775503   1.9306137283
1268  H      4.0813909092   0.4554992998    1.7427890339
1269  H      3.7135197703   2.3725141047    1.8121507511
1270  H      5.523375463    1.7350671718    3.5016190493
1271  H      4.8922781457   1.0621015232    5.0141151076
1272  H      6.2112169049   -0.6453724711   3.8112202498
1273  H      4.5178381471   -1.1170472943   3.9012237673
1274  Core RigidRotor
1275  SymmetryFactor      0.5
1276  End
1277  Rotor      Hindered
1278  Group              12 13 14
1279  Axis                1 2
1280  Symmetry            3
1281  Potential[kcal/mol] 2
1282  0.0  2.67
1283  End
1284  Rotor      Hindered
1285  Group              1 15 16
1286  Axis                2 3
1287  Symmetry            1
1288  Potential[kcal/mol] 6
1289  0.0  3.65  0.35  3.58  0.11  4.85
1290  End
1291  Rotor      Hindered
1292  Group              2 17 18
1293  Axis                3 4
1294  Symmetry            1
1295  Potential[kcal/mol] 6
1296  0.0  3.62  3.52  7.16  2.3  4.35
1297  End
1298  Rotor      Hindered

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1299      Group                3
1300      Axis                  4 5
1301      Symmetry              1
1302      Potential[kcal/mol]    6
1303      0.0  4.34  1.96  3.49  2.51  4.26
1304      End
1305      Frequencies [1/cm]      61
1306      137.43      213.77      281.84      312.2      325.01
398.84
1307      439.85      453.7      491.96      625.21      645.82
768.75      835.27      892.8      901.75      926.95
1308      933.8      964.43      983.42      1045.88      1086.19
1091.89      1117.92      1142.79      1169.43      1180.56
1309      1198.71      1249.45      1257.22      1281.48      1303.56
1313.76      1360.67      1366.41      1382.13      1407.28
1310      1412.88      1424.63      1451.48      1456.04      1480.58
1482.44      1499.74      1511.8      1512.2      1526.22
1311      1584.42      3013.39      3020.91      3037.01      3055.89
3063.9      3067.95      3097.22      3101.18      3106.34
1312      3112.89      3133.5      3134.98      3150.67      3198.43
1313      !29.75      65.87      78.98      178.46!
1314      ZeroEnergy[kcal/mol]    21.8
1315      ElectronicLevels [1/cm]  1
1316      0  2
1317      End
1318      Tunneling                Eckart
1319      ImaginaryFrequency [1/cm] 1763.4704
1320      WellDepth[kcal/mol]      15.8
1321      WellDepth[kcal/mol]      19.6
1322      End
1323      End
1324      Bimolecular      P4      # CCCOCO[CH2] + C=C
1325      Fragment CCCOCO[CH2]
1326      RRHO
1327      Geometry[angstrom]      18
1328      C      0.0311661217      0.0273945471      -0.0073920717
1329      O      0.0008726024      -0.0003344328      1.3470971999
1330      C      1.2718969625      -0.0010868223      1.9625522936
1331      O      2.0371738652      -1.0984453087      1.6053349774
1332      C      1.5046898095      -2.3365310186      2.0569645026
1333      C      2.3492102059      -3.4541398315      1.4846601166
1334      C      2.3025725506      -3.4829732554      -0.0378694179
1335      H      -0.9417292694      -0.0219034321      -0.4666927815
1336      H      0.9209060385      -0.3283557532      -0.5065696589
1337      H      1.8325501568      0.8825769852      1.6535709655
1338      H      1.0659106826      0.0161076734      3.0355048638
1339      H      1.5127942182      -2.3523341223      3.1526831659
1340      H      0.4678291934      -2.4341429204      1.7204628624

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1341 H 3.3773835247 -3.3296150904 1.8290629402
1342 H 1.9846590054 -4.3981463638 1.8940489802
1343 H 2.7040927723 -2.5582183692 -0.4491108344
1344 H 2.8824681573 -4.3140906107 -0.4365831457
1345 H 1.2744294983 -3.5876778898 -0.389485947
1346 Core RigidRotor
1347 SymmetryFactor 1.0
1348 End
1349 Rotor Hindered
1350 Group 8 9
1351 Axis 1 2
1352 Symmetry 1
1353 Potential[kcal/mol] 6
1354 0.0 4.95 0.1 0.21 0.02 4.6
1355 End
1356 Rotor Hindered
1357 Group 1
1358 Axis 2 3
1359 Symmetry 1
1360 Potential[kcal/mol] 6
1361 0.0 4.26 2.5 2.86 2.44 3.18
1362 End
1363 Rotor Hindered
1364 Group 2 10 11
1365 Axis 3 4
1366 Symmetry 1
1367 Potential[kcal/mol] 8
1368 0.0 7.1 2.28 2.38 2.11 4.66 3.93 4.87
1369 End
1370 Rotor Hindered
1371 Group 3
1372 Axis 4 5
1373 Symmetry 1
1374 Potential[kcal/mol] 8
1375 0.0 1.83 1.29 1.32 1.19 7.27 2.94 3.12
1376 End
1377 Rotor Hindered
1378 Group 4 12 13
1379 Axis 5 6
1380 Symmetry 1
1381 Potential[kcal/mol] 6
1382 0.0 4.98 0.13 3.74 0.48 3.62
1383 End
1384 Rotor Hindered
1385 Group 5 14 15
1386 Axis 6 7
1387 Symmetry 1
1388 Potential[kcal/mol] 6
```

```
1389      0.0  2.64  0.0  2.64  0.0  2.64
1390      End
1391      Frequencies [1/cm]      42
1392      302.98      320.4      403.52      484.76
1393      547.99      651.91      771.94      901.65      924.85
1394      964.05      992.83      1089.89      1113.29      1146.62
1395      1185.12      1193.4      1241.82      1269.08      1286.98
1396      1309.09      1347.55      1378.42      1412.76      1430.59
1397      1447.63      1484.95      1492.6      1497.44      1511.48
1398      1521.44      1528.95      3024.07      3057.9      3061.28
1399      3063.87      3075.38      3106.52      3116.5      3132.47
1400      3148.95      3164.17      3304.07
1401      !38.26      72.94      136.42      190.27      212.06      270.87!
1402      ZeroEnergy [kcal/mol]      0
1403      ElectronicLevels [1/cm]      1
1404      0  2
1405      End
1406      Fragment  C=C
1407      RRHO
1408      Geometry [angstrom]      6
1409      C      0.00000000      0.00000000      0.00000000
1410      H      0.00000000      0.00000000      1.08216909
1411      H      0.96588500      0.00000000      -0.48801240
1412      C      -1.12558139      -0.00000000      -0.69239269
1413      H      -1.12558139      -0.00000000      -1.77456178
1414      H      -2.09146639      -0.00000000      -0.20438028
1415      Core      RigidRotor
1416      SymmetryFactor      2
1417      End
1418      Frequencies [1/cm]      12
1419      829.14  990.4  1002.92  1070.96  1243.08  1388.11  1473.77  1718.56
1420      3159.71  3175.83  3235.53  3261.92
1421      !!torsions
1422      ZeroEnergy [kcal/mol]      0
1423      ElectronicLevels [1/cm]      1
1424      0  1
1425      End
1426      GroundEnergy [kcal/mol]      26.0
1427      End
1428      Barrier      B8  W3  P4      # TS_C=C_CCCOCO [CH2] _E26_m062x.log
1429      Variational
1430      RRHO
1431      Geometry [angstrom]      24
1432      C      0.0015933747      0.0000014138      0.0035392005
1433      C      0.0006558822      0.0009953422      1.5266282417
1434      C      1.3979507206      -0.0028765102      2.1081622597
1435      O      2.0667982075      1.1782752931      1.6855191368
1436      C      3.3851282544      1.2524974518      2.1063561057
```

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1432   O      3.5147016605   1.4139628202   3.4981727382
1433   C      3.1056148385   2.6218344363   3.9824718183
1434   C      0.9121834886   2.5883630207   4.4226582797
1435   C      0.5295685905   3.7148319043   5.065368704
1436   H      0.2236691434   4.5975545296   4.5208540968
1437   H      0.5716947109   3.7932301797   6.1430771723
1438   H      0.5157791633   0.879755479    -0.3792566823
1439   H     -1.0133258758    -0.0021895913   -0.3912219649
1440   H      0.514014336    -0.8831926412   -0.3817301337
1441   H     -0.530918643     0.8765707059   1.9045591329
1442   H     -0.5244552338    -0.8768906286   1.907739157
1443   H      1.368017764     -0.0384697763   3.1998972061
1444   H      1.9603260063    -0.8763831273   1.7533708186
1445   H      3.9272656625     0.3326564034   1.8729997662
1446   H      3.8266894116     2.1087168353   1.5918247277
1447   H      3.4629732991     2.8007843444   4.986176226
1448   H      3.1333689348     3.4497521014   3.279753961
1449   H      0.7423325661     2.4719377359   3.3602548392
1450   H      1.0841678559     1.6743592897   4.97824026
1451   Core RigidRotor
1452       SymmetryFactor      1.0
1453   End
1454   Rotor      Hindered
1455       Group                12 13 14
1456       Axis                  1 2
1457       Symmetry                3
1458       Potential [kcal/mol]    2
1459       0.0  2.73
1460   End
1461   Rotor      Hindered
1462       Group                1 15 16
1463       Axis                  2 3
1464       Symmetry                1
1465       Potential [kcal/mol]    6
1466       0.0  3.48  0.29  3.21  0.14  4.69
1467   End
1468   Rotor      Hindered
1469       Group                2 17 18
1470       Axis                  3 4
1471       Symmetry                1
1472       Potential [kcal/mol]    8
1473       0.0  4.12  3.52  6.61  2.3  2.8  2.22  2.44
1474   End
1475   Rotor      Hindered
1476       Group                3
1477       Axis                  4 5
1478       Symmetry                1
1479       Potential [kcal/mol]    6

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```
1480      0.0  11.0  4.74  5.24  3.41  4.25
1481 End
1482 Rotor      Hindered
1483   Group                4 19 20
1484   Axis                  5 6
1485   Symmetry              1
1486   Potential[kcal/mol]   6
1487     0.0  8.67  2.89  3.11  2.97  3.73
1488 End
1489 Rotor      Hindered
1490   Group                5
1491   Axis                  6 7
1492   Symmetry              1
1493   Potential[kcal/mol]   4
1494     0.0  4.85  0.87  6.02
1495 End
1496 Rotor      Hindered
1497   Group                6 21 22
1498   Axis                  7 8
1499   Symmetry              1
1500   Potential[kcal/mol]   6
1501     0.0  1.13  0.48  2.39  0.11  1.59
1502 End
1503 Frequencies [1/cm]      58
1504     220.08      286.59      296.93
1505     320.08      391.21      431.29      497.65      578.89
1506 654.7      768.85      826.38      846.57      888.05
1507     899.47      927.95      961.77      997.18      1001.26
1508 1040.6      1090.6      1113.09      1143.18      1180.12
1509     1193.27      1238.41      1240.52      1263.17      1283.32
1510     1308.6      1313.88      1350.93      1381.36      1414.34
1511     1427.66      1450.58      1469.31      1482.91      1487.48
1512     1499.89      1512.1      1519.84      1529.01      1591.18
1513     3011.61      3053.0      3063.52      3066.83      3085.34
1514     3104.75      3107.32      3109.68      3133.64      3149.64
1515     3151.14      3167.6      3232.3      3250.11      3260.29
1516     !41.33      60.43      81.11      84.5      117.8      136.51
1517     187.67!
1518 ZeroEnergy[kcal/mol]    33.2
1519 ElectronicLevels [1/cm]  1
1520     0  2
1521 End
1522 Tunneling      Eckart
1523 ImaginaryFrequency [1/cm]  493.4911
1524 WellDepth[kcal/mol]     27.2
1525 WellDepth[kcal/mol]     7.2
1526 End
1527 End
```

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1522 !-----
1523 !-----WELL 4 to Products -----
1524 !-----
1525 Bimolecular      P5      # Bi_CCCOC=O_E4-4  +  CC[CH2]_E6-5
1526   Fragment      Bi_CCCOC=O_E4-4
1527     RRHO
1528   Geometry[angstrom]      14
1529     C      0.0240964182      0.0095221715      0.0177319524
1530     C      -0.0030425293      -0.0039903355      1.5406932512
1531     C      1.3810526487      0.0075489273      2.1477852797
1532     O      2.0145018277      1.2430203364      1.7720768004
1533     C      3.2624172943      1.4051392265      2.20525629
1534     O      3.8765204621      0.6198108646      2.8648746235
1535     H      0.5240548293      0.9039028938      -0.3506417673
1536     H      -0.9838521124      -0.009648659      -0.3935102324
1537     H      0.5610273437      -0.858905151      -0.3666945599
1538     H      -0.5595170156      0.8555979426      1.9180905613
1539     H      -0.514632694      -0.8978448249      1.9021761279
1540     H      1.3548784005      -0.0512964009      3.2356710446
1541     H      1.9904306763      -0.8198792418      1.7803288283
1542     H      3.6490536234      2.3730992117      1.8666815551
1543   Core RigidRotor
1544     SymmetryFactor      1.0
1545   End
1546   Rotor      Hindered
1547     Group      7 8 9
1548     Axis      1 2
1549     Symmetry      3
1550     Potential[kcal/mol]      2
1551     0.0  2.75
1552   End
1553   Rotor      Hindered
1554     Group      1 10 11
1555     Axis      2 3
1556     Symmetry      1
1557     Potential[kcal/mol]      6
1558     0.0  3.6  0.28  3.6  0.03  4.82
1559   End
1560   Rotor      Hindered
1561     Group      2 12 13
1562     Axis      3 4
1563     Symmetry      1
1564     Potential[kcal/mol]      8
1565     0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
1566   End
1567   Rotor      Hindered
1568     Group      3
1569     Axis      4 5

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1570      Symmetry                1
1571      Potential [kcal/mol]     4
1572      0.0  12.84  5.12  12.83
1573      End
1574      Frequencies [1/cm]      32
1575      299.37      351.0      467.28      768.7      797.8
1576      912.78
1577      922.75      957.98      1065.81      1089.78      1136.59
1578      1180.37      1260.59      1287.64      1312.35      1381.12
1579      1413.84      1417.13      1428.14      1484.81      1501.99
1580      1513.24      1520.99      1852.3      3066.48      3071.27
1581      3076.24      3084.0      3107.9      3126.48      3138.05
1582      3150.08
1583      !55.58      128.77      199.8      261.94!
1584      ZeroEnergy [kcal/mol]   0
1585      ElectronicLevels [1/cm]  1
1586      0  1
1587      End
1588      Fragment  CC[CH2]_E6-5
1589      RRHO
1590      Geometry [angstrom]     10
1591      C      0.0039810468      -0.0002188188      0.0092042733
1592      C      -0.0088483198      0.0002930088      1.5351197712
1593      C      1.3565534595      0.0092394493      2.1204521286
1594      H      0.5040514096      0.8903711756      -0.371400763
1595      H      -1.00586973      -0.025183384      -0.398163844
1596      H      0.541628334      -0.8708029617      -0.3683706538
1597      H      -0.575496772      0.8591900883      1.9045845297
1598      H      -0.5626721837      -0.881435076      1.8869769385
1599      H      1.5205634067      0.2906855121      3.1494183006
1600      H      2.1839808894      -0.4237198291      1.5766300632
1601      Core RigidRotor
1602      SymmetryFactor      1.0
1603      End
1604      Rotor      Hindered
1605      Group                4 5 6
1606      Axis                1 2
1607      Symmetry            3
1608      Potential [kcal/mol]  2
1609      0.0  3.01
1610      End
1611      Rotor      Hindered
1612      Group                1 7 8
1613      Axis                2 3
1614      Symmetry            1
1615      Potential [kcal/mol]  12
1616      0.0  0.05  0.01  0.28  0.26  0.28  0.0  0.05  0.01  0.28  0.26
1617      0.28

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1613 End
1614 Frequencies [1/cm]      22
1615      373.58      453.53      756.21      896.17      928.95
      1053.02      1101.17      1178.18
1616      1271.23      1363.51      1410.57      1469.66      1474.78
      1502.4      1508.75      2984.28      3059.08      3062.57
1617      3130.39      3139.2      3166.94      3270.35
1618      !93.61      253.67!
1619 ZeroEnergy [kcal/mol]      0
1620 ElectronicLevels [1/cm]      1
1621      0 2
1622 End
1623 GroundEnergy [kcal/mol]      -7.9
1624 End
1625 Barrier      B9 W4 P5      # TS_CCCOC=0_CC[CH2]_E10-8_m062x.log
1626 Variational
1627      RRHO
1628 Geometry [angstrom]      24
1629 C      0.0355582487      -0.0169682364      -0.024441075
1630 C      -0.0174643074      0.0319156001      1.497679403
1631 C      1.3377549595      0.0133839198      2.1127552365
1632 O      1.9675796799      -1.6870469738      1.851598868
1633 C      1.1303926374      -2.6232702254      1.8742289959
1634 H      0.5340194479      -2.9258124172      1.0182470626
1635 O      0.6903709664      -3.1886318632      3.0181647772
1636 C      1.4805170906      -2.9522444514      4.1838711104
1637 C      0.9669881192      -3.8564485148      5.2832694929
1638 C      1.1387818653      -5.3333553412      4.9531277396
1639 H      0.5329320481      0.8703898738      -0.4176804113
1640 H      -0.9617894819      -0.0664137513      -0.4588386977
1641 H      0.6018424877      -0.8863596783      -0.3590532796
1642 H      -0.5646478328      0.9191540018      1.8302386245
1643 H      -0.587727851      -0.8235792453      1.881647916
1644 H      2.1236143005      0.5424004711      1.5895613189
1645 H      1.3915417151      0.0993418245      3.1908928274
1646 H      2.527795135      -3.163351405      3.9520223574
1647 H      1.4045370614      -1.9018504516      4.4687781353
1648 H      1.5052610019      -3.6074484959      6.1998255835
1649 H      -0.0858183929      -3.6284183895      5.4596076675
1650 H      2.1914264139      -5.5735874229      4.7960334853
1651 H      0.7667981359      -5.9635921894      5.7595732225
1652 H      0.5973224969      -5.5876727571      4.0435866402
1653 Core RigidRotor
1654      SymmetryFactor      1.0
1655 End
1656 Rotor      Hindered
1657      Group      11 12 13
1658      Axis      1 2

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```
1659 Symmetry 3
1660 Potential [kcal/mol] 2
1661 0.0 2.74
1662 End
1663 Rotor Hindered
1664 Group 1 14 15
1665 Axis 2 3
1666 Symmetry 1
1667 Potential [kcal/mol] 6
1668 0.0 6.53 0.79 2.22 1.17 2.7
1669 End
1670 Rotor Hindered
1671 Group 2 16 17
1672 Axis 3 4
1673 Symmetry 1
1674 Potential [kcal/mol] 6
1675 0.0 3.15 2.32 4.61 1.01 2.11
1676 End
1677 Rotor Hindered
1678 Group 8
1679 Axis 7 5
1680 Symmetry 1
1681 Potential [kcal/mol] 4
1682 0.0 6.95 1.32 6.28
1683 End
1684 Rotor Hindered
1685 Group 9 18 19
1686 Axis 8 7
1687 Symmetry 1
1688 Potential [kcal/mol] 8
1689 0.0 0.52 0.28 7.45 0.76 0.93 0.62 0.8
1690 End
1691 Rotor Hindered
1692 Group 10 20 21
1693 Axis 9 8
1694 Symmetry 1
1695 Potential [kcal/mol] 6
1696 0.0 3.68 0.32 3.63 0.05 4.9
1697 End
1698 Rotor Hindered
1699 Group 22 23 24
1700 Axis 10 9
1701 Symmetry 1
1702 Potential [kcal/mol] 6
1703 0.0 2.7 -0.0 2.7 0.0 2.7
1704 End
1705 Frequencies [1/cm] 58
1706 224.92 262.22 303.5
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1707      313.96      380.55      456.05      466.63      710.75
      722.51      759.25      767.72      811.04      904.7
1708      909.15      922.5      941.85      956.95      979.1
      1085.43      1092.72      1113.51      1133.89      1178.57
1709      1194.17      1199.12      1282.74      1283.18      1310.55
      1349.7      1375.0      1380.35      1412.83      1414.96
1710      1423.73      1473.8      1481.74      1482.86      1485.4
      1500.04      1501.16      1511.52      1512.35      1523.2
1711      3016.66      3055.65      3055.94      3063.73      3064.7
      3067.62      3100.64      3108.27      3130.6      3135.24
1712      3141.82      3145.03      3151.0      3160.53      3233.34
1713      !30.49      35.17      67.64      114.45      125.63      168.78
      194.4!
1714      ZeroEnergy [kcal/mol]      15.8
1715      ElectronicLevels [1/cm]      1
1716      0 2
1717      End
1718      Tunneling      Eckart
1719      ImaginaryFrequency [1/cm]      777.0171
1720      WellDepth[kcal/mol]      13.6
1721      WellDepth[kcal/mol]      23.7
1722      End
1723      End
1724      End

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E.6 CCOC[O]

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1 TemperatureList [K]      500 510 520 530 540 550 560 570 580
      590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750
      760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920
      930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060 1070
      1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200
      1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320 1330
      1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460
      1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580 1590
      1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710 1720
      1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840 1850
      1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980
      1990 2000
2 PressureList [atm]      0.00001 0.001 0.01 0.1 1 10 100.
3 !PressureList [bar]      1.
4 EnergyStepOverTemperature      .2
5 ExcessEnergyOverTemperature      30
6 ModelEnergyLimit [kcal/mol]      400
7 CalculationMethod      direct
8 !CalculationMethod      low-eigenvalue !direct
9 WellCutoff      10
10 ChemicalEigenvalueMax      0.2

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11 Model
12   EnergyRelaxation
13     Exponential
14       Factor [1/cm]           200
15       Power                   .85
16       ExponentCutoff         15
17     End
18   CollisionFrequency
19     LennardJones
20       Epsilons [1/cm]       94.87   292.09   !Ar and CCOC[O]
21       Sigmas [angstrom]     3.33    6.03
22       Masses [amu]          39.88   75.09
23     End
24 !-----
25 !-----WELL 1 to Products -----
26 !-----
27 Well          W1          # W_CCOC[O]_m062x.log
28   Species
29     RRHO
30     Geometry [angstrom]      12
31     O          -0.0000136479   -0.0158947662   0.0001300488
32     C           0.0003804679   -0.0116558615   1.4194515571
33     C           1.4348826083   0.0041591029   1.8907607535
34     C          -1.2747334222   -0.0278957055   -0.5487163989
35     H          -1.1614851697   0.0929277806   -1.6352880151
36     H          -1.8740917079   0.8342817878   -0.1867784254
37     H          -0.5391724883   0.8746145099   1.7772187915
38     O          -2.0241910818   -1.1168828411   -0.3006299029
39     H          -0.5240324399   -0.896234416    1.7892024768
40     H           1.948419974    0.8871976315    1.5138163786
41     H           1.4763606257    0.0127262847    2.9791096444
42     H           1.9577182949   -0.8794154994    1.528544097
43   Core RigidRotor
44     SymmetryFactor          1
45   End
46   Rotor          Hindered
47     Group          4
48     Axis           1 2
49     Symmetry       1
50     Potential [kcal/mol]   8
51     0.0  1.74  0.99  4.51  1.17  1.18  1.07  1.41
52   End
53   Rotor          Hindered
54     Group          5 6 8
55     Axis           4 1
56     Symmetry       1
57     Potential [kcal/mol]   6
58     0.0  2.32  0.0  3.36  2.24  3.36

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59 End
60 Rotor      Hindered
61   Group          10 11 12
62   Axis           3 2
63   Symmetry       3
64   Potential[kcal/mol] 2
65     0.0  3.09
66 End
67 Frequencies [1/cm] 27
68   281.68   401.61   637.56   797.03   825.93
69 885.15   1048.18
70   1081.1   1134.03   1187.87   1193.87   1245.45
71   1310.9   1355.19   1393.15   1409.18   1442.46
72   1487.8   1505.84   1535.9    2884.66   3009.4
73 3011.82   3075.12   3078.04   3151.9    3154.27
74
75 !70.21   146.84   248.71! Torsions
76 ZeroEnergy[kcal/mol] 0
77 ElectronicLevels [1/cm] 1
78   0 2
79 End
80 End
81 Well      W2      # W_CCO[CH]O_m062x.log
82 Species
83   RRHO
84 Geometry[angstrom] 12
85   C      0.0000433788   0.0024700771   -0.0001972596
86   C      0.0000555856   -0.0060724026   1.5095492025
87   O      1.3609586911   -0.0100016927   1.9407270439
88   C      1.5529542565   0.1873578303   3.2577024765
89   O      0.7754147405   -0.6270805274   4.0474432603
90   H      0.5027965156   0.8916338309   -0.3770671566
91   H      -1.0222238956   -0.0077779008   -0.3761901143
92   H      0.5193106247   -0.8752249686   -0.3821236336
93   H      -0.4942982298   0.8805352656   1.9164680211
94   H      -0.508055467    -0.8872933108   1.901618396
95   H      0.8746968719   -0.3531018135   4.9619264266
96   H      2.6096999086   0.2443476066   3.5075233557
97 Core RigidRotor
98   SymmetryFactor 1
99 End
100 Rotor      Hindered
101   Group          6 7 8
102   Axis           1 2
103   Symmetry       3
104   Potential[kcal/mol] 2
105     0.0  3.1
106 End

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104 Rotor      Hindered
105   Group                4
106   Axis                 3 2
107   Symmetry             1
108   Potential [kcal/mol] 6
109   0.0  1.05  0.43  3.78  0.05  1.21
110 End
111 Rotor      Hindered
112   Group                5 12
113   Axis                 4 3
114   Symmetry             1
115   Potential [kcal/mol] 6
116   0.0  3.12  1.53  2.78  2.13  2.67
117 End
118 Rotor      Hindered
119   Group                11
120   Axis                 5 4
121   Symmetry             1
122   Potential [kcal/mol] 6
123   0.0  0.91  0.64  1.57  1.55  1.56
124 End
125 Frequencies [1/cm]    26
126   295.7      388.13      632.61      818.14      868.85
127   956.6
128   1061.23     1129.08     1139.35     1185.94     1203.81
129   1306.09     1325.06     1392.69     1417.9      1443.11
130   1487.63     1505.16     1533.66     3050.46     3073.56
131   3104.54     3122.4      3150.03     3153.21     3906.57
132   !61.97      154.12      229.46      246.96!
133 ZeroEnergy [kcal/mol] -8.0
134 ElectronicLevels [1/cm] 1
135   0  2
136 End
137 Barrier      B1  W1  W2  # W_CC0 [CH] 0_m062x.log
138 Variational
139   RRHO
140   Geometry [angstrom] 12
141   C      -0.000495912  -0.0129654119  -0.001674686
142   C      0.0016077345  0.0396372445  1.5064494001
143   O      1.3644538144  0.0385229135  1.9358970487
144   C      1.5650231361  0.1847645992  3.2573361323
145   O      0.6563462207  -0.3015643612  4.1463779212
146   H      0.5197404715  0.8487322661  -0.4163625889
147   H      -1.0242354078  -0.0151333828  -0.3731718261
148   H      0.4966091561  -0.9170525219  -0.3494129069
149   H      -0.4803039534  0.9497488699  1.8775900663

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149   H          -0.5156237198   -0.8134623023   1.94316343
150   H          0.8396393715    0.8946228362    4.0485015736
151   H          2.6226861131    0.1265612566    3.5050854493
152   Core RigidRotor
153       SymmetryFactor      0.5
154   End
155   Rotor          Hindered
156       Group                6 7 8
157       Axis                  1 2
158       Symmetry              3
159       Potential [kcal/mol]   2
160       0.0  3.1
161   End
162   Rotor          Hindered
163       Group                4
164       Axis                  3 2
165       Symmetry              1
166       Potential [kcal/mol]   6
167       0.0  1.46  0.33  6.63  0.48  1.66
168   End
169   Rotor          Hindered
170       Group                2
171       Axis                  3 4
172       Symmetry              1
173       Potential [kcal/mol]   4
174       0.0  6.39  2.86  5.3
175   End
176   Frequencies [1/cm]      26
177       279.4      384.9      650.65      756.54      822.09
878.14      1012.36
178       1064.16      1138.55      1186.18      1188.04      1279.22
       1311.71      1381.02      1403.58      1436.45      1490.02
179       1505.09      1531.23      2323.33      3044.84      3075.33
       3117.39      3132.2      3152.64      3155.74
180       !86.45      184.54      242.61!
181   ZeroEnergy [kcal/mol]   24.9
182   ElectronicLevels [1/cm]  1
183       0  2
184   End
185   Tunneling                Eckart
186   ImaginaryFrequency [1/cm] 1814.2957
187   WellDepth [kcal/mol]     24.9
188   WellDepth [kcal/mol]     32.9
189   End
190 End
191 Well          W3          # W_C[CH]OCO_m062x.log
192   Species
193       RRHO

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194 Geometry [angstrom]      12
195 C      0.0004564886      -0.0000249976      -0.000991796
196 C      -0.000737671      0.0130950412      1.4790860616
197 O      1.2433878871      -0.0123497744      2.0435730865
198 C      1.2481614968      -0.0486442093      3.4482040185
199 O      0.754882183      -1.2515320109      3.9529452249
200 H      0.6357579886      0.7967984946      -0.3909132844
201 H      -1.0092294668      0.1421233641      -0.3814256615
202 H      0.383274109      -0.9462746894      -0.4027243023
203 H      1.3381403125      -1.9616079289      3.6698040167
204 H      -0.7901844682      -0.4555533757      2.0539256901
205 H      2.2848377266      0.1242307419      3.7374850965
206 H      0.6013924262      0.7346113427      3.8465078376
207 Core RigidRotor
208     SymmetryFactor      1
209 End
210 Rotor      Hindered
211     Group      6 7 8
212     Axis      1 2
213     Symmetry      1
214     Potential [kcal/mol]      6
215     0.0  1.35  0.0  1.35  0.0  1.35
216 End
217 Rotor      Hindered
218     Group      4
219     Axis      3 2
220     Symmetry      1
221     Potential [kcal/mol]      6
222     0.0  3.98  1.7  2.57  1.45  4.53
223 End
224 Rotor      Hindered
225     Group      5 11 12
226     Axis      4 3
227     Symmetry      1
228     Potential [kcal/mol]      6
229     0.0  2.92  2.25  3.03  0.88  5.82
230 End
231 Rotor      Hindered
232     Group      9
233     Axis      5 4
234     Symmetry      1
235     Potential [kcal/mol]      4
236     0.0  3.79  1.87  3.45
237 End
238 Frequencies [1/cm]      26
239     192.58      412.79      581.44      643.53      900.2
1023.24

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240      1054.01      1105.96      1115.94      1165.06      1233.43
      1315.86      1382.36      1394.78      1429.31      1465.7
241      1470.31      1495.98      1533.53      3008.62      3072.48
      3090.17      3127.17      3146.72      3183.56      3870.29
242
243      !81.75      136.16      278.45      371.56! Torsions
244      ZeroEnergy[kcal/mol]      -9.8
245      ElectronicLevels [1/cm]      1
246      0 2
247      End
248      End
249      Barrier      B2  W1  W3      # W_C[CH]OCO_m062x.log
250      Variational
251      RRHO
252      Geometry[angstrom]      12
253      C      -0.0028669845      0.0124688762      0.0329675519
254      C      0.0296622093      0.0145978304      1.524947518
255      O      1.3231640274      0.0322625014      2.0472670249
256      C      1.1651753608      0.7495049941      3.2565127917
257      O      0.3086696827      1.8090378537      2.9743251821
258      H      0.5451798726      0.8683853881      -0.3560561568
259      H      -1.027316072      0.0357601353      -0.3337583574
260      H      0.4765682159      -0.8963906411      -0.3391791118
261      H      -0.3450618306      1.098537956      2.0202827976
262      H      -0.6152742937      -0.7238595711      2.0162037757
263      H      0.7459317725      0.0796102228      4.0201803272
264      H      2.1325603922      1.1377591664      3.5798597608
265      Core RigidRotor
266      SymmetryFactor      0.5
267      End
268      Rotor      Hindered
269      Group      6 7 8
270      Axis      1 2
271      Symmetry      3
272      Potential[kcal/mol]      2
273      0.0 2.36
274      End
275      Frequencies [1/cm]      28
276      138.51      266.44      425.96      548.14      712.57
      841.13      900.44      1007.32      1097.43
277      1114.53      1144.01      1160.76      1173.86      1258.84
      1305.05      1373.9      1410.55      1426.9      1478.35
278      1488.98      1541.2      1888.35      2993.62      3036.13
      3056.7      3098.98      3129.49      3162.73
279      !206.95! Torsions
280      ZeroEnergy[kcal/mol]      20.3
281      ElectronicLevels [1/cm]      1
282      0 2

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283 End
284 Tunneling Eckart
285 ImaginaryFrequency [1/cm] 1776.8973
286 WellDepth[kcal/mol] 20.3
287 WellDepth[kcal/mol] 30.1
288 End
289 End
290 Well W4 # W_[CH2]COCO_m062x.log
291 Species
292 RRHO
293 Geometry[angstrom] 12
294 C 0.0020189982 0.0160214494 0.0079808931
295 C -0.0011068789 -0.0107611031 1.491695066
296 O 1.3138665327 -0.0044799478 2.0340728911
297 C 1.9504732489 1.2341013732 1.9297213108
298 O 1.3752386068 2.2050155801 2.7591146397
299 H 1.4665801644 1.9092547911 3.6694630063
300 H -0.8305830737 0.4279129436 -0.5405010272
301 H 0.7545916178 -0.5440867673 -0.5269618518
302 H -0.5787944972 0.8243553346 1.8972422432
303 H -0.4567196771 -0.9333686733 1.8667518137
304 H 2.9943151448 1.0495217498 2.1874254768
305 H 1.8770537949 1.6324342886 0.9147145292
306 Core RigidRotor
307 SymmetryFactor 1
308 End
309 Rotor Hindered
310 Group 7 8
311 Axis 1 2
312 Symmetry 1
313 Potential[kcal/mol] 4
314 0.0 1.66 0.0 1.66
315 End
316 Rotor Hindered
317 Group 4
318 Axis 3 2
319 Symmetry 1
320 Potential[kcal/mol] 6
321 0.0 1.89 0.52 1.89 1.03 3.18
322 End
323 Rotor Hindered
324 Group 5 11 12
325 Axis 4 3
326 Symmetry 1
327 Potential[kcal/mol] 6
328 0.0 3.75 3.08 3.82 1.25 7.35
329 End
330 Rotor Hindered
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331      Group                6
332      Axis                 5 4
333      Symmetry             1
334      Potential [kcal/mol] 4
335      0.0  3.8  1.97  4.01
336      End
337      Frequencies [1/cm]   26
338      197.85      461.35      526.27      597.23      848.63
339      942.06
339      1053.71      1061.06      1104.25      1133.55      1168.91
340      1279.69      1325.05      1390.63      1393.54      1453.75
340      1459.94      1493.77      1531.99      3027.43      3060.81
341      3073.6      3111.96      3173.81      3283.94      3869.91
342      !79.29      187.13      313.1      359.39!
343      ZeroEnergy [kcal/mol] -3.0
344      ElectronicLevels [1/cm] 1
345      0 2
346      End
347      End
348      Barrier      B3  W1  W4      # W_ [CH2]COCO_m062x.log
349      Variational
350      RRHO
351      Geometry [angstrom] 12
352      C              0.0330815491      -0.0299443728
353      0.0032413357
354      C              0.0505711386      -0.0132639494
355      1.5137513189
356      O              1.3822464438      0.0067349515      1.998019554
357      C              2.0678044661      -1.1106234354
358      1.5006877424
359      O              2.226632952      -1.0574978407
360      0.1250709843
361      H              1.0539801123      -0.7130359604
362      -0.2491314131
363      H              0.2848761441      0.9186162715
364      -0.4624067274
365      H              -0.8201809608      -0.5218149587
366      -0.4546175024
367      H              -0.4337242566      0.878778394
368      1.9119831239
369      H              -0.4694162922      -0.8932364273
370      1.9095650939
371      H              3.0707064228      -1.0985879864      1.935888386
372      H              1.5384364757      -2.0243473483
373      1.8090746643
374      Core RigidRotor
375      SymmetryFactor      1

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366 End
367 Frequencies [1/cm]      29
368      178.48 365.86 424.71 493.28 579.88 723.75 857.66 921.55
1016.75 1065.85 1096.36 1132.22 1144.87 1191.2 1255.59 1284.64
1319.16 1382.08 1425.69 1454.3 1497.77 1508.5 1563.7 2984.23 3027.42
3079.43 3103.38 3117.44 3202.21
369  ! !
370 ZeroEnergy [kcal/mol]      16.7
371 ElectronicLevels [1/cm]    1
372      0 2
373 End
374 Tunneling                  Eckart
375 ImaginaryFrequency [1/cm]  1627.79
376 WellDepth [kcal/mol]      16.70
377 WellDepth [kcal/mol]      19.7
378 End
379 End
380 Bimolecular      P1      # C=O  +  CC[O]
381 Fragment  C=O
382      RRHO
383 Geometry [angstrom]      4
384      O      -0.000000016      -0.0000022088      0.0061054213
385      C      -0.0000000144      0.0000068137      1.2014608526
386      H      0.9375275336      -0.0000022726      1.7838372267
387      H      -0.9375275608      0.0000246367      1.7838372291
388 Core RigidRotor
389      SymmetryFactor      2
390 End
391 Frequencies [1/cm]      6
392      1216.69      1279.34      1545.84      1876.79      2940.94
3011.91
393  !!
394 ZeroEnergy [kcal/mol]      0
395 ElectronicLevels [1/cm]    1
396      0 1
397 End
398 Fragment  CC[O]
399      RRHO
400 Geometry [angstrom]      6
401      C      0.0155365932      -0.0000000007      0.0171987239
402      C      0.0029660543      0.0000000002      1.5560358386
403      O      1.3181854365      -0.0000000006      1.942937121
404      H      -1.0120743165      0.0000000013      -0.3413302391
405      H      0.5253156863      0.8861747108      -0.3533063308
406      H      -0.5179168516      0.8981336306      1.9058855675
407 Core RigidRotor
408      SymmetryFactor      1
409 End
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410 Rotor      Hindered
411   Group                4 5 6
412   Axis                  1 2
413   Symmetry              1
414   Potential [kcal/mol]  6
415   0.0  2.34  0.0  2.35  0.0  2.34
416 End
417 Frequencies [1/cm]      17
418   389.37   759.82   914.81   971.51   1034.8
1156.42   1266.06   1316.76   1389.99
419   1481.94   1503.1   1546.86   3008.76   3055.73
   3081.36   3164.27   3170.31
420 !244.47! Torsions
421 ZeroEnergy [kcal/mol]   0
422 ElectronicLevels [1/cm] 1
423   0  2
424 End
425 GroundEnergy [kcal/mol] 18.5
426 End
427 Barrier      B4  W1  P1  # TS_CC[0]+C=0_m062x.log
428 Variational
429   RRHO
430 Geometry [angstrom]     12
431 C      -0.0036292853    -0.0069715059    -0.004787059
432 C      0.0055451657     0.0052156433     1.5095753484
433 O      1.2868547532     0.0024082279     2.0619025642
434 C      1.8908586856     1.6659620251     2.4563858684
435 O      1.8277593448     2.1202822645     1.3025123835
436 H      0.4085951259     0.9309296114     -0.3722360157
437 H     -1.0208202027     -0.1248729846     -0.3780202194
438 H      0.6062373243     -0.8280072188     -0.3778300604
439 H     -0.5884670004     0.8292628686     1.9170835203
440 H     -0.4257465282     -0.9279039418     1.9043200986
441 H      1.1205153644     1.9238811198     3.1964227131
442 H      2.8458432615     1.3250549017     2.8724518577
443 Core RigidRotor
444   SymmetryFactor      1
445 End
446 Rotor      Hindered
447   Group                6 7 8
448   Axis                  1 2
449   Symmetry              3
450   Potential [kcal/mol]  2
451   0.0  2.91
452 End
453 Rotor      Hindered
454   Group                1 9 10
455   Axis                  2 3

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456     Symmetry                1
457     Potential [kcal/mol]    6
458     0.0  1.91  1.32  2.23  0.59  4.2
459     End
460     Rotor      Hindered
461     Group                5 11 12
462     Axis                 4 3
463     Symmetry            1
464     Potential [kcal/mol]  6
465     0.0  2.25  0.60  6.68  4.68  6.26
466     End
467     Frequencies [1/cm]     26
468     281.54      375.03      464.19      776.99      846.6
906.94      1029.11
469     1107.66      1156.08      1220.65      1244.06      1270.16
1389.17      1407.08      1426.16      1466.48      1483.8
470     1503.12      1609.99      2981.16      2984.81      3057.7
3068.11      3071.94      3150.02      3161.37
471     !109.15      130.6      213.03!
472     ZeroEnergy [kcal/mol]  22.9
473     ElectronicLevels [1/cm]  1
474     0  2
475     End
476     Tunneling      Eckart
477     ImaginaryFrequency [1/cm]  620.8219
478     WellDepth [kcal/mol]    22.88
479     WellDepth [kcal/mol]    4.41
480     End
481     End
482     Bimolecular      P2      # CCOC=0 + [H]
483     Fragment      CCOC=0
484     RRHO
485     Geometry [angstrom]    11
486     O      0.0001875982      0.0001810121      -0.0000045809
487     C      0.0000360448      0.0001495603      1.1954700817
488     H      0.9006620095      0.000133797      1.8198581397
489     O      -1.0833263564      0.0001288025      1.9687150237
490     C      -2.3413617547      0.0001474237      1.272369565
491     C      -3.4340641981      0.0001156125      2.3120371537
492     H      -2.3828528182      0.8801670343      0.6309353146
493     H      -2.3828502516      -0.8798347151      0.6308837924
494     H      -3.3624530972      0.8838386974      2.9438172999
495     H      -4.407993839      0.0001325389      1.8247539829
496     H      -3.3624553661      -0.8836477651      2.9437612352
497     Core RigidRotor
498     SymmetryFactor    1
499     End
500     Rotor      Hindered

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501      Group                5
502      Axis                 4 2
503      Symmetry             1
504      Potential [kcal/mol]  4
505      0.0  12.99  5.27  12.99
506      End
507      Rotor      Hindered
508      Group                6 7 8
509      Axis                 5 4
510      Symmetry             1
511      Potential [kcal/mol]  6
512      0.0  1.12  0.01  6.55  0.01  1.12
513      End
514      Rotor      Hindered
515      Group                9 10 11
516      Axis                 6 5
517      Symmetry             1
518      Potential [kcal/mol]  6
519      0.0  3.12  0.0  3.12  0.0  3.12
520      End
521      Frequencies [1/cm]    24
522      237.16      389.93      806.77      814.71      883.19
1062.71      1063.87
523      1145.7      1187.56      1261.98      1310.78      1399.55
      1413.17      1434.43      1490.84      1503.7      1528.65
524      1852.53      3076.3      3081.04      3086.08      3124.94
      3153.11      3158.28
525      !77.65      236.19      344.76!
526      ZeroEnergy [kcal/mol]  18.5
527      ElectronicLevels [1/cm]  1
528      0  1
529      End
530      Fragment      H
531      Atom
532      Mass [amu]      1
533      ElectronicLevels [1/cm]  1
534      0  2
535      End
536      GroundEnergy [kcal/mol]  1.9
537      End
538      Barrier      B5  W1  P2      # TS_CCOC=0+[H]_m062x.log
539      Variational
540      RRHO
541      Geometry [angstrom]  12
542      C      0.0099622992      -0.0195631625      0.0098023554
543      C      -0.005631246      0.0063995797      1.5246746767
544      O      1.3250247148      -0.0080232284      2.0606508365
545      C      1.9729632713      -1.1867030096      1.9862101831

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546 O      1.4433825342   -2.2580708185    1.7381640787
547 H      0.6261873741    0.7917436431   -0.3768624373
548 H     -1.0031151047    0.1041366251   -0.3711757773
549 H      0.3984760925   -0.9681865205   -0.3565643908
550 H     -0.4388342122    0.9295401224    1.9008521432
551 H     -0.5587814771   -0.8411343653    1.926889221
552 H      2.7352069567   -1.0053390519    0.5886432043
553 H      2.9492917892   -1.0945288078    2.4817478997
554 Core RigidRotor
555     SymmetryFactor      1
556 End
557 Rotor      Hindered
558     Group          6 7 8
559     Axis           1 2
560     Symmetry       3
561     Potential[kcal/mol] 2
562     0.0  3.15
563 End
564 Rotor      Hindered
565     Group          4
566     Axis           3 2
567     Symmetry       1
568     Potential[kcal/mol] 6
569     0.0  6.81  0.43  1.64  0.2  1.56
570 End
571 Rotor      Hindered
572     Group          5 11 12
573     Axis           4 3
574     Symmetry       1
575     Potential[kcal/mol] 4
576     0.0  10.83  4.59  11.1
577 End
578 Frequencies [1/cm]      26
579     323.87    440.07    545.76    630.86    760.87
829.12    872.74
580     1035.35    1119.68    1126.8    1192.57    1220.88
     1338.14    1372.07    1397.73    1423.22    1488.94
581     1502.05    1513.24    1675.71    3032.3    3071.74
     3099.68    3141.21    3148.04    3164.57
582     !112.16    206.86    255.04! Torsions
583 ZeroEnergy[kcal/mol]    12.8
584 ElectronicLevels [1/cm] 1
585     0  2
586 End
587 Tunneling      Eckart
588 ImaginaryFrequency [1/cm] 1089.5335
589 WellDepth[kcal/mol]    12.8
590 WellDepth[kcal/mol]    10.9

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591 End
592 End
593 !-----
594 !-----WELL 2 to Products -----
595 !-----
596 Barrier      B6  W2  W3      # W_C[CH]OCO_m062x.log
597 Variational
598 RRHO
599 Geometry [angstrom]      12
600 C      0.0355619539      0.0416762584      0.0370615052
601 C      -0.0112738058      -0.0235741654      1.5299232092
602 O      1.2746920873      -0.0285172415      2.144631517
603 C      1.1666856207      1.2438026194      2.7128464394
604 H      1.0608141319      1.248147706      3.7975014404
605 O      2.1422278535      2.1159992294      2.3288013842
606 H      0.5660877945      0.9357401208      -0.2969715773
607 H      -0.9714225967      0.0654336357      -0.376635257
608 H      0.5582300261      -0.8279853245      -0.3709708399
609 H      -0.0867205469      1.2589641504      2.1246090392
610 H      -0.6878632551      -0.7490294149      1.975811977
611 H      2.4073981864      1.8885376401      1.4312247248
612 Core RigidRotor
613 SymmetryFactor      0.25
614 End
615 Rotor      Hindered
616 Group      7 8 9
617 Axis      1 2
618 Symmetry      3
619 Potential [kcal/mol]      2
620 0.0 2.71
621 End
622 Rotor      Hindered
623 Group      12
624 Axis      6 4
625 Symmetry      1
626 Potential [kcal/mol]      4
627 0.0 3.91 2.05 3.08
628 End
629 Frequencies [1/cm]      27
630 89.62      245.02      409.31      514.2      617.48
631 832.84      899.1      993.24
632 1059.28      1121.72      1137.12      1150.17      1196.6
633 1265.11      1347.5      1368.8      1403.45      1433.0
634 1478.84      1489.73      1911.77      3039.58      3096.91
635 3105.99      3128.46      3146.25      3858.27
636 !214.06      320.78!
637 ZeroEnergy [kcal/mol]      29.1
638 ElectronicLevels [1/cm]      1

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636      0  2
637      End
638      Tunneling                      Eckart
639      ImaginaryFrequency [1/cm]      1975.6035
640      WellDepth[kcal/mol]            37.1
641      WellDepth[kcal/mol]            38.9
642      End
643      End
644      Barrier      B7  W2  W4      # W_[CH2]COCO_m062x.log
645      Variational
646      RRHO
647      Geometry[angstrom]              12
648      C      0.0101776697      0.0085592581      0.0040915509
649      C      0.0135812119      -0.0105137826      1.5083146517
650      O      1.3886575449      0.04579091      1.9380873378
651      C      2.1751066387      -0.6325188378      1.026749986
652      H      2.3048699515      -1.6981934462      1.228032958
653      O      3.3948688613      -0.0457908878      0.8575557741
654      H      1.3356924844      -0.5167646673      0.0074371442
655      H      0.0973026982      0.9818291601      -0.4677619359
656      H      -0.6492832335      -0.676208698      -0.5136874113
657      H      -0.4813661762      0.8405189596      1.9722707519
658      H      -0.4438887183      -0.9283885377      1.8858389625
659      H      3.2669830792      0.9083526515      0.8944641679
660      Core RigidRotor
661      SymmetryFactor                    0.5
662      End
663      Rotor      Hindered
664      Group      12
665      Axis      6 4
666      Symmetry      1
667      Potential[kcal/mol]              4
668      0.0  3.67  3.16  5.22
669      End
670      Frequencies [1/cm]              28
671      120.85      182.09      424.93      542.35      577.84
672      683.07      850.5      904.33      996.03
673      1036.57      1079.59      1118.15      1172.02      1213.2
674      1268.71      1305.3      1373.28      1416.37      1445.65
675      1461.81      1527.09      1726.22      3057.82      3079.46
676      3124.06      3136.64      3227.07      3854.3
677      !360.0!
678      ZeroEnergy[kcal/mol]              16.3
679      ElectronicLevels [1/cm]          1
680      0  2
681      End
682      Tunneling                      Eckart
683      ImaginaryFrequency [1/cm]      1817.3507

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681 WellDepth[kcal/mol]          24.3
682 WellDepth[kcal/mol]          19.3
683 End
684 End
685 Barrier      B8  W2  P2      # TS_CCOC=0_[H]_m062x.log
686 Variational
687 RRHO
688 Geometry[angstrom]          12
689 O                      1.42029000   -0.82782200   -0.43457200
690 C                      1.25749600    0.16903000    0.25069700
691 O                      0.18028600    0.97564900    0.19040600
692 C                      -0.95394600    0.44887800   -0.51255500
693 C                      -1.65739900   -0.62019100    0.29861700
694 H                      0.97604100   -0.57931100    1.63917400
695 H                      2.07872400    0.69940000    0.75225700
696 H                      -1.59624300    1.31068100   -0.67415200
697 H                      -0.62478300    0.05951500   -1.47490300
698 H                      -2.57392700   -0.92257000   -0.20667000
699 H                      -1.02460400   -1.49875600    0.41151600
700 H                      -1.91672200   -0.23788700    1.28556000
701 Core RigidRotor
702 SymmetryFactor          0.5
703 End
704 Rotor      Hindered
705 Group              4
706 Axis              3 2
707 Symmetry          1
708 Potential[kcal/mol] 4
709 0.0 11.1 4.59 10.83
710 End
711 Rotor      Hindered
712 Group              5 8 9
713 Axis              4 3
714 Symmetry          1
715 Potential[kcal/mol] 6
716 0.0 1.56 0.20 1.64 0.43 6.81
717 End
718 Rotor      Hindered
719 Group              10 11 12
720 Axis              5 4
721 Symmetry          3
722 Potential[kcal/mol] 2
723 0.0 3.15
724 End
725 Frequencies [1/cm]    26
726 323.87 440.07 545.76 630.86 760.87
829.12 872.74

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727      1035.35      1119.68      1126.8      1192.57      1220.88
      1338.14      1372.07      1397.73      1423.22      1488.94
728      1502.05      1513.24      1675.71      3032.3      3071.74
      3099.68      3141.21      3148.04      3164.57
729      !112.16      206.86      255.04!
730      ZeroEnergy [kcal/mol]      13.1
731      ElectronicLevels [1/cm]      1
732      0 2
733      End
734      Tunneling      Eckart
735      ImaginaryFrequency [1/cm]      1089.53
736      WellDepth[kcal/mol]      21.1 #change this
737      WellDepth[kcal/mol]      11.2 Change this
738      End
739      End
740      Bimolecular      P3      # O=CO + [CH2]C
741      Fragment      O=CO
742      RRHO
743      Geometry [angstrom]      5
744      O      0.0131557082      0.0000001595      0.0113773429
745      C      0.0039093905      -0.0000001902      1.2040046496
746      O      1.0959786514      0.000000353      1.9766481878
747      H      1.867089127      0.000001062      1.391359079
748      H      -0.896731242      -0.0000010008      1.8269687049
749      Core RigidRotor
750      SymmetryFactor      1.0
751      End
752      Rotor      Hindered
753      Group      1 5
754      Axis      2 3
755      Symmetry      1
756      Potential [kcal/mol]      4
757      0.0 12.62 4.68 12.62
758      End
759      Frequencies [1/cm]      8
760      645.48      1078.39      1164.58      1323.79      1418.04
      1880.73      3099.61      3797.64
761      !682.34!
762      ZeroEnergy [kcal/mol]      0
763      ElectronicLevels [1/cm]      1
764      0 1
765      End
766      Fragment      [CH2]C
767      RRHO
768      Geometry [angstrom]      7
769      C      0.0002983383      -0.0005389889      0.0004031088
770      C      0.0047388604      -0.0084680438      1.4846485597
771      H      1.0125028336      -0.0004449026      -0.404522378

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772   H      -0.4985399523   0.8907396606   -0.4014899118
773   H      -0.5291032253   -0.8632636678   -0.4045194797
774   H      0.770457535    0.5135203684    2.0371553306
775   H      -0.8406008348   -0.3881967978    2.037158663
776   Core RigidRotor
777       SymmetryFactor      1.0
778   End
779   Rotor      Hindered
780       Group              3 4 5
781       Axis                1 2
782       Symmetry            1
783       Potential[kcal/mol]  12
784       0.0  0.07  0.0  0.08  0.0  0.07  0.0  0.08  0.0  0.07  0.0
0.08
785   End
786   Frequencies [1/cm]    14
787       444.91      810.81      982.95      1081.35      1195.68
1403.91      1471.58      1487.61      1489.49
788       3004.53      3085.23      3128.72      3174.72      3276.16
789       !125.25!
790   ZeroEnergy[kcal/mol]    0
791   ElectronicLevels [1/cm]  1
792       0  2
793   End
794   GroundEnergy[kcal/mol]  -18.6
795   End
796   Barrier      B9  W2  P3  # TS_C[CH2]_0=CO_m062x.log
797   Variational
798       RRHO
799   Geometry[angstrom]      12
800   C      0.0044939866   0.0131629173   0.0042243499
801   C      -0.0033355631   -0.0061896502   1.4908118003
802   O      1.7705109138   0.0083192681   1.9801088228
803   C      2.5414097919   0.6942424321   1.2688222001
804   H      3.0337831409   0.3375640884   0.3698523993
805   O      2.6088583844   2.0424052828   1.3982386482
806   H      0.5636645464   0.876656145    -0.3659586897
807   H      -1.006845848   0.0875954588   -0.4017265142
808   H      0.4650166474   -0.8897463421   -0.3962904458
809   H      -0.3747230679   0.8809636764   1.9884967752
810   H      -0.2801187622   -0.9293183723   1.9788268854
811   H      2.1638178298   2.2741450956   2.2222467686
812   Core RigidRotor
813       SymmetryFactor      1.0
814   End
815   Rotor      Hindered
816       Group              7 8 9
817       Axis                1 2

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818      Symmetry                1
819      Potential [kcal/mol]    6
820      0.0  1.23  0.0  1.21  0.0  1.23
821      End
822      Rotor      Hindered
823      Group                1 10 11
824      Axis                 2 3
825      Symmetry             1
826      Potential [kcal/mol]  4
827      0.0  1.76  1.23  1.81
828      End
829      Rotor      Hindered
830      Group                12
831      Axis                 4 6
832      Symmetry             1
833      Potential [kcal/mol]  4
834      0.0  6.8  2.7  8.07
835      End
836      Frequencies [1/cm]     26
837      127.36      263.95      380.69      606.61      715.3
838      767.1      859.18
839      915.31      1046.43      1096.98      1113.96      1225.87
840      1294.76      1338.56      1400.42      1484.91      1488.61
841      1493.35      1512.97      3043.68      3098.61      3130.06
842      3154.48      3174.28      3246.86      3838.56
843      !52.74      175.38      509.41!
844      ZeroEnergy [kcal/mol]   5.8
845      ElectronicLevels [1/cm] 1
846      0 2
847      End
848      Tunneling              Eckart
849      ImaginaryFrequency [1/cm] 786.3561
850      WellDepth [kcal/mol]    13.8
851      WellDepth [kcal/mol]    24.4
852      End
853      End
854      !-----
855      !-----WELL 3 to Products -----
856      !-----
857      Bimolecular      P4      # CC=O_E4-80 + [CH2]O_E4-80
858      Fragment      CC=O_E4-80
859      RRHO
860      Geometry [angstrom]    7
861      C      0.0018814559      0.0000017976      -0.0001381206
862      C      0.0031292531      0.0000006426      1.4991972767
863      H      1.0033145885      0.0000269684      1.9745983086
864      O      -0.9863570005      -0.0000264084      2.1767693385
865      H      -1.0168597697      -0.0000237514      -0.377470613

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863   H          0.540287054   -0.8770154643   -0.3636967341
864   H          0.5402427993   0.8770466646   -0.3636956282
865   Core RigidRotor
866       SymmetryFactor          1.0
867   End
868   Rotor          Hindered
869       Group          5 6 7
870       Axis          1 2
871       Symmetry          3
872       Potential [kcal/mol]          2
873       0.0  1.2
874   End
875   Frequencies [1/cm]          14
876       513.29      776.08      900.41      1138.06      1146.18
877       1379.68      1433.59      1464.85      1474.9
878       1874.28      2942.79      3063.52      3127.31      3180.67
879       !157.82!
880   ZeroEnergy [kcal/mol]          0
881   ElectronicLevels [1/cm]          1
882       0  1
883   End
884   Fragment [CH2]O_E4 -80
885       RRHO
886   Geometry [angstrom]          5
887       C          0.0017120689   0.0006775385   0.0060328527
888       O          0.0003046754   -0.0110369781   1.3662657057
889       H          0.9891031273   0.0055497388   -0.425004445
890       H          -0.8280009474   0.4619203835   -0.510815411
891       H          -0.8993933768   0.068252049   1.6902446555
892   Core RigidRotor
893       SymmetryFactor          1.0
894   End
895   Rotor          Hindered
896       Group          3 4
897       Axis          1 2
898       Symmetry          1
899       Potential [kcal/mol]          4
900       0.0  4.31  0.0  5.13
901   End
902   Frequencies [1/cm]          8
903       605.38      1066.47      1240.91      1364.7      1496.89
904       3154.31      3293.73      3901.11
905       !413.46!
906   ZeroEnergy [kcal/mol]          0
907   ElectronicLevels [1/cm]          1
908       0  2
909   End
910   GroundEnergy [kcal/mol]          0.4

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909 End
910 Barrier      B10  W3  P4      # TS_CC=0_[CH2]O_E19-08_m062x.log
911   Variational
912     RRHO
913   Geometry[angstrom]      12
914   C      0.0012282983      0.000171847      -0.0002578412
915   C      -0.0009891069      0.0001393909      1.494070945
916   H      0.9645484119      -0.0011986766      2.0135991487
917   O      -1.0598667002      0.1071190181      2.1520400767
918   C      -1.6682358888      1.9662294404      2.2833975279
919   O      -0.569364828      2.6892587847      1.9845829764
920   H      0.8931279391      -0.4787582699      -0.4017622807
921   H      -0.019107577      1.0324996439      -0.3667585382
922   H      -0.8880767949      -0.5052235063      -0.375762331
923   H      -2.4136621759      1.9966557738      1.5054523068
924   H      -1.989066137      1.9180641157      3.31385606
925   H      0.0546685291      2.6513114473      2.7153229607
926   Core RigidRotor
927     SymmetryFactor      1.0
928   End
929   Rotor      Hindered
930     Group      7 8 9
931     Axis      1 2
932     Symmetry      3
933     Potential[kcal/mol]      2
934     0.0  0.33
935   End
936   Rotor      Hindered
937     Group      6 10 11
938     Axis      5 4
939     Symmetry      1
940     Potential[kcal/mol]      4
941     0.0  3.93  3.21  3.59
942   End
943   Rotor      Hindered
944     Group      12
945     Axis      6 5
946     Symmetry      1
947     Potential[kcal/mol]      4
948     0.0  3.39  0.63  5.6
949   End
950   Frequencies [1/cm]      26
951     108.25      217.63      436.15      504.11      664.94
952     702.63      911.23
953     941.51      1026.42      1086.7      1122.55      1216.47
954     1343.08      1382.52      1390.42      1464.18      1476.47
955     1513.43      1526.66      3028.89      3034.39      3105.66
956     3150.49      3159.62      3291.15      3869.05

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954      !81.32      91.28      317.16!
955      ZeroEnergy[kcal/mol]      15.1
956      ElectronicLevels [1/cm]      1
957      0 2
958      End
959      Tunneling      Eckart
960      ImaginaryFrequency [1/cm]      656.9909
961      WellDepth[kcal/mol]      24.9
962      WellDepth[kcal/mol]      14.7
963      End
964      End
965      !-----
966      !-----WELL 4 to Products -----
967      !-----
968      Bimolecular      P5      # C=C + OC[O]_E10-83
969      Fragment C=C
970      RRHO
971      Geometry[angstrom]      6
972      C      0.0000005934      -0.0000013257      0.005740686
973      C      -0.00000068      0.0000017949      1.3272371407
974      H      0.9217469077      -0.0000000153      -0.5612441874
975      H      -0.9217446282      -0.0000053139      -0.5612459638
976      H      0.9217445416      0.000005783      1.8942237904
977      H      -0.9217469943      0.0000004844      1.894222014
978      Core RigidRotor
979      SymmetryFactor      4
980      End
981      Frequencies [1/cm]      12
982      829.14      990.39      1002.91      1070.95      1243.09
983      1388.1      1473.76      1718.54      3159.72      3175.83
984      3235.55      3261.94
985      ! !
986      ZeroEnergy[kcal/mol]      0
987      ElectronicLevels [1/cm]      1
988      0 1
989      End
990      Fragment OC[O]_E10-83
991      RRHO
992      Geometry[angstrom]      6
993      O      -0.0179552501      0.0302415143      -0.006361056
994      C      0.0041382763      0.0110589374      1.3314866849
995      O      1.2589086436      0.0840212439      1.9357400001
996      H      -0.5947076421      0.8417540232      1.7323338284
997      H      -0.5341035012      -0.9194312946      1.6108216799
998      H      1.8532698239      -0.5108496864      1.4687292972
999      Core RigidRotor
1000     SymmetryFactor      1.0
1000     End

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1001 Rotor      Hindered
1002   Group                1 4 5
1003   Axis                  2 3
1004   Symmetry              1
1005   Potential[kcal/mol]   6
1006   0.0  0.34  0.0  2.89  2.85  2.89
1007 End
1008 Frequencies [1/cm]      11
1009   558.99   759.52   1020.09   1132.89   1167.89
1010   1315.09   1364.87   1423.56   2878.54
1011   3001.58   3871.87
1012   !222.92!
1013 ZeroEnergy[kcal/mol]   0
1014 ElectronicLevels [1/cm] 1
1015   0  2
1016 End
1017 GroundEnergy[kcal/mol]  14.7
1018 End
1019 Barrier      B11  W4  P5  # TS_OC[O]C=C_E14-13_m062x.log
1020 Variational
1021   RRHO
1022 Geometry[angstrom]      12
1023   C      0.0017283294   0.0009604065   -0.0042823292
1024   H      0.0085101916   0.0061042776   1.0766073696
1025   H      0.9610513573   -0.0026343736   -0.5015232257
1026   C     -1.155823243   0.0864589269   -0.6950038853
1027   O     -1.4137172979   2.1264059571   -0.7865721885
1028   C     -0.30084044   2.7030378402   -1.3076505758
1029   O      0.7494328262   2.8881078541   -0.3913913128
1030   H     -1.1679294103   -0.007854312   -1.7715198108
1031   H     -2.1085252448   0.0060969228   -0.1941930089
1032   H      0.1305888705   2.1416967919   -2.1437788387
1033   H     -0.6517027368   3.6756368555   -1.6973913782
1034   H      0.3557108433   3.2130938657   0.4240661984
1035 Core RigidRotor
1036   SymmetryFactor      1.0
1037 End
1038 Rotor      Hindered
1039   Group                1 8 9
1040   Axis                  4 5
1041   Symmetry              1
1042   Potential[kcal/mol]   4
1043   0.0  2.94  0.35  1.25
1044 End
1045 Rotor      Hindered
1046   Group                7 10 11
1047   Axis                  6 5
1048   Symmetry              1

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1048     Potential [kcal/mol]          4
1049     0.0  10.88  3.32  8.11
1050     End
1051     Rotor      Hindered
1052     Group              12
1053     Axis              7 6
1054     Symmetry          1
1055     Potential [kcal/mol]          6
1056     0.0  2.0  2.0  3.92  3.56  3.82
1057     End
1058     Frequencies [1/cm]      25
1059     205.02      309.72      409.5      574.59      826.52
1060     938.49      972.05
1061     1008.55      1028.23      1056.41      1138.11      1233.16
1062     1242.7      1319.63      1336.84      1422.04      1469.26
1063     1476.69      1604.51      2937.27      3041.72      3174.9
1064     3182.94      3257.42      3281.89      3866.28
1065     !83.87      132.89      265.51!
1066     ZeroEnergy [kcal/mol]      20.1
1067     ElectronicLevels [1/cm]    1
1068     0  2
1069     End
1070     Tunneling      Eckart
1071     ImaginaryFrequency [1/cm]  486.1776
1072     WellDepth[kcal/mol]      23.1
1073     WellDepth[kcal/mol]      5.4
1074     End
1075 End
1076 End

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E.7 CCCOC[O]

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1 TemperatureList [K]          500 510 520 530 540 550 560 570
  580 590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740
  750 760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910
  920 930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060
  1070 1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190
  1200 1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320
  1330 1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450
  1460 1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580
  1590 1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710
  1720 1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840
  1850 1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970
  1980 1990 2000
2 PressureList [atm]          0.00001 0.001 0.01 0.1 1 10
  100.
3 !PressureList [bar]          1.
4 EnergyStepOverTemperature    .2

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5 ExcessEnergyOverTemperature          30
6 ModelEnergyLimit [kcal/mol]          400
7 CalculationMethod                     direct
8 !CalculationMethod                   low-eigenvalue !direct
9 WellCutoff                            10
10 ChemicalEigenvalueMax                0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor [1/cm]                  200 ! He
15       Power                          .85
16       ExponentCutoff                  15
17   End
18   CollisionFrequency
19     LennardJones
20       Epsilons [1/cm]                94.87  304.14 !Ar and CCCOC[O]
21       Sigmas [angstrom]               3.33   6.34
22       Masses [amu]                    39.88  89.11
23     End
24 !-----
25 !-----WELL 1 to Products -----
26 !-----
27 Well          W1          # W_CCCOC[O]
28   Species
29     RRHO
30   Geometry [angstrom]                15
31     O          0.0533340676          0.0524975625          0.0276926138
32     C          0.0247111721          -0.0115849308          1.3707476695
33     O          1.2527276949          0.0015027426          2.0170390537
34     C          2.059460825           -1.1279289307          1.7188172707
35     C          3.3438158934          -1.0246840295          2.5127091364
36     C          3.1029266468          -1.0437506459          4.0164691369
37     H          -0.5565050223          0.83610001            1.7604186659
38     H          -0.5438276209          -0.9343351991          1.6128169707
39     H          1.5133966609          -2.0420950005          1.9917873502
40     H          2.2628029419          -1.1606993273          0.6457993422
41     H          3.9906011024          -1.8539256038          2.220074996
42     H          3.8526904915          -0.1037539302          2.2232315106
43     H          2.6109166569          -1.9703669905          4.3171943809
44     H          4.039235916           -0.9672944128          4.567330343
45     H          2.4638926709          -0.2131978417          4.3110017184
46   Core RigidRotor
47     SymmetryFactor                    1
48   End
49   Rotor          Hindered
50     Group                    1 7 8
51     Axis                    2 3
52     Symmetry                    1

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53     Potential [kcal/mol]          6
54     0.0  2.35  0.05  3.26  2.17  3.36
55 End
56 Rotor      Hindered
57   Group          2
58   Axis           3 4
59   Symmetry       1
60   Potential [kcal/mol]          4
61     0.0  7.19  0.78  1.44
62 End
63 Rotor      Hindered
64   Group          3 9 10
65   Axis           4 5
66   Symmetry       1
67   Potential [kcal/mol]          6
68     0.0  3.64  0.35  3.58  0.1  4.82
69 End
70 Rotor      Hindered
71   Group          4 11 12
72   Axis           5 6
73   Symmetry       1
74   Potential [kcal/mol]          6
75     0.0  2.74  -0.0  2.74  0.0  2.74
76 End
77 Frequencies [1/cm]      35
78     294.3      322.94      469.02      636.93      769.87
806.52
79     907.93      929.04      963.69      1059.99      1095.67
     1133.72      1169.32      1196.54      1240.41      1284.46
80     1314.35      1354.75      1379.33      1400.27      1413.51
     1439.76      1483.62      1500.31      1513.05      1527.32
81     2886.01      2995.25      3008.58      3063.95      3066.97
     3081.76      3107.34      3134.25      3151.03
82     !49.19      109.4      164.27      212.14!
83 ZeroEnergy [kcal/mol]    0.0
84 ElectronicLevels [1/cm]  1
85     0  2
86 End
87 End
88 !-----
89 !-----WELLS 2-----
90 !-----
91 Well      W2      # W_ [CH2]CCOCO
92 Species
93     RRHO
94 Geometry [angstrom]      15
95   C      -0.0007888382      0.0423351303      -0.0027660947
96   C      -0.0026569732      -0.0222994013      1.4810808463

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97      C      1.3954396268      -0.012193007      2.0709667963
98      O      2.0798316791      -1.1633522226      1.6054012759
99      C      3.4067213268      -1.2288520676      2.0233321666
100     O      3.5346401403      -1.4238657135      3.4043393464
101     H      3.1472899944      -2.276518766      3.6218707052
102     H      -0.8603273783      0.4094489955      -0.5414377257
103     H      0.7832224869      -0.4508016972      -0.5563299571
104     H      -0.5682271238      0.8110930702      1.9036203748
105     H      -0.5021093211      -0.9371608412      1.8290169461
106     H      1.9378513661      0.8853714741      1.7486770913
107     H      1.3571743255      -0.0159910203      3.1624496215
108     H      3.8559659857      -2.0468707726      1.4579598384
109     H      3.929077731      -0.2919791707      1.8102347725
110     Core RigidRotor
111         SymmetryFactor      1
112     End
113     Rotor      Hindered
114         Group      8 9
115         Axis      1 2
116         Symmetry      2
117         Potential[kcal/mol]      2
118         0.0 0.65
119     End
120     Rotor      Hindered
121         Group      1 10 11
122         Axis      2 3
123         Symmetry      1
124         Potential[kcal/mol]      6
125         0.0 5.02 0.16 3.47 0.31 3.48
126     End
127     Rotor      Hindered
128         Group      2 12 13
129         Axis      3 4
130         Symmetry      1
131         Potential[kcal/mol]      8
132         0.0 1.32 0.34 6.11 1.08 1.15 0.74 1.0
133     End
134     Rotor      Hindered
135         Group      3
136         Axis      4 5
137         Symmetry      1
138         Potential[kcal/mol]      6
139         0.0 3.91 2.72 3.99 2.05 6.56
140     End
141     Rotor      Hindered
142         Group      4 14 15
143         Axis      5 6
144         Symmetry      1

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145      Potential [kcal/mol]          4
146      0.0  3.57  1.84  3.98
147      End
148      Frequencies [1/cm]          34
149      263.15      335.9      450.62      499.73      628.5
150      770.23      922.4      962.66      1041.24      1062.12
151      1093.67      1113.58      1144.89      1192.39      1230.52
152      1295.08      1310.03      1375.66      1391.93      1419.38
153      1455.23      1459.56      1470.97      1526.03      1534.85
154      2993.96      3018.46      3052.46      3083.16      3088.24
155      3106.21      3179.01      3285.1      3870.83
156      !45.45      116.55      167.27      189.57      368.88!
157      ZeroEnergy [kcal/mol]      -4.9
158      ElectronicLevels [1/cm]    1
159      0  2
160      End
161      End
162      #-----
163      Barrier      B1  W1  W2      # W_[CH2]CCOCO
164      Variational
165      RRHO
166      Geometry [angstrom]          15
167      C      0.0471343566      0.0165551784      -0.0037644318
168      C      0.0143163212      0.0215167537      1.5041082537
169      C      1.4070205885      -0.0018369492      2.1286099
170      O      2.1419884307      1.1888159482      1.9336824731
171      C      2.5605925246      1.4075881583      0.6181389723
172      O      1.5883114589      1.9334120307      -0.210638619
173      H      0.7218224199      1.0045839168      -0.3284352832
174      H      -0.9096865757      0.1880381388      -0.4899977536
175      H      0.5819506228      -0.8266423538      -0.4399525816
176      H      -0.5134895133      0.9059060495      1.8635778249
177      H      -0.5357006684      -0.8534508264      1.8648079513
178      H      1.3271917484      -0.1244099688      3.2072444451
179      H      1.9757431805      -0.8544703514      1.7324844702
180      H      3.3502343755      2.163312085      0.6536722189
181      H      2.9728092338      0.4739652581      0.2070155769
182      Core RigidRotor
183      SymmetryFactor      1
184      End
185      Frequencies [1/cm]          38
186      150.65      195.29      324.56      402.01      458.63
187      519.39      609.89      642.63      819.0      893.89
188      927.38      965.0      1057.26      1076.35      1112.23
189      1127.87      1167.28      1199.69      1254.36      1275.52
190      1303.63      1338.71      1384.58      1405.58      1430.72
191      1455.87      1468.0      1471.78      1480.91      1510.03

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186          2984.38      3005.03      3046.28      3075.74      3092.16
          3108.67      3125.24      3176.81
187      ! !
188      ZeroEnergy [kcal/mol]      11.3
189      ElectronicLevels [1/cm]      1
190      0 2
191      End
192      Tunneling      Eckart
193      ImaginaryFrequency [1/cm]      1560.3939
194      WellDepth [kcal/mol]      11.3
195      WellDepth [kcal/mol]      16.2
196      End
197      End
198      !-----
199      !-----WELLS 3-----
200      !-----
201      Well      W3      # W_C [CH] COCO
202      Species
203      RRHO
204      Geometry [angstrom]      15
205      C      -0.0003548893      0.0015419689      -0.0003085236
206      C      -0.0003519064      -0.0015829022      1.485736156
207      C      1.2853762052      -0.0007448143      2.2369764143
208      O      2.1932106763      -1.0002631954      1.7745101317
209      C      1.8021159842      -2.2998574132      2.101286603
210      O      1.8711999495      -2.5530635343      3.4772671151
211      H      0.1728201785      1.0104926277      -0.3975719067
212      H      -0.9507456963      -0.3425494202      -0.4060523454
213      H      0.7985240253      -0.630387483      -0.3899414723
214      H      2.7864767578      -2.4467754168      3.7520998739
215      H      -0.9084173895      0.2366524593      2.02092318
216      H      1.8237677586      0.9425862606      2.0921971333
217      H      1.1100414512      -0.1243678831      3.3075349303
218      H      0.7619123612      -2.4832727158      1.8203793749
219      H      2.4665305229      -2.9558125592      1.5365383229
220      Core RigidRotor
221      SymmetryFactor      1
222      End
223      Rotor      Hindered
224      Group      7 8 9
225      Axis      1 2
226      Symmetry      3
227      Potential [kcal/mol]      2
228      0.0 0.26
229      End
230      Rotor      Hindered
231      Group      1 11
232      Axis      2 3

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233     Symmetry                1
234     Potential [kcal/mol]    4
235     0.0  4.68  0.46  2.58
236   End
237   Rotor      Hindered
238     Group                2 12 13
239     Axis                 3 4
240     Symmetry             1
241     Potential [kcal/mol]  6
242     0.0  4.14  0.93  1.93  0.91  2.26
243   End
244   Rotor      Hindered
245     Group                3
246     Axis                 4 5
247     Symmetry             1
248     Potential [kcal/mol]  6
249     0.0  7.06  0.58  3.74  2.99  3.6
250   End
251   Rotor      Hindered
252     Group                4 14 15
253     Axis                 5 6
254     Symmetry             1
255     Potential [kcal/mol]  4
256     0.0  3.97  1.6  3.8
257   End
258   Frequencies [1/cm]      34
259     237.15      368.23      386.92      596.38      607.18
260     885.64      924.94      956.34      993.99      1056.17
261     1105.09     1112.35     1155.8      1169.94     1283.64
262     1327.65     1378.38     1390.04     1392.22     1416.91
263     1455.72     1480.35     1489.04     1495.43     1529.74
264     3000.91     3023.66     3057.71     3089.36     3091.45
265     3108.18     3138.14     3207.15     3870.55
266     !46.38      67.34      98.83      201.97      347.27!
267   ZeroEnergy [kcal/mol]   -6.6
268   ElectronicLevels [1/cm]  1
269     0  2
270   End
271   End
272   !-----
273   Barrier      B2  W1  W3      #  W_C [CH] COCO
274   Variational
275   RRHO
276   Geometry [angstrom]     15
277   C      0.0122708786      0.00904156      0.0152456969
278   C      -0.0176660359      0.0293530846      1.5212246116
279   C      1.3294933784      0.0056425315      2.2138303234
280   O      1.2595198607      0.598212452      3.4955347899

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278   C      0.7961776672    1.9173346208    3.3677505012
279   O     -0.5121696781    1.9718317063    2.9238224013
280   H      0.6099317312    0.8321348896   -0.377003671
281   H     -0.9881628705    0.0768434577   -0.4069847715
282   H      0.4604242497   -0.9226483584   -0.3430827717
283   H     -0.475372933    1.0950513045    1.9435975461
284   H     -0.7201762656   -0.6754776804    1.9643140861
285   H      1.6829993468   -1.0159651621    2.3615956415
286   H      2.0682847267    0.5384882161    1.5996286089
287   H      0.814520719    2.3670418002    4.3645756777
288   H      1.4739938326    2.4699198249    2.6993322295
289   Core RigidRotor
290       SymmetryFactor      0.5
291   End
292   Rotor      Hindered
293       Group                7 8 9
294       Axis                  1 2
295       Symmetry              3
296       Potential [kcal/mol]   2
297       0.0  2.24
298   End
299   Frequencies [1/cm]      37
300       114.26    220.14    347.54    392.48    476.3
301   498.74    672.23    794.02    909.59
302       935.35    992.94    1069.32    1084.26    1119.49
303       1129.39    1153.87    1191.83    1261.85    1317.19
304       1330.58    1334.55    1393.86    1410.87    1429.67
305       1488.72    1491.85    1495.96    1508.06    1593.35
306       2976.52    3005.04    3043.31    3073.39    3096.18
307       3108.28    3121.59    3150.93
308       !186.49!
309   ZeroEnergy [kcal/mol]    12.0
310   ElectronicLevels [1/cm]  1
311       0  2
312   End
313   Tunneling      Eckart
314   ImaginaryFrequency [1/cm]  1417.0484
315   WellDepth[kcal/mol]      12.0
316   WellDepth[kcal/mol]      18.6
317   End
318   End
319   !-----
320   !-----WELLS 4-----
321   !-----
322   Well      W4      # W_CC [CH] OCO
323   Species
324       RRHO
325   Geometry [angstrom]      15

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322   C      0.0003569795   0.0020586305   0.0003532474
323   C     -0.0000298536   -0.0013546711   1.5292935205
324   C      1.368719835   -0.0010106197   2.1027893036
325   O      2.1506353068   1.0450770468   1.7012980214
326   C      3.4406480251   1.0619505147   2.2586316308
327   O      3.4258183243   1.309410035    3.6307438825
328   H      0.5278495072   0.8762239886   -0.3773509146
329   H     -1.0163329842   0.0189901444   -0.390203997
330   H      0.5033199421   -0.8856916341   -0.3830183079
331   H     -0.5559868679   0.8759228805   1.8876066363
332   H     -0.5267887786   -0.8781230132   1.9070473059
333   H      3.0674900423   2.1896109788   3.7771400448
334   H      1.5768027316   -0.3939030689   3.0905834202
335   H      3.9166456622   0.0885998471   2.131110015
336   H      3.9825981532   1.830899958    1.7078931773
337   Core RigidRotor
338       SymmetryFactor    1
339   End
340   Rotor      Hindered
341       Group                7 8 9
342       Axis                 1 2
343       Symmetry              3
344       Potential [kcal/mol]   2
345       0.0  2.84
346   End
347   Rotor      Hindered
348       Group                1 10 11
349       Axis                 2 3
350       Symmetry              1
351       Potential [kcal/mol]   6
352       0.0  1.53  0.17  1.59  0.04  2.12
353   End
354   Rotor      Hindered
355       Group                2 13
356       Axis                 3 4
357       Symmetry              1
358       Potential [kcal/mol]   4
359       0.0  5.8  2.28  4.14
360   End
361   Rotor      Hindered
362       Group                3
363       Axis                 4 5
364       Symmetry              1
365       Potential [kcal/mol]   6
366       0.0  5.81  0.75  2.96  2.23  2.91
367   End
368   Rotor      Hindered
369       Group                4 14 15

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370      Axis                5 6
371      Symmetry            1
372      Potential [kcal/mol] 4
373      0.0  3.45  1.86  3.8
374      End
375      Frequencies [1/cm]   33
376      327.62      472.64      589.3      675.71
377      775.22      910.43      983.75      1055.26      1076.55
378      1110.85      1122.4      1146.52      1227.15      1284.83
379      1320.79      1362.25      1394.1      1399.34      1416.8
380      1468.32      1471.53      1499.37      1512.4      1532.3
381      2990.97      3067.85      3072.11      3101.26      3126.88
382      3138.16      3149.54      3180.26      3871.17
383      !367.29      47.81      93.71      163.29      207.29      282.77!
384      ZeroEnergy [kcal/mol] -10.0
385      ElectronicLevels [1/cm] 1
386      0 2
387      End
388      End
389      !-----
390      Barrier      B3  W1  W4      # W_CC [CH] OCO
391      Variational
392      RRHO
393      Geometry [angstrom] 15
394      C      0.0013116439      -0.004451816      0.0000690726
395      C      -0.000217632      0.002330939      1.5242335275
396      C      1.3814142069      -0.0022082611      2.1004753635
397      O      2.1562470771      -1.0872420571      1.6849885304
398      C      3.4600221698      -0.5439539344      1.6141043987
399      O      3.3279866905      0.7246958295      1.056657381
400      H      0.5135272532      0.8767503475      -0.3863999681
401      H      -1.0152543703      -0.010298084      -0.3889946521
402      H      0.5217990909      -0.8831937267      -0.3747997253
403      H      -0.5352385545      0.8696607525      1.9137020088
404      H      -0.5183648753      -0.8848788045      1.9048234022
405      H      2.0948501239      0.8934918743      1.5985683708
406      H      1.4497073146      0.1780675686      3.1794924553
407      H      3.8875743281      -0.5009232226      2.6252713189
408      H      4.0798745582      -1.164546411      0.9643835043
409      Core RigidRotor
410      SymmetryFactor      0.5
411      End
412      Rotor      Hindered
413      Group                7 8 9
414      Axis                1 2
415      Symmetry            3
416      Potential [kcal/mol] 2
417      0.0  2.4

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415 End
416 Rotor          Hindered
417   Group                1 10 11
418   Axis                  2 3
419   Symmetry              1
420   Potential [kcal/mol]  6
421   0.0  3.7  0.47  3.19  0.62  2.99
422 End
423 Frequencies [1/cm]    36
424   113.04    282.95    304.96    519.57    554.96
711.73    771.82    899.54
425   927.55    982.71    1017.61    1098.87    1119.24
   1141.3    1150.3    1171.48    1251.33    1280.55
426   1308.25    1369.55    1380.66    1414.52    1425.16
   1467.09    1499.96    1510.33    1541.72    1878.0
427   2994.55    3033.33    3042.61    3073.82    3099.53
   3102.45    3144.04    3159.46
428   !79.88    203.61!
429 ZeroEnergy [kcal/mol]  19.4
430 ElectronicLevels [1/cm]  1
431   0  2
432 End
433 Tunneling                Eckart
434 ImaginaryFrequency [1/cm]  1741.1981
435 WellDepth [kcal/mol]    19.4
436 WellDepth [kcal/mol]    29.4
437 End
438 End
439 !-----
440 !-----W1 - > P1-----
441 !-----
442 Bimolecular      P1      # CCCOC=0 + [H]
443 Fragment CCCOC=0
444   RRHO
445 Geometry [angstrom]    14
446   C      0.0240964182    0.0095221715    0.0177319524
447   C      -0.0030425293    -0.0039903355    1.5406932512
448   C      1.3810526487    0.0075489273    2.1477852797
449   O      2.0145018277    1.2430203364    1.7720768004
450   C      3.2624172943    1.4051392265    2.20525629
451   O      3.8765204621    0.6198108646    2.8648746235
452   H      0.5240548293    0.9039028938    -0.3506417673
453   H      -0.9838521124    -0.009648659    -0.3935102324
454   H      0.5610273437    -0.858905151    -0.3666945599
455   H      -0.5595170156    0.8555979426    1.9180905613
456   H      -0.514632694    -0.8978448249    1.9021761279
457   H      1.3548784005    -0.0512964009    3.2356710446
458   H      1.9904306763    -0.8198792418    1.7803288283

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459   H          3.6490536234    2.3730992117    1.8666815551
460   Core RigidRotor
461     SymmetryFactor    1
462   End
463   Rotor      Hindered
464     Group                7 8 9
465     Axis                 1 2
466     Symmetry             3
467     Potential [kcal/mol] 2
468     0.0  2.75
469   End
470   Rotor      Hindered
471     Group                1 10 11
472     Axis                 2 3
473     Symmetry             1
474     Potential [kcal/mol] 6
475     0.0  3.6  0.28  3.6  0.03  4.82
476   End
477   Rotor      Hindered
478     Group                2 12 13
479     Axis                 3 4
480     Symmetry             1
481     Potential [kcal/mol] 8
482     0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
483   End
484   Rotor      Hindered
485     Group                3
486     Axis                 4 5
487     Symmetry             1
488     Potential [kcal/mol] 4
489     0.0  12.84  4.65  12.83
490   End
491   Frequencies [1/cm]    32
492     261.94    351.0    467.28    768.7    797.8
912.78
493     922.75    957.98    1065.81    1089.78    1136.59
     1180.37    1260.59    1287.64    1312.35    1381.12
494     1413.84    1417.13    1428.14    1484.81    1501.99
     1513.24    1520.99    1852.3    3066.48    3071.27
495     3076.24    3084.0    3107.9    3126.48    3138.05
     3150.08
496     !55.58    128.77    199.8    299.37!
497   ZeroEnergy [kcal/mol] 0
498   ElectronicLevels [1/cm] 1
499     0 1
500   End
501   Fragment      H
502   Atom

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503      Mass [amu]      1
504      ElectronicLevels [1/cm]      1
505      0 2
506      End
507      GroundEnergy [kcal/mol]      1.5
508      End
509      !-----
510      Barrier      B4  W1  P1      # TS_CCCOC=O_H
511      Variational
512      RRHO
513      Geometry [angstrom]      15
514      C      0.054140414      0.0251811368      0.0206005523
515      C      0.0015816414      -0.0114492624      1.5424551698
516      C      1.3759153991      0.0213345372      2.1715115793
517      O      1.9884433581      1.2686744176      1.8227636788
518      C      3.2710567471      1.4026456716      2.2072578252
519      O      3.8285066051      0.6831939706      3.0197304403
520      H      0.5415419008      0.935245658      -0.3255241915
521      H      -0.9456428412      -0.0092894826      -0.4092685592
522      H      0.6163087432      -0.8260350729      -0.3666515369
523      H      -0.5782248599      0.8312629162      1.9228256059
524      H      -0.4973300195      -0.9205463655      1.8829044693
525      H      1.3352763899      -0.062192662      3.2573400932
526      H      2.0070473244      -0.7897996943      1.7960411102
527      H      4.0062334779      0.8124679712      0.8971036043
528      H      3.6341465541      2.4022383547      1.9321667243
529      Core RigidRotor
530      SymmetryFactor      0.5
531      End
532      Rotor      Hindered
533      Group      7 8 9
534      Axis      1 2
535      Symmetry      3
536      Potential [kcal/mol]      2
537      0.0 2.62
538      End
539      Rotor      Hindered
540      Group      1 10 11
541      Axis      2 3
542      Symmetry      1
543      Potential [kcal/mol]      6
544      0.0 3.65 0.34 3.63 0.1 4.85
545      End
546      Rotor      Hindered
547      Group      2 12 13
548      Axis      3 4
549      Symmetry      1
550      Potential [kcal/mol]      4

```

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551      0.0  7.73  0.42  1.54
552  End
553  Rotor      Hindered
554      Group      3
555      Axis      4 5
556      Symmetry   1
557      Potential [kcal/mol] 4
558      0.0  10.33  3.83  10.24
559  End
560  Frequencies [1/cm] 34
561      259.39      317.29      465.42      544.73      603.91
562 767.92
563      789.84      909.72      921.95      958.58      1089.28
564 1119.08      1136.9      1179.25      1225.21      1286.86
565      1311.4      1373.29      1380.5      1414.81      1427.41
566 1484.01      1500.91      1512.09      1519.11      1676.16
567      3035.67      3053.24      3065.2      3070.85      3107.34
568      3116.84      3136.44      3149.44
569 !52.03      116.3      187.2      221.67!
570 ZeroEnergy [kcal/mol] 11.6
571 ElectronicLevels [1/cm] 1
572      0 2
573  End
574  Tunneling      Eckart
575  ImaginaryFrequency [1/cm] 1073.8059
576  WellDepth [kcal/mol] 11.6
577  WellDepth [kcal/mol] 10.1
578  End
579  End
580  !-----
581  !-----W1 - > P2-----
582  !-----
583  Bimolecular      P2      # CCC[O] + CH2O
584  Fragment CCC[O]
585  RRHO
586  Geometry [angstrom] 11
587  C      0.0123289889      0.0008284765      0.0157060082
588  C      -0.0102318725      -0.0063326812      1.5374674503
589  C      1.3947992388      -0.0037428312      2.122950554
590  O      2.1545760773      1.0809214006      1.7772294789
591  H      0.5824550629      0.8549966456      -0.3476429006
592  H      -0.9928461086      0.0595956019      -0.3983845671
593  H      0.4825717163      -0.9054375589      -0.369798953
594  H      -0.5391724294      0.8719988963      1.911966076
595  H      -0.5434565335      -0.8824344933      1.9127449196
596  H      1.3956084458      -0.1128711697      3.2172441153
597  H      1.966221157      -0.8766033662      1.7562262415
598  Core RigidRotor

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595     SymmetryFactor    1
596 End
597 Rotor      Hindered
598   Group          5 6 7
599   Axis           1 2
600   Symmetry       3
601   Potential[kcal/mol]  2
602     0.0  2.78
603 End
604 Rotor      Hindered
605   Group          1 8 9
606   Axis           2 3
607   Symmetry       1
608   Potential[kcal/mol]  6
609     0.0  3.15  0.44  3.15  0.0  3.29
610 End
611 Frequencies [1/cm]    25
612   312.26   474.66   506.23   792.85   885.51
613 984.56   1001.42   1097.32
614   1115.56   1223.19   1291.87   1361.37   1373.72
615   1386.87   1421.11   1486.1   1502.31   1511.67
616   2936.28   2996.28   3062.53   3066.56   3102.81
617   3133.89   3147.38
618   !141.59   231.1!
619 ZeroEnergy[kcal/mol]  0
620 ElectronicLevels [1/cm]  1
621   0  2
622 End
623 Fragment  CH2O
624   RRHO
625 Geometry[angstrom]    4
626   O      -0.000000016  -0.0000022088  0.0061054213
627   C      -0.0000000144  0.0000068137  1.2014608526
628   H       0.9375275336  -0.0000022726  1.7838372267
629   H      -0.9375275608  0.0000246367  1.7838372291
630 Core RigidRotor
631   SymmetryFactor    2
632 End
633 Frequencies [1/cm]    6
634   1216.69   1279.34   1545.84   1876.79   2940.94
635   3011.91
636   !  !
637 ZeroEnergy[kcal/mol]  0
638 ElectronicLevels [1/cm]  1
639   0  1
640 End
641 GroundEnergy[kcal/mol]  13.6
642 End

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639 !-----
640 Barrier      B5  W1  P2    # TS_CH20_CCC[O]
641 Variational
642 RRHO
643 Geometry[angstrom]      15
644 C      0.0019699561      -0.0000919431      -0.0015719815
645 C      -0.0015799842      0.0002768644      1.5195420225
646 C      1.4022922402      0.0001829883      2.1046037522
647 O      2.236333603      0.993185311      1.5957294832
648 C      2.1914332554      2.5287451669      2.5611079796
649 O      0.9863306899      2.7757680319      2.3925327458
650 H      0.5031151667      0.8893064065      -0.3790237071
651 H      -1.0138939147      -0.0117409793      -0.3930313354
652 H      0.5239991516      -0.8748858761      -0.3938569219
653 H      -0.5132216713      0.8858378107      1.8979762609
654 H      -0.5247471892      -0.8773730621      1.9055139309
655 H      1.3891032127      0.0242382859      3.1990624291
656 H      1.9269066352      -0.9211440386      1.8006808972
657 H      2.5429046081      2.1056754089      3.512581186
658 H      2.9558292389      3.0379776351      1.9629972382
659 Core RigidRotor
660 SymmetryFactor      1
661 End
662 Rotor      Hindered
663 Group      7 8 9
664 Axis      1 2
665 Symmetry      1
666 Potential[kcal/mol]      6
667 0.0 2.71 0.0 2.71 0.0 2.71
668 End
669 Rotor      Hindered
670 Group      1 10 11
671 Axis      2 3
672 Symmetry      1
673 Potential[kcal/mol]      6
674 0.0 3.63 0.46 2.75 0.82 4.23
675 End
676 Rotor      Hindered
677 Group      2 12 13
678 Axis      3 4
679 Symmetry      1
680 Potential[kcal/mol]      6
681 0.0 2.24 1.76 3.76 2.5 5.82
682 End
683 Rotor      Hindered
684 Group      3
685 Axis      4 5
686 Symmetry      1

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687      Potential [kcal/mol]          6
688      0.0  2.41  0.83  7.7  5.7  8.11
689      End
690      Frequencies [1/cm]          34
691      265.59      304.52      400.22      522.65      772.25
848.85
692      874.11      889.61      983.63      1067.44      1115.95
      1154.97      1221.77      1246.04      1250.84      1301.38
693      1349.54      1387.6      1419.44      1425.44      1467.39
      1484.01      1500.09      1510.43      1612.22      2964.83
694      2984.8      3053.74      3063.19      3070.24      3071.36
      3115.5      3135.64      3153.42
695      !47.67      111.45      152.89      230.11!
696      ZeroEnergy [kcal/mol]          22.1
697      ElectronicLevels [1/cm]          1
698      0  2
699      End
700      Tunneling                      Eckart
701      ImaginaryFrequency [1/cm]          605.8983
702      WellDepth[kcal/mol]          22.1
703      WellDepth[kcal/mol]          8.5
704      End
705      End
706      !-----
707      !-----WELL 2 to Products -----
708      !-----
709      Well          W5          # W_CCCO [CH] OH
710      Species
711      RRHO
712      Geometry [angstrom]          15
713      C          -0.1409798046      -0.0341013083      0.0763015037
714      C          0.0121541307      0.0370002934      1.5891725723
715      H          1.0676670275      0.0848289751      1.8652901911
716      C          -0.6738050233      1.2582768935      2.1805893645
717      O          -2.0438012216      1.3562875298      1.8149918464
718      C          -2.826007979      0.3625459895      2.3247248681
719      O          -4.1216274451      0.4735529442      1.9401598926
720      H          0.2459142346      0.869209414      -0.3980264374
721      H          -1.1912815929      -0.130879985      -0.196474374
722      H          0.3954301383      -0.888254189      -0.3338765581
723      H          -0.5926792487      1.2570308265      3.2729237666
724      H          -0.2147890825      2.1721592248      1.8052571425
725      H          -0.3974944842      -0.8647860678      2.0472240876
726      H          -2.7195578926      0.1620168852      3.3909299896
727      H          -4.1358407166      0.8273336402      1.0444402337
728      Core RigidRotor
729      SymmetryFactor          1
730      End

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731 Rotor          Hindered
732   Group                8 9 10
733   Axis                 1 2
734   Symmetry             3
735   Potential [kcal/mol] 2
736   0.0  2.72
737 End
738 Rotor          Hindered
739   Group                1 3 13
740   Axis                 2 4
741   Symmetry             1
742   Potential [kcal/mol] 6
743   0.0  3.61  0.44  3.17  0.7  4.61
744 End
745 Rotor          Hindered
746   Group                2 11 12
747   Axis                 4 5
748   Symmetry             1
749   Potential [kcal/mol] 4
750   0.0  1.5  0.03  4.93
751 End
752 Rotor          Hindered
753   Group                4
754   Axis                 5 6
755   Symmetry             1
756   Potential [kcal/mol] 4
757   0.0  5.27  2.1  2.33
758 End
759 Rotor          Hindered
760   Group                5 14
761   Axis                 6 7
762   Symmetry             1
763   Potential [kcal/mol] 4
764   0.0  2.87  2.39  3.44
765 End
766 Frequencies [1/cm] 34
767   297.55    363.93    468.2    577.42    777.93
768   883.61    917.35    947.38    992.2    1067.71
769 1116.61    1173.66    1193.27    1222.05    1300.26
770   1310.77    1351.42    1378.19    1398.57    1414.36
771   1441.83    1483.23    1499.12    1507.57    1515.9
772   3036.05    3063.11    3068.6    3093.88    3100.04
773   3122.51    3134.95    3145.13    3859.58
774   !60.69    79.12    158.53    248.41    251.0!
775 ZeroEnergy [kcal/mol] -9.0
776 ElectronicLevels [1/cm] 1
777   0 2
778 End

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776 End
777 !-----
778 Barrier          B6  W2  W5      # W_CCCO [CH] OH
779 Variational
780 RRHO
781 Geometry [angstrom]          15
782 C          0.0004933203      -0.0002683619      -0.0001444953
783 H          0.0001392167      -0.0001247247      1.0865831687
784 H          0.9970944499      -0.0021910808      -0.428201126
785 C          -1.0172736301      -0.9076612767      -0.6429719458
786 C          -2.422275895       -0.3302877511      -0.4886880841
787 O          -2.5000774019      0.9524249394      -1.1069066509
788 C          -1.6903956588      1.8922113716      -0.5049469765
789 O          -2.0856510568      2.2492305485      0.7758052609
790 H          -0.8079291931      -1.0218908243      -1.7074629191
791 H          -1.0098692701      -1.9088611765      -0.1998149958
792 H          -3.1632020894      -0.9483688706      -0.9899781151
793 H          -2.6870358301      -0.2459274728      0.5687789542
794 H          -0.5624784656      1.2171508409      -0.288941986
795 H          -1.5563190952      2.7321128059      -1.1856237846
796 H          -2.9676353604      2.6368580963      0.7351987235
797 Core RigidRotor
798 SymmetryFactor          0.5
799 End
800 Rotor          Hindered
801 Group          15
802 Axis          8 7
803 Symmetry          1
804 Potential [kcal/mol]          4
805 0.0  1.76  0.53  1.65
806 End
807 Frequencies [1/cm]          37
808 139.07          160.34          303.61          417.14          491.46
542.82          602.58          650.19          826.84
809 899.43          929.61          948.53          1032.08          1047.44
1095.0          1129.62          1171.6          1191.24          1242.94
810 1285.39          1307.39          1362.64          1374.81          1410.46
1449.76          1455.31          1479.01          1511.56          1578.88
811 3036.76          3059.91          3100.98          3108.23          3117.09
3143.74          3202.16          3811.26
812 !273.86!
813 ZeroEnergy [kcal/mol]          11.0
814 ElectronicLevels [1/cm]          1
815 0 2
816 End
817 Tunneling          Eckart
818 ImaginaryFrequency [1/cm]          1734.3756
819 WellDepth [kcal/mol]          15.9

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820 WellDepth [kcal/mol]          18.0
821 End
822 End
823 !-----
824 !-----
825 !-----
826 Bimolecular          P3      # [CH2] OCOH  +  C=C
827 Fragment    [CH2] OCOH
828      RRHO
829 Geometry [angstrom]          9
830   C          0.0004242915      -0.0000363321      0.0000815993
831   O          0.0001503754      0.0000678304      1.3573274535
832   C          1.2812584108      0.00041206       1.9419188129
833   O          1.9858635589      -1.1721603274      1.6812220126
834   H          0.8587661489      -0.420451383      -0.5044915023
835   H          -0.9848098531      -0.0361202249      -0.433865058
836   H          1.8794068052      0.8132560077      1.5276025639
837   H          1.1083169825      0.1519565878      3.0072090351
838   H          1.5181302731      -1.9071692222      2.0883780825
839 Core RigidRotor
840     SymmetryFactor      1
841 End
842 Rotor          Hindered
843     Group                5 6
844     Axis                  1 2
845     Symmetry              1
846     Potential [kcal/mol]  6
847     0.0  4.96  0.0  4.87  0.47  0.51
848 End
849 Rotor          Hindered
850     Group                1
851     Axis                  2 3
852     Symmetry              1
853     Potential [kcal/mol]  8
854     0.0  3.94  3.78  3.91  1.94  2.97  2.16  3.24
855 End
856 Rotor          Hindered
857     Group                2 7 8
858     Axis                  3 4
859     Symmetry              1
860     Potential [kcal/mol]  4
861     0.0  3.41  1.08  4.54
862 End
863 Frequencies [1/cm]      18
864     396.61      601.46      613.01      991.83      1063.89
     1122.38      1199.26
865     1269.0      1316.15      1395.84      1447.11      1494.35
     1533.68      3074.17      3129.72      3160.7      3300.39

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866          3869.46
867      !162.73      260.33      372.97!
868      ZeroEnergy [kcal/mol]      0
869      ElectronicLevels [1/cm]      1
870          0  2
871      End
872      Fragment  C=C
873      RRHO
874      Geometry [angstrom]  6
875      C          0.00000000      0.00000000      0.00000000
876      H          0.00000000      0.00000000      1.08216909
877      H          0.96588500      0.00000000      -0.48801240
878      C          -1.12558139      -0.00000000      -0.69239269
879      H          -1.12558139      -0.00000000      -1.77456178
880      H          -2.09146639      -0.00000000      -0.20438028
881      Core      RigidRotor
882      SymmetryFactor      4
883      End
884      Frequencies [1/cm]      12
885      829.14  990.4  1002.92  1070.96  1243.08  1388.11  1473.77  1718.56
      3159.71  3175.83  3235.53  3261.92
886      !!torsions
887      ZeroEnergy [kcal/mol]      0
888      ElectronicLevels [1/cm]      1
889      0  1
890      End
891      GroundEnergy [kcal/mol]      15.6
892      End
893      !-----
894      Barrier      B7  W2  P3      # TS_[CH2]OCO_H_C=C
895      Variational
896      RRHO
897      Geometry [angstrom]      15
898      C          0.0263795788      0.1012610411      -0.0777414441
899      H          0.1067962175      0.1356612      1.0003690486
900      H          0.9494112323      0.1045374881      -0.6412513109
901      C          -1.174588009      0.1223070847      -0.6986384714
902      C          -1.8284554476      2.2225386781      -1.1381741645
903      O          -0.7722865345      2.8318913691      -1.7448325637
904      C          0.1435479081      3.4248112457      -0.8546338498
905      O          -0.3892741708      4.5472130136      -0.2215425078
906      H          -1.2346087326      -0.0609839998      -1.7632377594
907      H          -2.0866571114      -0.0322884042      -0.1360904856
908      H          -2.6291578774      2.0024961307      -1.8310536181
909      H          -2.0979077326      2.5990179807      -0.1576281188
910      H          0.4058991384      2.721218317      -0.0645154199
911      H          1.0162116121      3.6678058856      -1.4609383166
912      H          -0.5809850679      5.2116296398      -0.8896757886

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913 Core RigidRotor
914     SymmetryFactor    1
915 End
916 Rotor      Hindered
917     Group          1 9 10
918     Axis           4 5
919     Symmetry       1
920     Potential[kcal/mol] 6
921     0.0  1.02  0.62  1.54  0.23  0.37
922 End
923 Rotor      Hindered
924     Group          4 11 12
925     Axis           5 6
926     Symmetry       1
927     Potential[kcal/mol] 4
928     0.0  6.7  0.22  4.78
929 End
930 Rotor      Hindered
931     Group          5
932     Axis           6 7
933     Symmetry       1
934     Potential[kcal/mol] 4
935     0.0  5.29  0.33  2.7
936 End
937 Rotor      Hindered
938     Group          6 13 14
939     Axis           7 8
940     Symmetry       1
941     Potential[kcal/mol] 4
942     0.0  3.56  1.95  3.94
943 End
944 Frequencies [1/cm]    34
945     122.64      193.09      383.87      443.33      560.22
946     606.09
947     819.05      850.99      876.81      982.01      1001.63
948     1034.51     1065.84     1115.05     1197.19     1243.92
949     1250.5      1308.34     1318.91     1392.68     1444.17
950     1461.68     1497.03     1537.08     1589.01     3079.85
951     3120.6      3138.88     3150.01     3165.81     3229.19
952     3245.24     3258.58     3869.91
953     !55.3      75.24      262.59      369.26!
954 ZeroEnergy[kcal/mol]    23.1
955 ElectronicLevels [1/cm]  1
956     0  2
957 End
958 Tunneling      Eckart
959 ImaginaryFrequency [1/cm]  509.5638
960 WellDepth[kcal/mol]      28.0
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957 WellDepth[kcal/mol]          7.5
958 End
959 End
960 !-----
961 !-----WELL 3 to Products -----
962 !-----
963 Barrier      B8   W3   W5   # TS C[CH]COCO <=> CCCO[CH]OH
964 Variational
965 RRHO
966 Geometry[angstrom]          15
967 C      0.0028356065      -0.0028728929      0.0131504744
968 C      0.0027164622      0.0079084147      1.51414265
969 H      0.9884947858      0.0120013202      1.9748118025
970 C     -1.0104892599     -0.8378853967      2.2438728701
971 O     -1.4785688727     -0.0787009194      3.3712565412
972 C     -1.529620761      1.2592975236      3.0219733813
973 O     -1.2041609063      2.078099782       4.0648173566
974 H      0.3329372683     -0.9662367512     -0.3897051759
975 H      0.6693072016     0.759342913      -0.3892208251
976 H     -0.9990249146     0.1825244209     -0.3785067698
977 H     -1.8536180925     -1.0681980694     1.583466329
978 H     -0.6203964274     -1.7718560672     2.6457770228
979 H     -0.6119584216     1.1592060097     2.041310814
980 H     -2.4739842082     1.584252324      2.5799903955
981 H     -0.4897976077     1.6561383996     4.5541550108
982 Core RigidRotor
983 SymmetryFactor      0.25
984 End
985 Rotor      Hindered
986 Group      8 9 10
987 Axis      1 2
988 Symmetry   3
989 Potential[kcal/mol] 2
990 0.0 1.87
991 End
992 Rotor      Hindered
993 Group      15
994 Axis      7 6
995 Symmetry   1
996 Potential[kcal/mol] 6
997 0.0 4.91 3.12 3.44 0.62 0.67
998 End
999 Frequencies [1/cm]    36
1000 99.34 128.44 177.22 377.94 496.87
1001 551.33 624.97 810.21
1002 913.28 946.24 988.83 1052.37 1089.73
1003 1118.9 1137.08 1164.86 1210.88 1262.26

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1002          1305.58          1335.16          1399.26          1410.13          1418.36
          1450.42          1486.86          1497.76          1524.17          1724.44
1003          3027.0          3032.9          3079.87          3089.08          3113.87
          3124.89          3136.99          3855.45
1004      !185.34          338.46!
1005      ZeroEnergy [kcal/mol]          14.3
1006      ElectronicLevels [1/cm]          1
1007          0  2
1008      End
1009      Tunneling          Eckart
1010      ImaginaryFrequency [1/cm]          1794.304
1011      WellDepth[kcal/mol]          20.9
1012      WellDepth[kcal/mol]          23.3
1013      End
1014      End
1015      !-----
1016      !-----
1017      !-----
1018      Bimolecular          P4          # C=CC + [O]COH
1019      Fragment          C=CC
1020          RRHO
1021      Geometry [angstrom]          9
1022      C          -0.0036173945          -0.0000157516          0.0051672399
1023      C          0.0040011912          -0.000049678          1.5008982519
1024      H          0.9797799476          -0.000127773          1.9768349341
1025      C          -1.079110104          0.0000087324          2.2615933185
1026      H          0.5151885421          0.876581567          -0.3868008481
1027      H          -1.0214504945          0.000056787          -0.3822056223
1028      H          0.5150788396          -0.8766602561          -0.3868403603
1029      H          -1.0141839757          -0.0000194025          3.3409791477
1030      H          -2.0713139546          0.0000868059          1.8258205252
1031      Core RigidRotor
1032          SymmetryFactor          1
1033      End
1034      Rotor          Hindered
1035          Group          5 6 7
1036          Axis          1 2
1037          Symmetry          3
1038          Potential [kcal/mol]          2
1039          0.0  2.01
1040      End
1041      Frequencies [1/cm]          20
1042          430.51          596.0          938.41          947.42          967.29
1036.32          1079.5          1195.46          1330.57
1043          1407.13          1454.25          1484.54          1497.22          1742.34
          3056.62          3111.88          3138.7          3159.03          3168.59
1044          3248.77
1045      !206.03!

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1046 ZeroEnergy [kcal/mol]      0
1047 ElectronicLevels [1/cm]   1
1048   0  1
1049 End
1050 Fragment   [O] COH
1051   RRHO
1052 Geometry [angstrom]       6
1053   O      -0.0179086386    0.0302114826    -0.0063445877
1054   C      0.0041353263    0.011029922     1.3315040021
1055   O      1.2588889626    0.0839062173    1.9358024239
1056   H      -0.5946672698    0.8417674225    1.7323279478
1057   H      -0.5341812063    -0.9194223458    1.6108213777
1058   H      1.8532254387    -0.5110076245    1.4688149448
1059 Core RigidRotor
1060   SymmetryFactor   1
1061 End
1062 Rotor           Hindered
1063   Group           1 4 5
1064   Axis            2 3
1065   Symmetry        1
1066   Potential [kcal/mol] 6
1067   0.0  0.34  0.0  2.89  2.85  2.89
1068 End
1069 Frequencies [1/cm]   11
1070   558.99    759.52    1020.09    1132.89    1167.89
1071   1315.09    1364.87    1423.56    2878.54
1072   3001.58    3871.87
1073   !222.92!
1074 ZeroEnergy [kcal/mol]      0
1075 ElectronicLevels [1/cm]   1
1076   0  2
1077 End
1078 GroundEnergy [kcal/mol]    11.7
1079 End
1080 !-----
1081 Barrier           B9  W3  P4  # TS_ [O] COH_CC=C
1082 Variational
1083   RRHO
1084 Geometry [angstrom]       15
1085   C      0.0185437987    -0.1312956575    0.0796816176
1086   C      -0.0145806727    -0.0520296972    1.5645188906
1087   H      0.9412851349    -0.0685416726    2.075478971
1088   C      -1.15048733    -0.0556461536    2.2963676225
1089   O      -1.5119003381    -2.1054989383    2.4029249915
1090   C      -0.4053491109    -2.739054531     2.8666078844
1091   O      0.5897574347    -2.9690387118    1.8948216374
1092   H      0.5678736959    -1.021775022     -0.2320220895
1093   H      0.5407905317    0.7283577276     -0.3460757619

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1093   H           -0.9861651356   -0.1728916396   -0.337196289
1094   H           -1.1220846839    0.0639226529    3.3696630475
1095   H           -2.1141344899    0.0486063206    1.8187621407
1096   H            0.0974982749   -2.1996285978    3.6765420067
1097   H           -0.7745278226   -3.6967487099    3.2736131566
1098   H            0.1477506622   -3.3405279549    1.1251076998
1099   Core RigidRotor
1100       SymmetryFactor      1
1101   End
1102   Rotor           Hindered
1103       Group                8 9 10
1104       Axis                  1 2
1105       Symmetry                3
1106       Potential [kcal/mol]    2
1107       0.0  1.4
1108   End
1109   Rotor           Hindered
1110       Group                2 11 12
1111       Axis                  4 5
1112       Symmetry                1
1113       Potential [kcal/mol]    4
1114       0.0  3.13  0.0  1.32
1115   End
1116   Rotor           Hindered
1117       Group                4
1118       Axis                  5 6
1119       Symmetry                1
1120       Potential [kcal/mol]    4
1121       0.0  11.03  3.7  8.28
1122   End
1123   Rotor           Hindered
1124       Group                5 13 14
1125       Axis                  6 7
1126       Symmetry                1
1127       Potential [kcal/mol]    6
1128       0.0  2.84  2.68  3.53  3.05  3.24
1129   End
1130   Frequencies [1/cm]      33
1131       136.85      228.45      303.06      432.61      578.3
688.5
1132       935.51      946.74      960.36      994.49      1016.92
1047.88      1051.54      1132.09      1201.74      1232.7
1133       1307.15      1337.66      1394.7      1417.95      1445.82
1471.01      1475.92      1494.9      1624.27      2945.59
1134       3043.31      3052.88      3107.01      3144.97      3177.09
3184.41      3268.64      3862.44
1135       !67.66      112.52      150.22      336.33!
1136   ZeroEnergy [kcal/mol]    14.8

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1137 ElectronicLevels [1/cm]      1
1138     0  2
1139 End
1140 Tunneling                      Eckart
1141 ImaginaryFrequency [1/cm]     409.8372
1142 WellDepth[kcal/mol]          21.4
1143 WellDepth[kcal/mol]          3.1
1144 End
1145 End
1146 !-----
1147 !-----WELL 4 to Products -----
1148 !-----
1149 Bimolecular      P5      # CCC=O  +  [CH2]OH
1150 Fragment      CCC=O
1151      RRHO
1152 Geometry[angstrom]      10
1153   C      -0.0000566396      0.0062360295      -0.0000851688
1154   C      0.0002269459      -0.0058860377      1.5176215585
1155   C      1.3811361699      -0.0034523604      2.1113838536
1156   H      1.4229848487      -0.0120720663      3.2179002795
1157   O      2.393691471      0.0069513451      1.4676073164
1158   H      0.5150796789      0.8884132091      -0.3758097392
1159   H      -1.0166443986      0.0040558499      -0.3884237127
1160   H      0.524187663      -0.8644258075      -0.3898116873
1161   H      -0.5289339007      0.8570574089      1.9342051971
1162   H      -0.5199028418      -0.8808265682      1.9203230958
1163 Core RigidRotor
1164     SymmetryFactor      1
1165 End
1166 Rotor      Hindered
1167     Group                      6 7 8
1168     Axis                        1 2
1169     Symmetry                    3
1170     Potential[kcal/mol]        2
1171     0.0  2.12
1172 End
1173 Rotor      Hindered
1174     Group                      1 9 10
1175     Axis                        2 3
1176     Symmetry                    1
1177     Potential[kcal/mol]        6
1178     0.0  2.36  1.42  2.11  1.42  2.36
1179 End
1180 Frequencies [1/cm]      22
1181     266.82      673.44      677.86      873.63      908.86
1182     1008.52      1121.87      1156.86
1183     1283.93      1372.83      1414.21      1430.39      1457.55
1184     1497.45      1504.73      1866.92      2945.02      3050.32

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1183          3077.74          3081.28          3153.86          3156.87
1184      !148.66          238.11!
1185      ZeroEnergy [kcal/mol]          0
1186      ElectronicLevels [1/cm]          1
1187          0  1
1188      End
1189      Fragment  [CH2]OH
1190          RRHO
1191      Geometry [angstrom]          5
1192      C          0.0017104629          0.0006805334          0.006036701
1193      O          0.0003059126          -0.011024407          1.3662696453
1194      H          0.9891006186          0.005542419          -0.425002778
1195      H          -0.8280003133          0.4619257545          -0.5108130333
1196      H          -0.8993908337          0.0682737923          1.6902499792
1197      Core RigidRotor
1198          SymmetryFactor          1
1199      End
1200      Rotor          Hindered
1201          Group          3 4
1202          Axis          1 2
1203          Symmetry          1
1204          Potential [kcal/mol]          4
1205          0.0  4.41  0.0  4.7
1206      End
1207      Frequencies [1/cm]          8
1208          605.38          1066.47          1240.91          1364.7          1496.89
1209          3154.31          3293.73          3901.11
1209      !413.46!
1210      ZeroEnergy [kcal/mol]          0
1211      ElectronicLevels [1/cm]          1
1212          0  2
1213      End
1214      GroundEnergy [kcal/mol]          -1.1
1215      End
1216      !-----
1217      Barrier          B10  W4  P5          # TS_CCC=O_[CH2]OH
1218      Variational
1219          RRHO
1220      Geometry [angstrom]          15
1221      C          0.0055772018          -0.0245570763          0.0031798375
1222      C          -0.0061060076          0.0193262645          1.523519484
1223      C          1.3710238776          -0.0155499813          2.120354704
1224      H          1.4464168115          -0.1650017094          3.2051619105
1225      O          2.4169678187          0.1018376156          1.4406785191
1226      C          3.0228402306          -1.5750326439          0.6650856755
1227      O          2.132966505          -2.4830525743          1.1127056781
1228      H          0.6242318656          0.7756793818          -0.3994722334
1229      H          -1.0019293687          0.0791630355          -0.3962846412

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1230   H           0.4136546961   -0.9727248948   -0.3455081377
1231   H          -0.5098258795    0.9274835882    1.876145547
1232   H          -0.5890664712   -0.8126688856    1.9297083642
1233   H           2.9093956255   -1.3565630707   -0.3842231321
1234   H           4.0146405217   -1.5758440753    1.0948908028
1235   H           2.2716825869   -2.6436949599    2.051446609
1236   Core RigidRotor
1237       SymmetryFactor      1
1238   End
1239   Rotor           Hindered
1240       Group                8 9 10
1241       Axis                  1 2
1242       Symmetry              1
1243       Potential [kcal/mol]   6
1244       0.0  2.58  0.0  2.59  0.0  2.58
1245   End
1246   Rotor           Hindered
1247       Group                1 11 12
1248       Axis                  2 3
1249       Symmetry              1
1250       Potential [kcal/mol]   4
1251       0.0  0.95  0.39  1.29
1252   End
1253   Rotor           Hindered
1254       Group                3
1255       Axis                  5 6
1256       Symmetry              1
1257       Potential [kcal/mol]   4
1258       0.0  4.07  3.24  3.82
1259   End
1260   Rotor           Hindered
1261       Group                15
1262       Axis                  7 6
1263       Symmetry              1
1264       Potential [kcal/mol]   4
1265       0.0  2.9  0.43  5.3
1266   End
1267   Frequencies [1/cm]      34
1268       116.67      217.85      312.31      439.59      628.0
678.56
1269       702.65      818.42      879.42      936.61      1009.78
1077.19      1089.4      1113.56      1215.44      1270.04
1270       1341.18      1363.03      1384.78      1406.79      1466.13
1495.16      1506.28      1519.92      1526.38      3013.76
1271       3026.18      3058.36      3075.48      3145.51      3151.0
3155.67      3289.3      3854.19
1272       !55.62      96.39      254.08      277.94!
1273   ZeroEnergy [kcal/mol]      14.4

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1274 ElectronicLevels [1/cm]      1
1275     0  2
1276 End
1277 Tunneling                      Eckart
1278 ImaginaryFrequency [1/cm]     649.7726
1279 WellDepth[kcal/mol]          24.4
1280 WellDepth[kcal/mol]          15.5
1281 End
1282 End
1283 !-----
1284 !-----
1285 !-----
1286 Bimolecular      P6      # C=COCO + [CH3]
1287 Fragment C=COCO
1288 RRHO
1289 Geometry[angstrom]      11
1290 C      0.0013601933      0.0057058929      -0.0003134127
1291 C      0.0016491502      -0.0036923609      1.3245431897
1292 H      0.9170463758      -0.0206423495      1.9008590388
1293 O      -1.0738188154      -0.0025648474      2.1582830484
1294 C      -2.3378811366      -0.1866279717      1.5724223705
1295 O      -2.7663939592      0.914462695      0.8351387573
1296 H      0.9496318576      -0.0285387338      -0.5135908198
1297 H      -0.9003197225      0.0760488618      -0.5886499238
1298 H      -2.3067080309      -1.0285364804      0.87890601
1299 H      -3.0036461967      -0.4011762725      2.4085064045
1300 H      -2.8311556979      1.6717785765      1.4237413182
1301 Core RigidRotor
1302     SymmetryFactor      1
1303 End
1304 Rotor      Hindered
1305     Group      1 3
1306     Axis      2 4
1307     Symmetry      1
1308     Potential[kcal/mol]      4
1309     0.0  4.72  0.92  4.75
1310 End
1311 Rotor      Hindered
1312     Group      2
1313     Axis      4 5
1314     Symmetry      1
1315     Potential[kcal/mol]      6
1316     0.0  9.0  1.08  4.48  1.42  4.61
1317 End
1318 Rotor      Hindered
1319     Group      4 9 10
1320     Axis      5 6
1321     Symmetry      1

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1322     Potential [kcal/mol]          4
1323     0.0  2.16  0.6  3.84
1324     End
1325     Frequencies [1/cm]          24
1326     365.26    496.28    665.29    735.43    894.99
1327     925.35    1016.4
1328     1028.45    1095.18    1139.24    1246.95    1301.96
1329     1364.75    1396.66    1431.58    1471.29    1533.28
1330     1726.67    3073.86    3127.55    3198.16    3216.26
1331     3292.08    3872.9
1332     !168.43    199.6    307.74!
1333     ZeroEnergy [kcal/mol]        0
1334     ElectronicLevels [1/cm]     1
1335     0  1
1336     End
1337     Fragment  [CH3]
1338     RRHO
1339     Geometry [angstrom]          4
1340     C          0.00000000    0.00000000    0.00000000
1341     H          0.00000000    0.00000000    1.07652900
1342     H          0.93230200    0.00000000    -0.53826500
1343     H          -0.93230200   -0.00000000   -0.53826500
1344     Core RigidRotor
1345     SymmetryFactor        6
1346     End
1347     Frequencies [1/cm]          6
1348     436.03    1412.64    1412.73    3144.41    3323.11
1349     3323.14
1350     !  !
1351     ZeroEnergy [kcal/mol]        0
1352     ElectronicLevels [1/cm]     1
1353     0  2
1354     End
1355     GroundEnergy [kcal/mol]     12.6
1356     End
1357     !-----
1358     Barrier      B11  W4  P6    # TS_[CH3]_C=COCOH
1359     Variational
1360     RRHO
1361     Geometry [angstrom]          15
1362     C          0.0099326936    0.0134730456   -0.0060153825
1363     C          -0.004342837    -0.0060842891    2.2640991858
1364     C          1.2596630616    -0.0086612646    2.7412367849
1365     H          1.8087404664    0.9010300062    2.9371578014
1366     O          2.0583985969    -1.0962758198    2.9247660037
1367     C          1.516690575    -2.3549569593    2.6135399846
1368     O          0.5266394069    -2.7568610064    3.5077872822
1369     H          -1.049331931    -0.0894932564   -0.1967175195

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1366   H           0.6276253731   -0.8367971282   -0.2576616415
1367   H           0.4418282762   0.984799225    -0.1972112281
1368   H           -0.5286146523   0.9367693364   2.2689929907
1369   H           -0.6053942044   -0.9023242524   2.26343908
1370   H           1.0494195921   -2.3339399677   1.6285607817
1371   H           2.3700758369   -3.0330923183   2.6169713626
1372   H           0.9124567393   -2.8133973554   4.3866075076
1373   Core RigidRotor
1374       SymmetryFactor      1
1375   End
1376   Rotor           Hindered
1377       Group                8 9 10
1378       Axis                  1 2
1379       Symmetry                3
1380       Potential[kcal/mol]      2
1381       0.0  0.2
1382   End
1383   Rotor           Hindered
1384       Group                6
1385       Axis                  5 3
1386       Symmetry                1
1387       Potential[kcal/mol]      4
1388       0.0  3.33  0.28  4.0
1389   End
1390   Rotor           Hindered
1391       Group                3
1392       Axis                  5 6
1393       Symmetry                1
1394       Potential[kcal/mol]      6
1395       0.0  8.5  0.0  4.14  1.79  4.42
1396   End
1397   Rotor           Hindered
1398       Group                5 13 14
1399       Axis                  6 7
1400       Symmetry                1
1401       Potential[kcal/mol]      4
1402       0.0  2.3  0.99  3.86
1403   End
1404   Frequencies [1/cm]      34
1405       124.86      287.4      372.08      484.59      507.81
1406   526.08
1407       655.57      761.74      809.75      910.81      933.7
1408   961.41      1031.02      1092.75      1136.71      1234.63
1409       1297.11      1331.97      1394.47      1420.14      1426.16
1410       1429.53      1467.39      1537.14      1605.69      3080.42
1411       3108.86      3133.42      3193.87      3224.87      3264.79
1412       3270.98      3284.95      3871.22
1413   !52.79      84.62      169.35      324.88!

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1410 ZeroEnergy [kcal/mol]      21.2
1411 ElectronicLevels [1/cm]   1
1412     0  2
1413 End
1414 Tunneling                   Eckart
1415 ImaginaryFrequency [1/cm]  595.1808
1416 WellDepth[kcal/mol]      31.2
1417 WellDepth[kcal/mol]      8.6
1418 End
1419 End
1420 !-----
1421 !-----WELL 5 to Products -----
1422 !-----
1423 Bimolecular      P7      # CC[CH2] + O=C0
1424   Fragment      CC[CH2]
1425     RRHO
1426   Geometry [angstrom]      10
1427     C              -1.21576400   -0.24393400   -0.03513100
1428     C              0.07906700    0.55925200    0.04786100
1429     C              1.29106100   -0.29615900   -0.03188100
1430     H              -1.27316400   -0.78426700   -0.98002700
1431     H              -2.09049500    0.40029700    0.04349600
1432     H              -1.26327100   -0.97710700    0.77093600
1433     H              0.10443800    1.31177800   -0.74483100
1434     H              0.08395300    1.13114900    0.98641300
1435     H              2.25628600    0.12468300   -0.26877100
1436     H              1.25606300   -1.32148700    0.30769100
1437   Core RigidRotor
1438     SymmetryFactor      1
1439   End
1440   Rotor              Hindered
1441     Group              4 5 6
1442     Axis                1 2
1443     Symmetry            3
1444     Potential [kcal/mol]  6
1445     0. 3.0 0. 3.0 0. 3.0
1446   End
1447   Rotor              Hindered
1448     Group              9 10
1449     Axis                3 2
1450     Symmetry            2
1451     Potential [kcal/mol]  2
1452     0. 0.26
1453   End
1454   Frequencies [1/cm]    22
1455   373.58 453.53 756.21 896.17 928.95 1053.02
1456   1101.17 1178.18 1271.23 1363.51 1410.57 1469.66
1457   1474.78 1502.4 1508.75 2984.28 3059.08 3062.57

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1458 3130.39 3139.2 3166.94 3270.35
1459 ! 93.61 253.67 ! Torsions
1460 ZeroEnergy [kcal/mol] 0
1461 ElectronicLevels [1/cm] 1
1462 0 1
1463 End
1464 Fragment O=CO
1465 RRHO
1466 Geometry [angstrom] 5
1467 O -1.12637500 -0.26441800 0.00000000
1468 C -0.13498100 0.39859000 0.00000000
1469 H -0.10944700 1.49339600 0.00000000
1470 O 1.11063300 -0.08930300 0.00000000
1471 H 1.04527400 -1.05517000 0.00000000
1472 Core RigidRotor
1473 SymmetryFactor 1
1474 End
1475 Rotor Hindered
1476 Group 5
1477 Axis 4 2
1478 Symmetry 1
1479 Potential [kcal/mol] 4
1480 0.0 12.62 4.68 12.62
1481 End
1482 Frequencies [1/cm] 8
1483 645.59 1077.81 1164.30 1323.84 1418.68 1881.20 3099.91 3799.58
1484 ! 680.89 !
1485 ZeroEnergy [kcal/mol] 0
1486 ElectronicLevels [1/cm] 1
1487 0 2
1488 End
1489 GroundEnergy [kcal/mol] -18.5
1490 End
1491 !-----
1492 Barrier B12 W5 P7 # TS_CC [CH2]_O=CO
1493 Variational
1494 RRHO
1495 Geometry [angstrom] 15
1496 C 2.12326100 -0.78051400 -0.19320400
1497 C 1.32670200 0.12577600 0.73728900
1498 C 0.62133900 1.21307100 0.00667400
1499 O -0.71729600 0.36770200 -0.93138400
1500 C -1.30714500 -0.56586900 -0.33753400
1501 H -0.97976700 -1.60104300 -0.33630300
1502 O -2.26108900 -0.31984700 0.59343300
1503 H 1.47512300 -1.20300500 -0.96105600
1504 H 2.59299000 -1.59826200 0.35116400
1505 H 2.90728800 -0.21535800 -0.69843200

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```
1506 H 0.58398800 -0.46237600 1.29097400
1507 H 1.98157200 0.55751200 1.50036800
1508 H 0.05459900 1.91947800 0.60064900
1509 H 1.13107000 1.65500300 -0.83912600
1510 H -2.50472700 0.61042400 0.51601200
1511 Core RigidRotor
1512 SymmetryFactor 1
1513 End
1514 Rotor Hindered
1515 Group 4 13 14
1516 Axis 3 2
1517 Symmetry 1
1518 Potential[kcal/mol] 6
1519 0.0 2.75 1.2 2.14 1.18 6.58
1520 End
1521 Rotor Hindered
1522 Group 5
1523 Axis 4 3
1524 Symmetry 1
1525 Potential[kcal/mol] 4
1526 0.0 2.25 1.44 3.15
1527 End
1528 Rotor Hindered
1529 Group 8 9 10
1530 Axis 1 2
1531 Symmetry 3
1532 Potential[kcal/mol] 2
1533 0.0 2.76
1534 End
1535 Rotor Hindered
1536 Group 15
1537 Axis 7 5
1538 Symmetry 1
1539 Potential[kcal/mol] 4
1540 0.0 6.79 2.67 7.95
1541 End
1542 Frequencies[1/cm] 34
1543 141.79 289.91 346.88 423.27 606.94 710.97 756.12 797.86 910.05
1544 940.14 969.04 1072.03 1100.97 1124.80 1194.71 1282.06 1296.69
1545 1336.40 1375.41 1414.26 1475.59 1481.20
1546 1497.72 1509.19 1515.12 3019.91 3054.81 3064.95 3131.92 3143.57
1547 3146.64 3169.47 3236.30 3838.45
1548 !62.20 107.56 201.78 506.83!
1549 ZeroEnergy[kcal/mol] 5.0
1550 ElectronicLevels[1/cm] 1
1551 0 2
1552 End
1553 Tunneling Eckart
```

```

1552   ImaginaryFrequency [1/cm]      775.36
1553   WellDepth[kcal/mol]           14.0
1554   WellDepth[kcal/mol]           23.5
1555   End
1556 End
1557 End

```

E.8 CCOCO[CH2]

```

1 TemperatureList [K]                500 510 520 530 540 550 560 570 580
   590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750
   760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920
   930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060 1070
   1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200
   1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320 1330
   1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460
   1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580 1590
   1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710 1720
   1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840 1850
   1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980
   1990 2000
2 PressureList [atm]                 0.00001 0.001 0.01 0.1 1 10 100.
3 !PressureList [bar]                1.
4 EnergyStepOverTemperature          .2
5 ExcessEnergyOverTemperature        30
6 ModelEnergyLimit [kcal/mol]        400
7 CalculationMethod                  direct
8 !CalculationMethod                 low-eigenvalue !direct
9 WellCutoff                          10
10 ChemicalEigenvalueMax              0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor [1/cm]                200
15       Power                        .85
16       ExponentCutoff               15
17   End
18   CollisionFrequency
19     LennardJones
20       Epsilons [1/cm]              94.87 268.26 !Ar and CCOCO[CH2]
21       Sigmas [angstrom]             3.33 5.83
22       Masses [amu]                  39.88 89.11
23   End
24   !-----
25   !-----WELL 1 to Products -----
26   !-----
27 Well          W1          # W_CCOCO[CH2]_m062x.log
28   Species

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```
29      RRHO
30      Geometry [angstrom]      15
31      C      0.014783426      -0.0119935837      -0.0103422635
32      O      -0.0024138094      -0.0072930793      1.3451304474
33      C      1.2749942279      0.0030002078      1.9462362319
34      O      2.0172040058      -1.1279838406      1.6497614135
35      C      1.4631221731      -2.3265914553      2.1742206778
36      C      2.4147811714      -3.4570840431      1.8630714045
37      H      -0.9632988961      -0.0640728065      -0.4584452616
38      H      0.8927735478      -0.4012129986      -0.5058708057
39      H      1.8486369535      0.855942202      1.5802591448
40      H      1.0815352411      0.0864282337      3.0184158142
41      H      1.3243046626      -2.2143854687      3.2558566152
42      H      0.4817444164      -2.5049247984      1.7275679455
43      H      3.3886945035      -3.2685235324      2.3119151449
44      H      2.025993717      -4.3974046839      2.251629836
45      H      2.5446136254      -3.5535303802      0.7862036653
46      Core RigidRotor
47      SymmetryFactor      1
48      End
49      Rotor      Hindered
50      Group      7 8
51      Axis      1 2
52      Symmetry      1
53      Potential [kcal/mol]      4
54      0.0 11.55 0.67 5.05
55      End
56      Rotor      Hindered
57      Group      1
58      Axis      2 3
59      Symmetry      1
60      Potential [kcal/mol]      6
61      0.0 4.28 1.6 2.6 2.18 2.93
62      End
63      Rotor      Hindered
64      Group      5
65      Axis      4 3
66      Symmetry      1
67      Potential [kcal/mol]      6
68      0.0 6.91 1.95 4.46 3.8 4.79
69      End
70      Rotor      Hindered
71      Group      6 11 12
72      Axis      5 4
73      Symmetry      1
74      Potential [kcal/mol]      8
75      0.0 1.63 1.05 1.12 1.07 4.61 0.77 1.23
76      End
```

```

77 Rotor      Hindered
78   Group          13 14 15
79   Axis           6 5
80   Symmetry       3
81   Potential [kcal/mol] 2
82     0.0  3.05
83 End
84 Frequencies [1/cm] 34
85     302.16    359.65    462.79    573.73    649.76
86     821.45    881.67    991.14    1065.83    1107.19
87     1161.87    1185.76    1199.09    1246.95    1269.05
88     1309.95    1345.91    1400.15    1433.72    1446.61
89     1488.63    1491.73    1505.56    1519.45    1536.64
90     3024.66    3057.19    3073.81    3076.5    3115.41
91     3150.44    3152.21    3161.74    3302.14
92     !57.06    80.74    241.97    172.0    273.48! Torsions
93 ZeroEnergy [kcal/mol] 0
94 ElectronicLevels [1/cm] 1
95     0 2
96 End
97 End
98 Well      W2      # W_CCO[CH]OC_m062x.log
99 Species
100 RRHO
101 Geometry [angstrom] 15
102 C      0.0699272834    -0.2329127203    0.1220920593
103 C      0.0572517118    0.0547689702    1.6103102573
104 O      1.3705742127    0.05159696    2.1723508234
105 C      2.0559467553    -1.1022857866    2.0595549147
106 O      1.3401533619    -2.2095278274    2.4168176471
107 C      2.0643469632    -3.4083486534    2.2438179794
108 H      2.9744115926    -3.4034632774    2.8507258204
109 H      1.4223319889    -4.2223348495    2.5672777004
110 H      0.7322124267    0.4618336631    -0.3930385392
111 H      -0.9354490276    -0.1246549191    -0.2841290767
112 H      0.4131887368    -1.2483510453    -0.0717335853
113 H      -0.3228015833    1.0539334302    1.8111880621
114 H      -0.5649783367    -0.6662397399    2.141132132
115 H      2.3375939447    -3.5467752781    1.1952853545
116 H      3.0618994777    -1.0300334995    2.4702782091
117 Core RigidRotor
118   SymmetryFactor 1
119 End
120 Rotor      Hindered
121   Group          9 10 11
122   Axis           1 2
123   Symmetry       1
124   Potential [kcal/mol] 6

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122      0.0  3.03  0.0  3.03  0.0  3.04
123      End
124      Rotor      Hindered
125      Group      1 12 13
126      Axis      2 3
127      Symmetry   1
128      Potential [kcal/mol]      6
129      0.0  3.64  0.48  1.17  -0.03  1.28
130      End
131      Rotor      Hindered
132      Group      5 15
133      Axis      4 3
134      Symmetry   1
135      Potential [kcal/mol]      8
136      0.0  2.95  2.9  2.93  2.4  2.72  2.46  3.17
137      End
138      Rotor      Hindered
139      Group      6
140      Axis      5 4
141      Symmetry   1
142      Potential [kcal/mol]      4
143      0.0  2.01  1.51  9.16
144      End
145      Rotor      Hindered
146      Group      7 8 14
147      Axis      6 5
148      Symmetry   3
149      Potential [kcal/mol]      2
150      0.0  1.68
151      End
152      Frequencies [1/cm]      34
153      261.43      359.21      465.24      608.02      814.33
154      868.02      935.18      1035.69      1078.87      1117.23
155      1181.07      1189.85      1203.18      1257.75      1294.09
156      1334.16      1367.61      1402.81      1437.73      1484.97
157      1489.09      1499.82      1500.37      1515.64      1526.76
158      3033.69      3069.78      3087.02      3092.63      3110.12
159      3131.62      3145.65      3155.53      3167.04
160      !58.3      86.38      156.53      199.9      264.34! Torsions
161      ZeroEnergy [kcal/mol]      0.9
162      ElectronicLevels [1/cm]      1
163      0 2
164      End
165      End
166      Barrier      B1  W1  W2      # W_CCO[CH]OC_m062x.log
167      Variational
168      RRHO
169      Geometry [angstrom]      15

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167 C -0.0031229326 -0.0002946779 0.0024794799
168 O 0.0010685985 0.0005787559 1.4166009498
169 C 1.3964138969 0.0001817209 1.5568609442
170 O 1.9293318661 1.0718202924 2.1876269907
171 C 1.5337121159 2.339622929 1.6687003979
172 C 2.2122302579 3.4086224443 2.4903582059
173 H -0.4293786919 -0.8951424429 -0.4414621763
174 H -0.3088045542 0.9475030211 -0.4352966762
175 H 1.9089376396 3.3310624749 3.5330777801
176 H 1.9394878892 4.3962048525 2.1209410053
177 H 3.2942743371 3.3015707085 2.4361730227
178 H 0.4474446291 2.4278705118 1.7192874346
179 H 1.8355968218 2.3940791411 0.6170400505
180 H 1.4057443327 -0.023697597 0.1675068693
181 H 1.7934807387 -0.9217531164 1.9781027147
182 Core RigidRotor
183 SymmetryFactor 0.5
184 End
185 Rotor Hindered
186 Group 5
187 Axis 4 3
188 Symmetry 1
189 Potential [kcal/mol] 6
190 0.0 4.17 3.02 4.24 2.25 5.16
191 End
192 Rotor Hindered
193 Group 6 12 13
194 Axis 5 4
195 Symmetry 1
196 Potential [kcal/mol] 6
197 0.0 1.82 0.58 5.03 0.88 1.43
198 End
199 Rotor Hindered
200 Group 9 10 11
201 Axis 6 5
202 Symmetry 3
203 Potential [kcal/mol] 2
204 0.0 3.06
205 End
206 Frequencies [1/cm] 35
207 72.17 110.51 285.9 379.03 418.52
633.32 675.32 827.93
208 876.15 950.42 1053.38 1078.82 1111.84
1115.76 1156.82 1171.94 1189.82 1248.11
209 1308.35 1313.71 1378.97 1402.65 1435.5
1481.13 1488.77 1506.59 1534.82 1898.59
210 3034.38 3075.73 3082.39 3099.53 3124.65
3153.12 3155.12 3194.63

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211      !72.17      169.36      252.96! Torsions
212      ZeroEnergy[kcal/mol]      39.0
213      ElectronicLevels [1/cm]      1
214      0 2
215      End
216      Tunneling      Eckart
217      ImaginaryFrequency [1/cm]      1970.1498
218      WellDepth[kcal/mol]      39.0
219      WellDepth[kcal/mol]      38.01
220      End
221      End
222      Well      W3      # W_C[CH]OCOC_m062x.log
223      Species
224      RRHO
225      Geometry[angstrom]      15
226      C      -0.0002279902      0.0061809167      0.0003026867
227      C      -0.0040373378      -0.000581162      1.4805027374
228      O      1.2387260795      -0.0064992508      2.0463699564
229      C      1.2415577268      0.0515942031      3.452565855
230      O      0.7500033514      1.2536271627      3.9421447285
231      C      1.554435286      2.3631284082      3.5962623325
232      H      2.5794865858      2.2235594912      3.9542365888
233      H      1.1211626686      3.235272807      4.0778759228
234      H      -1.0124289015      -0.1123419807      -0.3815468419
235      H      0.615661016      -0.8080059985      -0.3849228637
236      H      0.4069314615      0.9406473      -0.40554913
237      H      1.5755193419      2.5152821638      2.5155919351
238      H      -0.7847400456      0.4836138141      2.0545226728
239      H      0.6012324122      -0.7318230706      3.8610473116
240      H      2.2845443533      -0.0978417948      3.7436230713
241      Core RigidRotor
242      SymmetryFactor      1
243      End
244      Rotor      Hindered
245      Group      9 10 11
246      Axis      1 2
247      Symmetry      1
248      Potential[kcal/mol]      6
249      0.0 1.32 -0.0 1.32 0.0 1.32
250      End
251      Rotor      Hindered
252      Group      1 13
253      Axis      2 3
254      Symmetry      1
255      Potential[kcal/mol]      4
256      0.0 4.53 1.35 4.31
257      End
258      Rotor      Hindered

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259      Group                5 14 15
260      Axis                  4 3
261      Symmetry               1
262      Potential [kcal/mol]    6
263      0.0  8.67  1.63  2.71  2.34  2.96
264      End
265      Rotor      Hindered
266      Group                6
267      Axis                  5 4
268      Symmetry               1
269      Potential [kcal/mol]    6
270      0.0  6.57  2.12  3.82  2.99  4.25
271      End
272      Rotor      Hindered
273      Group                7 8 12
274      Axis                  6 5
275      Symmetry               3
276      Potential [kcal/mol]    2
277      0.0  1.68
278      End
279      Frequencies [1/cm]    34
280      273.74      367.73      465.44      573.91      661.75
281      900.08      986.06      1022.77      1092.72      1112.32
282      1163.45      1190.54      1214.72      1223.09      1276.07
283      1350.93      1383.16      1427.77      1456.74      1470.03
284      1485.59      1497.12      1498.86      1516.09      1524.33
285      3006.98      3033.17      3054.74      3089.06      3100.99
286      3115.39      3146.67      3162.32      3184.8
287      !65.87      86.32      137.71      180.69      228.59! Torsions
288      ZeroEnergy [kcal/mol]  -1.2
289      ElectronicLevels [1/cm]  1
290      0  2
291      End
292      End
293      Barrier      B2  W1  W3      # W_C[CH]OCOC_m062x.log
294      Variational
295      RRHO
296      Geometry [angstrom]    15
297      C      0.004383189      -0.0071387273      0.0249854039
298      C      0.0269540707      0.0220603329      1.5202150774
299      O      1.3386914694      0.0852174634      1.9898389405
300      C      1.4479984124      0.2448632454      3.3795120904
301      O      0.4092586481      1.0141291867      3.9308795512
302      C      -0.0737710045      1.9991652361      3.0807011571
303      H      0.6852812779      2.6858150747      2.7016628415
304      H      -0.9417923716      2.4717419417      3.5244502692
305      H      0.5097743458      0.8709219823      -0.3771344514
306      H      -1.0219782253      -0.0178215861      -0.3377524636

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304 H      0.5161545567   -0.8933738703   -0.3584156985
305 H      -0.421612267    1.1973988844    2.0181227965
306 H      -0.5710446087   -0.7403936671    2.0273666926
307 H      1.4006475727    -0.720092979    3.8909192945
308 H      2.41753255     0.7215556695    3.5456862711
309 Core RigidRotor
310     SymmetryFactor    0.5
311 End
312 Rotor      Hindered
313     Group          9 10 11
314     Axis           1 2
315     Symmetry       3
316     Potential[kcal/mol] 2
317     0.0  2.37
318 End
319 Frequencies [1/cm]  37
320     132.9    152.82    249.58    328.88    430.01
540.36    576.58    702.33    878.91
321     903.33    993.52    1074.16    1101.49    1126.58
     1151.22    1156.44    1180.53    1216.55    1255.7
322     1311.52    1366.33    1415.93    1444.67    1452.12
     1479.03    1479.64    1498.92    1535.41    1664.8
323     3043.07    3049.64    3059.54    3066.24    3089.78
     3116.0    3150.4    3205.22
324 !211.73! Torsions
325 ZeroEnergy[kcal/mol] 23.3
326 ElectronicLevels [1/cm] 1
327     0  2
328 End
329 Tunneling      Eckart
330 ImaginaryFrequency [1/cm] 1770.5051
331 WellDepth[kcal/mol] 23.3
332 WellDepth[kcal/mol] 24.5
333 End
334 End
335 Well      W4      # W_[CH2]COCOC_m062x.log
336 Species
337     RRHO
338 Geometry[angstrom] 15
339 C      -0.0075341675    0.0023776341    0.0122701686
340 O      0.0073388744    -0.0014187079    1.424348381
341 C      1.2964403514    0.0007211451    1.9548000676
342 O      2.0056208394    1.1689921347    1.6593652189
343 C      1.4814118147    2.3233746919    2.3030406568
344 C      1.7712258554    2.3389577521    3.7584644252
345 H      -1.0467300455    -0.0632700315    -0.2989061521
346 H      0.5423073761    -0.858351136    -0.382614588
347 H      0.4370584077    0.9153094886    -0.3882143849

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```

348   H           1.1292951908    2.8670831183    4.4459717034
349   H           2.7268079594    1.9773904448    4.1084002444
350   H           0.4060710255    2.4023228471    2.1185342023
351   H           1.9608507414    3.1691166887    1.7984384667
352   H           1.8910309154    -0.8157182285    1.5346881621
353   H           1.1750078469    -0.1237928542    3.0336974419
354   Core RigidRotor
355       SymmetryFactor      1
356   End
357   Rotor           Hindered
358       Group                7 8 9
359       Axis                  1 2
360       Symmetry              3
361       Potential [kcal/mol]   2
362       0.0  1.61
363   End
364   Rotor           Hindered
365       Group                1
366       Axis                  2 3
367       Symmetry              1
368       Potential [kcal/mol]   6
369       0.0  4.15  2.69  3.24  3.01  7.32
370   End
371   Rotor           Hindered
372       Group                5
373       Axis                  4 3
374       Symmetry              1
375       Potential [kcal/mol]   6
376       0.0  3.64  2.97  3.82  3.56  8.66
377   End
378   Rotor           Hindered
379       Group                6 12 13
380       Axis                  5 4
381       Symmetry              1
382       Potential [kcal/mol]   6
383       0.0  1.8  0.35  1.38  0.54  3.18
384   End
385   Rotor           Hindered
386       Group                10 11
387       Axis                  6 5
388       Symmetry              2
389       Potential [kcal/mol]   2
390       0.0  1.76
391   End
392   Frequencies [1/cm]      34
393       284.64    426.35    465.79    527.84    620.67
394       848.01    943.33    983.22    1055.39    1103.23
       1131.72    1168.46    1190.19    1209.24    1252.5

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395      1304.56      1351.95      1394.43      1445.49      1456.42
      1481.63      1494.05      1497.31      1515.94      1523.66
396      3026.27      3030.27      3046.47      3068.23      3097.74
      3100.29      3158.68      3174.21      3285.02
397      !57.34      93.26      148.52      192.02      227.12!
398      ZeroEnergy [kcal/mol]      5.8
399      ElectronicLevels [1/cm]      1
400      0 2
401      End
402      End
403      Barrier      B3  W1  W4      # W_ [CH2]COCOC_m062x.log
404      Variational
405      RRHO
406      Geometry [angstrom]      15
407      C      0.0018291926      -0.004510396      0.0058299264
408      C      0.0524769187      -0.026174463      1.5105568753
409      O      1.4099143023      -0.0126989668      1.9543096896
410      C      1.9284491563      -1.2732632054      2.2420864154
411      O      1.6750590947      -2.2226508558      1.2370483866
412      C      1.968161729      -1.7729676277      -0.0410481587
413      H      1.8815381305      -2.5928959702      -0.7464331268
414      H      2.906614622      -1.2195603264      -0.114777925
415      H      1.0151880971      -0.9044049275      -0.3075149484
416      H      0.3534931015      0.920301268      -0.4425046693
417      H      -0.9081878841      -0.3858916122      -0.446311622
418      H      -0.4168581169      0.860482263      1.9422119476
419      H      -0.4611241005      -0.9067664716      1.9049564771
420      H      3.004058993      -1.1270023671      2.3730189913
421      H      1.4818551953      -1.6961477678      3.1459338298
422      Core RigidRotor
423      SymmetryFactor      1
424      End
425      Frequencies [1/cm]      38
426      137.61      240.9      304.66      367.38      404.79
430.81      570.53      633.14      703.51      863.21
427      888.52      988.35      1022.95      1078.32      1098.96
      1165.48      1174.24      1185.98      1222.04      1255.53
428      1311.53      1334.49      1395.69      1409.11      1446.92
      1451.44      1471.95      1501.39      1520.51      1529.95
429      3044.1      3049.64      3062.77      3090.18      3095.3
      3117.7      3187.2      3203.4
430      !!Torsions
431      ZeroEnergy [kcal/mol]      22.8
432      ElectronicLevels [1/cm]      1
433      0 2
434      End
435      Tunneling      Eckart
436      ImaginaryFrequency [1/cm]      1728.3804

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437 WellDepth[kcal/mol]      22.8
438 WellDepth[kcal/mol]      17.0
439 End
440 End
441 Bimolecular      P1      # C=O  +  CCO[CH2]
442 Fragment C=O
443 RRHO
444 Geometry[angstrom]      4
445 O      -0.000000016      -0.0000022088      0.0061054213
446 C      -0.0000000144     0.0000068137      1.2014608526
447 H      0.9375275336      -0.0000022726     1.7838372267
448 H      -0.9375275608     0.0000246367      1.7838372291
449 Core RigidRotor
450 SymmetryFactor      2
451 End
452 Frequencies [1/cm]      6
453      1216.69      1279.34      1545.84      1876.79      2940.94
454      3011.91
455 !! Torsions
456 ZeroEnergy[kcal/mol]      0
457 ElectronicLevels [1/cm]      1
458      0  1
459 End
460 Fragment CCO[CH2]
461 RRHO
462 Geometry[angstrom]      11
463 O      -0.0014817113      -0.0155848882     0.0002794589
464 C      -0.0005868038      -0.0090032165     1.4196033317
465 C      1.4321878366      0.002078756      1.894442275
466 C      -1.2263142708      -0.008203098     -0.5632685818
467 H      -1.2161425723      0.0491526598     -1.6394562426
468 H      -2.0502495284      0.3960187506     0.0122880813
469 H      -0.5404318214      0.8764641954     1.7712477052
470 H      -0.53190841      -0.8946070834     1.779843481
471 H      1.9477347437      0.8859620831     1.5224489139
472 H      1.4686074424      0.0086994034     2.9829490596
473 H      1.9564191269      -0.8810975598     1.5333225193
474 Core RigidRotor
475 SymmetryFactor      1
476 End
477 Rotor      Hindered
478 Group      4
479 Axis      1  2
480 Symmetry      1
481 Potential[kcal/mol]      6
482      0.0  1.51  0.6  4.08  0.15  1.5
483 End
484 Rotor      Hindered
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484      Group                5 6
485      Axis                 4 1
486      Symmetry             1
487      Potential [kcal/mol] 6
488      0.0  5.25  0.0  0.3  0.0  4.79
489      End
490      Rotor      Hindered
491      Group                9 10 11
492      Axis                 3 2
493      Symmetry             3
494      Potential [kcal/mol] 2
495      0.0  3.0
496      End
497      Frequencies [1/cm]   24
498      303.35      487.19      593.22      821.8      883.99
1073.33      1122.2
499      1187.61      1234.87      1308.92      1313.32      1400.08
      1434.83      1488.69      1493.38      1506.22      1531.36
500      3029.29      3069.09      3075.45      3137.07      3152.88
      3154.08      3283.45
501      !99.2      239.29      290.05!
502      ZeroEnergy [kcal/mol] 0
503      ElectronicLevels [1/cm] 1
504      0 2
505      End
506      GroundEnergy [kcal/mol] 12.7
507      End
508      Barrier      B4  W1  P1  # TS_CC0[CH2]+C=O_m062x.log
509      Variational
510      RRHO
511      Geometry [angstrom] 15
512      C      -0.0126362017      -0.0167350269      -0.0036094738
513      C      -0.0028985098      0.0073244075      1.5044261861
514      O      1.3569275776      0.0075381778      1.9422594928
515      C      1.5111559737      0.2309457065      3.2453005624
516      O      1.2835517687      2.2118374673      3.3657040161
517      C      1.4702801407      2.7829202085      2.2743342918
518      H      0.6401989795      2.9808830755      1.5872667998
519      H      2.4735844614      3.0699371577      1.9459207157
520      H      0.486544643      0.8681404507      -0.3959216961
521      H      -1.0371055731      -0.0341244932      -0.37246207
522      H      0.5061090852      -0.8997410198      -0.3731759416
523      H      -0.4955242657      0.8991649057      1.8989726018
524      H      -0.4996793959      -0.8731416125      1.9228907883
525      H      0.6978205298      -0.0233475994      3.912462351
526      H      2.5303737997      0.1513601889      3.5869173613
527      Core RigidRotor
528      SymmetryFactor      1

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529 End
530 Rotor          Hindered
531   Group          9 10 11
532   Axis           1 2
533   Symmetry       3
534   Potential [kcal/mol] 2
535     0.0  3.01
536 End
537 Rotor          Hindered
538   Group          1 12 13
539   Axis           2 3
540   Symmetry       1
541   Potential [kcal/mol] 6
542     0.0  2.16  0.87  3.7  1.28  2.74
543 End
544 Rotor          Hindered
545   Group          5 14 15
546   Axis           4 3
547   Symmetry       1
548   Potential [kcal/mol] 4
549     0.0 13.46  2.08  7.72
550 End
551 Rotor          Hindered
552   Group          6
553   Axis           5 4
554   Symmetry       1
555   Potential [kcal/mol] 4
556     0.0  4.72  3.04  3.59
557 End
558 Frequencies [1/cm] 34
559   152.21    250.77    275.62    313.52    408.85
560 516.33    651.78
561   823.52    879.13    895.35    936.22    1072.73
562 1123.64    1185.68    1234.34    1249.56    1257.19
563   1308.65    1397.01    1402.08    1437.49    1486.72
564   1504.79    1518.67    1532.74    1581.9     3008.94
565   3042.43    3074.86    3087.49    3094.72    3148.47
566   3152.22    3154.29    3288.62
567   !67.63    110.38    207.35!
568 ZeroEnergy [kcal/mol] 25.2
569 ElectronicLevels [1/cm] 1
570   0 2
571 End
572 Tunneling          Eckart
573 ImaginaryFrequency [1/cm] 606.8734
574 WellDepth [kcal/mol] 25.21
575 WellDepth [kcal/mol] 12.5
576 End

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573 End
574 !-----
575 !-----WELL 2 to Products -----
576 !-----
577 Barrier      B5  W2  W4      # W_[CH2]COCOC_m062x.log
578 Variational
579 RRHO
580 Geometry[angstrom]      15
581 C      0.0004665243      0.0012264764      0.00012082
582 C      0.000205991      0.0001034846      1.5039700908
583 O      1.3754025349      -0.0006875452      1.9588537021
584 C      2.2379853956      0.4348991236      0.9772003995
585 H      3.0779655847      -0.2366129579      0.8224864415
586 O      2.7176629545      1.7077906116      1.1237395014
587 C      1.7293653338      2.6825231041      1.3899984385
588 H      1.3685569653      0.3605575271      -0.0249015063
589 H      -0.5853642353      0.7575306655      -0.5074149172
590 H      -0.0183544803      -0.96626422      -0.489062994
591 H      -0.5007523005      0.883470427      1.9057091931
592 H      -0.4628121328      -0.886027322      1.9348411675
593 H      0.968301959      2.685171994      0.6029648204
594 H      1.2521460322      2.5001796088      2.3536929883
595 H      2.2313528794      3.645374994      1.4073388295
596 Core RigidRotor
597 SymmetryFactor      0.5
598 End
599 Rotor      Hindered
600 Group      7
601 Axis      6 4
602 Symmetry      1
603 Potential[kcal/mol]      6
604 0.0 3.64 1.34 2.74 0.82 3.99
605 End
606 Rotor      Hindered
607 Group      13 14 15
608 Axis      7 6
609 Symmetry      1
610 Potential[kcal/mol]      6
611 0.0 2.53 0.0 2.53 0.0 2.53
612 End
613 Frequencies [1/cm]      36
614 152.47      178.85      333.19      474.32      576.96
615 649.78      699.63      845.3
616 893.96      977.75      1006.69      1036.25      1090.94
1153.41      1171.14      1183.77      1214.52      1254.65
1266.99      1363.96      1388.31      1415.37      1466.27
1482.23      1498.4      1516.18      1534.41      1706.37

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617          3034.25      3065.48      3109.0      3119.09      3139.3
          3146.9      3168.13      3224.66
618      !113.16      237.76!
619      ZeroEnergy [kcal/mol]      25.5
620      ElectronicLevels [1/cm]      1
621          0  2
622      End
623      Tunneling      Eckart
624      ImaginaryFrequency [1/cm]      1749.2129
625      WellDepth [kcal/mol]      24.6
626      WellDepth [kcal/mol]      19.7
627      End
628      End
629      Bimolecular      P2      # Bi_0=COC_E2-75      +      [CH2]C
630      Fragment      Bi_0=COC_E2-75
631      RRHO
632      Geometry [angstrom]      8
633      O      0.0418924661      0.0001246289      0.0116965965
634      C      0.0167993753      0.0000166154      1.2063812612
635      O      1.0865652314      -0.0000631766      1.9997896845
636      C      2.3431972004      -0.0000105584      1.318127389
637      H      -0.8942447797      -0.0000317404      1.8147181938
638      H      3.1023784274      -0.0000881096      2.0924532518
639      H      2.4312544895      -0.8854855669      0.6918659719
640      H      2.4312687749      0.885578481      0.6920292162
641      Core RigidRotor
642      SymmetryFactor      1.0
643      End
644      Rotor      Hindered
645      Group      1 5
646      Axis      2 3
647      Symmetry      1
648      Potential [kcal/mol]      4
649      0.0  13.48  5.51  13.48
650      End
651      Rotor      Hindered
652      Group      2
653      Axis      3 4
654      Symmetry      3
655      Potential [kcal/mol]      2
656      0.0  1.12
657      End
658      Frequencies [1/cm]      16
659      319.89      792.46      984.42      1064.87      1192.28
          1207.29      1273.14      1410.45
660      1481.65      1497.47      1509.45      1856.01      3083.57
          3088.44      3158.89      3195.05
661      !155.75      343.39!

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662 ZeroEnergy [kcal/mol]      0
663 ElectronicLevels [1/cm]   1
664   0  1
665 End
666 Fragment   [CH2]C
667   RRHO
668 Geometry [angstrom]       7
669   C      0.0002983383    -0.0005389889    0.0004031088
670   C      0.0047388604    -0.0084680438    1.4846485597
671   H      1.0125028336    -0.0004449026    -0.404522378
672   H     -0.4985399523     0.8907396606    -0.4014899118
673   H     -0.5291032253    -0.8632636678    -0.4045194797
674   H      0.770457535    0.5135203684    2.0371553306
675   H     -0.8406008348    -0.3881967978    2.037158663
676 Core RigidRotor
677   SymmetryFactor           1.0
678 End
679 Rotor      Hindered
680   Group                3 4 5
681   Axis                  1 2
682   Symmetry              1
683   Potential [kcal/mol]   12
684   0.0  0.07  0.0  0.08  0.0  0.07  0.0  0.08  0.0  0.07  0.0
685   0.08
686 End
687 Frequencies [1/cm]      14
688   444.91      810.81      982.95      1081.35      1195.68
689   1403.91     1471.58     1487.61     1489.49
690   3004.53     3085.23     3128.72     3174.72     3276.16
691   !125.25!
692 ZeroEnergy [kcal/mol]      0
693 ElectronicLevels [1/cm]   1
694   0  2
695 End
696 GroundEnergy [kcal/mol]   -10.1
697 End
698 Barrier      B6  W2  P2  # TS_C[CH2]_COC=0_E9-19_m062x.log
699 Variational
700   RRHO
701 Geometry [angstrom]       15
702   C      0.0129958622    -0.0472878214    0.0051768466
703   C     -0.0043234375     0.0120890428    1.4921754805
704   O      1.7447963624    -0.0000412445    2.0205324676
705   C      2.6224009901    -0.2457458213    1.1562992952
706   H      3.0693174825     0.4999060305    0.5066969116
707   O      2.9346035332    -1.5024581724    0.7666288127
708   C      2.3997365092    -2.5410471892    1.5722559441
709   H      0.5957874919     0.7790284508    -0.4064620928

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708   H      -0.9949407565   0.0230300161   -0.4093652809
709   H      0.4557787819  -0.9794192134   -0.3497070049
710   H      -0.3109117808   0.9472815886   1.940094423
711   H      -0.3695585512  -0.8610028794   2.0169819706
712   H      2.6436667486  -2.3809861672   2.6224196991
713   H      1.3151333867  -2.5967731632   1.4676831822
714   H      2.8484474121  -3.4635104441   1.2168283353
715   Core RigidRotor
716       SymmetryFactor           1.0
717   End
718   Rotor      Hindered
719       Group                8 9 10
720       Axis                  1 2
721       Symmetry              3
722       Potential[kcal/mol]   2
723       0.0  1.14
724   End
725   Rotor      Hindered
726       Group                1
727       Axis                  2 3
728       Symmetry              1
729       Potential[kcal/mol]   4
730       0.0  2.29  1.0  1.65
731   End
732   Rotor      Hindered
733       Group                7
734       Axis                  6 4
735       Symmetry              1
736       Potential[kcal/mol]   4
737       0.0  7.72  1.93  6.85
738   End
739   Rotor      Hindered
740       Group                13 14 15
741       Axis                  7 6
742       Symmetry              1
743       Potential[kcal/mol]   6
744       0.0  1.09  0.0  1.09  0.0  1.1
745   End
746   Frequencies [1/cm]      34
747       154.43      289.57      324.48      439.06      701.73
722.97
748       771.24      856.37      921.81      979.66      1068.28
1105.26      1184.61      1195.76      1223.39      1226.69
749       1349.53      1401.57      1448.0      1485.1      1488.97
1493.32      1501.27      1510.25      1518.0      3048.0
750       3059.06      3108.04      3121.84      3124.62      3153.38
3170.37      3174.84      3240.03
751   !56.0      99.37      178.85      203.48!

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752 ZeroEnergy [kcal/mol]      15.6
753 ElectronicLevels [1/cm]   1
754   0 2
755 End
756 Tunneling                  Eckart
757 ImaginaryFrequency [1/cm] 791.3312
758 WellDepth [kcal/mol]      14.7
759 WellDepth [kcal/mol]      25.7
760 End
761 End
762 Bimolecular      P3      # CCOC=0 + [CH3]
763 Fragment CCOC=0
764   RRHO
765 Geometry [angstrom]      11
766   O      0.0001875982      0.0001810121      -0.0000045809
767   C      0.0000360448      0.0001495603      1.1954700817
768   H      0.9006620095      0.000133797      1.8198581397
769   O      -1.0833263564      0.0001288025      1.9687150237
770   C      -2.3413617547      0.0001474237      1.272369565
771   C      -3.4340641981      0.0001156125      2.3120371537
772   H      -2.3828528182      0.8801670343      0.6309353146
773   H      -2.3828502516      -0.8798347151      0.6308837924
774   H      -3.3624530972      0.8838386974      2.9438172999
775   H      -4.407993839      0.0001325389      1.8247539829
776   H      -3.3624553661      -0.8836477651      2.9437612352
777 Core RigidRotor
778   SymmetryFactor          1.0
779 End
780 Rotor      Hindered
781   Group          1 3
782   Axis           2 4
783   Symmetry       1
784   Potential [kcal/mol] 4
785     0.0 12.99 5.27 12.99
786 End
787 Rotor      Hindered
788   Group          2
789   Axis           4 5
790   Symmetry       1
791   Potential [kcal/mol] 6
792     0.0 1.12 0.01 6.55 0.01 1.12
793 End
794 Rotor      Hindered
795   Group          4 7 8
796   Axis           5 6
797   Symmetry       1
798   Potential [kcal/mol] 6
799     0.0 3.12 0.0 3.12 0.0 3.12
```

```
800 End
801 Frequencies [1/cm]      24
802      237.16      389.93      806.77      814.71      883.19
      1062.71      1063.87
803      1145.7      1187.56      1261.98      1310.78      1399.55
      1413.17      1434.43      1490.84      1503.7      1528.65
804      1852.53      3076.3      3081.04      3086.08      3124.94
      3153.11      3158.28
805      !77.65      236.19      344.76!
806 ZeroEnergy [kcal/mol]      0
807 ElectronicLevels [1/cm]      1
808      0 1
809 End
810 Fragment [CH3]
811      RRHO
812 Geometry [angstrom]      4
813      C      0.      0.      0.
814      H      0.      0.      1.0765291468
815      H      0.9323015891      0.      -0.5382645734
816      H      -0.9323015891      0.      -0.5382645734
817 Core RigidRotor
818      SymmetryFactor      6.0
819 End
820 Frequencies [1/cm]      6
821      436.03      1412.64      1412.73      3144.41      3323.11
      3323.14
822      !!
823 ZeroEnergy [kcal/mol]      0
824 ElectronicLevels [1/cm]      1
825      0 2
826 End
827 GroundEnergy [kcal/mol]      -12.6
828 End
829 Barrier      B7 W2 P3      # TS_CCOC=0_[CH3]_E10-34_m062x.log
830 Variational
831      RRHO
832 Geometry [angstrom]      15
833      C      0.0023743634      0.0161461555      0.006978212
834      C      -0.0017707082      -0.0123431369      1.5217506171
835      O      1.3295426905      -0.0088055975      2.0462635879
836      C      2.0098507254      1.1496383336      1.9424611857
837      H      3.043169333      1.037193216      2.2592431337
838      O      1.4459651558      2.2595726382      1.7936265056
839      C      0.7470175462      3.027148304      3.2998826895
840      H      0.4386393622      0.9460650747      -0.3538159623
841      H      -1.0174011965      -0.0569525977      -0.3699679938
842      H      0.5790265479      -0.8203033123      -0.3853633626
843      H      -0.5563991334      0.8348404914      1.9244357714
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844   H      -0.4435010827   -0.9313650019   1.8997341219
845   H      0.3207480141    2.1896056453    3.8365114546
846   H      1.6176965773    3.4767902391    3.754981222
847   H      0.0344678096    3.719180553     2.8762348137
848   Core RigidRotor
849     SymmetryFactor      1.0
850   End
851   Rotor      Hindered
852     Group          8 9 10
853     Axis           1 2
854     Symmetry       1
855     Potential[kcal/mol] 6
856     0.0  3.02  0.0  3.02  0.0  3.02
857   End
858   Rotor      Hindered
859     Group          1 11 12
860     Axis           2 3
861     Symmetry       1
862     Potential[kcal/mol] 6
863     0.0  1.12  0.1  1.2  0.66  5.68
864   End
865   Rotor      Hindered
866     Group          2
867     Axis           3 4
868     Symmetry       1
869     Potential[kcal/mol] 4
870     0.0  7.64  2.44  9.18
871   End
872   Rotor      Hindered
873     Group          13 14 15
874     Axis           7 6
875     Symmetry       1
876     Potential[kcal/mol] 6
877     0.0  0.4  0.0  0.4  0.0  0.4
878   End
879   Frequencies [1/cm]    34
880     112.74      325.73      347.05      460.3      692.9
881     736.52
882     757.47      813.74      829.66      875.63      1032.08
883     1066.01     1121.89     1190.07     1207.3     1332.33
884     1354.97     1391.46     1418.0     1442.78     1447.61
885     1479.1     1492.3     1504.3     1527.63     3072.7
886     3093.86     3110.91     3138.43     3147.8     3155.85
887     3162.69     3258.74     3274.46
888     !60.97     85.53     164.81     228.76!
889   ZeroEnergy[kcal/mol] 16.5
890   ElectronicLevels [1/cm] 1
891     0  2

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888 End
889 Tunneling                      Eckart
890 ImaginaryFrequency [1/cm]      880.1354
891 WellDepth[kcal/mol]           15.6
892 WellDepth[kcal/mol]           29.1
893 End
894 End
895 !-----
896 !-----WELL 3 to Products -----
897 !-----
898 Bimolecular      P4      # CC=0 + CO[CH2]_E3-61
899 Fragment  CC=0
900      RRHO
901 Geometry [angstrom]           7
902 C      0.0168373546      0.0074667344      0.0239483472
903 C      0.0532684252      -0.0026225916      1.5228064476
904 O      1.0089808942      0.305132101      2.1786132672
905 H      -0.2265979192      -0.9922483978      -0.340091758
906 H      0.9738375724      0.3312736039      -0.375444231
907 H      -0.7794935524      0.6722088819      -0.315449875
908 H      -0.8836735886      -0.3212103319      2.0198178019
909 Core RigidRotor
910      SymmetryFactor           1.0
911 End
912 Rotor      Hindered
913      Group                    4 5 6
914      Axis                     1 2
915      Symmetry                 1
916      Potential [kcal/mol]     6
917      0.0 1.2 0.01 1.2 0.0 1.19
918 End
919 Frequencies [1/cm]           14
920      513.29      776.08      900.41      1138.06      1146.18
921      1379.69      1433.6      1464.85      1474.9
922      1874.29      2942.78      3063.51      3127.31      3180.67
923      !157.82!
924 ZeroEnergy [kcal/mol]       0
925 ElectronicLevels [1/cm]     1
926      0 1
927 End
928 Fragment  CO[CH2]_E3-61
929      RRHO
930 Geometry [angstrom]           8
931 C      0.0026902296      -0.0018733009      0.0160456217
932 O      -0.0078291385      0.0076990299      1.3645690081
933 C      1.273786629      0.0049260623      1.95715442
934 H      -0.9758393198      0.0608442139      -0.431273488
935 H      0.877362312      0.3899910944      -0.4891132431

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935   H          1.8220579152   -0.8982084317   1.6804741972
936   H          1.8440457298   0.8825642786   1.6409888636
937   H          1.1333897905   0.0323929123   3.0337908614
938   Core RigidRotor
939       SymmetryFactor          1.0
940   End
941   Rotor          Hindered
942       Group          4 5
943       Axis          1 2
944       Symmetry          1
945       Potential [kcal/mol]          6
946       0.0  0.29  0.0  5.48  0.0  5.4
947   End
948   Rotor          Hindered
949       Group          1
950       Axis          2 3
951       Symmetry          1
952       Potential [kcal/mol]          6
953       0.0  1.56  0.0  1.56  0.0  1.56
954   End
955   Frequencies [1/cm]          16
956       445.06          597.39          1006.96          1150.37          1184.95
957       1269.45          1323.39          1465.29
958       1498.89          1507.76          1515.58          3037.89          3099.15
959       3133.66          3168.24          3282.25
960       !171.34          290.38!
961   ZeroEnergy [kcal/mol]          0
962   ElectronicLevels [1/cm]          1
963       0  2
964   End
965   GroundEnergy [kcal/mol]          7.8
966   End
967   Barrier          B8  W3  P4  # TS_CC=0_C0 [CH2] _E18-12_m062x.log
968   Variational
969   RRHO
970   Geometry [angstrom]          15
971   C          0.0317419102   0.0308463666   0.016964234
972   C          -0.0311620838   -0.0103136546   1.508658573
973   H          0.9117575303   -0.0447957299   2.0669606279
974   O          -1.113688194   0.1189456755   2.1244161273
975   C          -1.6706203211   1.999108624   2.2185220311
976   O          -0.5069501117   2.6576450908   2.1690019564
977   C          0.2069939266   2.64030135   3.3952372329
978   H          -0.8429111005   -0.4581019599   -0.4114357185
979   H          0.938138769   -0.4382180667   -0.362543433
980   H          0.0294586299   1.0747017254   -0.318346403
981   H          -2.2518592346   2.0854090635   1.3140183026
982   H          -2.1789745589   1.9356825238   3.1724390117

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```
981 H -0.3338034931 3.2169985413 4.1499666012
982 H 0.331039549 1.6138151989 3.7437547989
983 H 1.1755467298 3.0946372684 3.2105710721
984 Core RigidRotor
985 SymmetryFactor 1.0
986 End
987 Rotor Hindered
988 Group 8 9 10
989 Axis 1 2
990 Symmetry 3
991 Potential [kcal/mol] 2
992 0.0 0.5
993 End
994 Rotor Hindered
995 Group 2
996 Axis 4 5
997 Symmetry 1
998 Potential [kcal/mol] 4
999 0.0 4.93 3.33 3.84
1000 End
1001 Rotor Hindered
1002 Group 7
1003 Axis 6 5
1004 Symmetry 1
1005 Potential [kcal/mol] 4
1006 0.0 10.46 2.64 6.85
1007 End
1008 Rotor Hindered
1009 Group 13 14 15
1010 Axis 7 6
1011 Symmetry 3
1012 Potential [kcal/mol] 2
1013 0.0 1.92
1014 End
1015 Frequencies [1/cm] 34
1016 111.15 248.53 407.81 478.12 499.65
662.39
1017 704.65 908.78 939.76 1004.63 1026.06
1123.02 1154.43 1185.55 1265.51 1283.96
1018 1354.07 1389.76 1463.83 1469.36 1476.2
1495.16 1513.67 1516.68 1528.96 3023.74
1019 3037.01 3044.66 3103.72 3112.14 3143.18
3151.58 3176.67 3279.52
1020 !67.34 95.87 149.45 178.93!
1021 ZeroEnergy [kcal/mol] 22.4
1022 ElectronicLevels [1/cm] 1
1023 0 2
1024 End
```

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1025 Tunneling                      Eckart
1026 ImaginaryFrequency [1/cm]      655.7407
1027 WellDepth[kcal/mol]            23.6
1028 WellDepth[kcal/mol]            14.6
1029 End
1030 End
1031 !-----
1032 !-----WELL 4 to Products -----
1033 !-----
1034 Bimolecular          P5      # C=C  +  [O]COC
1035 Fragment  C=C
1036          RRHO
1037 Geometry[angstrom]      6
1038 C          0.0000005934   -0.0000013257   0.005740686
1039 C          -0.00000068    0.0000017949   1.3272371407
1040 H          0.9217469077   -0.0000000153   -0.5612441874
1041 H          -0.9217446282   -0.0000053139   -0.5612459638
1042 H          0.9217445416    0.000005783    1.8942237904
1043 H          -0.9217469943    0.0000004844    1.894222014
1044 Core RigidRotor
1045     SymmetryFactor      4.0
1046 End
1047 Frequencies [1/cm]      12
1048     829.14      990.39      1002.91      1070.95      1243.09
1049     1388.1      1473.76      1718.54      3159.72      3175.83
1050     3235.55      3261.94
1051 !!
1052 ZeroEnergy[kcal/mol]    0
1053 ElectronicLevels [1/cm] 1
1054     0  1
1055 End
1056 Fragment  [O]COC
1057          RRHO
1058 Geometry[angstrom]      9
1059 O          0.6190925539    1.2333026374    0.1745233226
1060 C          0.9876560396    1.6303870496    1.4046807256
1061 O          0.4947479953    0.8876174447    2.469301145
1062 C          -0.9151817518    0.9194994719    2.5570147608
1063 H          2.0837969907    1.6157267218    1.4807404905
1064 H          0.6693669199    2.6924348993    1.4784997506
1065 H          -1.2719639526    1.9471586296    2.6879247658
1066 H          -1.3752133308    0.4934711935    1.6640667461
1067 H          -1.1965461365    0.3309141128    3.4254024352
1068 Core RigidRotor
1069     SymmetryFactor      1.0
1070 End
1071 Rotor          Hindered
1072     Group              2

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1072      Axis                3 4
1073      Symmetry            3
1074      Potential [kcal/mol] 2
1075      0.0  1.7
1076      End
1077      Rotor      Hindered
1078      Group                1 5 6
1079      Axis                2 3
1080      Symmetry            1
1081      Potential [kcal/mol] 6
1082      0.0  2.19  0.04  3.53  2.25  3.54
1083      End
1084      Frequencies [1/cm]   19
1085      363.19      613.76      810.76      976.59      1076.02
1086      1152.39      1189.69      1224.58
1087      1273.63      1355.26      1400.69      1485.0      1497.47
1088      1521.26      2881.46      3014.09      3026.92      3102.78
1089      3166.67
1090      !132.13      202.72!
1091      ZeroEnergy [kcal/mol] 0
1092      ElectronicLevels [1/cm] 1
1093      0  2
1094      End
1095      GroundEnergy [kcal/mol] 23.9
1096      End
1097      Barrier      B9  W4  P5      # TS_CO2C[0]_C=C_E14-03_m062x.log
1098      Variational
1099      RRHO
1100      Geometry [angstrom] 15
1101      C      0.0099792477      0.0057414095      -0.0163221748
1102      H      0.0394840421      0.0246198733      1.0641611622
1103      H      0.9586407167      -0.0111077785      -0.5333432198
1104      C      -1.1607454082      0.0923300166      -0.6842231582
1105      O      -1.4110944857      2.1331579164      -0.7853241691
1106      C      -0.2984505195      2.7027686085      -1.3194182368
1107      O      0.7788879599      2.8663094478      -0.4390966055
1108      C      0.4432650295      3.6055448958      0.7144572404
1109      H      -1.195022608      -0.0126301152      -1.7593882654
1110      H      -2.1036408607      0.0242749283      -0.1635075777
1111      H      0.1039091516      2.1470428531      -2.1727916156
1112      H      -0.6416067418      3.6937893187      -1.6748528992
1113      H      0.0445177693      4.5896508011      0.4435789093
1114      H      -0.2994364616      3.0826867368      1.3188123991
1115      H      1.356841189      3.7372620636      1.2885442607
1116      Core RigidRotor
1117      SymmetryFactor      1.0
1118      End
1119      Rotor      Hindered

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1118      Group          1  9 10
1119      Axis           4  5
1120      Symmetry       1
1121      Potential [kcal/mol] 4
1122      0.0  2.92  0.34  1.24
1123      End
1124      Rotor          Hindered
1125      Group          7 11 12
1126      Axis           6  5
1127      Symmetry       1
1128      Potential [kcal/mol] 4
1129      0.0 15.0  2.66  8.8
1130      End
1131      Rotor          Hindered
1132      Group          8
1133      Axis           7  6
1134      Symmetry       1
1135      Potential [kcal/mol] 6
1136      0.0  6.26  3.1  5.41  2.68  4.41
1137      End
1138      Rotor          Hindered
1139      Group          13 14 15
1140      Axis           8  7
1141      Symmetry       3
1142      Potential [kcal/mol] 2
1143      0.0  1.64
1144      End
1145      Frequencies [1/cm] 33
1146      187.56      230.32      379.93      422.91      623.62
1147      826.32
1148      937.6      960.23      987.25      1018.47      1045.37
1149      1129.88      1181.25      1190.55      1218.27      1242.37
1150      1289.66      1328.58      1402.43      1448.87      1476.15
1151      1481.56      1494.35      1520.67      1603.59      2917.56
1152      3024.4      3048.12      3099.37      3155.94      3173.92
1153      3181.75      3257.03      3281.68
1154      !70.01      76.43      124.06      258.12!
1155      ZeroEnergy [kcal/mol] 28.9
1156      ElectronicLevels [1/cm] 1
1157      0  2
1158      End
1159      Tunneling          Eckart
1160      ImaginaryFrequency [1/cm] 490.0031
1161      WellDepth [kcal/mol] 23.1
1162      WellDepth [kcal/mol] 5.0
1163      End
1164      End
1165      End
```

E.9 CCCOCO[CH2]

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1 TemperatureList [K]                500 510 520 530 540 550 560 570 580
   590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750
   760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920
   930 940 950 960 970 980 990 1000 1010 1020 1030 1040 1050 1060 1070
   1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200
   1210 1220 1230 1240 1250 1260 1270 1280 1290 1300 1310 1320 1330
   1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460
   1470 1480 1490 1500 1510 1520 1530 1540 1550 1560 1570 1580 1590
   1600 1610 1620 1630 1640 1650 1660 1670 1680 1690 1700 1710 1720
   1730 1740 1750 1760 1770 1780 1790 1800 1810 1820 1830 1840 1850
   1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980
   1990 2000
2 PressureList [atm]                0.00001 0.001 0.01 0.1 1 10 100.
3 !PressureList [bar]                1.
4 EnergyStepOverTemperature          .2
5 ExcessEnergyOverTemperature        30
6 ModelEnergyLimit [kcal/mol]        400
7 CalculationMethod                  direct
8 !CalculationMethod                 low-eigenvalue !direct
9 WellCutoff                          10
10 ChemicalEigenvalueMax             0.2
11 Model
12   EnergyRelaxation
13     Exponential
14       Factor [1/cm]                200
15       Power                        .85
16       ExponentCutoff               15
17   End
18   CollisionFrequency
19     LennardJones
20       Epsilons [1/cm]              94.87 280.62 !Ar and CCCOCO[CH2]
21       Sigmas [angstrom]             3.33 6.14
22       Masses [amu]                  49.88 103.14
23   End
24 !-----
25 !-----WELL 1 to Products -----
26 !-----
27 Well          W1          # W_CCCOCO[CH2]_m062x.log
28   Species
29     RRHO
30   Geometry [angstrom]              18
31   C          0.0311661217          0.0273945471          -0.0073920717
32   O          0.0008726024          -0.0003344328          1.3470971999
33   C          1.2718969625          -0.0010868223          1.9625522936
34   O          2.0371738652          -1.0984453087          1.6053349774
35   C          1.5046898095          -2.3365310186          2.0569645026

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36   C      2.3492102059   -3.4541398315   1.4846601166
37   C      2.3025725506   -3.4829732554   -0.0378694179
38   H     -0.9417292694   -0.0219034321   -0.4666927815
39   H      0.9209060385   -0.3283557532   -0.5065696589
40   H      1.8325501568   0.8825769852   1.6535709655
41   H      1.0659106826   0.0161076734   3.0355048638
42   H      1.5127942182   -2.3523341223   3.1526831659
43   H      0.4678291934   -2.4341429204   1.7204628624
44   H      3.3773835247   -3.3296150904   1.8290629402
45   H      1.9846590054   -4.3981463638   1.8940489802
46   H      2.7040927723   -2.5582183692   -0.4491108344
47   H      2.8824681573   -4.3140906107   -0.4365831457
48   H      1.2744294983   -3.5876778898   -0.389485947
49   Core RigidRotor
50       SymmetryFactor      1
51   End
52   Rotor      Hindered
53       Group          8 9
54       Axis           1 2
55       Symmetry       1
56       Potential[kcal/mol]      6
57       0.0  4.95  0.1  0.21  0.02  4.6
58   End
59   Rotor      Hindered
60       Group          1
61       Axis           2 3
62       Symmetry       1
63       Potential[kcal/mol]      10
64       0.0  4.26  3.39  3.65  2.5  2.79  2.48  2.86  2.44  3.18
65   End
66   Rotor      Hindered
67       Group          2 10 11
68       Axis           3 4
69       Symmetry       1
70       Potential[kcal/mol]      8
71       0.0  7.1  2.28  2.38  2.11  4.66  3.93  4.87
72   End
73   Rotor      Hindered
74       Group          3
75       Axis           4 5
76       Symmetry       1
77       Potential[kcal/mol]      8
78       0.0  1.83  1.29  1.32  1.19  7.27  2.94  3.12
79   End
80   Rotor      Hindered
81       Group          4 12 13
82       Axis           5 6
83       Symmetry       1

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84      Potential [kcal/mol]          6
85      0.0  4.98  0.13  3.74  0.48  3.62
86      End
87      Rotor      Hindered
88      Group              16 17 18
89      Axis              7 6
90      Symmetry          1
91      Potential [kcal/mol]          6
92      0.0  2.64  0.0  2.64  0.0  2.64
93      End
94      Frequencies [1/cm]      42
95      302.98      320.4      403.52      484.76
96      547.99      651.91      771.94      901.65      924.85
97      964.05      992.83      1089.89      1113.29      1146.62
98      1185.12      1193.4      1241.82      1269.08      1286.98
99      1309.09      1347.55      1378.42      1412.76      1430.59
100     1447.63      1484.95      1492.6      1497.44      1511.48
101     1521.44      1528.95      3024.07      3057.9      3061.28
102     3063.87      3075.38      3106.52      3116.5      3132.47
103     3148.95      3164.17      3304.07
104     !38.26      72.94      136.42      190.27      212.06      270.87!
105     ZeroEnergy [kcal/mol]      0
106     ElectronicLevels [1/cm]      1
107     0  2
108     End
109     End
110     !-----
111     !-----WELLS 2-----
112     !-----
113     Well      W2      # W_CC[CH]OCOC_E-1-8_m062x.log
114     Species
115     RRHO
116     Geometry [angstrom]      18
117     C      0.0028423816      -0.0249239537      0.0030295185
118     C      0.0005044272      0.0174150195      1.5380352406
119     C      1.3678050207      0.0016653397      2.113363171
120     O      2.0509353064      -1.1601337519      1.8936556461
121     C      3.3950807684      -1.142286269      2.3107121127
122     O      4.1632646334      -0.223649471      1.6095705534
123     C      4.238538618      -0.5041693767      0.2263584152
124     H      4.5983363856      -1.5241071383      0.0568889623
125     H      4.9422911205      0.202235123      -0.2050416611
126     H      0.5214882623      0.8435640275      -0.4046240996
127     H      -1.0123105919      -0.0344141692      -0.3933531335
128     H      0.5154022368      -0.9213300521      -0.3446132147
129     H      -0.5137009449      0.9135868098      1.8862503877
130     H      -0.555261177      -0.8435335937      1.918272619
131     H      3.2648274917      -0.3886903531      -0.2543700634

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128   H           1.969506135    0.9010265374    2.1800738419
129   H           3.458610755   -0.8567632591    3.3619874133
130   H           3.7556961192   -2.1623735123    2.154802268
131   Core RigidRotor
132       SymmetryFactor      1
133   End
134   Rotor           Hindered
135       Group                10 11 12
136       Axis                  1 2
137       Symmetry              3
138       Potential [kcal/mol]   2
139       0.0  3.18
140   End
141   Rotor           Hindered
142       Group                1 13 14
143       Axis                  2 3
144       Symmetry              1
145       Potential [kcal/mol]   6
146       0.0  2.27  0.23  1.75  0.38  1.71
147   End
148   Rotor           Hindered
149       Group                2 16
150       Axis                  3 4
151       Symmetry              1
152       Potential [kcal/mol]   6
153       0.0  5.11  1.84  4.56  3.32  5.68
154   End
155   Rotor           Hindered
156       Group                3
157       Axis                  4 5
158       Symmetry              1
159       Potential [kcal/mol]   6
160       0.0  6.92  1.78  2.86  2.5  3.19
161   End
162   Rotor           Hindered
163       Group                4 17 18
164       Axis                  5 6
165       Symmetry              1
166       Potential [kcal/mol]   6
167       0.0  6.64  2.0  4.29  3.22  4.48
168   End
169   Rotor           Hindered
170       Group                8 9 15
171       Axis                  7 6
172       Symmetry              3
173       Potential [kcal/mol]   2
174       0.0  1.77
175   End
```

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176   Frequencies [1/cm]      42
177       283.58      310.77      406.83      479.47
178       619.62      658.05      782.12      911.25      969.67
      988.56      1059.02      1099.56      1120.62      1164.85
179       1190.42      1215.04      1221.16      1266.95      1301.16
      1335.82      1351.98      1392.97      1419.34      1459.67
180       1477.17      1488.23      1496.41      1498.39      1510.72
      1515.11      1525.21      3032.22      3054.8      3055.97
181       3060.11      3098.14      3107.6      3115.62      3131.47
      3141.77      3161.95      3174.3
182       !46.9      67.92      114.68      149.75      212.4      237.0!
183   ZeroEnergy [kcal/mol]      -1.0
184   ElectronicLevels [1/cm]      1
185       0  2
186   End
187 End
188 !-----
189 Barrier      B1  W1  W2      # W_CC[CH]OCOC_E-1-8_m062x.log
190   Variational
191     RRHO
192   Geometry [angstrom]      18
193   C      0.0038526119      0.0305653071      0.0015185603
194   C      0.0000084586      -0.0149788276      1.5264671357
195   C      1.3870186623      0.0011838062      2.0994709805
196   O      2.1070485088      -1.1370647318      1.7243508416
197   C      3.4889774642      -0.923835811      1.7170206742
198   O      3.8463143631      -0.0062018604      0.7232399138
199   C      3.3768794474      1.2711695708      1.01156829
200   H      3.2970841683      1.8638853232      0.1070179808
201   H      3.9201685954      1.7585714645      1.8248871848
202   H      0.4433240804      0.9631021092      -0.3544740395
203   H      -1.0067978731      -0.0421749505      -0.3973039247
204   H      0.5930508278      -0.7922162412      -0.4000778069
205   H      -0.5511973325      0.8333458598      1.9350786679
206   H      -0.5128158275      -0.9206974979      1.8680402839
207   H      2.1395561773      0.9811703869      1.5405487547
208   H      1.4550938371      0.1869699507      3.1760262117
209   H      3.8186974441      -0.5577910451      2.7007314494
210   H      3.9623433901      -1.8694898203      1.473558817
211   Core RigidRotor
212     SymmetryFactor      0.5
213   End
214   Rotor      Hindered
215     Group      10 11 12
216     Axis      1 2
217     Symmetry      1
218     Potential [kcal/mol]      6
219     0.0  2.46  0.0  2.46  0.0  2.46

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220 End
221 Rotor          Hindered
222   Group          1 13 14
223   Axis           2 3
224   Symmetry       1
225   Potential [kcal/mol] 6
226   0.0  3.82  0.43  3.09  0.5  3.08
227 End
228 Frequencies [1/cm] 45
229   67.38   235.18   297.53   376.14   409.7
444.69   513.23   610.1
230   669.19   777.23   902.98   954.37   980.84
1001.69  1068.8   1108.29  1128.45  1131.01
231   1161.79   1180.98   1221.61   1256.89   1301.83
   1328.8   1363.12   1366.84   1411.44   1435.31
232   1441.01   1476.11   1479.37   1499.78   1510.64
   1523.94   1627.99   2990.43   3031.63   3046.56
233   3051.59   3068.21   3098.18   3136.74   3150.98
   3170.49   3192.23
234   !91.87   172.73!
235 ZeroEnergy [kcal/mol] 18.8
236 ElectronicLevels [1/cm] 1
237   0 2
238 End
239 Tunneling          Eckart
240 ImaginaryFrequency [1/cm] 1716.6001
241 WellDepth [kcal/mol] 18.8
242 WellDepth [kcal/mol] 19.8
243 End
244 End
245 !-----
246 !-----WELLS 3-----
247 !-----
248 Well          W3          # W_C [CH] COCOC_E2 -4_m062x.log
249 Species
250   RRHO
251 Geometry [angstrom] 18
252   C          -0.0151155348   0.0251243656   0.0220460786
253   C          0.0185385656   0.0018804974   1.5075658012
254   C          1.3214764469   -0.0209672625   2.2283356905
255   O          2.2242949304   0.9832774407   1.7678353321
256   C          1.8358575763   2.2799829911   2.1158880674
257   O          1.8771207436   2.5108678271   3.490267469
258   C          3.1831441766   2.4366474857   4.021725255
259   H          3.116842277   2.6924019807   5.0759273853
260   H          3.8464738174   3.148292961   3.5189327148
261   H          -0.9652205541   0.4007787668   -0.3557422099
262   H          0.1219929081   -0.980639303   -0.3966552721

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263 H 0.7909392206 0.6434538384 -0.374497348
264 H 3.6006773723 1.4337539746 3.9143550563
265 H -0.8796457033 -0.2353425061 2.059540505
266 H 1.1698636531 0.0790236462 3.3054876763
267 H 1.8520293688 -0.9631376226 2.0502085926
268 H 2.529491376 2.9427536065 1.5898077629
269 H 0.8048003922 2.4781113324 1.8122054517
270 Core RigidRotor
271 SymmetryFactor 1.0
272 End
273 Rotor Hindered
274 Group 10 11 12
275 Axis 1 2
276 Symmetry 1
277 Potential[kcal/mol] 6
278 0.0 0.25 0.0 0.25 -0.0 0.25
279 End
280 Rotor Hindered
281 Group 1 14
282 Axis 2 3
283 Symmetry 1
284 Potential[kcal/mol] 8
285 0.0 2.48 0.47 0.68 0.67 6.64 1.96 1.99
286 End
287 Rotor Hindered
288 Group 2 15 16
289 Axis 3 4
290 Symmetry 1
291 Potential[kcal/mol] 6
292 0.0 2.11 0.7 1.55 0.5 4.08
293 End
294 Rotor Hindered
295 Group 3
296 Axis 4 5
297 Symmetry 1
298 Potential[kcal/mol] 6
299 0.0 3.49 2.64 3.9 3.19 8.12
300 End
301 Rotor Hindered
302 Group 4 17 18
303 Axis 5 6
304 Symmetry 1
305 Potential[kcal/mol] 8
306 0.0 4.16 2.69 3.07 2.87 3.79 3.08 7.33
307 End
308 Rotor Hindered
309 Group 8 9 13
310 Axis 7 6
```

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311 Symmetry 1
312 Potential [kcal/mol] 6
313 0.0 1.61 -0.0 1.61 0.0 1.61
314 End
315 Frequencies [1/cm] 42
316 253.42 342.57 383.19 444.25
317 606.04 622.4 885.11 926.99 953.88
318 983.94 996.37 1102.31 1109.71 1156.62
319 1168.35 1189.95 1209.25 1251.41 1311.17
320 1350.6 1378.7 1392.86 1417.0 1445.5
321 1480.99 1481.04 1489.87 1494.3 1497.28
322 1514.79 1522.93 3001.02 3021.45 3028.87
323 3043.73 3083.86 3091.1 3096.05 3097.75
324 3137.11 3158.07 3209.22
325 !38.72 61.31 81.88 107.75 157.14 208.82!
326 ZeroEnergy [kcal/mol] 2.7
327 ElectronicLevels [1/cm] 1
328 0 2
329 End
330 End
331 !-----
332 Barrier B2 W1 W3 # W_C [CH] COCOC_E2 -4_m062x.log
333 Variational
334 RRHO
335 Geometry [angstrom] 18
336 C 0.013332019 0.0462895608 0.0301809319
337 C -0.0157956863 -0.0228217745 1.5322451633
338 C 1.3280523964 -0.0145554422 2.2200800187
339 O 1.2092559542 0.467203913 3.5564481504
340 C 1.4720632631 1.8296530341 3.6912270355
341 O 0.8106218676 2.6213099197 2.7378621518
342 C -0.5408355356 2.3333452749 2.6179652592
343 H -1.0149312613 3.059695028 1.9663102548
344 H -1.0519850548 2.1841203651 3.5710003801
345 H -0.9916626882 0.0620222494 -0.3895223737
346 H 0.5366590376 -0.8106184706 -0.4069398061
347 H 0.5346140228 0.9469709471 -0.3014299359
348 H -0.5512757375 1.1420412806 2.0022234596
349 H -0.6922749534 -0.7693709522 1.944745563
350 H 1.7454078684 -1.0221660587 2.2915769124
351 H 2.036040409 0.6039745878 1.6584474927
352 H 1.1516405072 2.0934373584 4.7027654135
353 H 2.5337666755 2.0493242538 3.5506939724
354 Core RigidRotor
355 SymmetryFactor 0.5
356 End
357 Rotor Hindered
358 Group 10 11 12

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355      Axis                1 2
356      Symmetry            1
357      Potential [kcal/mol] 6
358      0.0  2.03  0.0  2.03  0.0  2.03
359      End
360      Frequencies [1/cm]   46
361      65.99      146.93      272.93      310.47      350.82
362      393.66      433.37      496.98      574.42
363      670.67      849.45      912.37      930.36      975.22
364      1001.36     1090.4      1103.57     1135.55     1160.98
365      1174.14     1178.58     1219.7      1254.65     1302.91
366      1334.09     1336.9      1399.22     1409.42     1427.85
367      1447.41     1472.23     1490.36     1494.84     1502.05
368      1524.76     1529.74     3028.71     3035.54     3044.33
369      3064.81     3077.93     3087.26     3095.24     3118.83
370      3134.49     3189.65
371      !185.1!
372      ZeroEnergy [kcal/mol] 20.8
373      ElectronicLevels [1/cm] 1
374      0 2
375      End
376      Tunneling            Eckart
377      ImaginaryFrequency [1/cm] 1694.8723
378      WellDepth [kcal/mol] 20.8
379      WellDepth [kcal/mol] 18.1
380      End
381      End
382      !-----
383      !-----WELLS 4-----
384      !-----
385      Well      W4      # W_[CH2]CCOCOC_E5-7_m062x.log
386      Species
387      RRHO
388      Geometry [angstrom] 18
389      C      0.0087443749      -0.0009686721      -0.0019382697
390      C      0.0012366037      -0.0051500282      1.484358929
391      C      1.4054364741      -0.0037323494      2.0679125979
392      O      2.0668425775      -1.1716224307      1.6153728279
393      C      3.4093871382      -1.2294376141      1.9894588583
394      O      4.1797277591      -0.2099840296      1.4327687306
395      C      4.1783071283      -0.2289587236      0.0206562464
396      H      4.4581089383      -1.218702392      -0.3553455502
397      H      4.9111448224      0.5020309211      -0.3105755504
398      H      3.1955429729      0.032609855      -0.3795584903
399      H      -0.6893251476      0.5983117692      -0.5646432906
400      H      0.6115965171      -0.7235404158      -0.5297056763
401      H      -0.5398212772      0.8583975316      1.8728790725
402      H      -0.5125201048      -0.8985727251      1.8624255165

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398 H 1.951289928 0.8853370012 1.7403019962
399 H 1.3712316293 -0.0035042691 3.1638016122
400 H 3.5197420091 -1.1254951656 3.0728144271
401 H 3.7637737098 -2.2098462683 1.6568590309
402 Core RigidRotor
403 SymmetryFactor 1.0
404 End
405 Rotor Hindered
406 Group 11 12
407 Axis 1 2
408 Symmetry 1
409 Potential[kcal/mol] 6
410 0.0 0.03 0.03 0.63 -0.0 0.62
411 End
412 Rotor Hindered
413 Group 1 13 14
414 Axis 2 3
415 Symmetry 1
416 Potential[kcal/mol] 6
417 0.0 5.21 0.24 3.75 0.61 3.65
418 End
419 Rotor Hindered
420 Group 2 15 16
421 Axis 3 4
422 Symmetry 1
423 Potential[kcal/mol] 6
424 0.0 1.83 0.71 4.91 1.83 2.55
425 End
426 Rotor Hindered
427 Group 3
428 Axis 4 5
429 Symmetry 1
430 Potential[kcal/mol] 4
431 0.0 2511.67 190.34 1876.7
432 End
433 Rotor Hindered
434 Group 4 17 18
435 Axis 5 6
436 Symmetry 1
437 Potential[kcal/mol] 6
438 0.0 7.15 2.91 4.99 3.06 4.39
439 End
440 Rotor Hindered
441 Group 8 9 10
442 Axis 7 6
443 Symmetry 1
444 Potential[kcal/mol] 6
445 0.0 1.79 0.0 1.79 0.0 1.79
```

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446 End
447 Frequencies [1/cm]      42
448      272.11      309.13      409.79      467.51
449      518.4      659.86      756.65      921.37      956.17
450 984.03      1064.2      1087.81      1113.22      1147.69
451      1183.72      1192.07      1211.6      1244.78      1253.49
452      1301.96      1343.27      1364.76      1416.29      1444.55
453      1459.94      1472.62      1485.84      1498.49      1514.27
454      1521.31      1532.54      3005.67      3020.69      3027.01
455      3036.94      3076.82      3087.7      3090.65      3104.27
456      3157.34      3180.16      3286.06
457 !40.71      81.71      104.05      147.71      176.95      235.43!
458 ZeroEnergy [kcal/mol]      4.6
459 ElectronicLevels [1/cm]      1
460      0      2
461 End
462 End
463 !-----
464 Barrier      B3      W1      W4      #      W_ [CH2]CCOCOC_E5-7_m062x.log
465 Variational
466 RRHO
467 Geometry [angstrom]      18
468 C      0.0217818783      -0.0053373722      0.0053519893
469 C      -0.0009547028      0.0302106621      1.5104545302
470 C      1.4035162348      0.0105308793      2.109165689
471 O      2.3261231784      0.8631817117      1.4483128941
472 C      2.1793802984      2.2206209103      1.6941476668
473 O      1.0214091643      2.7770667567      1.1266030435
474 C      0.8892327909      2.5142287019      -0.230369056
475 H      1.8334754381      2.5556898181      -0.7779624182
476 H      0.1129151372      3.1469791813      -0.6489734089
477 H      0.4688496093      1.2640932298      -0.3283286917
478 H      -0.950877751      -0.077793005      -0.4721713229
479 H      0.7619521152      -0.6680564913      -0.4366731754
480 H      -0.5400307011      0.9174362539      1.8481950632
481 H      -0.5394101907      -0.8326716343      1.9188800198
482 H      1.3706502264      0.2614522097      3.1753427714
483 H      1.8294567895      -0.9876507914      2.0079186906
484 H      2.106185363      2.4289085138      2.7652047245
485 H      3.0667436674      2.6944380206      1.2650609322
486 Core RigidRotor
487 SymmetryFactor      1.0
488 End
489 Frequencies [1/cm]      47
490      93.88      230.37      265.83      279.91      328.04
491 364.55      441.18      499.06      537.05      654.25
492      696.83      805.96      890.18      929.32      957.78
493 991.47      1060.99      1102.42      1113.22      1171.62

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488      1175.28      1196.76      1207.46      1258.07      1264.42
      1323.8      1354.41      1383.39      1412.07      1418.78
489      1447.03      1456.82      1465.49      1481.21      1495.95
      1505.71      1521.37      3025.02      3035.62      3041.53
490      3058.67      3082.74      3093.97      3105.99      3113.56
      3180.11      3188.87
491      !      !
492      ZeroEnergy [kcal/mol]      20.7
493      ElectronicLevels [1/cm]      1
494      0      2
495      End
496      Tunneling      Eckart
497      ImaginaryFrequency [1/cm]      1690.6325
498      WellDepth [kcal/mol]      20.7
499      WellDepth [kcal/mol]      16.1
500      End
501      End
502      !-----
503      !-----W1 - > P1-----
504      !-----
505      Bimolecular      P1      # CCCO[CH2]_E7-7 + CH2O_E6-5
506      Fragment      CCCO[CH2]_E7-7
507      RRHO
508      Geometry [angstrom]      14
509      C      0.0070851475      0.0232118319      0.0109696271
510      C      0.0058550135      -0.0033377688      1.5332072907
511      C      1.4126553548      -0.0158334403      2.1083640106
512      O      2.1877841031      1.0872630349      1.6603269035
513      C      1.8048504376      2.2857337517      2.1470205263
514      H      0.5081713734      0.9191365584      -0.3532886702
515      H      -1.007670756      0.0150590007      -0.3838679522
516      H      0.5345133038      -0.8424832541      -0.3925986491
517      H      -0.5302933857      0.8650499511      1.9213899356
518      H      -0.5138666687      -0.8899359573      1.9025516626
519      H      1.3868472355      -0.0128997673      3.2032344178
520      H      1.9530152869      -0.9020974475      1.7767367299
521      H      1.3125870489      2.3071560172      3.1128682676
522      H      2.4215295358      3.1077684911      1.8213449113
523      Core RigidRotor
524      SymmetryFactor      1.0
525      End
526      Rotor      Hindered
527      Group      6 7 8
528      Axis      1 2
529      Symmetry      3
530      Potential [kcal/mol]      2
531      0.0 2.78
532      End

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533 Rotor      Hindered
534   Group          1  9 10
535   Axis           2  3
536   Symmetry       1
537   Potential [kcal/mol] 6
538   0.0  3.74  0.47  3.46  0.73  4.79
539 End
540 Rotor      Hindered
541   Group          2 11 12
542   Axis           3  4
543   Symmetry       1
544   Potential [kcal/mol] 8
545   0.0  1.6  0.11  1.17  1.1  1.41  1.01  5.99
546 End
547 Rotor      Hindered
548   Group          3
549   Axis           4  5
550   Symmetry       1
551   Potential [kcal/mol] 6
552   0.0  5.36  0.0  5.54  0.6  0.64
553 End
554 Frequencies [1/cm] 32
555   282.38      440.57      525.81      631.8      771.33
880.55
556   921.94      967.17      1074.67      1120.36      1156.41
   1221.23      1279.48      1307.55      1338.15      1379.84
557   1410.34      1423.03      1481.32      1485.96      1500.86
   1509.25      1520.27      3037.27      3063.03      3066.28
558   3097.68      3120.11      3127.22      3134.42      3146.23
   3276.88
559   !70.3      168.24      232.83      307.28!
560 ZeroEnergy [kcal/mol] 0
561 ElectronicLevels [1/cm] 1
562   0  2
563 End
564 Fragment  CH2O_E6 -5
565   RRHO
566 Geometry [angstrom] 4
567   O      -0.000000016  -0.0000022088  0.0061054213
568   C      -0.0000000144  0.0000068137  1.2014608526
569   H      0.9375275336  -0.0000022726  1.7838372267
570   H      -0.9375275608  0.0000246367  1.7838372291
571 Core RigidRotor
572   SymmetryFactor  2.0
573 End
574 Frequencies [1/cm] 6
575   1216.69      1279.34      1545.84      1876.79      2940.94
   3011.91

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576      !      !
577      ZeroEnergy [kcal/mol]      0
578      ElectronicLevels [1/cm]    1
579      0      1
580      End
581      GroundEnergy [kcal/mol]    13.2
582      End
583      !-----
584      Barrier      B4      W1      P1      # TS_CH20_CCCO [CH2] _E18 -0_m062x.log
585      Variational
586      RRHO
587      Geometry [angstrom]      18
588      C      0.004569429      -0.0382212236      0.0022661482
589      C      0.0015684435      0.0222930036      1.5242762327
590      C      1.3935548921      0.0008175665      2.1138990233
591      O      1.9997166134      -1.2546481475      1.8012542879
592      C      3.2569451126      -1.3778140286      2.2202898358
593      O      4.2977981142      -0.3817630222      0.8288952344
594      C      3.6800232701      -0.2510189576      -0.2438631868
595      H      3.0963936722      0.6505990505      -0.4565186239
596      H      3.6712823964      -1.0444740262      -0.9976133752
597      H      0.5167137176      0.8288241017      -0.4174993791
598      H      -1.0107328559      -0.0520138352      -0.3914222651
599      H      0.5200586808      -0.9326356047      -0.3449769452
600      H      -0.4935131432      0.9328620281      1.8666148052
601      H      -0.5584975015      -0.819372932      1.9354966433
602      H      2.0172005237      0.8017179817      1.705507451
603      H      1.3644748401      0.1060256495      3.2026995147
604      H      3.5793728774      -0.7803101764      3.0631013026
605      H      3.6787069832      -2.3569564452      2.0624083305
606      Core RigidRotor
607      SymmetryFactor      1.0
608      End
609      Rotor      Hindered
610      Group      10 11 12
611      Axis      1 2
612      Symmetry      1
613      Potential [kcal/mol]      6
614      0.0 3.05 0.0 3.06 -0.0 3.05
615      End
616      Rotor      Hindered
617      Group      1 13 14
618      Axis      2 3
619      Symmetry      1
620      Potential [kcal/mol]      6
621      0.0 4.63 0.41 3.88 0.7 3.72
622      End
623      Rotor      Hindered

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624      Group                2 15 16
625      Axis                 3 4
626      Symmetry             1
627      Potential [kcal/mol] 6
628      0.0  2.58  1.21  7.72  2.7  4.41
629      End
630      Rotor                Hindered
631      Group                3
632      Axis                 4 5
633      Symmetry             1
634      Potential [kcal/mol] 4
635      0.0  15.89  2.72  9.56
636      End
637      Rotor                Hindered
638      Group                4 17 18
639      Axis                 5 6
640      Symmetry             1
641      Potential [kcal/mol] 4
642      0.0  4.91  3.47  4.1
643      End
644      Frequencies [1/cm]   42
645      232.41      286.06      309.81      364.13      424.14
646      536.31      648.0      765.93      886.55      902.05
647      923.71      940.33      966.73      1094.54      1125.48
648      1174.54      1234.04      1241.4      1255.91      1281.77
649      1316.45      1381.92      1400.31      1415.19      1432.26
650      1480.74      1499.8      1510.42      1514.96      1526.0
651      1582.62      3010.99      3037.48      3064.57      3067.73
652      3082.95      3096.11      3107.71      3135.81      3147.75
653      3149.53      3290.61
654      !77.53      92.54      112.51      168.64      215.71!
655      ZeroEnergy [kcal/mol] 25.2
656      ElectronicLevels [1/cm] 1
657      0 2
658      End
659      Tunneling              Eckart
660      ImaginaryFrequency [1/cm] 599.9148
661      WellDepth [kcal/mol] 25.2
662      WellDepth [kcal/mol] 12.0
663      End
664      End
665      !-----
666      !-----WELL 2 to Products -----
667      !-----
668      Bimolecular          P2      # CCC=O_E3-61 + CO[CH2]_E3-61
669      Fragment            CCC=O_E3-61
670      RRHO
671      Geometry [angstrom] 10

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668   C      -0.0000566396    0.0062360295   -0.0000851688
669   C      0.0002269459   -0.0058860377    1.5176215585
670   C      1.3811361699   -0.0034523604    2.1113838536
671   H      1.4229848487   -0.0120720663    3.2179002795
672   O      2.393691471    0.0069513451    1.4676073164
673   H      0.5150796789    0.8884132091   -0.3758097392
674   H     -1.0166443986    0.0040558499   -0.3884237127
675   H      0.524187663   -0.8644258075   -0.3898116873
676   H     -0.5289339007    0.8570574089    1.9342051971
677   H     -0.5199028418   -0.8808265682    1.9203230958
678   Core RigidRotor
679       SymmetryFactor    1.0
680   End
681   Rotor      Hindered
682       Group                6 7 8
683       Axis                 1 2
684       Symmetry              3
685       Potential [kcal/mol]   2
686       0.0  2.12
687   End
688   Rotor      Hindered
689       Group                1 9 10
690       Axis                 2 3
691       Symmetry              1
692       Potential [kcal/mol]   6
693       0.0  2.36  1.42  2.11  1.42  2.36
694   End
695   Frequencies [1/cm]    22
696       266.82    673.44    677.86    873.63    908.86
1008.52    1121.87    1156.86
697       1283.93    1372.83    1414.21    1430.39    1457.55
       1497.45    1504.73    1866.92    2945.02    3050.32
698       3077.74    3081.28    3153.86    3156.87
699       !148.66    238.11!
700   ZeroEnergy [kcal/mol]    0
701   ElectronicLevels [1/cm]  1
702       0  1
703   End
704   Fragment    CO[CH2]_E3-61
705       RRHO
706   Geometry [angstrom]    8
707   C      0.0026902296   -0.0018733009    0.0160456217
708   O     -0.0078291385    0.0076990299    1.3645690081
709   C      1.273786629    0.0049260623    1.95715442
710   H     -0.9758393198    0.0608442139   -0.431273488
711   H      0.877362312    0.3899910944   -0.4891132431
712   H      1.8220579152   -0.8982084317    1.6804741972
713   H      1.8440457298    0.8825642786    1.6409888636

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714   H          1.1333897905    0.0323929123    3.0337908614
715   Core RigidRotor
716       SymmetryFactor      1.0
717   End
718   Rotor      Hindered
719       Group              4 5
720       Axis                1 2
721       Symmetry            1
722       Potential [kcal/mol] 6
723       0.0  0.29  0.0  5.48  0.0  5.4
724   End
725   Rotor      Hindered
726       Group              1
727       Axis                2 3
728       Symmetry            1
729       Potential [kcal/mol] 6
730       0.0  1.56  0.0  1.56  0.0  1.56
731   End
732   Frequencies [1/cm]      16
733       445.06      597.39      1006.96      1150.37      1184.95
734       1269.45      1323.39      1465.29
735       1498.89      1507.76      1515.58      3037.89      3099.15
736       3133.66      3168.24      3282.25
737       !171.34      290.38!
738   ZeroEnergy [kcal/mol]    0
739   ElectronicLevels [1/cm]  1
740       0  2
741   End
742   GroundEnergy [kcal/mol]   7.6
743   End
744   !-----
745   Barrier      B5  W2  P2    # TS_CCC=O_CO [CH2]_E16 -71_m062x.log
746   Variational
747       RRHO
748   Geometry [angstrom]      18
749   C          -0.0011630263    0.0025368695    -0.0005050648
750   C          0.000876069     -0.0016432682    1.5236164973
751   C          1.381585976     -0.0007083721    2.1061770685
752   H          1.5086115545     0.390582317     3.1225973234
753   O          2.3479850031     -0.549905182    1.5269870771
754   C          2.3522672705     -2.4864727641    1.8028039032
755   O          1.7562365404     -2.6235585259    2.9930028445
756   C          2.5964237139     -2.2980432386    4.0891760791
757   H          0.4728163509     0.9060005189    -0.3832367711
758   H          -1.0168390478     -0.0467128565    -0.3900790764
759   H          0.559275012     -0.8470296056    -0.3862808893
760   H          -0.5565383202     0.8479088034     1.922487319
761   H          -0.5132036643     -0.9000532309    1.8926950377

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760   H          1.7401280718   -2.8175565231   0.9781367897
761   H          3.4254176705   -2.6234243712   1.7531883274
762   H          3.409368929    -3.024691174    4.1650028309
763   H          3.0148295225   -1.29879501    3.9589697701
764   H          1.9852853791   -2.3362483399   4.9856369225
765   Core RigidRotor
766       SymmetryFactor      1.0
767   End
768   Rotor          Hindered
769       Group                9 10 11
770       Axis                  1 2
771       Symmetry              3
772       Potential [kcal/mol]   2
773       0.0  2.26
774   End
775   Rotor          Hindered
776       Group                1 12 13
777       Axis                  2 3
778       Symmetry              1
779       Potential [kcal/mol]   6
780       0.0  0.25  0.13  0.66  0.15  1.1
781   End
782   Rotor          Hindered
783       Group                3
784       Axis                  5 6
785       Symmetry              1
786       Potential [kcal/mol]   6
787       0.0  3.99  3.56  3.69  2.78  3.65
788   End
789   Rotor          Hindered
790       Group                8
791       Axis                  7 6
792       Symmetry              1
793       Potential [kcal/mol]   6
794       0.0  10.17  2.13  2.85  1.81  6.08
795   End
796   Rotor          Hindered
797       Group                16 17 18
798       Axis                  8 7
799       Symmetry              3
800       Potential [kcal/mol]   2
801       0.0  1.89
802   End
803   Frequencies [1/cm]      42
804       140.51   256.74   291.43   411.09   481.61
805       585.87   688.38   710.94   809.48   888.65
931.38   1005.89   1014.21   1080.48   1113.95

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806      1154.65      1185.61      1258.54      1276.5      1285.47
      1350.54      1367.47      1406.84      1465.8      1469.32
807      1493.88      1496.49      1502.13      1513.47      1515.96
      1526.54      3000.53      3032.58      3045.05      3072.42
808      3089.59      3113.15      3139.71      3141.95      3150.85
      3175.11      3275.12
809      !42.64      60.58      92.11      175.79      211.29!
810      ZeroEnergy [kcal/mol]      22.6
811      ElectronicLevels [1/cm]      1
812      0 2
813      End
814      Tunneling      Eckart
815      ImaginaryFrequency [1/cm]      664.2086
816      WellDepth [kcal/mol]      23.6
817      WellDepth [kcal/mol]      15.0
818      End
819      End
820      !-----
821      !-----
822      Bimolecular      P3      # C=COCOC_E21 -90 + [CH3]
823      Fragment      C=COCOC_E21 -90
824      RRHO
825      Geometry [angstrom]      14
826      C      -0.0042800966      -0.0127363074      0.000882754
827      C      -0.0091071243      0.0177581663      1.3258701105
828      H      0.9044122917      0.0662452593      1.9036685686
829      O      -1.0844170454      -0.0100492049      2.157704227
830      C      -2.3398965536      -0.2645899287      1.574290547
831      O      -2.8074788365      0.7763954673      0.7880448361
832      C      -3.0135846937      1.9736060286      1.5100755402
833      H      0.9471989404      -0.0124121091      -0.5077237278
834      H      -0.9055287428      -0.013043779      -0.592143188
835      H      -2.2769011173      -1.141302371      0.9274444408
836      H      -3.0060010358      -0.4452064422      2.4220736225
837      H      -3.6822813906      1.8026023057      2.359974189
838      H      -2.0701641663      2.3808548695      1.8769606607
839      H      -3.4736414239      2.6823350448      0.8273313887
840      Core RigidRotor
841      SymmetryFactor      1.0
842      End
843      Rotor      Hindered
844      Group      1 3
845      Axis      2 4
846      Symmetry      1
847      Potential [kcal/mol]      4
848      0.0 4.73 1.0 4.9
849      End
850      Rotor      Hindered

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851      Group                2
852      Axis                 4 5
853      Symmetry            1
854      Potential [kcal/mol] 4
855      0.0  9.45  2.8  4.21
856      End
857      Rotor      Hindered
858      Group                4 10 11
859      Axis                 5 6
860      Symmetry            1
861      Potential [kcal/mol] 6
862      0.0  6.7  3.43  5.29  3.2  4.11
863      End
864      Rotor      Hindered
865      Group                5
866      Axis                 6 7
867      Symmetry            3
868      Potential [kcal/mol] 2
869      0.0  1.65
870      End
871      Frequencies [1/cm]   32
872      295.64      417.77      528.27      679.3      737.35
895.85
873      923.42      988.32      1017.02      1046.75      1142.16
      1190.24      1215.13      1241.44      1260.45      1351.18
874      1365.1      1429.97      1460.05      1489.2      1498.99
      1515.51      1524.42      1723.84      3032.33      3054.61
875      3104.55      3116.0      3164.69      3198.31      3215.11
      3292.5
876      !75.3      144.64      174.73      232.59!
877      ZeroEnergy [kcal/mol] 0
878      ElectronicLevels [1/cm] 1
879      0 1
880      End
881      Fragment  [CH3]
882      RRHO
883      Geometry [angstrom] 4
884      C          0.00000000  0.00000000  0.00000000
885      H          0.00000000  0.00000000  1.07652900
886      H          0.93230200  0.00000000 -0.53826500
887      H         -0.93230200 -0.00000000 -0.53826500
888      Core RigidRotor
889      SymmetryFactor 6
890      End
891      Frequencies [1/cm] 6
892      436.03      1412.64      1412.73      3144.41      3323.11
      3323.14
893      !  !

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```
894 ZeroEnergy [kcal/mol]      0
895 ElectronicLevels [1/cm]    1
896   0  2
897 End
898 GroundEnergy [kcal/mol]     21.6
899 End
900 !-----
901 Barrier      B6  W2  P3      # TS_[CH3]_C=COCOC_E29 -03_m062x.log
902 Variational
903   RRHO
904 Geometry [angstrom]        18
905   C      -0.0100032207      -0.0101254289      0.0043009665
906   C      0.0061409792      0.0059435675      2.2737739811
907   C      1.2778661742      0.0086729316      2.7313146353
908   H      1.83015515      0.9215467843      2.9029406904
909   O      2.0794216656      -1.0748012905      2.9198848531
910   C      1.5256965418      -2.3416168511      2.6562846801
911   O      0.5366781631      -2.7077079806      3.5563247829
912   C      1.0019863378      -2.812242977      4.8868345785
913   H      0.4404115132      0.9478451287      -0.2101158466
914   H      -1.073824061      -0.093213389      -0.1700701975
915   H      0.5853433359      -0.878462067      -0.2393180223
916   H      -0.5160290675      0.9500654196      2.272336116
917   H      -0.595769074      -0.8893222703      2.2922949564
918   H      1.0661715477      -2.3553488533      1.6672997828
919   H      2.3749105282      -3.0281505606      2.704393077
920   H      1.8528367466      -3.4986263903      4.9463628765
921   H      1.3028808328      -1.8389454666      5.2776059741
922   H      0.1814049321      -3.2041802813      5.4811171226
923 Core RigidRotor
924   SymmetryFactor      1.0
925 End
926 Rotor      Hindered
927   Group      9 10 11
928   Axis      1 2
929   Symmetry      3
930   Potential [kcal/mol]      2
931   0.0  0.21
932 End
933 Rotor      Hindered
934   Group      2 4
935   Axis      3 5
936   Symmetry      1
937   Potential [kcal/mol]      4
938   0.0  3.35  0.21  4.11
939 End
940 Rotor      Hindered
941   Group      3
```

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942      Axis                5 6
943      Symmetry            1
944      Potential [kcal/mol] 6
945      0.0  8.44  2.1  3.18  3.14  3.5
946      End
947      Rotor              Hindered
948      Group                5 14 15
949      Axis                6 7
950      Symmetry            1
951      Potential [kcal/mol] 6
952      0.0  6.56  3.23  5.4  3.18  4.14
953      End
954      Rotor              Hindered
955      Group                16 17 18
956      Axis                8 7
957      Symmetry            3
958      Potential [kcal/mol] 2
959      0.0  1.66
960      End
961      Frequencies [1/cm]  42
962      225.26      264.68      333.14      419.71      495.45
963      517.1      533.0      672.36      762.8      809.91
964      910.07      933.35      960.8      990.13      1045.78
965      1140.65      1190.08      1212.3      1236.95      1251.87
966      1331.12      1349.48      1419.86      1425.5      1429.5
967      1457.4      1488.41      1499.05      1515.96      1526.6
968      1605.05      3033.41      3058.71      3104.61      3107.39
969      3121.81      3164.18      3194.22      3221.39      3264.38
970      3268.84      3285.64
971      !59.33      67.41      70.32      119.01      149.08!
972      ZeroEnergy [kcal/mol] 30.2
973      ElectronicLevels [1/cm] 1
974      0 2
975      End
976      Tunneling              Eckart
977      ImaginaryFrequency [1/cm] 597.1092
978      WellDepth [kcal/mol] 31.2
979      WellDepth [kcal/mol] 8.6
980      End
981      End
982      !-----
983      !-----WELL 3 to Products -----
984      !-----
985      !-----WELL 3 -> Well 5 -----
986      !-----
987      Well      W5      # W_CCCO [CH] OC_E-2-17_m062x.log
988      Species

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986      RRHO
987      Geometry [angstrom]      18
988      C      0.0056925347      0.0044067557      0.0015999622
989      C      -0.0022423148      -0.0020167887      1.5240639341
990      H      1.0202126636      -0.0069673417      1.9066935904
991      C      -0.7456009953      1.1872020646      2.1085325526
992      O      -0.2498938736      2.4382908827      1.6258247597
993      C      1.0567165598      2.6755122063      1.8446701726
994      O      1.459722845      2.4287799297      3.1254055531
995      C      2.8445539972      2.6280186628      3.311818763
996      H      0.5225298623      0.8872116323      -0.3731939831
997      H      -1.0114020003      0.0190602357      -0.3932597238
998      H      0.508708402      -0.877232491      -0.39325078
999      H      -1.790417469      1.1738739896      1.8008031478
1000     H      -0.6996355274      1.1762590787      3.1979495002
1001     H      -0.4858755871      -0.905902841      1.9005490745
1002     H      1.388188563      3.6179790858      1.4113779235
1003     H      3.4205245525      1.9489848958      2.6789914016
1004     H      3.124033852      3.6586094571      3.0746000072
1005     H      3.0607628967      2.4294136094      4.3573431234
1006     Core RigidRotor
1007         SymmetryFactor      1.0
1008     End
1009     Rotor      Hindered
1010         Group      9 10 11
1011         Axis      1 2
1012         Symmetry      3
1013         Potential [kcal/mol]      2
1014             0.0  2.65
1015     End
1016     Rotor      Hindered
1017         Group      1 3 14
1018         Axis      2 4
1019         Symmetry      1
1020         Potential [kcal/mol]      6
1021             0.0  5.38  1.07  3.42  0.67  3.96
1022     End
1023     Rotor      Hindered
1024         Group      2 12 13
1025         Axis      4 5
1026         Symmetry      1
1027         Potential [kcal/mol]      9
1028             0.0  4.96  3.57  3.71  2.49  2.86  1.91  3.37  2.68
1029     End
1030     Rotor      Hindered
1031         Group      4
1032         Axis      5 6
1033         Symmetry      1
```

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1034 Potential [kcal/mol] 6
1035 0.0 3.36 2.17 2.72 2.66 3.5
1036 End
1037 Rotor Hindered
1038 Group 5 15
1039 Axis 6 7
1040 Symmetry 1
1041 Potential [kcal/mol] 6
1042 0.0 2.01 1.58 4.0 1.12 4.31
1043 End
1044 Rotor Hindered
1045 Group 6
1046 Axis 7 8
1047 Symmetry 1
1048 Potential [kcal/mol] 6
1049 0.0 1.68 0.0 1.68 0.0 1.68
1050 End
1051 Frequencies [1/cm] 42
1052 280.93 328.38 387.3 509.59
1053 616.8 769.08 878.88 916.68 924.7
1054 968.52 1060.43 1087.23 1120.2 1180.06
1055 1190.66 1195.24 1253.43 1285.2 1304.07
1056 1316.9 1368.72 1383.14 1414.16 1439.17
1057 1484.98 1488.95 1499.58 1501.07 1509.18
1058 1515.19 1519.42 3035.02 3062.93 3066.77
1059 3081.11 3093.63 3101.95 3112.16 3129.53
1060 3135.24 3144.09 3167.96
1061 !53.2 88.5 112.35 180.39 204.78 222.29!
1062 ZeroEnergy [kcal/mol] 0.9
1063 ElectronicLevels [1/cm] 1
1064 0 2
1065 End
1066 End
1067 !-----
1068 Barrier B7 W3 W5 # W_CCCO[CH]OC_E-2-17_m062x.log
1069 Variational
1070 RRHO
1071 Geometry [angstrom] 18
1072 C 0.0010976419 0.0007769054 0.0011240581
1073 C -0.0009818838 -0.0007991689 1.5064497278
1074 H 0.9777141295 -0.0015446348 1.9750424626
1075 C -1.0562309474 -0.8437124054 2.1715126496
1076 O -2.2557689941 -0.0415598397 2.2852748769
1077 C -1.9643957309 1.3065179632 2.2812899654
1078 O -2.0264548 1.9376736813 3.4938535658
1079 C -1.3169156789 1.2921460053 4.5312655126
1080 H 0.3538379792 -0.9548720991 -0.3978521351
1081 H 0.6430477634 0.7839688497 -0.4006672011

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1078   H      -1.0089760679   0.1600471213   -0.3817049931
1079   H      -1.3329804005  -1.720959764   1.5850120728
1080   H      -0.7485067804  -1.1711782052   3.1670902545
1081   H      -0.6855754965   1.1594165074   1.8613504691
1082   H      -2.5637270319   1.865045516   1.5676359021
1083   H      -1.7546948873   0.3185784458   4.7561648925
1084   H      -0.2650605201   1.1619285183   4.2561245709
1085   H      -1.3830332936   1.9320986561   5.4063003159
1086   Core RigidRotor
1087       SymmetryFactor      0.25
1088   End
1089   Rotor      Hindered
1090       Group                9 10 11
1091       Axis                  1 2
1092       Symmetry              3
1093       Potential[kcal/mol]   2
1094       0.0  2.02
1095   End
1096   Rotor      Hindered
1097       Group                8
1098       Axis                  7 6
1099       Symmetry              1
1100       Potential[kcal/mol]   6
1101       0.0  3.57  0.61  2.51  1.01  3.42
1102   End
1103   Rotor      Hindered
1104       Group                16 17 18
1105       Axis                  8 7
1106       Symmetry              1
1107       Potential[kcal/mol]   6
1108       0.0  2.42  0.0  2.41  0.0  2.42
1109   End
1110   Frequencies [1/cm]      44
1111       81.6      137.75      165.46      336.49      373.4
575.26      639.51
1112       695.84      793.67      902.09      930.18      961.35
992.46      1054.08      1067.08      1121.49      1153.82
1113       1160.67      1184.11      1213.26      1252.62      1263.46
1345.89      1379.42      1388.67      1411.77      1423.17
1114       1482.28      1491.21      1496.18      1498.88      1516.31
1530.5      1703.43      3032.24      3037.1      3058.93
1115       3096.51      3103.21      3106.78      3130.07      3145.06
3162.77      3167.48
1116       !187.62      197.45      253.39!
1117   ZeroEnergy[kcal/mol]   23.6
1118   ElectronicLevels [1/cm] 1
1119       0  2
1120   End

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1121 Tunneling                      Eckart
1122 ImaginaryFrequency [1/cm]      1725.1957
1123 WellDepth[kcal/mol]           20.9
1124 WellDepth[kcal/mol]           22.7
1125 End
1126 End
1127 !-----
1128 !-----
1129 !-----
1130 Bimolecular      P4      # C=CC_E11-71 + COC[0]_E11-71
1131 Fragment C=CC_E11-71
1132 RRHO
1133 Geometry[angstrom]           9
1134 C      -0.0036173945      -0.0000157516      0.0051672399
1135 C      0.0040011912      -0.000049678      1.5008982519
1136 H      0.9797799476      -0.000127773      1.9768349341
1137 C      -1.079110104      0.0000087324      2.2615933185
1138 H      0.5151885421      0.876581567      -0.3868008481
1139 H      -1.0214504945      0.000056787      -0.3822056223
1140 H      0.5150788396      -0.8766602561      -0.3868403603
1141 H      -1.0141839757      -0.0000194025      3.3409791477
1142 H      -2.0713139546      0.0000868059      1.8258205252
1143 Core RigidRotor
1144 SymmetryFactor      1.0
1145 End
1146 Rotor      Hindered
1147 Group      5 6 7
1148 Axis      1 2
1149 Symmetry      3
1150 Potential[kcal/mol]      2
1151 0.0 2.01
1152 End
1153 Frequencies [1/cm]      20
1154 430.51 596.0 938.41 947.42 967.29
1036.32 1079.5 1195.46 1330.57
1155 1407.13 1454.25 1484.54 1497.22 1742.34
3056.62 3111.88 3138.7 3159.03 3168.59
1156 3248.77
1157 !206.03!
1158 ZeroEnergy[kcal/mol]      0
1159 ElectronicLevels [1/cm]      1
1160 0 1
1161 End
1162 Fragment COC[0]_E11-71
1163 RRHO
1164 Geometry[angstrom]           9
1165 O      0.0382289661      0.0593540051      0.0002215994
1166 C      0.0163591446      -0.0053691118      1.3426864214

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1167 O 1.2470216178 0.0291171317 1.9848552562
1168 C 2.0739168416 -1.0665836523 1.6497473096
1169 H -0.5784125533 0.8290686934 1.7395124689
1170 H -0.5325957919 -0.941059928 1.5830535233
1171 H 1.5946834284 -2.0122857372 1.9263423625
1172 H 2.2976209058 -1.0792041752 0.5818999592
1173 H 2.9967462355 -0.9565845871 2.2118752179
1174 Core RigidRotor
1175 SymmetryFactor 1.0
1176 End
1177 Rotor Hindered
1178 Group 1 5 6
1179 Axis 2 3
1180 Symmetry 1
1181 Potential[kcal/mol] 6
1182 0.0 2.2 0.04 3.53 2.25 3.54
1183 End
1184 Rotor Hindered
1185 Group 2
1186 Axis 3 4
1187 Symmetry 3
1188 Potential[kcal/mol] 2
1189 0.0 1.7
1190 End
1191 Frequencies [1/cm] 19
1192 361.51 613.33 797.04 976.27 1074.59
1193 1151.14 1189.22 1223.98
1194 1273.03 1355.26 1400.31 1484.97 1497.95
1195 1521.41 2879.7 3012.82 3026.97 3103.17
1196 3167.4
1197 !132.69 204.03!
1198 ZeroEnergy[kcal/mol] 0
1199 ElectronicLevels [1/cm] 1
1200 0 2
1201 End
1202 GroundEnergy[kcal/mol] 21.4
1203 End
1204 !-----
1205 Barrier B8 W3 P4 # TS_CO2[0]_C=CC_E14-83_m062x.log
1206 Variational
1207 RRHO
1208 Geometry[angstrom] 18
1209 C 0.0725627534 -0.2581512192 0.0902507739
1210 C -0.004478305 -0.1046136918 1.5675602085
1211 H 0.9369868047 -0.08397223 2.1045997473
1212 C -1.1597095345 -0.0848849787 2.2681203162
1213 O -1.5122260274 -2.1320054686 2.4598551948
1214 C -0.395714855 -2.7453021389 2.931075682

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1213 O 0.6055726696 -2.9845156664 1.9745371002
1214 C 0.1575895909 -3.786013023 0.9043121795
1215 H 0.5974458395 0.5853620619 -0.3637312515
1216 H -0.9193449637 -0.3336968983 -0.3523967407
1217 H 0.6392456317 -1.1576303042 -0.1589793878
1218 H -1.1612002724 0.0860607652 3.3348071685
1219 H -2.1110693186 -0.0150305425 1.7606018363
1220 H 0.0975806778 -2.1870603892 3.7332468081
1221 H -0.7517981394 -3.7097289463 3.3405844154
1222 H -0.1873267399 -4.76105631 1.2663812613
1223 H -0.6595113597 -3.3056336616 0.3627094859
1224 H 1.0025332315 -3.9349736194 0.2358972602
1225 Core RigidRotor
1226 SymmetryFactor 1.0
1227 End
1228 Rotor Hindered
1229 Group 9 10 11
1230 Axis 1 2
1231 Symmetry 3
1232 Potential[kcal/mol] 2
1233 0.0 1.6
1234 End
1235 Rotor Hindered
1236 Group 2 12 13
1237 Axis 4 5
1238 Symmetry 1
1239 Potential[kcal/mol] 4
1240 0.0 3.24 0.03 1.4
1241 End
1242 Rotor Hindered
1243 Group 4
1244 Axis 5 6
1245 Symmetry 1
1246 Potential[kcal/mol] 6
1247 0.0 1.37 0.29 12.2 2.37 11.59
1248 End
1249 Rotor Hindered
1250 Group 5 14 15
1251 Axis 6 7
1252 Symmetry 1
1253 Potential[kcal/mol] 6
1254 0.0 6.83 4.14 5.26 2.17 4.03
1255 End
1256 Rotor Hindered
1257 Group 6
1258 Axis 7 8
1259 Symmetry 3
1260 Potential[kcal/mol] 2
```

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1261      0.0  1.82
1262      End
1263      Frequencies [1/cm]      41
1264      195.38      247.19      297.27      407.14      432.05
1265      620.12      685.71      935.49      944.71      949.02
1266      978.28      997.42      1042.04      1050.82      1128.54
1267      1179.63      1187.05      1201.42      1218.09      1293.17
1268      1311.07      1391.99      1403.1      1445.27      1454.19
1269      1473.88      1482.5      1493.58      1494.6      1522.73
1270      1624.19      2923.75      3023.66      3049.11      3052.2
1271      3094.78      3106.78      3143.08      3150.74      3177.37
1272      3182.68      3269.64
1273      !59.11      85.07      116.46      134.26      177.17!
1274      ZeroEnergy [kcal/mol]      24.1
1275      ElectronicLevels [1/cm]      1
1276      0  2
1277      End
1278      Tunneling      Eckart
1279      ImaginaryFrequency [1/cm]      412.3313
1280      WellDepth[kcal/mol]      21.4
1281      WellDepth[kcal/mol]      2.7
1282      End
1283      End
1284      !-----
1285      !-----WELL 4 to Products -----
1286      !-----
1287      Barrier      B9  W4  W5      # W_CCCO[CH]OC_E-2-17_m062x.log
1288      Variational
1289      RRHO
1290      Geometry [angstrom]      18
1291      C      -0.0254824206      0.0123942831      0.0093596899
1292      H      -0.0868588063      0.0771749799      1.0924065767
1293      H      0.9924278485      -0.0582674723      -0.358580221
1294      C      -1.0463476798      -0.8867014661      -0.6400477549
1295      C      -2.4292274841      -0.2386447978      -0.6114283095
1296      O      -2.4061370088      1.0055278987      -1.3056990103
1297      C      -1.5955434085      1.9438855892      -0.6970142396
1298      O      -2.0489284834      2.3804371351      0.5307910026
1299      C      -3.2356711965      3.1530424952      0.4486475843
1300      H      -0.7790398162      -1.0774465184      -1.6802990193
1301      H      -1.1148283618      -1.8570988297      -0.1376013223
1302      H      -3.1657975786      -0.8532605442      -1.1235548945
1303      H      -2.7557197503      -0.0789581346      0.420258726
1304      H      -0.5131515908      1.2348974904      -0.3803830498
1305      H      -1.4012045532      2.7528503003      -1.4042290067
1306      H      -3.0730899717      4.0427773736      -0.1668426414
1307      H      -4.0525945194      2.5694726611      0.020502296
1308      H      -3.4924204081      3.4562720943      1.4602777565

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1305 Core RigidRotor
1306     SymmetryFactor      0.5
1307 End
1308 Rotor      Hindered
1309     Group                9
1310     Axis                 8 7
1311     Symmetry             1
1312     Potential[kcal/mol]  6
1313     0.0  4.8  2.16  3.95  0.23  2.21
1314 End
1315 Rotor      Hindered
1316     Group                16 17 18
1317     Axis                 9 8
1318     Symmetry             1
1319     Potential[kcal/mol]  6
1320     0.0  1.67  0.0  1.67  0.0  1.67
1321 End
1322 Frequencies [1/cm]      45
1323     112.89      189.38      299.27      322.25      429.32
1324 492.97      570.51      636.56
1325     655.79      826.53      898.98      933.21      949.81
1326 996.68      1048.87      1085.04      1109.22      1164.68
1327     1173.49      1183.15      1189.05      1237.55      1248.26
1328     1302.12      1356.64      1372.09      1410.55      1441.51
1329     1456.04      1478.5      1481.61      1495.47      1512.14
1330     1516.7      1577.26      3035.76      3036.49      3057.35
1331     3083.07      3100.94      3103.68      3116.31      3142.43
1332     3159.37      3201.04
1333     !72.4 142.59!
1334 ZeroEnergy[kcal/mol]    20.1
1335 ElectronicLevels [1/cm]  1
1336     0  2
1337 End
1338 Tunneling      Eckart
1339     ImaginaryFrequency [1/cm]  1732.7857
1340     WellDepth[kcal/mol]    15.5
1341     WellDepth[kcal/mol]    19.2
1342 End
1343 End
1344 !-----
1345 !-----
1346 !-----
1347 Bimolecular      P5      # COCO[CH2]_E15-75 + C=C
1348     Fragment      COCO[CH2]_E15-75
1349     RRHO
1350     Geometry[angstrom]    12
1351     C      0.0197985211      -0.087165151      0.0620000365
1352     O      0.01946667      0.0123433083      1.4144452787

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1348   C      1.3033513113    0.0311999237    1.9991668647
1349   O      2.0080247069   -1.1421201916    1.7832282701
1350   C      1.4109833384   -2.2694954831    2.3939239059
1351   H      -0.9648560036   -0.14532655     -0.3706391162
1352   H      0.8812797475    -0.5336234028   -0.4138682818
1353   H      1.8984994652    0.8345471969    1.562446873
1354   H      1.1266582     0.2015697102    3.0640889162
1355   H      1.2881378939   -2.1058815072    3.4691277788
1356   H      0.4358203934   -2.4865939515    1.954487254
1357   H      2.0783884372   -3.1111023038    2.231721833
1358   Core RigidRotor
1359       SymmetryFactor    1.0
1360   End
1361   Rotor      Hindered
1362       Group                6 7
1363       Axis                  1 2
1364       Symmetry              1
1365       Potential [kcal/mol]   6
1366       0.0  4.94  0.3  0.36  0.01  4.58
1367   End
1368   Rotor      Hindered
1369       Group                1
1370       Axis                  2 3
1371       Symmetry              1
1372       Potential [kcal/mol]   8
1373       0.0  4.59  3.83  4.02  3.36  6.06  5.8  6.47
1374   End
1375   Rotor      Hindered
1376       Group                2 8 9
1377       Axis                  3 4
1378       Symmetry              1
1379       Potential [kcal/mol]   6
1380       0.0  6.82  2.13  4.68  3.81  4.95
1381   End
1382   Rotor      Hindered
1383       Group                3
1384       Axis                  4 5
1385       Symmetry              1
1386       Potential [kcal/mol]   6
1387       0.0  1.67  0.0  1.67  0.0  1.67
1388   End
1389   Frequencies [1/cm]    26
1390       339.67    453.44    580.33    624.75    980.8
1391       998.64
1391       1110.72    1182.67    1195.46    1222.42    1257.14
1391       1279.35    1349.19    1441.0     1475.73    1496.72
1392       1500.6     1515.37    1524.93    3033.95    3057.42
1392       3102.22    3117.1     3163.57    3164.38    3303.62

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1393
1394      !83.56      138.48      212.32      281.28!
1395      ZeroEnergy [kcal/mol]      0
1396      ElectronicLevels [1/cm]      1
1397      0 2
1398      End
1399      Fragment C=C
1400      RRHO
1401      Geometry [angstrom] 6
1402      C      0.00000000      0.00000000      0.00000000
1403      H      0.00000000      0.00000000      1.08216909
1404      H      0.96588500      0.00000000      -0.48801240
1405      C      -1.12558139      -0.00000000      -0.69239269
1406      H      -1.12558139      -0.00000000      -1.77456178
1407      H      -2.09146639      -0.00000000      -0.20438028
1408      Core RigidRotor
1409      SymmetryFactor 2
1410      End
1411      Frequencies [1/cm] 12
1412      829.14 990.4 1002.92 1070.96 1243.08 1388.11 1473.77 1718.56 3159.71
1413      3175.83 3235.53 3261.92
1414      !!torsions
1415      ZeroEnergy [kcal/mol] 0
1416      ElectronicLevels [1/cm] 1
1417      0 1
1418      End
1419      GroundEnergy [kcal/mol] 24.7
1420      End
1421      Barrier B10 W4 P5 # TS_C=C_COCCO [CH2] _E23 -71_m062x.log
1422      Variational
1423      RRHO
1424      Geometry [angstrom] 18
1425      C      -0.0084563854      0.0113946248      0.0102818023
1426      H      -0.0028056647      0.0318809306      1.0913826245
1427      H      0.9526089303      -0.0006686567      -0.4853111238
1428      C      -1.1640689608      0.071901169      -0.6889430574
1429      C      -1.7314054695      2.1976802129      -1.1008864362
1430      O      -2.7983603998      2.2570628036      -1.9499085498
1431      C      -4.0588434007      2.1982948195      -1.3295445703
1432      O      -4.3393648937      0.9557460081      -0.7810004328
1433      C      -4.5109616643      -0.0557125816      -1.7552873847
1434      H      -1.1621009229      -0.0867267465      -1.760595625
1435      H      -2.1183065145      -0.0506823553      -0.1935184875
1436      H      -1.9148757423      2.5321775922      -0.083874255
1437      H      -0.814185569      2.5124546371      -1.5770488189
1438      H      -4.1020446823      2.91490141      -0.5066844902
1439      H      -4.7768709737      2.4554489574      -2.1126865255
1440      H      -5.3327313879      0.1987353406      -2.4317163555

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1440   H          -3.6003188028   -0.2007752829   -2.3387756751
1441   H          -4.7510955195   -0.9732488777   -1.2253256447
1442   Core RigidRotor
1443       SymmetryFactor      1.0
1444   End
1445   Rotor          Hindered
1446       Group                6 12 13
1447       Axis                  5 4
1448       Symmetry              1
1449       Potential[kcal/mol]    6
1450       0.0  1.36  1.01  2.07  0.31  1.62
1451   End
1452   Rotor          Hindered
1453       Group                7
1454       Axis                  6 5
1455       Symmetry              1
1456       Potential[kcal/mol]    8
1457       0.0  1.3  0.87  2.27  2.17  2.76  2.47  3.8
1458   End
1459   Rotor          Hindered
1460       Group                8 14 15
1461       Axis                  7 6
1462       Symmetry              1
1463       Potential[kcal/mol]    7
1464       0.0  8.76  2.7  2.9  2.7  5.81  3.55
1465   End
1466   Rotor          Hindered
1467       Group                9
1468       Axis                  8 7
1469       Symmetry              1
1470       Potential[kcal/mol]    6
1471       0.0  10.44  3.0  4.16  3.14  4.23
1472   End
1473   Rotor          Hindered
1474       Group                16 17 18
1475       Axis                  9 8
1476       Symmetry              3
1477       Potential[kcal/mol]    2
1478       0.0  1.45
1479   End
1480   Frequencies [1/cm]      42
1481       214.81      290.15      340.53      393.53      474.57
1482       566.07      641.15      824.77      847.1      889.25
1483   978.43      997.95      1004.84      1039.94      1107.06
1484       1185.76      1192.58      1209.64      1239.75      1260.17
1485       1272.43      1309.75      1353.67      1442.22      1468.34
1486       1475.59      1493.92      1498.45      1516.06      1523.94
1487       1591.9      3037.01      3051.25      3106.83      3107.63

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1485      3109.99      3149.56      3165.46      3166.69      3231.58
      3250.33      3259.37
1486      !65.17      84.75      97.02      132.81      141.21!
1487      ZeroEnergy [kcal/mol]      32.2
1488      ElectronicLevels [1/cm]      1
1489      0 2
1490      End
1491      Tunneling      Eckart
1492      ImaginaryFrequency [1/cm]      493.5002
1493      WellDepth [kcal/mol]      27.6
1494      WellDepth [kcal/mol]      7.5
1495      End
1496      End
1497      !-----
1498      !-----WELL 5 to Products -----
1499      !-----
1500      Bimolecular      P6      # Bi_0=COC_E2-75 + CC[CH2]
1501      Fragment      Bi_0=COC_E2-75
1502      RRHO
1503      Geometry [angstrom]      8
1504      O      0.0418924661      0.0001246289      0.0116965965
1505      C      0.0167993753      0.0000166154      1.2063812612
1506      O      1.0865652314      -0.0000631766      1.9997896845
1507      C      2.3431972004      -0.0000105584      1.318127389
1508      H      -0.8942447797      -0.0000317404      1.8147181938
1509      H      3.1023784274      -0.0000881096      2.0924532518
1510      H      2.4312544895      -0.8854855669      0.6918659719
1511      H      2.4312687749      0.885578481      0.6920292162
1512      Core RigidRotor
1513      SymmetryFactor      1.0
1514      End
1515      Rotor      Hindered
1516      Group      1 5
1517      Axis      2 3
1518      Symmetry      1
1519      Potential [kcal/mol]      4
1520      0.0 13.48 5.51 13.48
1521      End
1522      Rotor      Hindered
1523      Group      6 7 8
1524      Axis      4 3
1525      Symmetry      3
1526      Potential [kcal/mol]      2
1527      0.0 1.12
1528      End
1529      Frequencies [1/cm]      16
1530      319.89      792.46      984.42      1064.87      1192.28
      1207.29      1273.14      1410.45

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1531      1481.65      1497.47      1509.45      1856.01      3083.57
          3088.44      3158.89      3195.05
1532      !155.75 343.39!
1533      ZeroEnergy [kcal/mol]      0
1534      ElectronicLevels [1/cm]      1
1535      0 1
1536      End
1537      Fragment CC[CH2]
1538      RRHO
1539      Geometry [angstrom]      10
1540      C      0.0039898156      -0.000284903      0.0092188719
1541      C      -0.008868217      0.0003344799      1.5351340559
1542      C      1.3565231458      0.0092275888      2.1204915126
1543      H      0.5041293962      0.8902436397      -0.3714390075
1544      H      -1.0058550385      -0.0252075459      -0.3981664794
1545      H      0.5415835145      -0.8709328996      -0.3682851152
1546      H      -0.5754642035      0.8592966151      1.9045280897
1547      H      -0.5627597195      -0.8813306258      1.8870425312
1548      H      1.5205327058      0.2907319782      3.1494417973
1549      H      2.1839314077      -0.4238248045      1.576714433
1550      Core RigidRotor
1551      SymmetryFactor      1.0
1552      End
1553      Rotor      Hindered
1554      Group      4 5 6
1555      Axis      1 2
1556      Symmetry      3
1557      Potential [kcal/mol]      2
1558      0.0 3.01
1559      End
1560      Rotor      Hindered
1561      Group      1 7 8
1562      Axis      2 3
1563      Symmetry      1
1564      Potential [kcal/mol]      12
1565      0.0 0.05 0.01 0.28 0.26 0.28 0.0 0.05 0.01 0.28 0.26
          0.28
1566      End
1567      Frequencies [1/cm]      22
1568      373.58      453.53      756.21      896.17      928.95
1053.02      1101.17      1178.18
1569      1271.23      1363.51      1410.57      1469.66      1474.78
          1502.4      1508.75      2984.28      3059.08      3062.57
1570      3130.39      3139.2      3166.94      3270.35
1571      !93.61 253.67!
1572      ZeroEnergy [kcal/mol]      0
1573      ElectronicLevels [1/cm]      1
1574      0 2

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1575 End
1576 GroundEnergy [kcal/mol] -9.3
1577 End
1578 Barrier B11 W5 P6 # TS_CC[CH2]_0=COC_E10-62_m062x.log
1579 Variational
1580 RRHO
1581 Geometry [angstrom] 18
1582 C 0.0284366395 -0.0170060218 -0.0169333001
1583 C -0.0219067159 0.0303409796 1.505303022
1584 C 1.3343043082 0.0117089011 2.1180473682
1585 O 1.9650016396 -1.686966595 1.8522142967
1586 C 1.1294480776 -2.6245123574 1.8753301407
1587 H 0.5226080268 -2.9216718448 1.0251745569
1588 O 0.7027606488 -3.1987965225 3.020877944
1589 C 1.5069796255 -2.9532032456 4.1654627765
1590 H 0.5241095357 0.8712515011 -0.4102611894
1591 H -0.9696336878 -0.0672939418 -0.44949597
1592 H 0.5952533376 -0.8853391171 -0.3533023182
1593 H -0.5687307603 0.9169713444 1.8399050458
1594 H -0.5911746634 -0.825652915 1.8896373876
1595 H 2.1188139482 0.5425963857 1.5947417134
1596 H 1.3893963616 0.0966805284 3.1962521149
1597 H 2.5480689189 -3.2060795019 3.9636416677
1598 H 1.451491679 -1.9085276175 4.4692641653
1599 H 1.112290057 -3.5857189669 4.9546386048
1600 Core RigidRotor
1601 SymmetryFactor 1.0
1602 End
1603 Rotor Hindered
1604 Group 9 10 11
1605 Axis 1 2
1606 Symmetry 1
1607 Potential [kcal/mol] 6
1608 0.0 2.74 0.0 2.74 0.0 2.74
1609 End
1610 Rotor Hindered
1611 Group 1 12 13
1612 Axis 2 3
1613 Symmetry 1
1614 Potential [kcal/mol] 6
1615 0.0 5.51 1.57 3.37 1.87 3.29
1616 End
1617 Rotor Hindered
1618 Group 2 14 15
1619 Axis 3 4
1620 Symmetry 1
1621 Potential [kcal/mol] 6
1622 0.0 3.14 2.19 3.81 1.87 2.5
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1623 End
1624 Rotor          Hindered
1625   Group          8
1626   Axis           7 5
1627   Symmetry       1
1628   Potential [kcal/mol] 4
1629   0.0  7.5  1.69  6.68
1630 End
1631 Rotor          Hindered
1632   Group          16 17 18
1633   Axis           8 7
1634   Symmetry       3
1635   Potential [kcal/mol] 2
1636   0.0  0.94
1637 End
1638 Frequencies [1/cm] 42
1639   140.36   294.02   331.58   382.31   461.13
1640   703.89   708.9    760.43   810.97   910.03
1641  943.89   971.51   987.54   1090.0   1115.96
1642   1183.81  1194.46  1197.63  1223.9   1283.32
1643   1349.36  1375.37  1416.7   1448.81  1475.87
1644   1481.69  1496.73  1500.62  1508.53  1512.82
1645   1519.23  3017.68  3056.14  3063.97  3066.28
1646   3130.82  3133.59  3142.46  3145.57  3165.03
1647   3175.56  3234.18
1648   !38.57   96.58   127.86   181.41   214.12!
1649 ZeroEnergy [kcal/mol] 13.2
1650 ElectronicLevels [1/cm] 1
1651   0  2
1652 End
1653 Tunneling          Eckart
1654 ImaginaryFrequency [1/cm] 776.8227
1655 WellDepth [kcal/mol] 12.3
1656 WellDepth [kcal/mol] 22.5
1657 End
1658 End
1659 !-----
1660 !-----
1661 !-----
1662 Bimolecular      P7      # Bi_CCCOC=O_E4 -4 + [CH3]
1663 Fragment Bi_CCCOC=O_E4 -4
1664 RRHO
1665 Geometry [angstrom] 14
1666   C      0.0240964182  0.0095221715  0.0177319524
1667   C      -0.0030425293  -0.0039903355  1.5406932512
1668   C      1.3810526487  0.0075489273  2.1477852797
1669   O      2.0145018277  1.2430203364  1.7720768004
1670   C      3.2624172943  1.4051392265  2.20525629

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1667      O          3.8765204621    0.6198108646    2.8648746235
1668      H          0.5240548293    0.9039028938    -0.3506417673
1669      H          -0.9838521124    -0.009648659    -0.3935102324
1670      H          0.5610273437    -0.858905151    -0.3666945599
1671      H          -0.5595170156    0.8555979426    1.9180905613
1672      H          -0.514632694    -0.8978448249    1.9021761279
1673      H          1.3548784005    -0.0512964009    3.2356710446
1674      H          1.9904306763    -0.8198792418    1.7803288283
1675      H          3.6490536234    2.3730992117    1.8666815551
1676      Core RigidRotor
1677          SymmetryFactor          1.0
1678      End
1679      Rotor          Hindered
1680          Group          7 8 9
1681          Axis          1 2
1682          Symmetry          3
1683          Potential [kcal/mol]          2
1684          0.0  2.75
1685      End
1686      Rotor          Hindered
1687          Group          1 10 11
1688          Axis          2 3
1689          Symmetry          1
1690          Potential [kcal/mol]          6
1691          0.0  3.6  0.28  3.6  0.03  4.82
1692      End
1693      Rotor          Hindered
1694          Group          2 12 13
1695          Axis          3 4
1696          Symmetry          1
1697          Potential [kcal/mol]          8
1698          0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
1699      End
1700      Rotor          Hindered
1701          Group          3
1702          Axis          4 5
1703          Symmetry          1
1704          Potential [kcal/mol]          4
1705          0.0  12.84  4.65  12.83
1706      End
1707      Frequencies [1/cm]          32
1708          261.94          351.0          467.28          768.7          797.8
1709          912.78
1710          922.75          957.98          1065.81          1089.78          1136.59
          1180.37          1260.59          1287.64          1312.35          1381.12
          1413.84          1417.13          1428.14          1484.81          1501.99
          1513.24          1520.99          1852.3          3066.48          3071.27

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1711          3076.24          3084.0          3107.9          3126.48          3138.05
          3150.08
1712      !55.58          128.77          199.8          299.37 !
1713      ZeroEnergy [kcal/mol]          0
1714      ElectronicLevels [1/cm]          1
1715          0 1
1716      End
1717      Fragment [CH3]
1718          RRHO
1719      Geometry [angstrom]          4
1720      C          0. 0. 0.
1721      H          0. 0. 1.0765291468
1722      H          0.9323015891 0. -0.5382645734
1723      H          -0.9323015891 0. -0.5382645734
1724      Core RigidRotor
1725          SymmetryFactor          6.0
1726      End
1727      Frequencies [1/cm]          6
1728          436.03          1412.64          1412.73          3144.41          3323.11
          3323.14
1729      ! !
1730      ZeroEnergy [kcal/mol]          0
1731      ElectronicLevels [1/cm]          1
1732          0 2
1733      End
1734      GroundEnergy [kcal/mol]          -12.5
1735      End
1736      Barrier          B12 W5 P7 # TS_CCCOC=0_[CH3]_E11-74_m062x.log
1737      Variational
1738          RRHO
1739      Geometry [angstrom]          18
1740      C          0.0179906848 -0.0173519364 -0.0044379667
1741      C          -0.0076605888 0.0184238393 1.5182617704
1742      C          1.3803600465 0.0083999702 2.1190305173
1743      O          2.0454184047 1.2033066436 1.7008809262
1744      C          3.2906740238 1.3854777637 2.1794091652
1745      H          3.6942802614 2.3531674115 1.8937185402
1746      O          3.9866774718 0.4462998928 2.6316656258
1747      C          4.8265576836 -0.6087582945 1.3980626923
1748      H          0.5455409505 0.8494348829 -0.3991445919
1749      H          -0.9899181554 -0.0197959385 -0.4166469006
1750      H          0.5288099463 -0.9136288791 -0.3606662728
1751      H          -0.5340461001 0.9083705272 1.8671437259
1752      H          -0.5471792927 -0.8466003159 1.9084887306
1753      H          1.3521673638 -0.0133753658 3.2104808819
1754      H          1.9451036601 -0.8627271422 1.780334797
1755      H          5.7211910636 -0.0432680373 1.180758965
1756      H          4.9766989419 -1.5185186733 1.9601231634

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1757   H          4.1098656247   -0.6745173682   0.5894812211
1758   Core RigidRotor
1759       SymmetryFactor          1.0
1760   End
1761   Rotor          Hindered
1762       Group          9 10 11
1763       Axis          1 2
1764       Symmetry          3
1765       Potential [kcal/mol]      2
1766       0.0  2.76
1767   End
1768   Rotor          Hindered
1769       Group          1 12 13
1770       Axis          2 3
1771       Symmetry          1
1772       Potential [kcal/mol]      6
1773       0.0  3.66  0.35  3.68  0.06  4.92
1774   End
1775   Rotor          Hindered
1776       Group          2 14 15
1777       Axis          3 4
1778       Symmetry          1
1779       Potential [kcal/mol]      6
1780       0.0  4.13  0.9  5.81  0.18  1.22
1781   End
1782   Rotor          Hindered
1783       Group          3
1784       Axis          4 5
1785       Symmetry          1
1786       Potential [kcal/mol]      4
1787       0.0  6.93  2.16  7.75
1788   End
1789   Rotor          Hindered
1790       Group          16 17 18
1791       Axis          8 7
1792       Symmetry          1
1793       Potential [kcal/mol]      6
1794       0.0  0.39  0.0  0.39  -0.0  0.39
1795   End
1796   Frequencies [1/cm]      42
1797       188.33      259.51      313.59      363.53      467.44
1798       710.79      734.52      765.37      769.89      822.99
1799       906.39      921.7      958.47      1067.3      1089.94
1800       1133.56      1178.3      1203.46      1282.85      1309.71
1800       1353.97      1377.35      1412.38      1423.05      1443.38
1800       1447.1      1484.06      1487.81      1500.39      1512.34
1800       1523.74      3058.14      3063.8      3069.78      3099.28

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1801          3109.87          3110.85          3134.64          3149.96          3153.33
          3257.13          3274.57
1802      !29.42          59.39          101.34          138.09          197.6!
1803      ZeroEnergy [kcal/mol]          14.5
1804      ElectronicLevels [1/cm]          1
1805          0  2
1806      End
1807      Tunneling          Eckart
1808      ImaginaryFrequency [1/cm]          880.2786
1809      WellDepth [kcal/mol]          13.6
1810      WellDepth [kcal/mol]          27.0
1811      End
1812 End
1813 End
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