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.

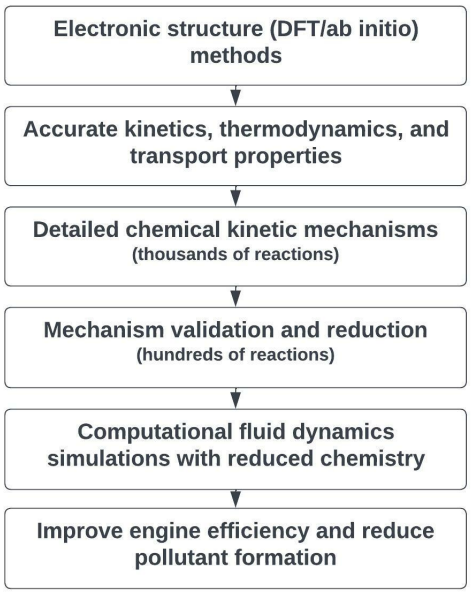

Fig. 1.1 Diagram of the layers of understanding for the simulation of combustion systems.

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 $\sim$30 reactions, while the mechanism for methane requires $\sim$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 CO_2 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 ($\phi \to \infty$) 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 unimolecularily 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, $CH_3 - (OCH_2)_n - CH_3$) 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 transfering 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).

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

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 were 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 and 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 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).

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

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

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

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.

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

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

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

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 O_2 addition, the product is a peroxy radical (ROȮ) that can either eliminate HO_2 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, HO_2 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 ROȮ 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.

$$\ln(k_i(T)) = \ln(k_0(T)) + m(x_i - x_0) \tag{2.8}$$

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]):

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

Here, $\Delta S^\dagger$ and $\Delta H^\dagger$ 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.

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

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.

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

$$E_a = E_{a,ref} + \sum_{i=1}^{N} \Delta\text{GAV}_{E_a}(X_i) \tag{2.12}$$

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 C_0-C_4 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

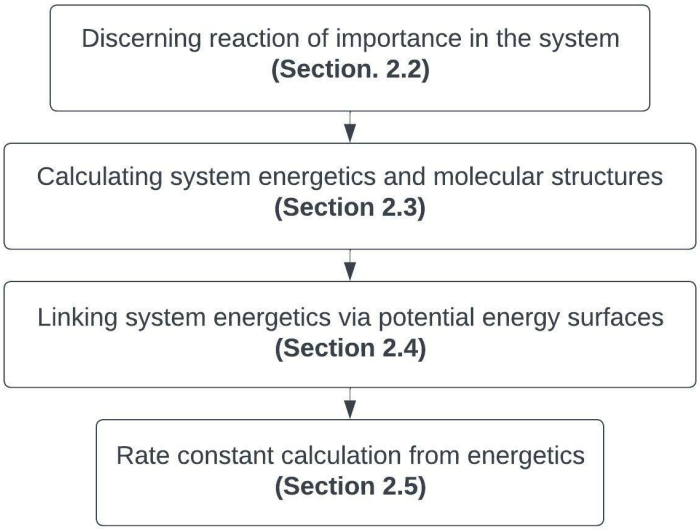

Fig. 2.1 Generalized computational steps required to calculate reaction rate constants from quantum mechanical principles.

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.

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2 \tag{2.13}$$

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).

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M\,, \qquad A^* \xrightarrow{k_2} \text{products} \tag{2.14}$$

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.

$$C_3H_7OCH_2OC_3H_7 \longrightarrow \dot{C}H_2CH_3 + \dot{C}H_2OCH_2OC_3H_7 \tag{2.15}$$

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.

$$\dot{C}H_2OCH_2OC_3H_7 \longrightarrow CH_2O + \dot{C}H_2OC_3H_7 \tag{2.16}$$

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.

$$\dot{C}H_2OCH_2OC_3H_7 \longrightarrow CH_3OCH_2OCH_2CH_2\dot{C}H_2 \tag{2.17}$$

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.

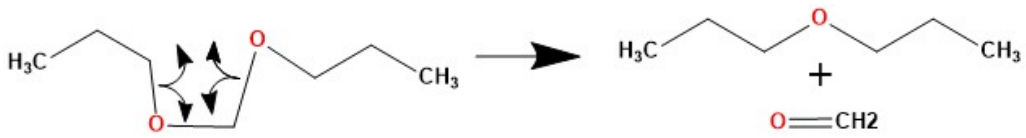

Fig. 2.2 Pericyclic reaction forming formaldehyde and dipropyl ether from DPM.

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 for 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 ($\dot{R}$) approaches a molecule and steals a hydrogen atom.

$$C_3H_7OCH_2OC_3H_7 + \dot{R} \longrightarrow C_3H_7O\dot{C}HOC_3H_7 + RH \tag{2.18}$$

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.

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

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 Shrödinger's equation, this system is governed by the Coulomb potential between the electron and the proton.

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{2.20}$$

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:

$$-\hbar\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\hat{L}^2\psi+2m_e r^2\left[-\frac{e^2}{4\pi\varepsilon_0 r}-E\right]\psi(r,\theta,\phi)=0 \tag{2.21}$$

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.

$$E_n=-\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}\quad n=1,2,3,... \tag{2.22}$$

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 polnomials L_{n+l}^{2l+1}:

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

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.

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

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 (MPn) [63], which rely on systematic improvements of the HF wave function through Rayleigh–Schrödinger perturbation theory of the n-th order. Unfortunately, MPn 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].

$$E = E[\rho] \tag{2.25}$$

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.

$$X - YZg \tag{2.26}$$

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						
		HF	MP2	MP3	MP4	CCSD(T)		Full configuration interaction
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 NxN 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 Section2.4) 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 be 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 of Z-matrix format.

An example of Cartesian vs. Z-Matrix descriptions for methyl ($\dot{C}H_3$) 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     1.07000000              -
B2     1.07000000              -
B3     1.07000000              -
A1   120.00000000              -
A2   120.00000000              -
D1  -180.00000000              -
```

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.

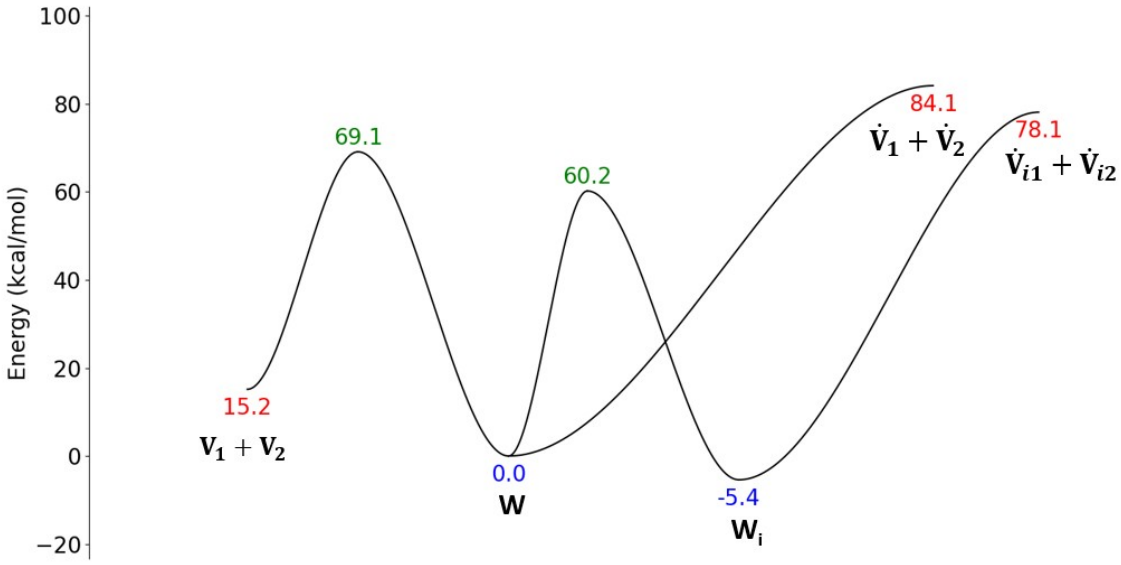

Fig. 2.5 Two-dimensional projections of the PES along a reaction coordinate for isomerization, elimination, and dissociation reactions. Free radicals are marked by a dot, and isomers are shown with a subscript *i*.

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, H_2 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 Section2.5). 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.

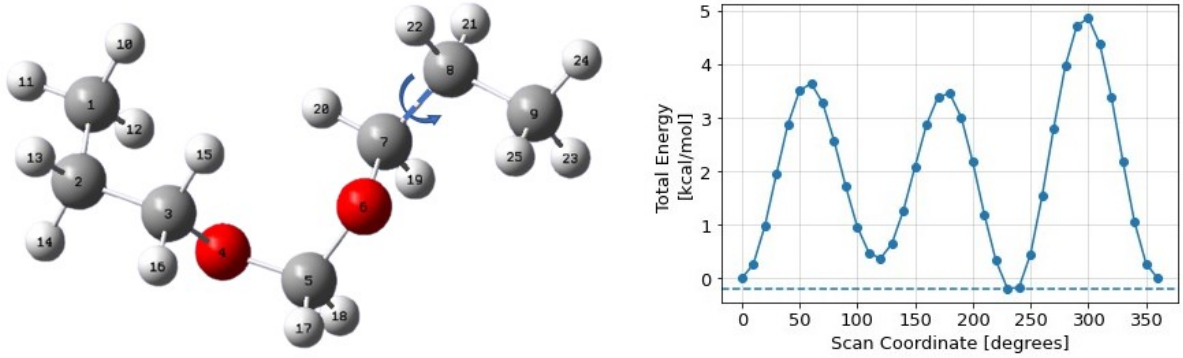

Fig. 2.6 Hindered rotor scan for the 7-8 bond of DPM, rotating a methyl group and the two hydrogen atoms attached to C8.

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].

$$\begin{aligned} \mathrm{E}_{high-level} = \mathrm{E}_{zero-point}[\mathrm{M06\text{-}2X/cc\text{-}pVTZ}] + \mathrm{E}[\mathrm{CCSD(T)/cc\text{-}pVTZ}] + \\ 0.4628 \times \{\mathrm{E}[\mathrm{CCSD(T)/cc\text{-}pVTZ}] - \mathrm{E}[\mathrm{CCSD(T)/cc\text{-}pVDZ}]\} \end{aligned} \tag{2.27}$$

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.

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

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:

$$\alpha = 2\pi\nu\sqrt{\frac{\mu}{2\text{BDE}}} \tag{2.29}$$

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

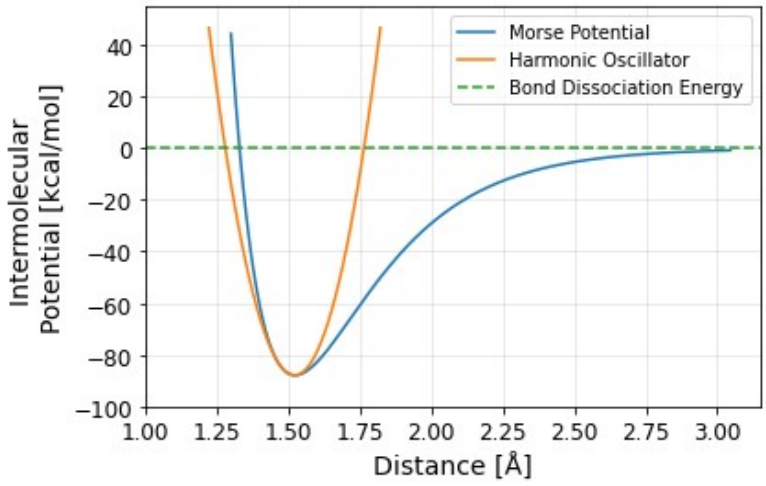

Fig. 2.7 Morse potential, harmonic oscillator approximation, and bond dissociation energy for the following DEM bond fission reaction: $C_2H_5OCH_2OC_2H_5 \longrightarrow C_2H_5O\dot{C}H_2 + \dot{O}C_2H_5$.

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.

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

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.

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M \tag{2.31}$$

$$A^* \xrightarrow{k_2} A^{\#} \xrightarrow{k^{\#}} P \tag{2.32}$$

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 $A^{\#}$ and from the transition state to the products P, the key assumption here is that $k^{\#} >> k_2$. Now, the expression for the rate of production can be derived from rate equations in terms of the concentration of the reactant $[A]$.

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

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

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

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 $k_{-1}[M] \to \infty$,

Eqn. 2.34 reduces to Eqn. 2.30. Since $k_2(E)$ is determined by the vibrational quantum states for $A^{\#}$, 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.

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

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 **J**, and its matrix form is outlined below.

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

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

All the diagonal terms of **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 **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 at 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 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.

$$V = \frac{-C_n}{R^n} \tag{2.38}$$

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

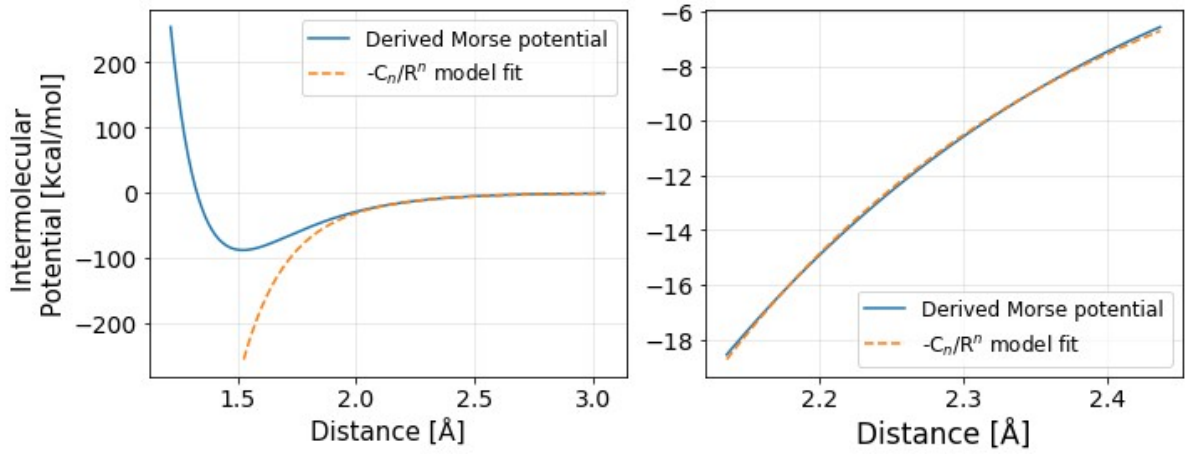

Fig. 2.8 Derived Morse potential and negative power law fit for modeling the following DEM bond fission reaction: $C_2H_5OCH_2OC_2H_5 \longrightarrow C_2H_5O\dot{C}H_2 + \dot{O}C_2H_5$. A zoomed in plot is shown on the right.

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 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.

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

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

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.

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

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

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

Here, c, n, and d are known parameters, all given in terms of F_cent by the following expressions:

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

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

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

This is know 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 is 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.

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

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.

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

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.

$$\varphi_i(x) = \cos[(i-1)acos(x)], \quad i = 1,2,3..., \tag{2.47}$$

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

$$\tilde{P} \rightarrow \frac{2\log P - \log P_{min} - \log P_{max}}{\log P_{max} - \log P_{min}} \tag{2.49}$$

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].

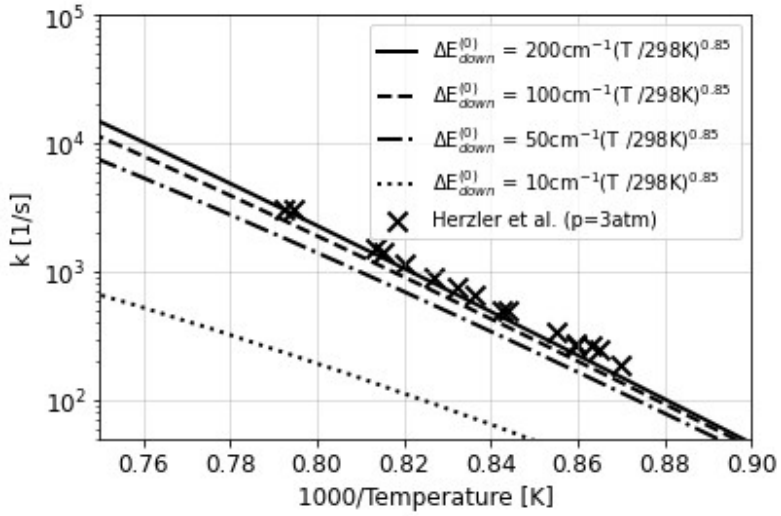

Fig. 2.9 Total experimental vs. theoretical rate of decomposition of DEM with different values for the ΔE_{down} energy relaxation model.

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 at 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

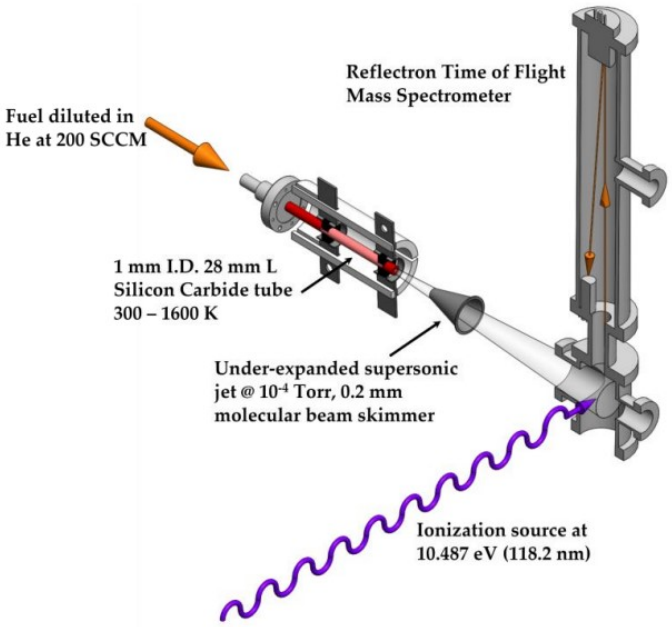

Fig. 2.10 Reflectron photoionization time-of-flight mass spectrometer with fixed ionization source of 10.487 eV.

can observe early kinetic processes by discerning thermal decomposition products formed at timescales of $\sim$100μs. 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.

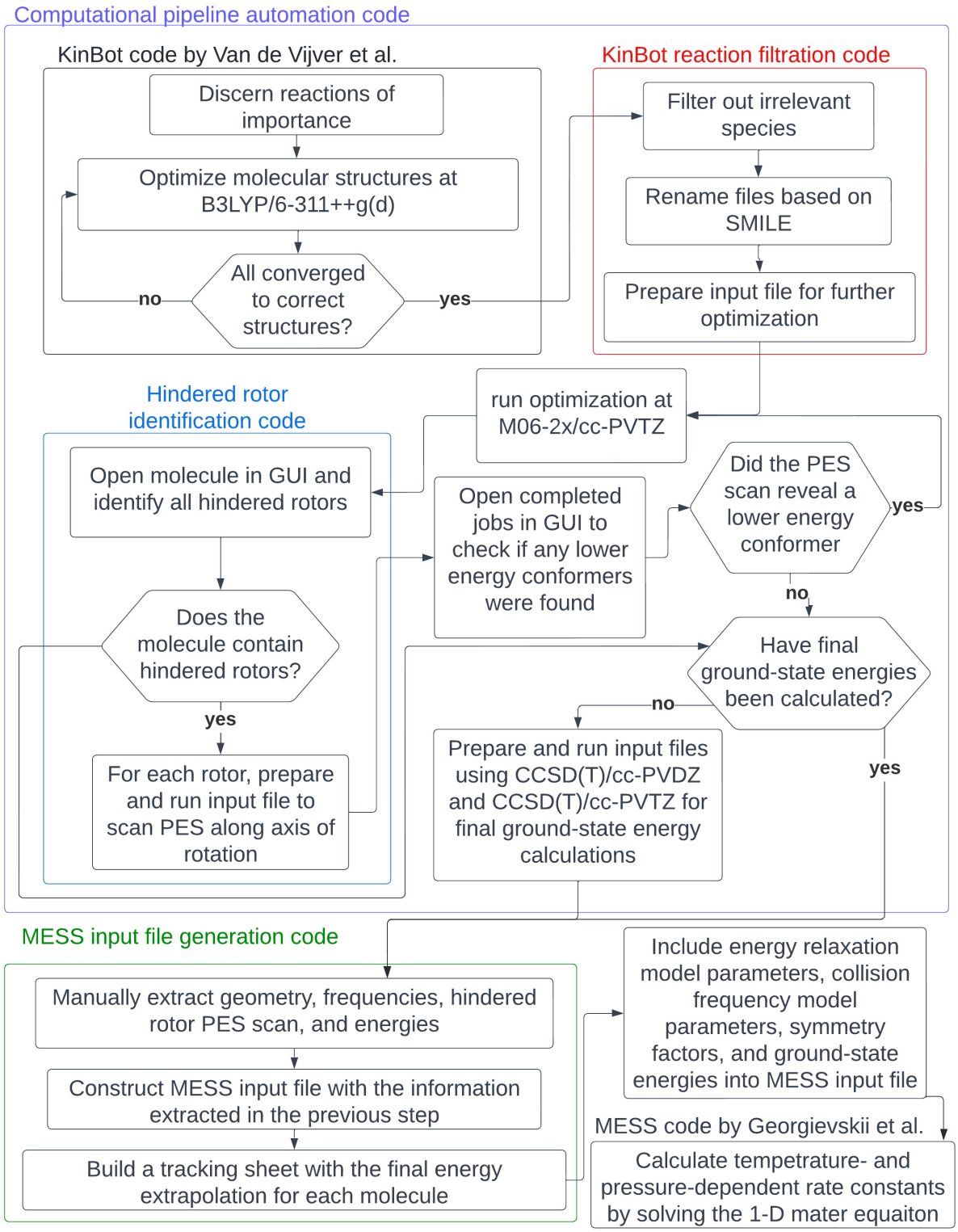

Fig. 3.1 Flow chart of the methods used in this work (that leverage previously developed codes and software [45, 75, 82, 94]) to calculate high-level rate coefficients, and the computational steps captured by the automation codes (in red, blue, green, and purple) developed in this work.

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-generate PES for $CH_3CH_2OCH\dot{O}$, a relevant radical in DEM pyrolysis, is shown in Fig. 3.2.

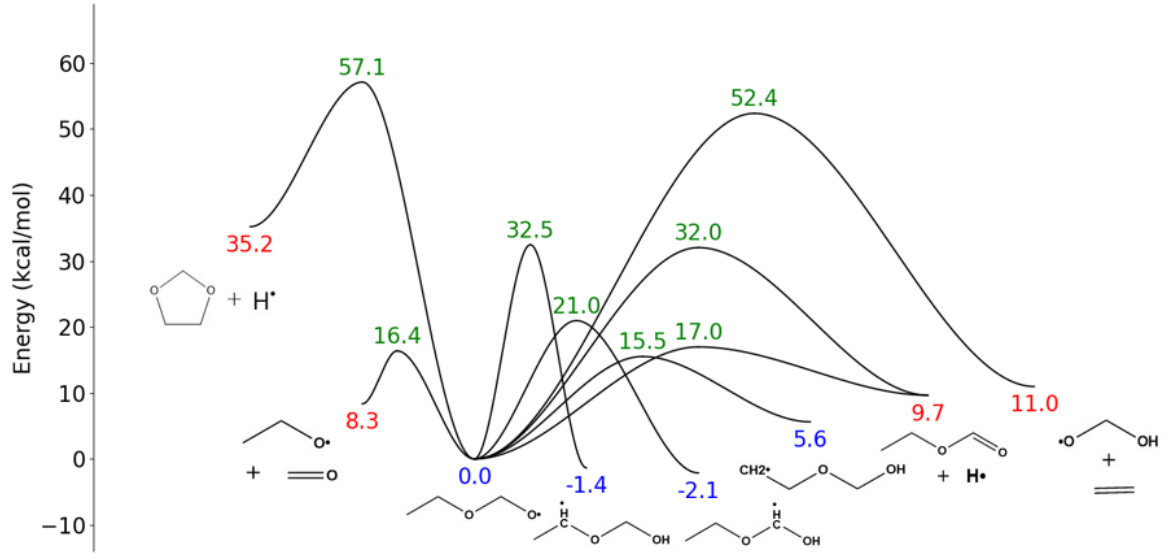

Fig. 3.2 KinBot-generated PES for $CH_3CH_2OCH\dot{O}$ with a cutoff of 60.0 kcal/mol. Isomerization, β-scission, and transition state energies are shown in blue, red, and green respectively.

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 $CH_3CH_2OCH\dot{O}$.

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 31067057000000000002_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*_E*energy*.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].

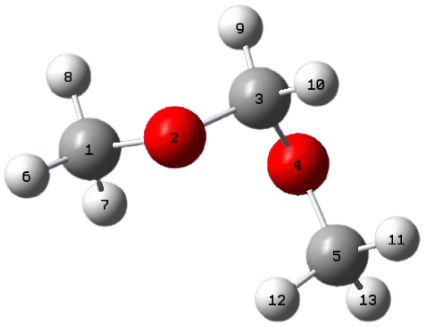

Fig. 3.3 Ball-and-stick model of dimethoxymethane using GaussView6.

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.

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

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.

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

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

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

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

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.

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

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 *.gjf* 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.

$$[[1,2],[2,3],[3,4],[4,5]] \overset{\text{[1,2] is a rotor}}{\rightarrow} [[2,3],[3,4],[4,5]] \overset{\text{[2,3] is a rotor}}{\rightarrow} [[3,4],[4,5]] \quad ...$$

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).

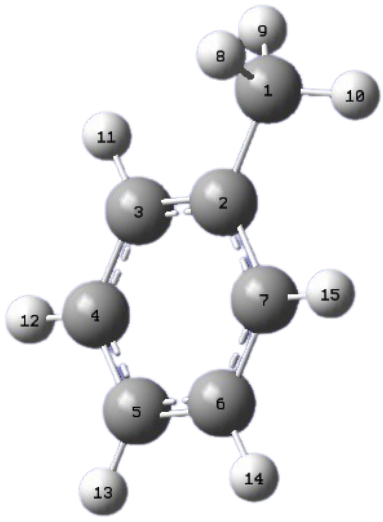

Fig. 3.4 Ball-and-stick model of toluene using GaussView6.

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

$$\text{bondgraph}: [[2,8,9,10],[1,3,7],[2,4,11],[3,5,12],[4,6,13],[5,7,14],[2,6,15],\\ [1],[1],[1],[3],[4],[5],[6],[7]]$$

$$\text{generalized}axes: [[1,2],[2,3],[2,7],[3,4],[4,5],[5,6],[6,7]]$$

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 it 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 Miscrosoft 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 abd 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 pericylic reactions in closed-shell molecule systems. In addition, the KinBot reaction

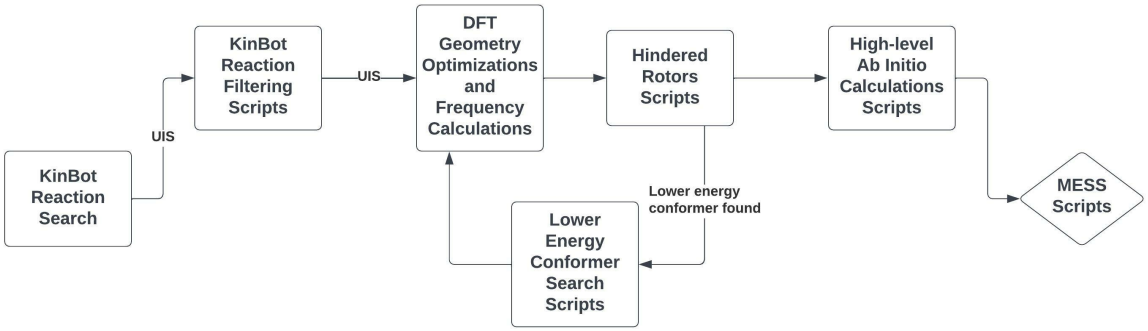

Fig. 3.5 Flow chart of the automation of the computational pipeline. UIS stands for user intervention step. The diamond-shaped box denotes the scripts that have not been integrated into the pipeline's automation at the moment of writing this thesis.

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 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 *.gjf* 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 a 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 studies 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 oxymethlyene 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 $CH_3OCH_2OCH_2OCH_2OCH_3$), or extending the end groups (i.e. diethoxymethane or $CH_3CH_2OCH_2OCH_2CH_3$). 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

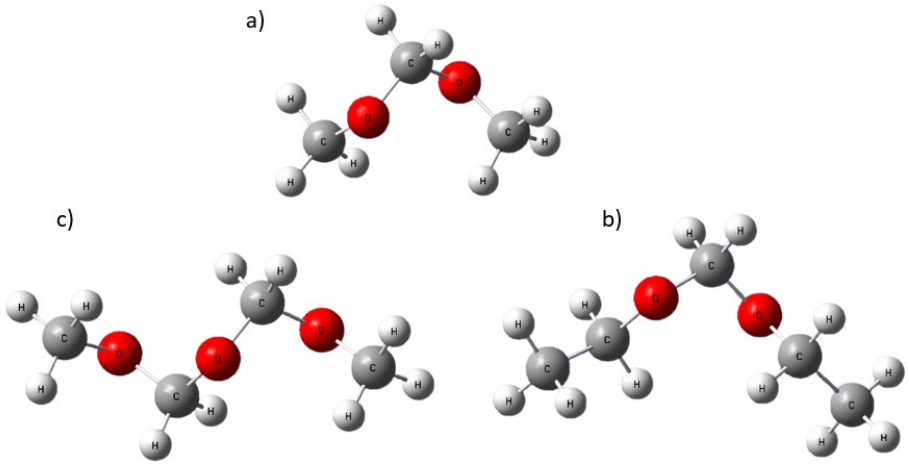

Fig. 4.1 Ball-and-stick models of dimethoxymethane (a), diethoxymethane (b), and 2,4,6 trioxaheptane (c) highlighting possible extended OME structures (b) and (c) from (a), the simplest OME

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 oxymehylene 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 $CH_3O\dot{C}HOCH_3$ breaks down into either methyl formate and methyl radical, or into 3 products: carbon monoxide, methane and methoxy radical. Additionally, they suggested that $\dot{C}H_2OCH_2OCH_3$ 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 ($\dot{C}H_2OCH_2OCH_3$) either unimolecularily decomposes into formaldehyde and methoxymethyl radical or adds to molecular oxygen; while dimethoxymethyl radical ($CH_3O\dot{C}HOCH_3$) 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/O_2 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.

$$CH_3OCH_2OCH_3 \longleftrightarrow CH_3OH + CH_3 + HCO \tag{4.1}$$

$$H + O_2 \longleftrightarrow O + OH \tag{4.2}$$

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 $CH_3OCH_2\dot{O} + CH_3$ 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 $\dot{H}$ and $\dot{C}H_3$, and concluded that abstraction from the central carbon is always favored, promoting the production of methyl formate.

4.2 OMEs with more oxymehtylene 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% $OME_{n=3-5}$ 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 a slight increase in the break thermal efficiency (BTE). Lastly, they found that that combustion duration was shortened with the addition of $OME_{n=3-5}$. 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 $OME_{n=3}$. 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 and also measured laminar burning velocities in a spherical combustion vessel at various equivalence ratios. They concluded that the combustion of $OME_{n=3}$ 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 $OME_{n=3}$ 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 $OME_{n=3}$ to n-heptane and saw faster, and less temperature- and pressure-sensitive flames for $OME_{n=3}$ 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 $OME_{n=3}$ 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 $OME_{n=3}$ 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 (NOx). 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 ($CH_3O[CH_2O]_nCH_3$ 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 $\Delta E^{(0)}_{down} = 200 cm^{-1}(T/298K)^{0.85}$. 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:

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

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:

$$\alpha = 2\pi\nu\sqrt{\frac{\mu}{2\mathrm{BDE}}} \tag{5.2}$$

The MESS parameters were chosen from a fit that matches the Morse potential between 30-50% increase of the equilibrium bond length r0. 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 $\pm$ 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 Δm/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>1000K, and the central C-O bond fission (5.4) comprises less than 10% of the reaction flux.

$$CH_3OCH_2OCH_3 \longrightarrow CH_3OCH_2\dot{O} + \dot{C}H_3 \tag{5.3}$$

$$CH_3OCH_2OCH_3 \longrightarrow CH_3O\dot{C}H_2 + \dot{O}CH_3 \tag{5.4}$$

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).

$$CH_3OCH_2OCH_3 + \dot{R} \longrightarrow CH_3O\dot{C}HOCH_3 + RH \tag{5.5}$$

$$CH_3O\dot{C}HOCH_3 \longrightarrow HCOOCH_3 + \dot{C}H_3 \tag{5.6}$$

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 methyl0terminated OMEs.

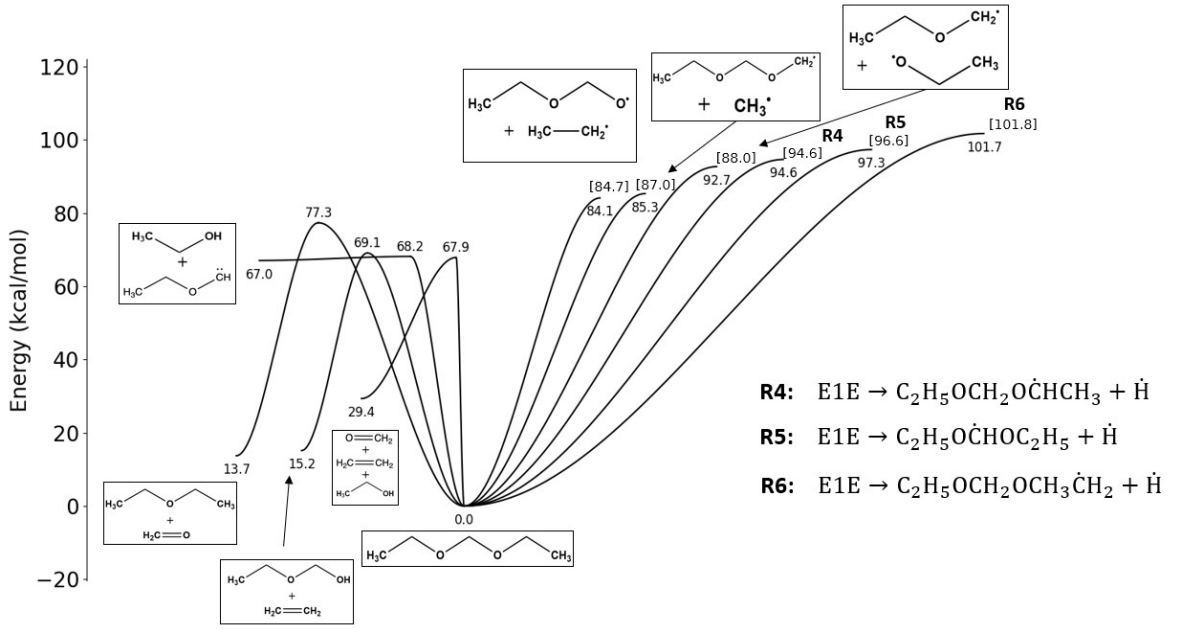

Fig. 5.1 Potential Energy Surface of unimolecular decomposition of E-1-E calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory. The zero point energy is located at the parent E-1-E molecule. Ground-state energies calculated by Jacobs et al. [51] are shown in square brackets.

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 at 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.

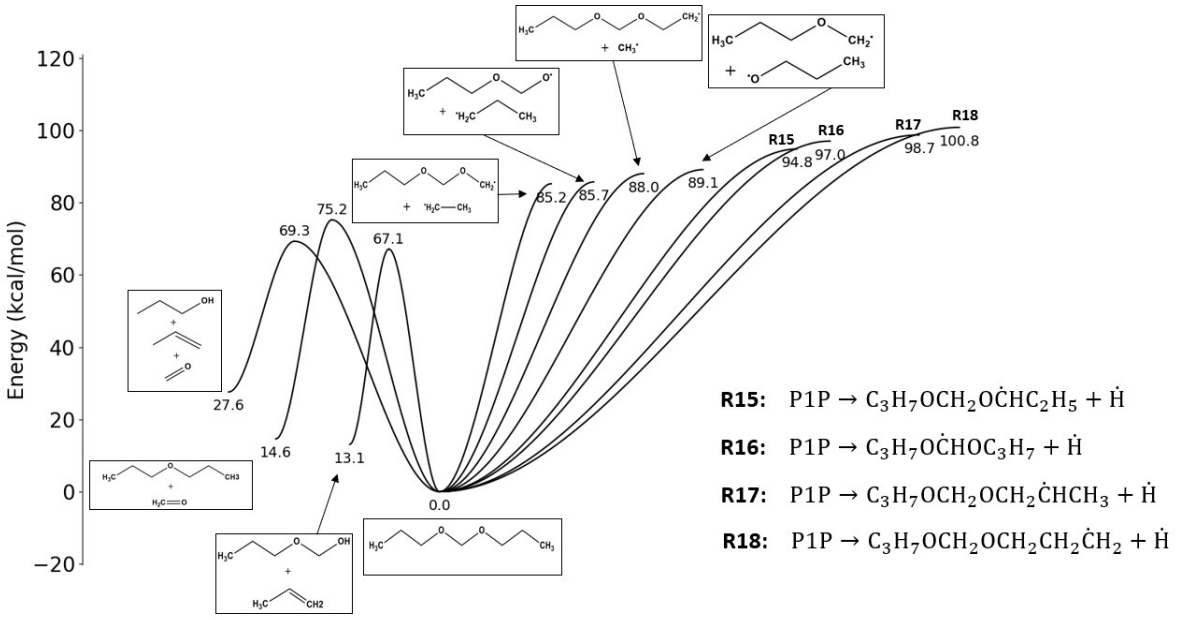

Fig. 5.2 Potential Energy Surface of unimolecular decomposition of P-1-P calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory. The zero point energy is located at the parent P-1-P molecule. Molecular and bond fission reactions are shown on the left and right, respectively.

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 *logP* [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 a analogous patterns to those of E-1-E, and the calculated BDEs show similar

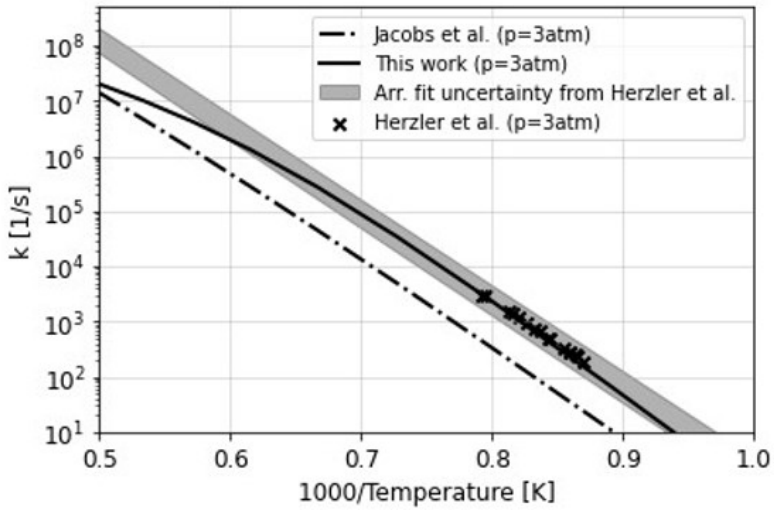

Fig. 5.3 Total rate coefficient of E-1-E calculated in this work compared to previous shock-tube and theoretical studies.

trends to the ones calculated by Cheng et al. [146, 147] for dipropyl ether (DPE). The $\alpha\ \beta$ C-C bond is the weakest and the $\beta\ \gamma$ 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.

$$\text{E1E} \longrightarrow C_2H_5OCH_2\dot{O} + \dot{C}H_2CH_3 \quad \text{(R1)}$$
$$\text{E1E} \longrightarrow C_2H_5OCH_2O\dot{C}H_2 + \dot{C}H_3 \quad \text{(R2)}$$
$$\text{E1E} \longrightarrow C_2H_5O\dot{C}H_2 + \dot{O}C_2H_5 \quad \text{(R3)}$$
$$\text{E1E} \longrightarrow C_2H_5OCH_2O\dot{C}HCH_3 + \dot{H} \quad \text{(R4)}$$
$$\text{E1E} \longrightarrow C_2H_5O\dot{C}HOC_2H_5 + \dot{H} \quad \text{(R5)}$$
$$\text{E1E} \longrightarrow C_2H_5OCH_2OCH_2\dot{C}H_2 + \dot{H} \quad \text{(R6)}$$
$$\text{E1E} \longrightarrow C_2H_5OCH_2OH + C_2H_4 \quad \text{(R7)}$$
$$\text{E1E} \longrightarrow C_2H_5OC_2H_5 + CH_2O \quad \text{(R8)}$$
$$\text{E1E} \longrightarrow C_2H_5OH + C_2H_5O\ddot{C}H \quad \text{(R9)}$$
$$\text{E1E} \longrightarrow C_2H_5OH + CH_2O + C_2H_4 \quad \text{(R10)}$$
$$\text{P1P} \longrightarrow C_3H_7OCH_2O\dot{C}H_2 + \dot{C}H_2CH_3 \quad \text{(R11)}$$
$$\text{P1P} \longrightarrow C_3H_7OCH_2\dot{O} + \dot{C}H_2C_2H_5 \quad \text{(R12)}$$
$$\text{P1P} \longrightarrow C_3H_7O\dot{C}H_2 + \dot{O}C_3H_7 \quad \text{(R13)}$$
$$\text{P1P} \longrightarrow C_3H_7OCH_2OCH_2\dot{C}H_2 + \dot{C}H_3 \quad \text{(R14)}$$

$$P1P \longrightarrow C_3H_7OCH_2O\dot{C}HC_2H_5 + \dot{H} \quad (R15)$$
$$P1P \longrightarrow C_3H_7O\dot{C}HOC_3H_7 + \dot{H} \quad (R16)$$
$$P1P \longrightarrow C_3H_7OCH_2OCH_2\dot{C}HCH_3 + \dot{H} \quad (R17)$$
$$P1P \longrightarrow C_3H_7OCH_2OCH_2CH_2\dot{C}H_2 + \dot{H} \quad (R18)$$
$$P1P \longrightarrow C_3H_7OCH_2OH + C_3H_6 \quad (R19)$$
$$P1P \longrightarrow C_3H_7OC_3H_7 + CH_2O \quad (R20)$$
$$P1P \longrightarrow C_3H_7OH + CH_2O + C_3H_6 \quad (R21)$$

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 <800K), the decomposition of E-1-E is dominated an the alcohol cleavage reaction forming ethanol and a carbene (R9).

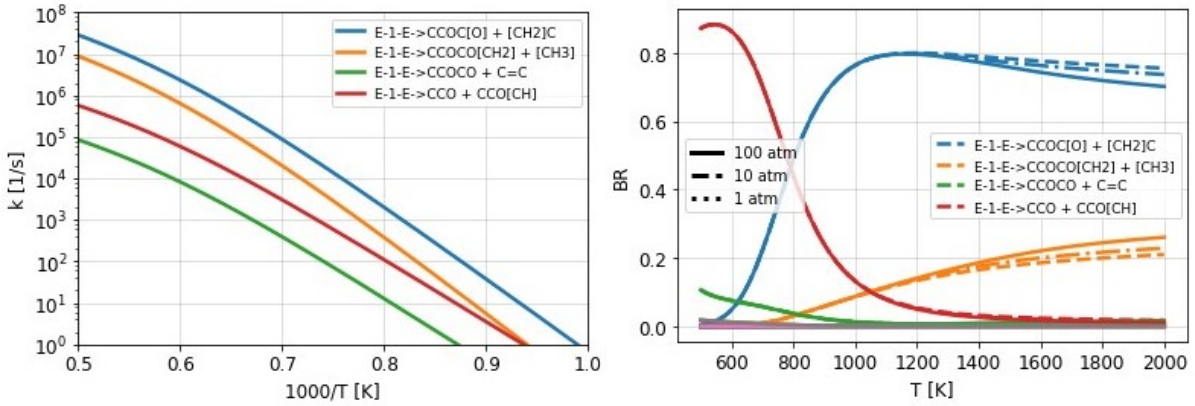

Fig. 5.4 Unimolecular rate constants at p = 10 atm (left) and branching ratios (right) for E-1-E. The four reaction channels shown here hold at least 1% of the total unimolecular reaction flux of E-1-E.

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.

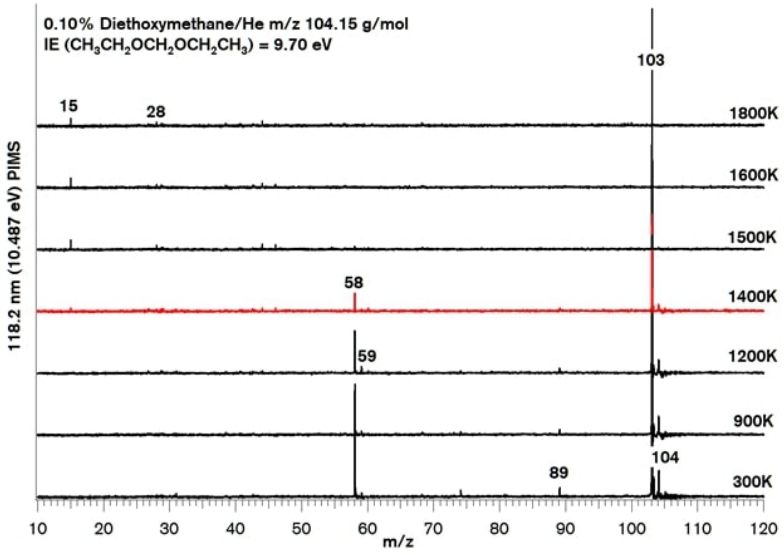

Fig. 5.5 PIMS of 0.1% diethoxymethane (E-1-E) in He in the micro reactor at 200 SCCM heated from 300 to 1700 L and ionized by 118.2 nm (10.487 eV) photons.

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 ∼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).

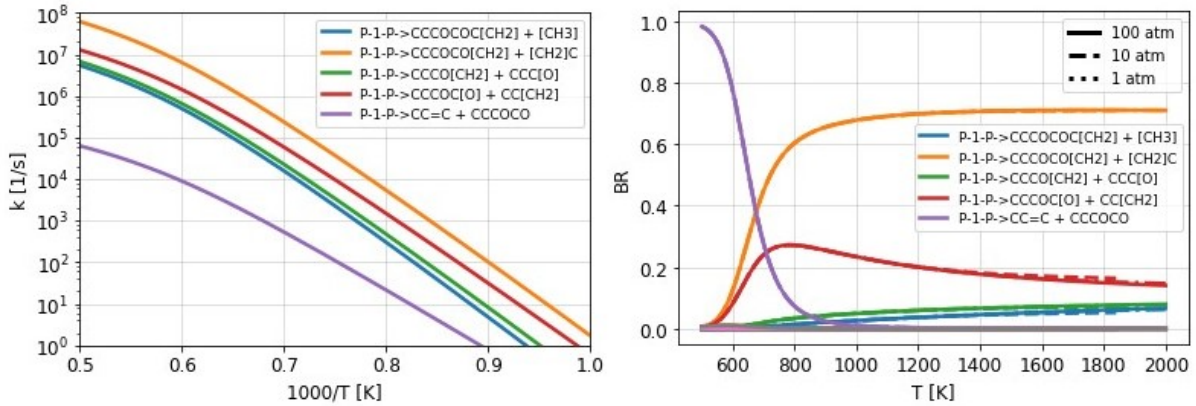

Fig. 5.6 Unimolecular rate constants at p = 10 atm (left) and branching ratios (right) for P-1-P.

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 $\dot{H}$, $\dot{C}H_3$ and $\dot{C}_2H_5$ 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.

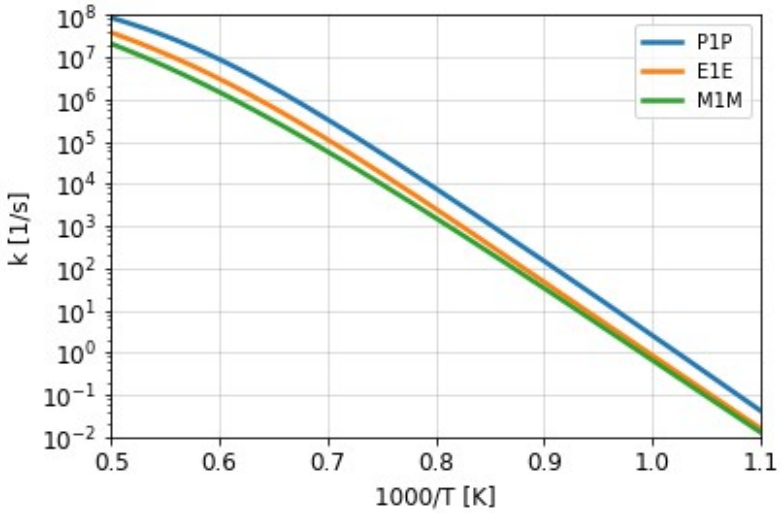

Fig. 5.7 Total rate constant for M-1-M, E-1-E, and P-1-P at p=10 atm.

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.

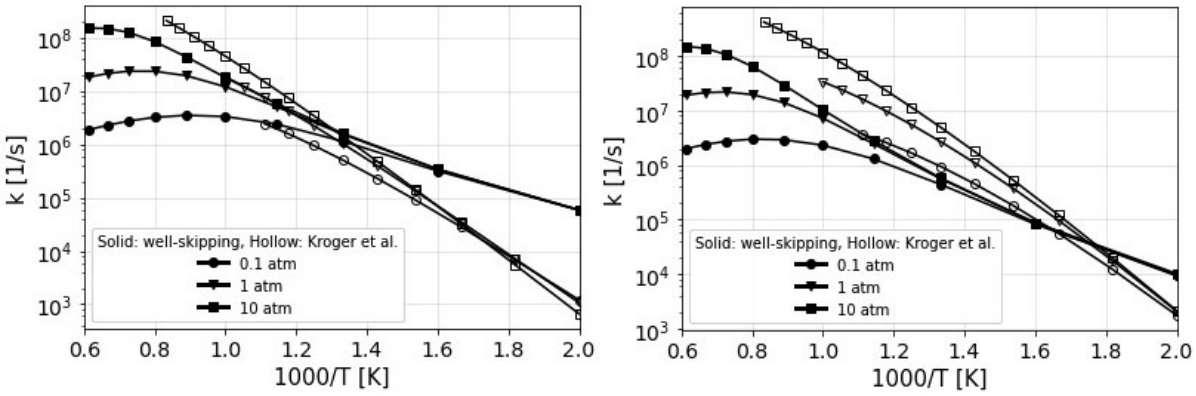

Fig. 5.8 Total well-skipping vs. β-scission rate constant for the decomposition of $CH_3CH_2OCH_2OCH_2\dot{C}H_2$ (left), and $CH_3CH_2OCH_2\dot{C}HCH_3$ (right) at multiple pressures.

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 $C_2H_5OCH_2\dot{O}$, $C_2H_5OCH_2O\dot{C}H_2$, $C_3H_7OCH_2O\dot{C}H_2$, $C_3H_7OCH_2\dot{O}$). 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 $\Delta E^{(0)}_{down} = 200cm^{-1}(T/298K)^{0.85}$. 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):

$CH_3CH_2OCH_2O\dot{C}HCH_3$	(DEMαR)
$CH_3CH_2OCH_2OCH_2\dot{C}H_2$	(DEMβR)
$CH_3CH_2O\dot{C}HOCH_2CH_3$	(DEMδR)
$C_2H_5OCH_2\dot{O}$	(DEMR1)
$C_2H_5OCH_2O\dot{C}H_2$	(DEMR2)
$CH_3CH_2CH_2OCH_2O\dot{C}HCH_2CH_3$	(DPMαR)
$CH_3CH_2CH_2OCH_2OCH_2\dot{C}HCH_3$	(DPMβR)
$CH_3CH_2CH_2OCH_2OCH_2CH_2\dot{C}H_2$	(DPMγR)
$CH_3CH_2CH_2O\dot{C}HOCH_2CH_2CH_3$	(DPMδR)
$C_3H_7OCH_2\dot{O}$	(DPMR1)
$C_3H_7OCH_2O\dot{C}H_2$	(DPMR2)

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: DEMαR, DEMβR, and DEMδR. Kroger et al. [141] showed that H-abstraction reactions by $\dot{H}$, $\dot{C}H_3$, and $\dot{C}H_2CH_3$ happen at similar rates forming DEMαR and DEMδR, 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 DEMαR, DEMβR, and DEMδR. 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 DEMαR to DEMβR, where a lower energy conformer was found in this work.

The increased contribution of this isomerization reactions (DEMαR to DEMβR) at low temperatures explains the discrepancies between the total rate of decomposition of DEMβR 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 $\dot{O}CH_2OC_2H_5$ (DEMR1) takes over. Additionally, this plot shows that chemically activated (well-skipping) reactions towards the products of DEMαR and DEMδR are relevant reaction pathways in the decomposition of DEMβR. 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

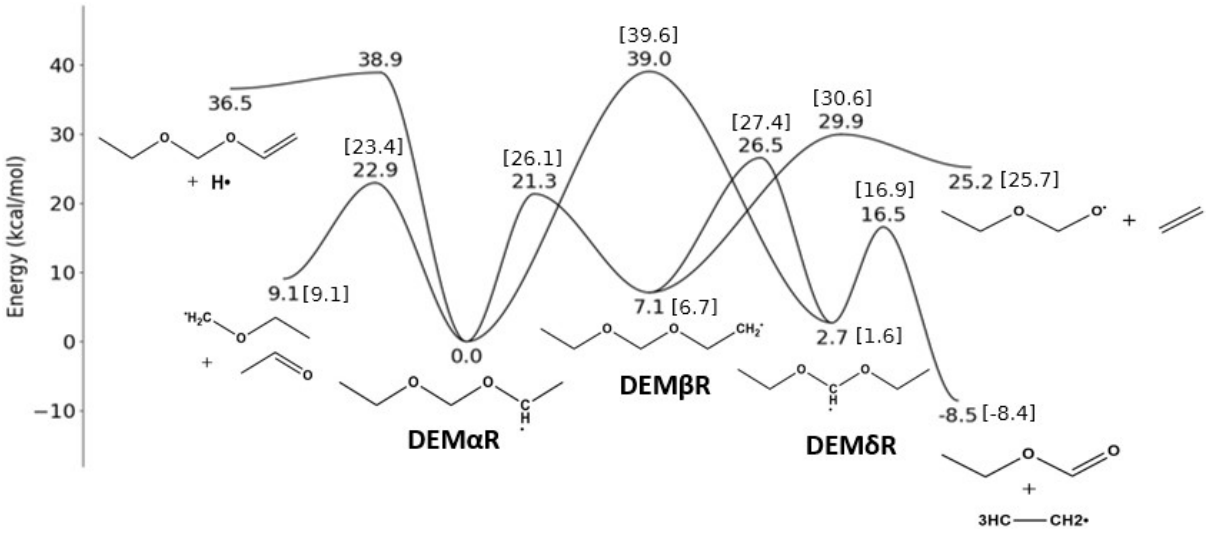

Fig. 6.1 PES of unimolecular decomposition of the E-1-E H-atom abstraction radicals calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory. The energy of W1.1 is used for reference. Ground-state energies calculated by Kroger et al. [141] are shown in brackets.

DEMαR 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 DEMαR is formed, its unimolecular decomposition does not vary significantly at different pressures and is dominated by the β-scission reaction forming acetaldehyde and $C_2H_5O\dot{C}H_2$. Acetaldehyde has been shown to decompose into methyl and formyl radicals at high temperatures [151], while $C_2H_5O\dot{C}H_2$ forms formaldehyde and ethyl radicals via a β-scission reaction. It is safe to assume that if DEMδR 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 DEMαR and DEMβR 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 (DPMαR, DPMβR, DPMγR, and DPMδR), and the PES for their isomerization-decomposition reactions is shown in Fig. 6.3.

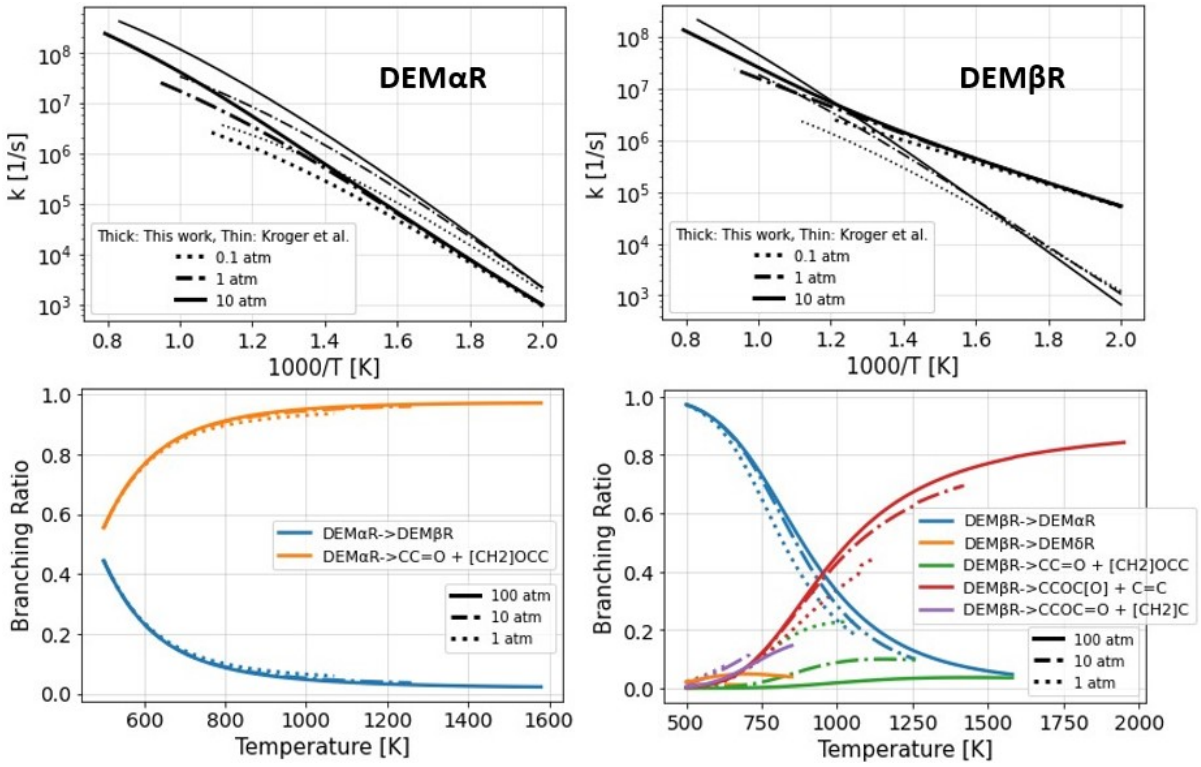

Fig. 6.2 Total isomerization-decomposition rate constant (top left, top right) and branching ratio (bottom left, bottom right) for the decomposition of DEMαR and DEMβR at multiple pressures.

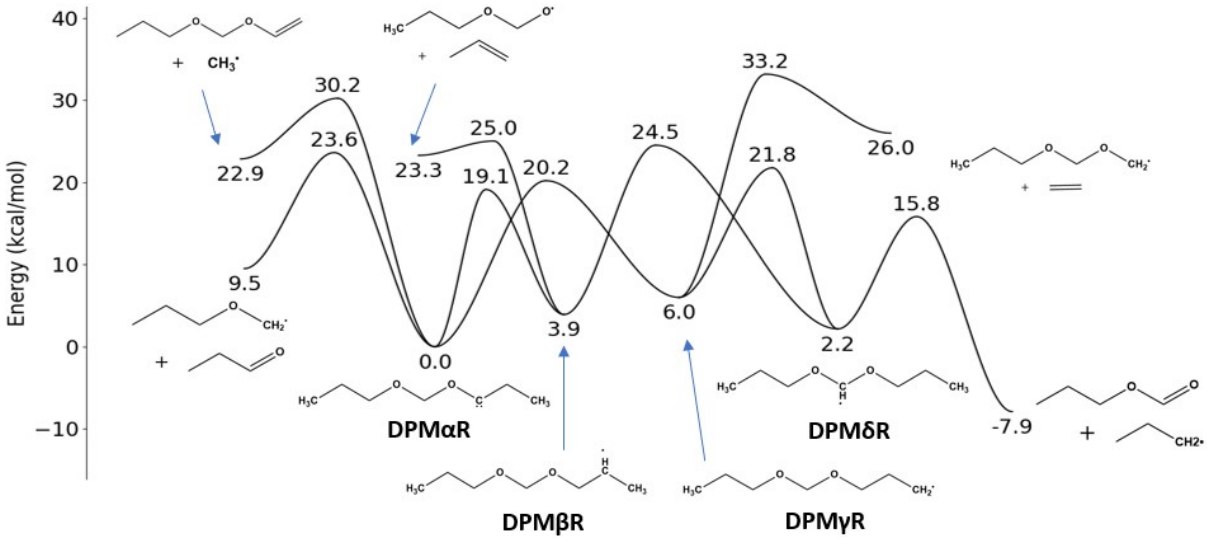

Fig. 6.3 PES of unimolecular decomposition of the P-1-P H-atom abstraction radicals calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory.

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 DPMδR (which is still heavily dominated by the low barrier of the β-scission reaction), it raises the rate of the isomerization reaction of DPMαR (which forms DPMβR) compared to that of DEMαR at low temperatures. Nevertheless, the high-temperature decomposition of DPMαR is dominated by its β-scission reaction forming propanaldehyde and $C_3H_7O\dot{C}H_2$, 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 (DPMβR and DPMγR). The branching ratios in the bottom show that DPMβR is more likely to isomerize (into DPMαR) than DPMγR, especially at low temperatures and high pressures.

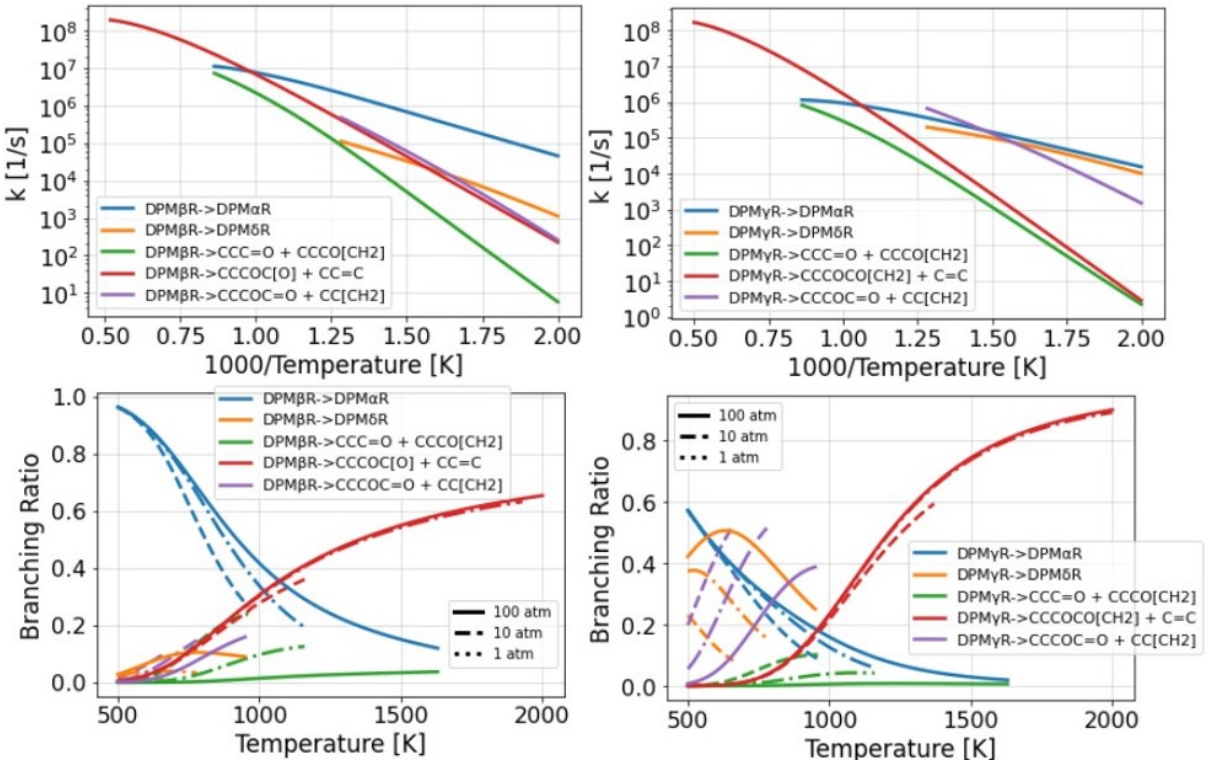

Fig. 6.4 Isomerization-decomposition rate constants (at atmospheric pressure) and corresponding branching ratio of DPMβR (left) and DPMγR (right) at multiple pressures.

At higher temperatures, DPMβR and DPMγR decompose into propylene and DPMR1, and ethylene and DPMR2, respectively. This reveals that DPMβR 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 (DEMR2) 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 DEMβR, chemically activated reactions through DPMαR and DPMδR show significant relevance at low temperatures for DPMβR and DPMγR, but further studies are required to predict these rates at higher temperatures.

6.3.2 The $CH_3CH_2OCH_2\dot{O}$ and $CH_3CH_2CH_2OCH_2\dot{O}$ radicals

The oxygen radicals (DEMR1 and DPMR1) 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.

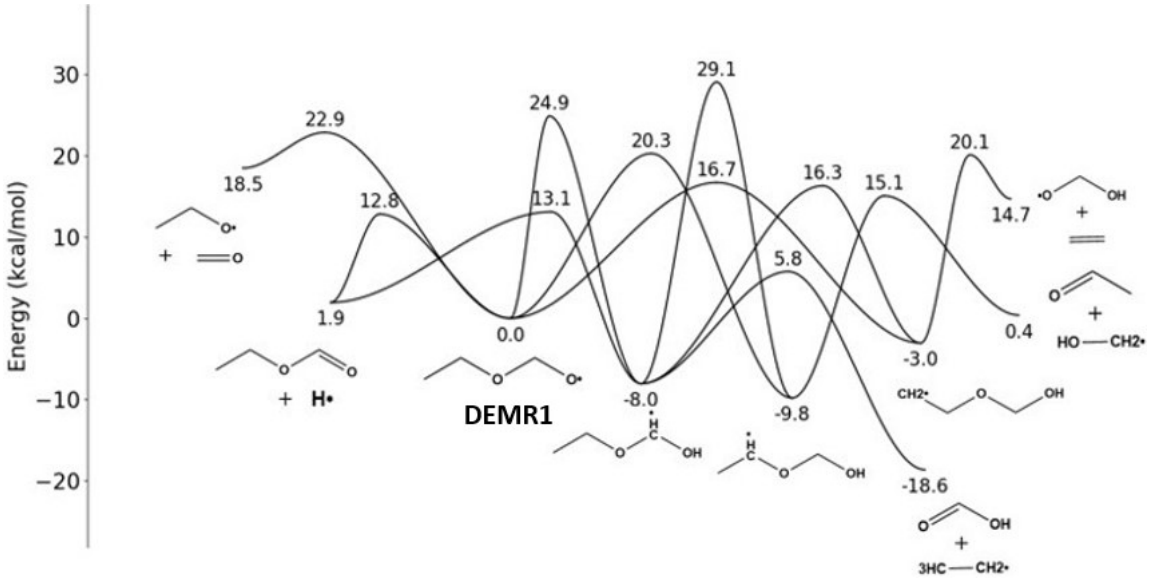

Fig. 6.5 PES of unimolecular decomposition of the oxygen radical and alcohol radical isomers for E-1-E calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory.

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.

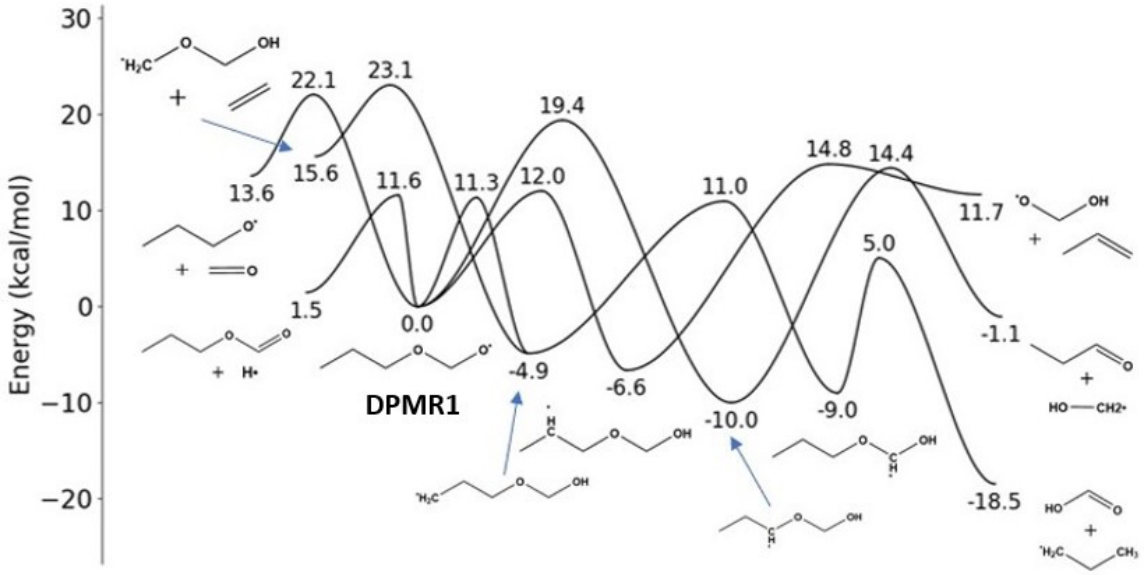

Fig. 6.6 PES of unimolecular decomposition of the oxygen radical and alcohol radical isomers for P-1-P calculated at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory.

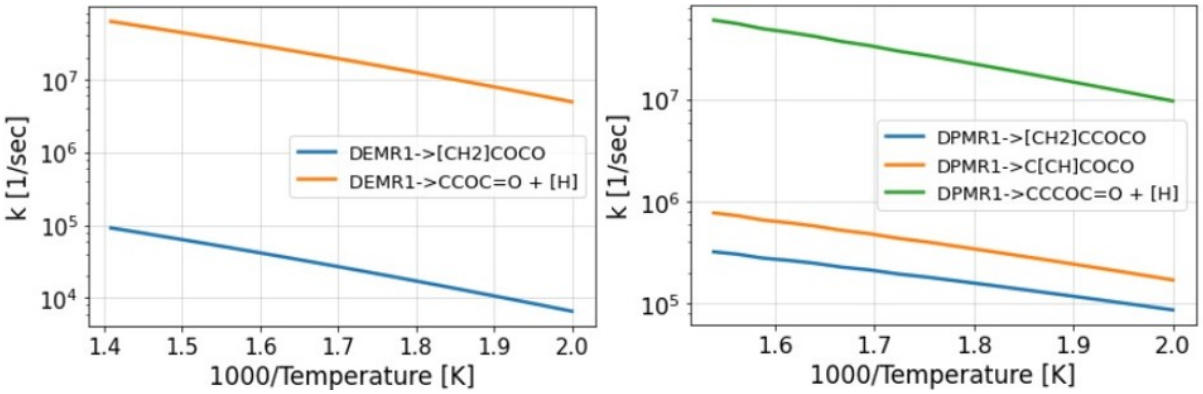

Fig. 6.7 Isomerization-decomposition rate constants (at atmospheric pressure) of DEMR1 (left) and DPMR1 (right).

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 ($CH_3\dot{O}$) and methoxy-methoxy ($CH_3OCH_2\dot{O}$) radicals [155, 156]. In addition, seeing that ethyl formate and propyl formate are also direct products of DEMδR and DPMδR, 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:

$$C_2H_5OCHO \longrightarrow HCOOH + C_2H_4 \tag{6.1}$$

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 $\dot{C}H_2OCH_2OC_2H_5$ and $\dot{C}H_2OCH_2OC_3H_7$ 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 $C_2H_5\dot{C}HOCH_2OCH_3$ is more accessible for DPMR2, it is dominant at low temperatures and stays relevant even at 1000 K.

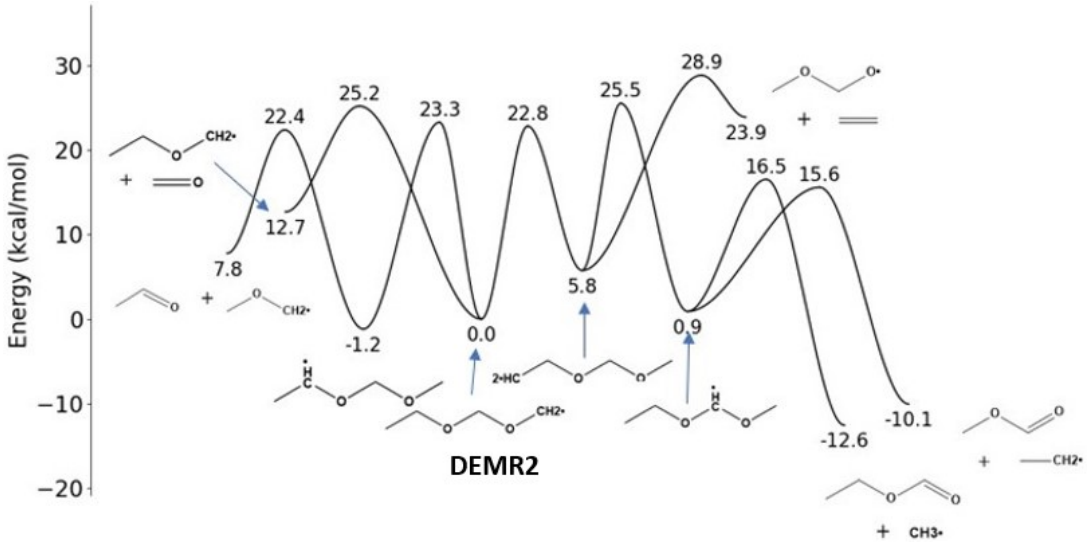

Fig. 6.8 PES of unimolecular decomposition of DEMR2 at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory.

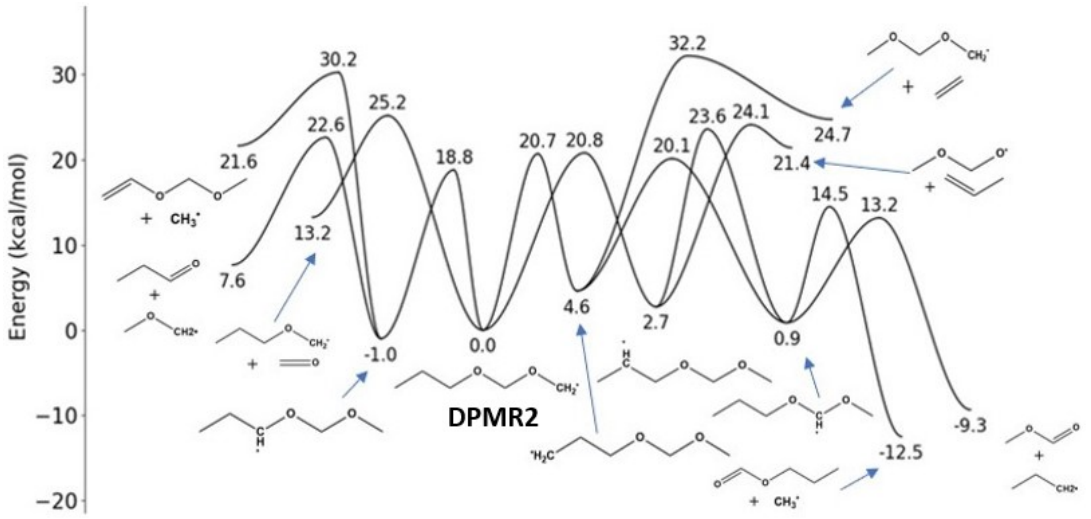

Fig. 6.9 PES of unimolecular decomposition of DPMR2 at the coupled-cluster CCSD(T)/cc-pV∞Z/M06-2X/cc-pVTZ level of theory.

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 temepratures, the decomposition of DPMR2 will be dominated by its β-scission reaction and is expected to favor formaldehyde production more heavily.

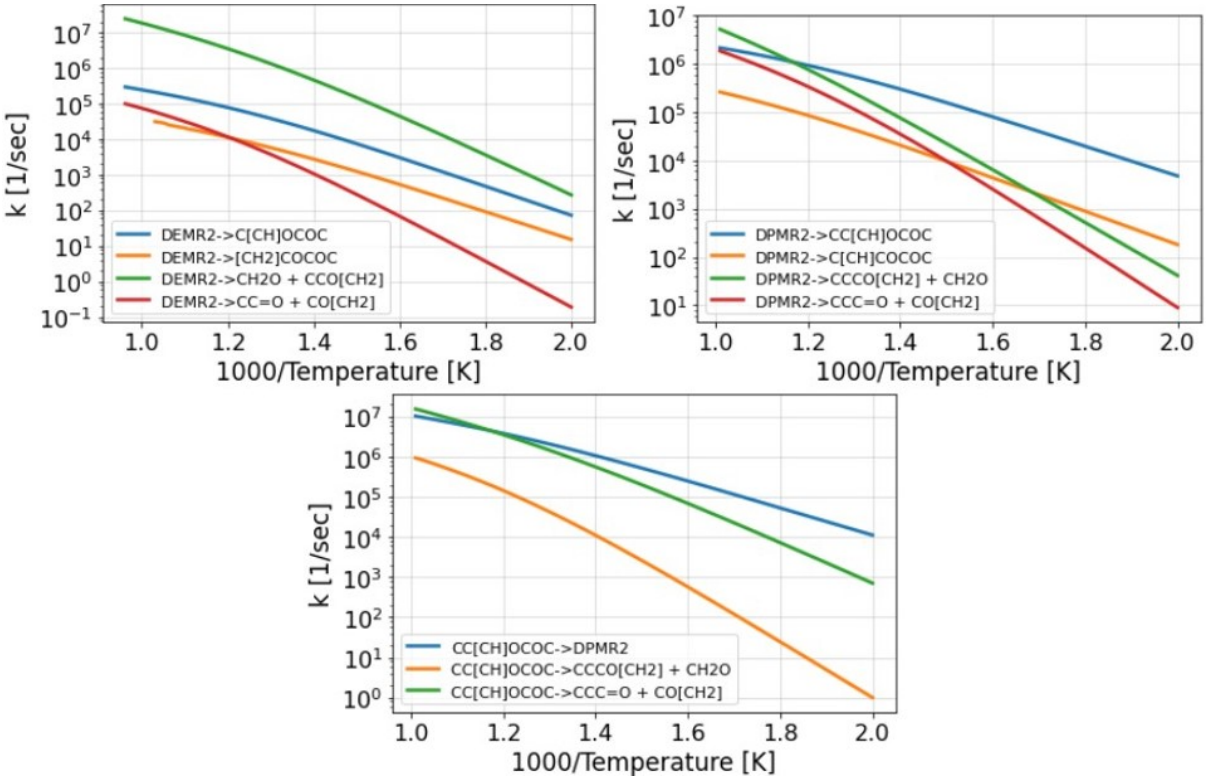

Fig. 6.10 Isomerization-decomposition rate constants (at atmospheric pressure) of DEMR2 (left), DPMR2 (right), and $C_2H_5\dot{C}HOCH_2OCH_3$ (bottom).

6.3.4 Chemically activated reactions

In Ch. 5, it was shown that $CH_3CH_2OCH_2O\dot{C}HCH_3$ (DEMαR) and $CH_3CH_2OCH_2OCH_2\dot{C}H_2$ (DEMβR) 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 DEMαR and DEMβR, 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.

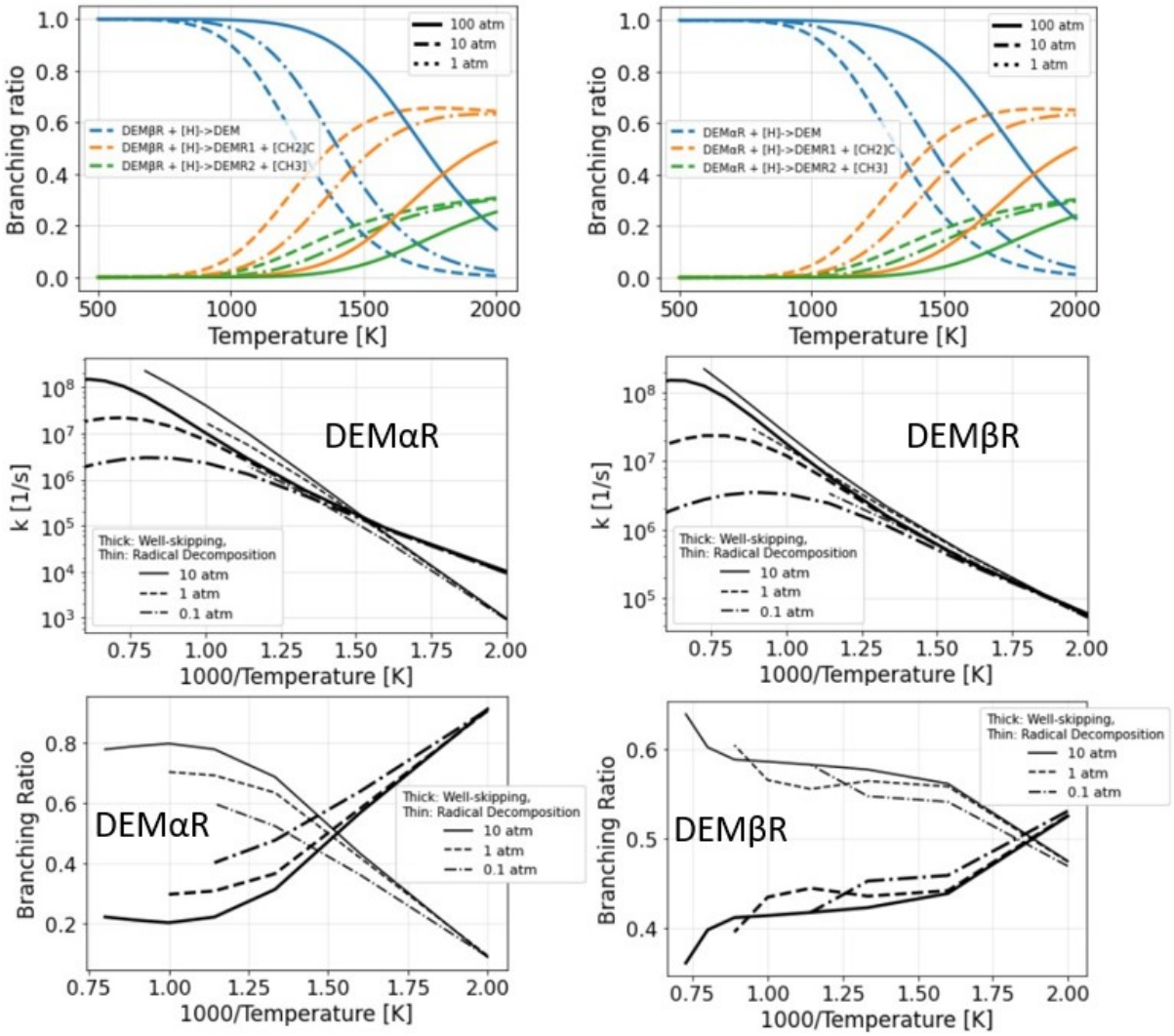

Fig. 6.11 Total well-skipping rates vs. radical decomposition rates for DEMαR (mid left) and DEMβR (mid right) at multiple pressures. The bottom row shows the branching ratio of the rates in the middle row, while the top row shows branching ratio comparing the recombination rate vs. well-skipping rate for the bimolecular reaction of DEMαR (left) and hydrogen atom, and DEMβR (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, $\dot{O}CH_2OC_2H_5$ (DEMR1), and $\dot{C}H_2OCH_2OC_2H_5$ (DEMR2) 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 DEMβR, 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 sharp29 turn-over at temperatures above 1000 K. For the case of DEMαR, 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 DEMβR and DEMδR) 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 $\dot{C}H_2OCH_2OC_3H_7$ (DPMR2) whose equivalent radical ($\dot{C}H_2OCH_2OC_2H_5$ (DEMR2) 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, $\dot{O}CH_2OC_3H_7$ (DEMR1) and $\dot{O}OCH_2OC_3H_7$ (DPMR1), 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 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 temepratures 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

```
#!/bin/bash
#SBATCH --partition=shas
#SBATCH --qos=long
#SBATCH --nodes=1
#SBATCH --ntasks-per-node=1
#SBATCH --time=00:10:00
#SBATCH --job-name=NZM
#SBATCH --account=ucb147_summit3

module purge
module load "gaussian/16_avx2"

newzmat -ichk -rebuildzmat -step 999 TS_C_CO_E82-99.chk TS_C_CO_E82-99.
    gjf

echo "Z-Matrix has been generated!"
```

A.2 run_all_gjfs.sh

```
#!/bin/bash
#SBATCH --partition=shas
#SBATCH --qos=normal
#SBATCH --nodes=1
#SBATCH --ntasks-per-node=11
#SBATCH --time=24:00:00
#SBATCH --job-name=83.35
#SBATCH --account=ucb146_summit3

module purge
```

```
module load "gaussian/16_avx2"

FILES=*.gjf
for f in $FILES
do
 name=$(echo "$f" | cut -f 1 -d '.')
 g16 <$name.gjf> $name.log
  echo "Processing $name file..."
done
echo "Finished all jobs."
```

A.3 get_input_gjf.py

```
import os, subprocess

# .log, .chk and newzmat.sh files must be in the same directory
def main(logfile,num_process=0,job='m062x'):
    # edits newzmat shell script and creates a gjf for each log file
    with open('newzmat.sh') as newzmatSC:
        scLines = newzmatSC.readlines()
        newzmatSC.close()
    gjfFile = logfile.replace('.log', '.gjf')
    for i, line in enumerate(scLines):
        if 'newzmat' in line:
            currentCHK = [item for item in line.split() if item.endswith('.chk')][0]
            currentGJF = [item for item in line.split() if item.endswith('.gjf')][0]
            scLines[i] = line.replace(currentCHK, logfile.replace('.log', '.chk')).replace(currentGJF, gjfFile)
    newzmatFile = open(f'newzmat.sh', 'w')
    newzmatFile.writelines(scLines)
    newzmatFile.close()

    subprocess.run(['sh', 'newzmat.sh'])

    # extracts route section informatino from log file
    lfile = open(logfile, 'r')
    lfileString = lfile.read()
    lfile.close()
    jobTitle = lfileString.split("#")[1].split('
    ----------------------------------------------------------------------
    ')[0]
    optTitle = jobTitle.split('opt')[-1]
    if 'ts' in optTitle.lower():
        ts = True
    else:
        ts = False
```

```
    procsLine = lfileString.split("%")[1].split('
    ----------------------------------------------------------------------
    ')[0]
    numProc = int(procsLine.split()[0].split('=')[-1])
    # adds route section to gjf file
    outputgjfFile = open(gjfFile, 'r')
    gjfLines = outputgjfFile.readlines()
    outputgjfFile.close()

    if job.lower() == 'M062X'.lower():
        if ts:
            gjfLines[0] = '\n#opt=(calcall,tight,ts) freq m062x/cc-pvtz
    maxdisk=500GB\n'
        else:
            gjfLines[0] = '\n#opt=(calcall,tight) freq m062x/cc-pvtz
    maxdisk=500GB\n'
    elif job.lower() == 'E'.lower():
        gjfLines[0] = '\n# ccsd(t,t1diag)/cc-pvdz maxdisk=500GB int=
    ultraFine\n'
    elif job.lower() == 'E1'.lower():
        gjfLines[0] = '\n# ccsd(t)/cc-pvtz maxdisk=500GB int=ultraFine\
    n'

    gjfLines.insert(0, f'\n%chk={gjfFile[:-4]}.chk')
    gjfLines.insert(0, '\n%mem=700MW')
    gjfLines.insert(0, f'%nprocshared={numProc + num_process}')
    outputgjfFile = open(gjfFile, 'w')
    outputgjfFile.writelines(gjfLines)
    outputgjfFile.close()
    #

    return gjfFile

if __name__ == '__main__':
    main(logfile='',num_process=0,job='m062x')
```

A.4 parsingPesviewer.py

```
#!/usr/bin/env python
# coding: utf-8

# In[1]:


# beginning of program

# -- Dependencies -- #
import os, shutil
```

```
import numpy as np
import subprocess
import collections
from geometryInfo import get_xyzGeom, get_frequencies
from xyz2mol import read_xyz_file, xyz2mol
import get_rotors, search_rotors, get_input_gjf

# gets list of kinbot logfiles of interest
def get_valid_logFiles():
    """
    This function is responsible for returning the log files for all species below the specified cutoff.

    :args None:
    returns: dictionary of log files.
    """

    try:
        # reads from pesviewer.inp
        pesviewer = open('pesviewer.inp', 'r')
        pesviewerLines = pesviewer.read()
        pesviewer.close()
    except FileNotFoundError:
        root = os.getcwd()
        print(f"Make sure pesviewer is in {root}")
    # parses pesviewer.inp and creates molecules + ground energies dictionaries
    keys = ["wells", "bimolec", "ts", "barrierless"]
    reactsProds = dict() # keys: keys, values: molecules
    groundEnergies = dict() # keys: molecules, values: ground energies
    for i, key in zip(range(3, 3+len(keys)), keys):
        entries = pesviewerLines.split('\n>')[i].split('\n')
        entries = [entry for entry in entries if len(entry)>1 and not entry.startswith(' ')]
        if key == 'barrierless':
            reactsProds[key] = [j.split(' ')[-1] for j in entries]
        # takes lower energy TS from different TS going to same products
        elif key == 'ts':
            allTSProds = dict()
            allTSReacts = dict()
            for j in entries:
                reacts, prods, energyBarrier = j.split(" ")[0], j.split(" ")[-1], j.split(" ")[1]
                if prods not in allTSProds:
                    allTSProds[prods] = float(energyBarrier)
                    allTSReacts[prods] = reacts
                    groundEnergies[reacts] = energyBarrier
```

```
                else:
                    if float(energyBarrier) < allTSProds[prods]:
                        allTSProds[prods] = float(energyBarrier)
                        del groundEnergies[allTSReacts[prods]]
                        groundEnergies[reacts] = energyBarrier
                        allTSReacts[prods] = reacts

            reactsProds[key] = allTSReacts.values()
        else:
            for k in entries:
                groundEnergies[k.split(' ')[0]] = k.split(' ')[1]
            reactsProds[key] = [j.split(' ')[0] for j in entries]

    # script assumes parent well is at the reference '0.0' energy
    parentWell = [energy for energy in groundEnergies if groundEnergies
[energy]=='0.0'][0]

    lowestTSEnergy = min([float(groundEnergies[value]) for value in
reactsProds["ts"]])
    print("Enter TS Energy cut-off: ")
    cutOff = float(input())
    minEnergy = lowestTSEnergy + cutOff

    allTSReacts = {v: k for k, v in allTSReacts.items()}

    # filters out products of TS with barriers larger than minimum
energy
    for mol in list(groundEnergies.keys()):
        if float(groundEnergies[mol]) > minEnergy:
            del groundEnergies[mol]
            if mol in allTSReacts:
                if allTSReacts[mol] in groundEnergies:
                    del groundEnergies[allTSReacts[mol]]

    validEnergies = list(groundEnergies.values())
    validMolecules = list()
    # -- potential bug, assumes only Bimolecular products have 1 '_' in
    their kinbot-generated name -- #
    for i in range(len(validEnergies)):
        molecule = list(groundEnergies.keys())[list(groundEnergies.
values()).index(validEnergies[i])]
        if len(molecule.split("_"))==2:
            validMolecules.append(molecule.split("_")[0])
            validMolecules.append(molecule.split("_")[1])
        else:
            validMolecules.append(molecule)
    # removes duplicates
    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
    != parentWell and "IRC" not in file:
106                 for key in groundEnergies:
107                     if molecule in key:
108                         validFiles[file] = groundEnergies[key]
109
110     validFilesTS = dict()
111     for file in validFiles:
112         fl = open(file, 'r')
113         flLines = fl.readlines()
114         fl.close()
115         isTS = False
116         for line in flLines:
117             if line.startswith(' #') and 'TS,' in line:
118                 isTS = True
119                 break
120         if isTS:
121             validFilesTS[file] = [True, validFiles[file]]
122         else:
123             validFilesTS[file] = [False, validFiles[file]]
124     os.chdir("./..")
125
126     return validFilesTS
127
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/
    newzmat.sh")
142         # 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
    foler
240     base_dir = os.getcwd()
241     jobAllocation = '1'
242     for file in os.listdir():
243         fileName = file
244         if "E" in file:
245             fileName = file.split("_E")[0]
246         if f'{fileName}.gjf' in moleculeDirectories:
247             # updates batch scripts - must be in parent directory!
248             bFile = open('run_all_gjfs.sh', 'r')
249             bArrayFile = open('run_all_gjfs_array.sh', 'r')
250             bLines = bFile.readlines()
251             bArrayLines = bArrayFile.readlines()
252             bFile.close()
253             bArrayFile.close()
254             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             bLines[4] = bLines[4].split('=')[0]+'='+jobNodes+'\n'
265             bArrayLines[4] = bArrayLines[4].split('=')[0]+'='+str(int(
    jobNodes)-3)+'\n' # used 3 nodes less for rotor jobs
266             bLines[5] = bLines[5].split('=')[0]+'='+jobTime+':00:00\n'
267             bArrayLines[5] = bArrayLines[5].split('=')[0]+'='+jobTime+'
    :00:00\n'
268             bLines[6] = bLines[6].split('=')[0]+'='+jobName+'\n'
269             bArrayLines[6] = bArrayLines[6].split('=')[0]+'='+jobName+'
    _rotors'+'\n'
270             bLines[7] = bLines[7].split('=')[0]+'='+allocations[
    jobAllocation]+'\n'
271             bArrayLines[7] = bArrayLines[7].split('=')[0]+'='+
    allocations[jobAllocation]+'\n'
272             # recycles through allocations
273             if jobAllocation=='4':
274                 jobAllocation = '1'
275             else:
276                 jobAllocation = str(int(jobAllocation)+1)
277             updatedBFile = open('run_all_gjfs.sh', 'w')
278             updatedBArrayFile = open('run_all_gjfs_array.sh', 'w')
279             updatedBFile.writelines(bLines)
280             updatedBArrayFile.writelines(bArrayLines)
281             updatedBFile.close()
282             updatedBArrayFile.close()
283
284             source = base_dir+'/run_all_gjfs.sh'
285             source_array = base_dir+'/run_all_gjfs_array.sh'
286             # print(os.listdir())
287             destination = f"{base_dir}/{file}/it1/run_all_gjfs.sh"
288             destination_array =  f"{base_dir}/{file}/it1/
    run_all_gjfs_array.sh"
289             shutil.copy(source, destination)
290             shutil.copy(source_array, destination_array)
291             print('\n ------------------------')
292
293
294 # Function Calling
295
```

```
validFilesTS = get_valid_logFiles()
xyzFileTS, procs, xyzGeoms = create_input_files(validFilesTS)
setupJobs(xyzFileTS, procs)
# runs search rotors within each molecule folder
base_dir = os.getcwd()
for fileName in os.listdir():
    if '_E' in fileName:
        os.chdir(f'{base_dir}/{fileName}/it1')
        search_rotors.main(xyzGeoms)
        os.chdir(base_dir)

# end of program
```

A.5 xyz2mol.py

```
"""
Module for generating rdkit molobj/smiles/molecular graph from free
    atoms

Implementation by Jan H. Jensen, based on the paper

    Yeonjoon Kim and Woo Youn Kim
    "Universal Structure Conversion Method for Organic Molecules: From
    Atomic Connectivity
    to Three-Dimensional Geometry"
    Bull. Korean Chem. Soc. 2015, Vol. 36, 1769-1777
    DOI: 10.1002/bkcs.10334

"""

import copy
import itertools

from rdkit.Chem import rdmolops
from rdkit.Chem import rdchem
try:
    from rdkit.Chem import rdEHTTools #requires RDKit 2019.9.1 or later
except ImportError:
    rdEHTTools = None

from collections import defaultdict

import numpy as np
import networkx as nx

from rdkit import Chem
from rdkit.Chem import AllChem, rdmolops
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',
    'dy',
43      'ho', 'er', 'tm', 'yb', 'lu', 'hf', 'ta', 'w',  're', 'os', 'ir',
    'pt',
44      'au', 'hg', 'tl', 'pb', 'bi', 'po', 'at', 'rn',
45      'fr', 'ra', 'ac', 'th', 'pa', 'u',  'np', 'pu']
46
47
48 global atomic_valence
49 global atomic_valence_electrons
50
51 atomic_valence = defaultdict(list)
52 atomic_valence[1] = [1]
53 atomic_valence[5] = [3,4]
54 atomic_valence[6] = [4]
55 atomic_valence[7] = [3,4]
56 atomic_valence[8] = [2,1,3]
57 atomic_valence[9] = [1]
58 atomic_valence[14] = [4]
59 atomic_valence[15] = [5,3] #[5,4,3]
60 atomic_valence[16] = [6,3,2] #[6,4,2]
61 atomic_valence[17] = [1]
62 atomic_valence[32] = [4]
63 atomic_valence[35] = [1]
64 atomic_valence[53] = [1]
65
66 atomic_valence_electrons = {}
67 atomic_valence_electrons[1] = 1
68 atomic_valence_electrons[5] = 3
69 atomic_valence_electrons[6] = 4
70 atomic_valence_electrons[7] = 5
71 atomic_valence_electrons[8] = 6
72 atomic_valence_electrons[9] = 7
73 atomic_valence_electrons[14] = 4
74 atomic_valence_electrons[15] = 5
75 atomic_valence_electrons[16] = 6
76 atomic_valence_electrons[17] = 7
77 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,
    valence_list)):
107         if not maxValence - valence > 0:
108             continue
109         UA.append(i)
110         DU.append(maxValence - valence)
111     return UA, DU
112
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         if number_of_bonds > valence:
139             return False
140 
141     return True
142 
143 def charge_is_OK(BO, AC, charge, DU, atomic_valence_electrons, atoms,
    valences,
144                  allow_charged_fragments=True):
145     # total charge
146     Q = 0
147 
148     # charge fragment list
149     q_list = []
150 
151     if allow_charged_fragments:
152 
153         BO_valences = list(BO.sum(axis=1))
154         for i, atom in enumerate(atoms):
155             q = get_atomic_charge(atom, atomic_valence_electrons[atom],
     BO_valences[i])
156             Q += q
157             if atom == 6:
158                 number_of_single_bonds_to_C = list(BO[i, :]).count(1)
159                 if number_of_single_bonds_to_C == 2 and BO_valences[i]
    == 2:
160                     Q += 1
161                     q = 2
162                 if number_of_single_bonds_to_C == 3 and Q + 1 < charge:
163                     Q += 2
164                     q = 1
165 
166             if q != 0:
167                 q_list.append(q)
168 
```

```
169     return (charge == Q)
170 
171 def BO_is_OK(BO, AC, charge, DU, atomic_valence_electrons, atoms,
    valences,
172     allow_charged_fragments=True):
173     """
174     Sanity of bond-orders
175 
176     args:
177         BO -
178         AC -
179         charge -
180         DU -
181 
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,
    atomic_valence_electrons, atoms, valences,
196                                 allow_charged_fragments)
197 
198     if check_charge and check_sum:
199         return True
200 
201     return False
202 
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     #              '[O:1]=[c:2][c-:3]>>[*-:1][*:2][*+0:3]',
234     #              '[O: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.GetMolFrags(mol,asMols=True,sanitizeFrags=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 BO2mol(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,
    generate an
265     rdkit molecule.
266
267     args:
268         mol - rdkit molecule
269         BO_matrix - bond order matrix of molecule
270         atoms - list of integer atomic symbols
271         atomic_valence_electrons -
272         mol_charge - total charge of molecule
273
274     optional:
275         allow_charged_fragments - bool - allow charged fragments
276
277     returns
278         mol - updated rdkit molecule with bond connectivity
279
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}
    differ'.format(l, l2))
288
289     rwMol = Chem.RWMol(mol)
290
291     bondTypeDict = {
292         1: Chem.BondType.SINGLE,
293         2: Chem.BondType.DOUBLE,
294         3: Chem.BondType.TRIPLE
295     }
296
297     for i in range(l):
298         for j in range(i + 1, l):
299             bo = int(round(BO_matrix[i, j]))
300             if (bo == 0):
301                 continue
```

```
            bt = bondTypeDict.get(bo, Chem.BondType.SINGLE)
            rwMol.AddBond(i, j, bt)

    mol = rwMol.GetMol()

    if allow_charged_fragments:
        mol = set_atomic_charges(
            mol,
            atoms,
            atomic_valence_electrons,
            BO_valences,
            BO_matrix,
            mol_charge)
    else:
        mol = set_atomic_radicals(mol, atoms, atomic_valence_electrons,
    BO_valences)

    return mol


def set_atomic_charges(mol, atoms, atomic_valence_electrons,
                       BO_valences, BO_matrix, mol_charge):
    """
    """
    q = 0
    for i, atom in enumerate(atoms):
        a = mol.GetAtomWithIdx(i)
        charge = get_atomic_charge(atom, atomic_valence_electrons[atom
   ], BO_valences[i])
        q += charge
        if atom == 6:
            number_of_single_bonds_to_C = list(BO_matrix[i, :]).count
   (1)
            if number_of_single_bonds_to_C == 2 and BO_valences[i] ==
   2:
                q += 1
                charge = 0
            if number_of_single_bonds_to_C == 3 and q + 1 < mol_charge:
                q += 2
                charge = 1

        if (abs(charge) > 0):
            a.SetFormalCharge(int(charge))

    #mol = clean_charges(mol)

    return mol

```

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

```
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 neighbourgs
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,
    use_graph=use_graph)
462             status = BO_is_OK(BO, AC, charge, DU_from_AC,
463                         atomic_valence_electrons, atoms, valences,
464                         allow_charged_fragments=allow_charged_fragments
    )
465             charge_OK = charge_is_OK(BO, AC, charge, DU_from_AC,
    atomic_valence_electrons, atoms, valences,
466                                      allow_charged_fragments=
    allow_charged_fragments)
467
468             if status:
469                 return BO, atomic_valence_electrons
470             elif BO.sum() >= best_BO.sum() and valences_not_too_large(
    BO, valences) and charge_OK:
471                 best_BO = BO.copy()
472
473     return best_BO, atomic_valence_electrons
474
475
476 def AC2mol(mol, AC, atoms, charge, allow_charged_fragments=True,
    use_graph=True):
477     """
478     """
479
```

```
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 = BO2mol(
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     # BO2mol returns an arbitrary resonance form. Let's make the rest
502     mols = rdchem.ResonanceMolSupplier(mol, Chem.UNCONSTRAINED_CATIONS,
    Chem.UNCONSTRAINED_ANIONS)
503     mols = [mol for mol in mols]
504 
505     return mols
506 
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 = []
```

```
    xyz_coordinates = []
    charge = 0
    title = ""

    with open(filename, "r") as file:
        for line_number, line in enumerate(file):
            if line_number == 0:
                num_atoms = int(line)
            elif line_number == 1:
                title = line
                if "charge=" in line:
                    charge = int(line.split("=")[1])
            else:
                atomic_symbol, x, y, z = line.split()
                atomic_symbols.append(atomic_symbol)
                xyz_coordinates.append([float(x), float(y), float(z)])

    atoms = [int_atom(atom) for atom in atomic_symbols]

    return atoms, charge, xyz_coordinates


def xyz2AC(atoms, xyz, charge, use_huckel=False):
    """

    atoms and coordinates to atom connectivity (AC)

    args:
        atoms - int atom types
        xyz - coordinates
        charge - molecule charge

    optional:
        use_huckel - Use Huckel method for atom connecitivty

    returns
        ac - atom connectivity matrix
        mol - rdkit molecule

    """

    if use_huckel:
        return xyz2AC_huckel(atoms, xyz, charge)
    else:
        return xyz2AC_vdW(atoms, xyz)


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
    and 0 is not
596
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
    facto
605
606     returns:
607         AC - adjacent matrix
608
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: #arbitry 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
    coordinates
674
675     args:
676         mol - rdkit molecule, with embeded conformer
677
678     """
679     Chem.SanitizeMol(mol)
680     Chem.DetectBondStereochemistry(mol, -1)
681     Chem.AssignStereochemistry(mol, flagPossibleStereoCenters=True,
    force=True)
682     Chem.AssignAtomChiralTagsFromStructure(mol, -1)
683
684     return
685
686
687 def xyz2mol(atoms, coordinates,
688     charge=0,
689     allow_charged_fragments=True,
690     use_graph=True,
691     use_huckel=False,
692     embed_chiral=True):
693     """
694     Generate a rdkit molobj from atoms, coordinates and a total_charge.
695
696     args:
697         atoms - list of atom types (int)
698         coordinates - 3xN Cartesian coordinates
699         charge - total charge of the system (default: 0)
700
701     optional:
702         allow_charged_fragments - alternatively radicals are made
703         use_graph - use graph (networkx)
704         use_huckel - Use Huckel method for atom connectivity prediction
705         embed_chiral - embed chiral information to the molecule
706
707     returns:
708         mols - list of rdkit molobjects
709
710     """
```

```
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

```
# program begins

import sys, math, os, shutil
from collections import Counter
from io import open
import numpy as np

## -- CONSTANTS -- ##

# threshold beyond average of covalent radiii to determine bond cutoff
bond_thresh = 1.2

# conversion from radians to degrees and vice versa
rad2deg = 180.0 / math.pi
deg2rad = 1.0 / rad2deg

# covalent (or ionic) radii by atomic element (Angstroms) from
# "Inorganic Chemistry" 3rd ed, Housecroft, Appendix 6, pgs 1013-1014
cov_rads_original = {  'H' : 0.37, 'C' : 0.77, 'O' : 0.73, 'N' : 0.75,
    'F' : 0.71,
  'P' : 1.10, 'S' : 1.03, 'Cl': 0.99, 'Br': 1.14, 'I' : 1.33, 'He':
    0.30,
  'Ne': 0.84, 'Ar': 1.00, 'Li': 1.02, 'Be': 0.27, 'B' : 0.88, 'Na':
    1.02,
  'Mg': 0.72, 'Al': 1.30, 'Si': 1.18, 'K' : 1.38, 'Ca': 1.00, 'Sc':
    0.75,
  'Ti': 0.86, 'V' : 0.79, 'Cr': 0.73, 'Mn': 0.67, 'Fe': 0.61, 'Co':
    0.64,
```

```
  'Ni': 0.55, 'Cu': 0.46, 'Zn': 0.60, 'Ga': 1.22, 'Ge': 1.22, 'As':
   1.22,
  'Se': 1.17, 'Kr': 1.03, 'X' : 0.00}

cov_rads = {  'H' : 0.31, 'C' : 0.76, 'O' : 0.66, 'N' : 0.71 }

## -- END OF CONSTANTS -- ##

## -- IO FUNCTIONS -- ##
# convert newzmat format into gaussview reformats
def get_gView_format(file_name):
    #Opens file for reading
    try:
        file = open(file_name, "r")
    except IOError:
        print('Error: file (%s) not found!\n' % (file_name))
        sys.exit()
    file_content = file.read()
    file.close()
    #Opens file for writing
    try:
        file_1 = open(file_name, "w")
    except IOError:
        print('Error: file (%s) not found!\n' % (file_name))
        sys.exit()
    # reformats zmatrix into correct array for
    fstring = '\n'.join('\n\n'.join(file_content.split('\n\n')[:-1]).
   split('\n')) # gets rid of extra numbers at the bottom
    ftring_header = '\n'.join(fstring.split('\n')[:7])
    fstring = '\n'.join([string.replace(',', 4*' ').replace('=', 4*' ')
   .replace('      Variables:', '')
                         for string in fstring.split('\n')[7:]])
    fstring = ftring_header + '\n' + fstring
    flines = fstring.split('\n')
    flines = [item+'\n' for item in flines]
    file_1.writelines(flines)
    file_1.close()


# read file data into a 2-d array
def get_file_string_array(file_name):
    #Opens file for array
    try:
        file = open(file_name, "r")
    except IOError:
        print('Error: file (%s) not found!\n' % (file_name))
        sys.exit()
    flines = file.readlines()
```

```
    #Opens file for string
    try:
        file_1 = open(file_name, "r")
    except IOError:
        print('Error: file (%s) not found!\n' % (file_name))
        sys.exit()
    file_content = file_1.read()
    file.close()
    file_1.close()

    array = []
    for line in flines:
        array.append(line.split())

    return array, file_content

# read in geometry from xyz file
def get_geom(xyz_array):
    # xyz_array = get_file_string_array(xyz_file_name)
    n_atoms = int(xyz_array[0][0])
    at_types = ['' for i in range(n_atoms)]
    coords = [[0.0 for j in range(3)] for i in range(n_atoms)]
    for i in range(n_atoms):
        at_types[i] = xyz_array[i+2][0]
        for j in range(3):
            coords[i][j] = float(xyz_array[i+2][j+1])
    geom = [at_types, coords]
    return geom

# input syntax and usage warnings
def get_inputs():
    if (not len(sys.argv) == 2):
        print('Usage: torsions.py XYZ_FILE\n')
        print('  XYZ_FILE: coordinates of target molecule\n')
        sys.exit()
    else:
        xyz_file_name = sys.argv[1]
        return xyz_file_name

# print list of torsion angles to screen
def print_torsions(geom, torsions):
    at_types = geom[0]
    n_torsions = len(torsions)
    print('%i torsion(s) found (degrees)' % (n_torsions))
    for q in range(n_torsions):
        n1, n2, n3, n4 = torsions[q][0:4]
        t1234 = torsions[q][4]
        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
    [n3], at_types[n4])
118         print(' %-15s  %-13s  %8.3f\n' % (nstr, tstr, t1234), end='')
119     print('\n', end='')
120 
121 ## -- END OF IO FUNCTIONS -- ##
122 
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 threshhold to catch double bonds
193             if bond_thresh == 1.2:
194                 double_bond_thresh = 1.2 * (covrad1*0.73 + covrad2
    *0.73)
195             if bond_thresh == 1.4:
196                 double_bond_thresh = 1.2 * (covrad1*0.74 + covrad2
    *0.74)
197             r12 = get_r12(coords[i], coords[j])
198             if (r12 < thresh):
199                 bond_graph[i].append(j)
200                 bond_graph[j].append(i)
201             if (r12 < double_bond_thresh):
202                 double_bonds.append([i, j])
203     return bond_graph, double_bonds
204 
205 # determine atoms which are covalently bonded from bond graph
206 def get_bonds(geom, bond_graph):
207     at_types, coords = geom[0:2]
208     n_atoms = len(at_types)
209     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 
```

```
# find axis where the second atom is not bonded to anything else!
    Extract that axis and redo!
# only caveat is that heavy atoms must bethe first ones in zmatrix!
def include_cyclics_branched(axes):
    rotor_axes = []
    check = True
    counter = 0
    while (check == True):
        for axis in axes:
            second_atom = axis[-1]
            first_atom = axis[0]
            counter_second = 0
            counter_first = 0
            for ax in axes:
                if second_atom in ax:
                    counter_second += 1
                if first_atom in ax:
                    counter_first += 1
            if counter_second == 1 or counter_first == 1:
                rotor_axes.append(axis)

        new_axes = [axis for axis in axes if axis not in rotor_axes]
        if axes == new_axes:
            check = False
        axes = new_axes
    if len(axes)>1:
        TS_ring = True
    else:
        TS_ring = False

    return rotor_axes, TS_ring

def get_all_rotors(bond_graph, bond_graph_woTSthresh=[]):
    #Fixes numbering system to match Gaussian
    from copy import deepcopy

    gauss_bond_graph_woTSthresh = deepcopy(bond_graph_woTSthresh)
    for bonds in gauss_bond_graph_woTSthresh:
        for i in range(len(bonds)):
            bonds[i] += 1

    gauss_bond_graph = deepcopy(bond_graph)
    for bonds in gauss_bond_graph:
        for i in range(len(bonds)):
            bonds[i] += 1

    #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
    dict bc unallow repeated elements
402 def get_rotor_dihedrals_method_2(torsions, zmat_array, bond_graph,
    bond_graph_woTSthresh=[]):
403     counter = 0
404     axes = []
405     rotors = []
406     zmat = []
407     rotor_rows = []
408     rotor_axes = get_all_rotors(bond_graph, bond_graph_woTSthresh)
409     for array in zmat_array:
410         if len(array)==0:
411             counter+=1
412         if counter==2:
413             zmat.append(array)
414     zmat = zmat[1:]
415 
416     largest_atomNums = []
417     for torsion in torsions:
418         ax = sorted(torsion[1:3])
419         if (ax in rotor_axes) and (ax not in axes):
420             if max(torsion[:4]) not in largest_atomNums:
421                 rotors.append(torsion[:4])
422                 axes.append(ax)
423             largest_atomNums.append(max(torsion[:4]))
424 
425     for rotor in rotors:
426         rotor_rows.append(zmat[max(rotor) + 1])
427     #adjusts 'D#' naming from the newzmat format
428     if 'R' in ' '.join(zmat_array[10]):
429         rotor_dihedrals = [f'D{int(row[6][1:])}' for row in rotor_rows]
430     else:
431         rotor_dihedrals = [row[6] for row in rotor_rows]
432 
```

```
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]+'_'+
    str(i)+'_'+'.'+filename.split('.')[1])
449 
450 # loops through the dihedrals and the gjf copies and parses 's 36 10.0'
     next to the corresponding diheral, for each copy
451 def write_new_files(rotor_dihedrals, originalFilenameLen):
452     directory=os.getcwd()
453     files=os.listdir(directory)
454     files = [file for file in files if file.endswith('gjf')]
455     for dihedral, filename in zip(rotor_dihedrals, files):
456         file = open(filename, "r")
457         file_lines = file.readlines()
458         for index, line in enumerate(file_lines):
459             if ((' '+dihedral+' ') in line) and (len(line.split())==2):
460                 value = line.split()[-1]
461                 file_lines[index] = line.replace(value, f'{value} s 36
    10.0')
462                 break
463         try:
464             file = open(filename, "w")
465         except IOError:
466             print('Error: file (%s) not found!\n' % (filename))
467             sys.exit()
468 
469         file.writelines(file_lines)
470         file.close()
471         newname=filename.split('.')[0][:originalFilenameLen]+"_"+str(
    dihedral)+"_rotor.gjf"
472         os.rename(filename,newname)
473 
474 ## -- END OF TOPOLOGY FUNCTIONS -- ##
475 
476 
```

```
## -- UPDATE_HEADER FUNCTION -- ## (by Katie L.)

def replace_header(ts, numProc):
    #user defined job type
    keyword='rotor'

    files=os.listdir(os.getcwd())
    for filename in files:
        #calls the function "replace_header" to edit the file header for the specific file type
        f=open(filename, 'r')
        count=0
        for line in f:
            if line == '\n' or line == '\r\n':
                f.close()
                break
            else:
                count = count + 1

        #determine which route we are using based on user specified input
        if keyword=='m062x':
            if ts:
                route="#opt=(calcall,tight,ts) freq m062x/cc-pvtz maxdisk=500GB int=ultrafine"
            if not ts:
                route="#opt=(calcall,tight) freq m062x/cc-pvtz maxdisk=500GB int=ultrafine"
        elif keyword=='b3lyp':
            if ts:
                route="#opt=(calcall,tight,ts) freq b3lyp/6-311++g* maxdisk=500GB int=ultrafine"
            if not ts:
                route="#opt=(calcall,tight) freq b3lyp/6-311++g* maxdisk=500GB int=ultrafine"

        elif keyword=='E':
            route="# roccsd(t,t1diag)/cc-pvdz maxdisk=500GB int=ultraFine"

        elif keyword=='E1':
            route="# roccsd(t,t1diag)/cc-pvtz maxdisk=500GB int=ultraFine"

        elif keyword=='E2':
            route="# roccsd(t)/cc-pvqz maxdisk=500GB int=ultraFine"

        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,
    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',"%
    chk="+title[0]+".chk",'\r\n',route,'\r\n']+lines[count:]
533         else:
534             text=["%nprocshared="+numProc,'\n',"%mem=500MW",'\n',"%chk=
    "+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)
    :
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         print(' %-15s  %-13s   %7.3f\n' % (nstr, tstr, a123), end='')
622     print('\n', end='')
623 
624 ## -- END OF UNUSED PRINTING FUNCTIONS -- ##
625 
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
     empty list for other cases.
10     '''
11     # looping through all gjfs and finding rotors for each one
12     directory=os.getcwd()
13     files=os.listdir(directory)
14     # convert all gjfs into gaussview reformats
15     for fileName in files:
16         if fileName.endswith('gjf'):
17             file = open(fileName, 'r')
18             fstring = file.read()
19             file.close()
20             if 'Variables' in fstring:
21                 get_gView_format(fileName)
22 
23     for fileName in files:
24         if fileName.endswith('gjf'):
25             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 opf processors used for m062x jobs (uses
    3 less for rotor jobs)
35            numProc = str(int(fstring.split('nprocshared=')[1].split()
    [0])-3)
36            file.close()
37
38            file_length = len(zmat_file.split(".gjf")[0])
39
40            # get original zmat array
41            zmat_array, zmat = get_file_string_array(zmat_file)
42
43            # read in z-matrix
44            # mol = zmat2xyz.molecule(zmat_file)
45            # convert to xyz-coordinates
46            # xyz_array = mol.zmat2xyz()
47
48            # extract xyz-coordinates from log file
49            if fileName[:-3]+'log' in os.listdir():
50                xyz_array = get_xyzGeom(fileName[:-3]+'log')
51            else:
52                xyz_array = xyzGeoms[fileName.split('_E')[0]+'.gjf']
53            xyz_array.insert(0, fileName)
54            xyz_array.insert(0, len(xyz_array[1:]))
55            xyz_array = [[item] for item in xyz_array]
56            for i, item in enumerate(xyz_array[2:]):
57                new_element = [float(elem) for elem in item[0].split(',
    ') if elem[-1].isdigit()]
58                new_element.insert(0, item[0].split(',')[0])
59                xyz_array[i+2] = new_element
60
61            # read in geometry, determine bond topology
62            geom = get_geom(xyz_array)
63            print(f'geom: {geom}')
64
65            if ts == 'y':
66                ts = True
67                # calculates bond graph without changing threshold.
    Used for extracting rotors of non-ring-structured TS
68                bond_thresh = 1.2
```

```
69                bond_graph_woTSthresh, 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_woTSthresh}')
87                rotor_dihedrals, rotors = get_rotor_dihedrals_method_2(
    torsions, zmat_array, bond_graph, bond_graph_woTSthresh)
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                             if '%chk' in line:
121                                 flines[j] = line.replace('_rotor', f'
    _rotor_{str(i)}')
122 
123                         fcopy = open(f'{fileName}_{str(i)}.gjf', 'w')
124                         fcopy.writelines(flines)
125                         fcopy.close()
126                 os.remove(file)
127             # moves rotor jobs shell script into rotor their dihedral
    rotor folder
128             for dihedral in rotor_dihedrals:
129                 os.mkdir(f'./{dihedral}')
130                 shutil.copy('./../run_all_gjfs_array.sh', f'./{dihedral
    }')
131             for file in os.listdir():
132                 if file.endswith('.gjf'):
133                     for dihedral in rotor_dihedrals:
134                         if dihedral in file:
135                             shutil.move(f'./{file}', f'./{dihedral}')
136             os.chdir(current_dir)
137 
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:
```

```
            if 'D' in line[0]:
                dihedral = line.split('--->')[0].strip()
                rotor_dihedrals.append(dihedral)
                rotor = line.split('--->')[1].strip()
                rotors.append(ast.literal_eval(rotor))
    else:
        rotor_dihedrals, rotors = [], []

    return rotor_dihedrals, rotors

    ## -- END FUNCTION CALLS AND MAIN BLOCKS -- ##

if __name__ == '__main__':
    main()
```

B.3 run_all_gjfs_array.sh

```
#!/bin/bash
#SBATCH --partition=shas
#SBATCH --qos=normal
#SBATCH --nodes=1
#SBATCH --ntasks-per-node=8
#SBATCH --time=24:00:00
#SBATCH --job-name=83.35_rotors
#SBATCH --account=ucb146_summit3
#SBATCH --array=1-36


module purge
module load "gaussian/16_avx2"

FILES=$(ls *.gjf | sed -n ${SLURM_ARRAY_TASK_ID}p)
echo "Processing $FILES ...."

g16 $FILES

echo "Finished all Jobs!"
date
```

Appendix C

Python scripts | MESS input file generation code

C.1 get_energies.py

```
import xlsxwriter
import numpy as np
import re
from scipy.signal import find_peaks

# Creates and populates energies spreadsheet from input energies dictionary
def write_energies_spreadsheet(energiesDictionary, non_repeated_non_ts, ts_prods, dissociations):
    # Create a workbook and add a worksheet.
    workbook = xlsxwriter.Workbook('Energies_SpreadSheet.xlsx')
    worksheet = workbook.add_worksheet('Energetics')
    # Some data we want to write to the worksheet.
    column_titles = ['m062X/cc-pVTZ', 'CCSD(T)/cc-pVDZ', 'CCSD(T)/cc-pVTZ', 'T1 diag', 'E(hartrees)']
    # Start from the first cell. Rows and columns are zero indexed.
    row = 0
    col = 0

    # Iterate over the data and write it out row by row.
    for column_title in (column_titles):
        col += 1
        worksheet.write(row, col, column_title)
    col = 0
    row += 1
    worksheet.write(row, col, 'Reactants/Products')

    row += 1

```

```
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' find_peaks
103 def get_peaks_valleys(dihedrals, m062xFileName):
104     moleculeName = m062xFileName.split('_m062x.log')[0]
105     # dictionary, conatins 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         # conditional for a different command in rotor header
116         if "#scan" in rotorFileString:
117             # use regex to find scanned energies at bottom of the file
118             print(rotorFileName)
119             energies = re.findall(r'\\HF=[-?\d*\.\d*,]*',
    rotorFileString)[0].split(',')
120             energies[0] = energies[0].split('=')[-1]
121         else:
122             rotorFile = open(rotorFileName, 'r')
123             rotorFileString = rotorFile.readlines()
124             rotorFile.close()
125             # use regex to find scanned energies throughout the file
126             print(rotorFileName)
127             search_optimization_line = re.compile(r'Optimization
    completed')
128             search_SCF_Done_line = re.compile(r'SCF Done')
129             num_lines = len(rotorFileString)
130             curr_line_num = 0
131             energies = []
132             while curr_line_num < num_lines:
133                 curr_line = str.strip(rotorFileString[curr_line_num])
134                 if search_SCF_Done_line.search(curr_line):
135                     SCF_Done_Line = curr_line
136                 if search_optimization_line.search(curr_line):
137                     SCF_Done_line_contents = SCF_Done_Line.split()
138                     energies.append(str(SCF_Done_line_contents[4]))
139                 curr_line_num = curr_line_num + 1
140
141         # adjusts energies with respect to initial energy and converts
    to kcal/mol
142         energies = np.array([float(energy)-float(energies[0]) for
    energy in energies][:-1])*627.51
143         peaks_and_valleys.append(energies[0])
144
145         # finds peaks and valleys using scipy.signal.find_peaks
146         peak_indices, _ = find_peaks(energies)
147         valley_indices, _  = find_peaks(-1*energies)
148
149         # creates list with all extreme energies
150         for i in range(len(peak_indices)):
151             try:
152                 peaks_and_valleys.append(energies[peak_indices[i]])
```

```
                peaks_and_valleys.append(energies[valley_indices[i]])
            except IndexError:
                pass
        # populates dicionary of dihedral-energies
        rotorEnergies[dihedral] =  peaks_and_valleys

    return rotorEnergies
```

C.2 geometryInfo.py

```
# Function for extracting XYZ Geometries from m062x files
import os
import re
from difflib import SequenceMatcher
from get_geometry import get_geom, get_bond_graph, get_bonds,
    get_angles, get_torsions, get_all_rotors

## ------------------------------------------------- TOPOLOGY FUNCTIONS
     ----------------------------------------------------------##

# get xyz geometry from the m062x file
def get_xyzGeom(m062xFileName):
    #open and strip \n from file, locate geom using regex and remove
    duplicates by using non-duplicate keys feature from dicts.
    #Regex: \d (digit), [A-Z] (caps letter), -? (0 or more appearances
    of '-'), \. (.), * (0 or more appearances of preceding call)
    m062xFile = open(m062xFileName, 'r')
    m062xFileString = m062xFile.read().replace('\n', '').replace(' ', '
    ')
    xyz_geom = list(dict.fromkeys(re.findall(r'[A-Z],-?\d\.\d*,-?\d\.\d
    *,-?\d\.\d*', m062xFileString)))
    idxs_toDelete = []
    for i in range(len(xyz_geom)):
        for j in range(len(xyz_geom)):
            # library used to compare how 2 strings match
            # used to delete repeated coordinates that differ to
    themeselves by a few orders of magnitude (redundant!)
            # ratios > 0.8 are accurate by 6 decimal places!
            if SequenceMatcher(a=xyz_geom[i], b=xyz_geom[j]).ratio() >
    0.8 and SequenceMatcher(a=xyz_geom[i], b=xyz_geom[j]).ratio() < 1.0:
                if sorted([i, j]) not in idxs_toDelete:
                    idxs_toDelete.append([i, j])
    # deletes repeated coordinates!
    idxs_toDelete = [max(item) for item in idxs_toDelete]
    for index in sorted(idxs_toDelete, reverse=True):
        del xyz_geom[index]

    m062xFile.close()
```

```
    return xyz_geom

# slightly different from rotor script, returns lists of rotors via atom numbering
def get_rotor_dihedrals(torsions, bond_graph, bond_graph_woTSthresh=[]):
    axes = []
    rotors = []
    rotor_rows = []
    maxAtomNumber = []

    rotor_axes = get_all_rotors(bond_graph, bond_graph_woTSthresh)

    for torsion in torsions:
        ax = sorted(torsion[1:3])
        if (ax in rotor_axes) and (ax not in axes) and (max(torsion[:4]) not in maxAtomNumber):
            rotors.append(torsion[:4])
            axes.append(ax)
            maxAtomNumber.append(max(torsion[:4]))

    return rotors

# pulls functions from get get_geomtry to get list of molecule's rotors
def get_rotors(xyz_geom, m062xFileName, bond_thresh, TS=False):
    #converts xyz_geom to xyz_array format compatible with get_rotors_gjf.py script!
    xyz_array = []
    xyz_array.append([len(xyz_geom)])
    xyz_array.append([m062xFileName])
    for i in range(len(xyz_geom)):
        line = [float(element) if len(element)>1 else element for element in xyz_geom[i].split(',')]
        xyz_array.append(line)
    ## -- Using functions from get_geometry script -- ##
    #read in geometry, determine bonded topology
    geom = get_geom(xyz_array)
    bond_graph, double_bonds = get_bond_graph(geom, bond_thresh)
    if TS:
        bond_thresh = 1.2
        bond_graph_woTSthresh, double_bonds = get_bond_graph(geom, bond_thresh)
    #calculate bond lengths, angles, and torsions
    bonds = get_bonds(geom, bond_graph)
    angles = get_angles(geom, bond_graph)
    torsions = get_torsions(geom, bond_graph)
    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
    lise (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:
```

```
                if all_frequencies[1:][i+1] < all_frequencies[1:][i]:
                    frequencies.append(all_frequencies[1:][i])
                    break
            except IndexError:
                frequencies.append(all_frequencies[1:][i])
                break
            else:
                frequencies.append(all_frequencies[1:][i])
    else:
        frequencies = []
    return frequencies, charge_multiplicity
```

C.3 messParsing.py

```
import os, math

# ------------------------------------------------ MESS PARSING FUNCTIONS ------------------------------------------------------ #

# ------------------------------------------- Writes MESS Input Header ----------------------------------------------------------#
def write_Header():
    MESSFile = open('MESSFile.inp', 'w')
    MESSFile.write('TemperatureList[K]                500. 625. 750. 875. 1000. 1125. 1250. 1375. 1500. 1625. 1750. 1875. 2000.\n')
    MESSFile.write('PressureList[atm]                 0.00001 0.001 0.01  0.1  1  10  100.\n')
    MESSFile.write('!PressureList[bar]                1.\n')
    MESSFile.write('EnergyStepOverTemperature         .2\n')
    MESSFile.write('ExcessEnergyOverTemperature       30\n')
    MESSFile.write('ModelEnergyLimit[kcal/mol]        400\n')
    MESSFile.write('CalculationMethod                 direct\n')
    MESSFile.write('!CalculationMethod                low-eigenvalue ! direct\n')
    MESSFile.write('WellCutoff                        10\n')
    MESSFile.write('ChemicalEigenvalueMax             0.2\n')
    MESSFile.write('Model\n  EnergyRelaxation\n    Exponential\n Factor[1/cm]'+' '*16+'200\n')
    MESSFile.write(' '*6+'Power                       .85\n')
    MESSFile.write(' ' *6+'ExponentCutoff'+'              15\n'+' '*4+'End\n')
    MESSFile.write('  CollisionFrequency\n    LennardJones\n Epsilons[1/cm]     --FILL HERE-- --FILL HERE--  !N2 and parent\n')
    MESSFile.write('  Sigmas[angstrom]       --FILL HERE-- --FILL HERE --\n  Masses[amu]            --FILL HERE-- --FILL HERE--\n    End\n')
    MESSFile.close()

```

```
# ------------------------------- CREATES AND WRITES THE BARRIER SECTION FOR A WELL  ------------------------------------ #
# Assumes all wells are connected to Well 1!
def write_Well_Barrier(TSW_xyz_geom, TSW_freqs, TSW_charge_multiplicity, TSW_rots, rotorEnergies, path_dir, m062xFileName):
    MESSFile = open('MESSFile.inp', 'a')
    # gets path folder name using os library
    pathway = os.path.basename(os.path.normpath(path_dir))
    # extracts the number from the pathway (ie. returns 8 for the P8 folder)
    path_num = ''.join([item for item in pathway if item.isdigit()])
    MESSFile.write('Barrier'+' '*8+'B'+str(int(path_num)-1)+' '*2+'W1'+' '*2+pathway+' '*4+'# '+m062xFileName+'\n')
    MESSFile.write(' '*4+'Variational\n')
    MESSFile.write(' '*8+'RRHO\n')
    MESSFile.write(' '*4+'Geometry[angstrom]'+' '*8+str(len(TSW_xyz_geom))+'\n')
    # writes geometry section
    for line in TSW_xyz_geom:
        line = line.split(',')
        MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+line[3]+'\n')
    MESSFile.write(' '*4+'Core RigidRotor\n')
    MESSFile.write(' '*8+'SymmetryFactor'+' '*4+'--- INCLUDE SYMMETRY FACTOR HERE ----\n')
    MESSFile.write(' '*4+'End\n')
    # writes rotor section
    for i in range(len(TSW_rots)):
        max_atom_number = max(TSW_rots[i])
        rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
        MESSFile.write(' '*4+'Rotor'+' '*8+'Hindered\n')
        MESSFile.write(' '*8+'Group'+' '*21+'numbers!\n')
        MESSFile.write(' '*8+'Axis'+' '*22+str(TSW_rots[i][1])+' '+str(TSW_rots[i][2])+'\n')
        # calculates rotor symmetry
        truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for energy in rotEnergies]
        rotorSymmetry = '1'
        if len(truncated_rotEnergies) == 4:
            if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
                rotorSymmetry = '2'
        if len(truncated_rotEnergies) == 6:
            if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
                rotorSymmetry = '3'
        if len(truncated_rotEnergies) == 8:
            if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
                rotorSymmetry = '4'
        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 frequecies section substracts number of rotors + 1
    imaginary frequency!
78      MESSFile.write(' '*4+'Frequencies[1/cm]'+' '*4+str(len(TSW_freqs)-(
    len(TSW_rots)+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 multplicity
    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,
    rotorEnergies, path_dir, m062xFileName):
101     MESSFile = open('MESSFile.inp', 'a')
102     # gets path folder name using os library
103     pathway = os.path.basename(os.path.normpath(path_dir))
104     MESSFile.write('Well'+' '*8+pathway+' '*8+'# '+m062xFileName+'\n')
105     MESSFile.write(' '*4+'Species\n')
106     MESSFile.write(' '*8+'RRHO\n')
107     MESSFile.write(' '*4+'Geometry[angstrom]'+' '*8+str(len(W_xyz_geom)
    )+'\n')
108     # writes geometry section
109     for line in W_xyz_geom:
110         line = line.split(',')
111         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
    line[3]+'\n')
112     MESSFile.write(' '*4+'Core RigidRotor\n')
113     MESSFile.write(' '*8+'SymmetryFactor'+' '*4+'--- INCLUDE SYMMETRY
    FACTOR HERE ----\n')
114     MESSFile.write(' '*4+'End\n')
115     # writes rotor section
116     for i in range(len(W_rots)):
117         max_atom_number = max(W_rots[i])
118         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
119         MESSFile.write(' '*4+'Rotor'+' '*8+'Hindered\n')
120         MESSFile.write(' '*8+'Group'+' '*21+'numbers!\n')
121         MESSFile.write(' '*8+'Axis'+' '*22+str(W_rots[i][1])+' '+str(
    W_rots[i][2])+'\n')
122         # calculates rotor symmetry
123         truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
    energy in rotEnergies]
124         rotorSymmetry = '1'
125         if len(truncated_rotEnergies) == 4:
126             if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
127                 rotorSymmetry = '2'
128         if len(truncated_rotEnergies) == 6:
129             if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
130                 rotorSymmetry = '3'
131         if len(truncated_rotEnergies) == 8:
132             if truncated_rotEnergies == truncated_rotEnergies[:2]*4:
133                 rotorSymmetry = '4'
134         MESSFile.write(' '*8+'Symmetry'+' '*19+rotorSymmetry+'\n')
135         rotEnergies = [round(energy, 2) for energy in rotEnergies]
136         MESSFile.write(' '*8+'Potential[kcal/mol]'+' '*8+str(int(len(
    rotEnergies)/int(rotorSymmetry)))+'\n')
137         MESSFile.write(' '*9)
138         if not rotorSymmetry == '1' :
139             for i in range(len(rotEnergies)):
140                 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 frequecies section substracts number of rotors
149     MESSFile.write(' '*4+'Frequencies[1/cm]'+' '*4+str(len(W_freqs)-(
    len(W_rots)))+'\n     ')
150     counter = 1
151     for freq in W_freqs:
152         MESSFile.write(' '*5)
153         MESSFile.write(' '+str(round(freq, 2)))
154         if counter == 10:
155             MESSFile.write('\n     ')
156             counter = 0
157         counter += 1
158     MESSFile.write('\n'+' '*5+'!------- INCLUDE ROTOR FREQUENCIES HERE
    ---------!')
159     MESSFile.write('\n'+' '*4+'ZeroEnergy[kcal/mol]'+' '*4+'--- ZERO
    ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
160     # change for higher excited states / pulls charge and multplicity
    from m062x file
161     MESSFile.write('\n'+' '*4+'ElectronicLevels[1/cm]'+' '*4+str(1)+'\n
    '+' '*8+W_charge_multiplicity[0]+' '*2+W_charge_multiplicity[1]+'\n'
    +' '*4+'End\n'+'End\n')
162     MESSFile.close()
163
164 # ---------------------------------- CREATES AND WRITES THE BARRIER
    SECTION FOR A TS  ---------------------------------------- #
165 def write_TS_Barrier(xyz_geom, rots, freqs, rotorEnergies,
    charge_multiplicity, path_dir, m062xFileName, number_of_wells,
    h_abstraction):
166     MESSFile = open('MESSFile.inp', 'a')
167     # gets path folder name using os library
168     pathway = os.path.basename(os.path.normpath(path_dir))
169     # extracts the number from the pathway (ie. returns 8 for the P8
    folder)
170     path_num = ''.join([item for item in pathway if item.isdigit()])
171     # ------------------------ Naming assumes Barrier connects W1 to
    products!(ie. B# W1 P#) ---------------------------------#
172     if h_abstraction:
173         MESSFile.write('Barrier'+' '*8+'B'+str(int(path_num)+
    number_of_wells)+' '*2+'W1'+' '*2+pathway+' '*4+'# '+m062xFileName+'
      +  [H]'+'\n')
174     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 frequecies section substracts 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 multplicity 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_CH2O_CCCOCCC_m062x.log)
241 # Fragment folder that stores must have the name of the TS: (ie. TS_CH2O_CCCOCCC)
242 # Fragment logs inside the folder must end with _m062x.log: (ie. CH2O_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,
    fragments_directory, path_dir, m062xFragmentFileList, fr_xyz_geom,
    fr_freqs, fr_rots, rotorEnergies, fr_charge_multiplicity,
    h_abstraction):
248     MESSFile = open('MESSFile.inp', 'a')
249     # gets path folder name using os library
250     pathway = os.path.basename(os.path.normpath(path_dir))
251     # makes it so Bimolecular header is writen only once!
252     if iteration == 1:
253         if h_abstraction:
254             MESSFile.write('Bimolecular'+' '*8+pathway+' '*4+'# '+
    fragments_naming+'  +  [H]'+'\n')
255         else:
256             MESSFile.write('Bimolecular'+' '*8+pathway+' '*4+'# '+
    fragments_naming+'\n')
257     MESSFile.write(' '*4+'Fragment'+' '*2+fragmentFile.split('_m062x.
    log')[0]+'\n')
258     MESSFile.write(' '*8+'RRHO\n')
259     MESSFile.write(' '*4+'Geometry[angstrom]'+' '*8+str(len(fr_xyz_geom
    ))+'\n')
260     # writes geometry section
261     for line in fr_xyz_geom:
262         line = line.split(',')
263         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
    line[3]+'\n')
264     MESSFile.write(' '*4+'Core RigidRotor\n')
265     MESSFile.write(' '*8+'SymmetryFactor'+' '*4+'--- INCLUDE SYMMETRY
    FACTOR HERE ----\n')
266     MESSFile.write(' '*4+'End\n')
267     # writes rotor section
268     for i in range(len(fr_rots)):
269         max_atom_number = max(fr_rots[i])
270         rotEnergies = rotorEnergies['D'+str(max_atom_number-3)]
271         MESSFile.write(' '*4+'Rotor'+' '*8+'Hindered\n')
272         MESSFile.write(' '*8+'Group'+' '*21+'numbers!\n')
273         MESSFile.write(' '*8+'Axis'+' '*22+str(fr_rots[i][1])+' '+str(
    fr_rots[i][2])+'\n')
274         # calculates rotor symmetry
275         truncated_rotEnergies = [math.floor(energy*10**2)/10**2 for
    energy in rotEnergies]
276         rotorSymmetry = '1'
277         if len(truncated_rotEnergies) == 4:
278             if truncated_rotEnergies == truncated_rotEnergies[:2]*2:
279                 rotorSymmetry = '2'
280         if len(truncated_rotEnergies) == 6:
281             if truncated_rotEnergies == truncated_rotEnergies[:2]*3:
282                 rotorSymmetry = '3'
283         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 frequecies section substracts 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 multplicity
    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 # Place two fragment m062x files in the pathway folder (ie. P3)
326 # Fragment files must begin with Bi_... and end with _m062x.log (ie.
    Bi_COH_E9-27_m062x.log)
327 # ----------------- Access each fragment's log file and extract
    geometries, rotors and frequencies --------------------------- #
328
329 # fragment#_info contains [xyz_geom, freqs, charge/multiplicity and
    rotors]
330 def write_BF_Barrier(fragments_naming, fragment1_info,
    fr1_rotorEnergies, fragment2_info, fr2_rotorEnergies,  pathway,
    number_of_wells, m062xFileName, h_abstraction):
331     MESSFile = open('MESSFile.inp', 'a')
332     # extracts the number from the pathway (ie. returns 8 for the P8
    folder)
333     path_num = ''.join([item for item in pathway if item.isdigit()])
334     # ------------------------ Naming assumes Barrier connects W1 to
    products!(ie. B# W1 P#) ---------------------------------#
335     if h_abstraction:
336         MESSFile.write('Barrier'+' '*8+'B'+str(int(path_num)+
    number_of_wells)+' '*2+'W1'+' '*2+pathway+' '*4+'# '+m062xFileName+'
      +  [H]'+'\n')
337     else:
338         MESSFile.write('Barrier'+' '*8+'B'+str(int(path_num)+
    number_of_wells)+' '*2+'W1'+' '*2+pathway+' '*4+'# '+
    fragments_naming+'\n')
339     MESSFile.write(' '*4+'RRHO\n')
340     MESSFile.write(' '*8+'Stoichiometry'+' '*8+'------ADD MOLECULAR
    FORMULA------\n')
341     MESSFile.write(' '*8+'Core'+' '*4+'PhaseSpaceTheory\n')
342     MESSFile.write(' '*4+'FragmentGeometry[angstrom]'+' '*8+str(len(
    fragment1_info[0]))+'\n')
343     # writes geometry section for fragment 1
344     for line in fragment1_info[0]:
345         line = line.split(',')
346         MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line[2]+' '*4+
    line[3]+'\n')
347     # writes geometry section for fragment 2
348     if h_abstraction:
349         MESSFile.write(' '*4+'FragmentGeometry[angstrom]        1\n'+'
    '*5+'H                  0.000000    0.000000    0.000000\n')
350     else:
351         MESSFile.write(' '*4+'FragmentGeometry[angstrom]'+' '*8+str(len
    (fragment2_info[0]))+'\n')
352         for line in fragment2_info[0]:
353             line = line.split(',')
```

```
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
    -3)]
401             MESSFile.write(' '*4+'Rotor'+' '*8+'Hindered\n')
402             MESSFile.write(' '*4+'Geometry[angstrom]'+' '*8+str(len(
    fragment2_info[0]))+'\n')
403             for line in fragment2_info[0]:
404                 line = line.split(',')
405                 MESSFile.write(' '*5+line[0]+' '*8+line[1]+' '*4+line
    [2]+' '*4+line[3]+'\n')
406             MESSFile.write(' '*8+'Group'+' '*21+'numbers!\n')
407             MESSFile.write(' '*8+'Axis'+' '*22+str(fragment2_info[3][i
    ][1])+' '+str(fragment2_info[3][i][2])+'\n')
408             # calculates rotor symmetry
409             fr2_truncated_rotEnergies = [math.floor(energy*10**2)/10**2
     for energy in fr2_rotEnergies]
410             rotorSymmetry = '1'
411             if len(fr2_truncated_rotEnergies) == 4:
412                 if fr2_truncated_rotEnergies ==
    fr2_truncated_rotEnergies[:2]*2:
413                     rotorSymmetry = '2'
414             if len(fr2_truncated_rotEnergies) == 6:
415                 if fr2_truncated_rotEnergies ==
    fr2_truncated_rotEnergies[:2]*3:
416                     rotorSymmetry = '3'
417             if len(fr2_truncated_rotEnergies) == 8:
418                 if fr2_truncated_rotEnergies ==
    fr2_truncated_rotEnergies[:2]*4:
419                     rotorSymmetry = '4'
420             MESSFile.write(' '*8+'Symmetry'+' '*19+rotorSymmetry+'\n')
421             fr2_rotEnergies = [round(energy, 2) for energy in
    fr2_rotEnergies]
422             MESSFile.write(' '*8+'Potential[kcal/mol]'+' '*8+str(int(
    len(fr2_rotEnergies)/int(rotorSymmetry)))+'\n')
423             MESSFile.write(' '*9)
424             if not rotorSymmetry == '1' :
425                 for i in range(len(fr2_rotEnergies)):
426                     MESSFile.write(str(fr2_rotEnergies[i])+'  ')
427                     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
    rotors for both fragments
435         total_frequencies = len(fragment1_info[1])+len(fragment2_info
    [1])-len(fragment1_info[3])-len(fragment2_info[3])
436     else:
437         total_frequencies = len(fragment1_info[1])-len(fragment1_info
    [3])
438     MESSFile.write(' '*4+'Frequencies[1/cm]'+' '*4+str(
    total_frequencies)+'\n     ')
439     counter = 1
440     for freq in fragment1_info[1]:
441         MESSFile.write(' '*5)
442         MESSFile.write(' '+str(round(freq, 2)))
443         if counter == 10:
444             MESSFile.write('\n     ')
445             counter = 0
446         counter += 1
447     MESSFile.write('\n     ')
448     counter = 1
449     if not h_abstraction:
450         for freq in fragment2_info[1]:
451             MESSFile.write(' '*5)
452             MESSFile.write(' '+str(round(freq, 2)))
453             if counter == 10:
454                 MESSFile.write('\n     ')
455                 counter = 0
456             counter += 1
457     MESSFile.write('\n'+' '*5+'!------- INCLUDE ROTOR FREQUENCIES HERE
    ---------!')
458     MESSFile.write('\n'+' '*4+'ZeroEnergy[kcal/mol]'+' '*4+'--- ZERO
    ENERGY VALUE FROM HIGH ENERGY CALCULATIONS ---')
459     # change for higher excited states / pulls charge and multplicity
    from m062x file
460     # for a BF, both fragments have charge and multplicity 0 2
461     MESSFile.write('\n'+' '*4+'ElectronicLevels[1/cm]'+' '*4+str(1)+'\n
    '+' '*8+fragment1_info[2][0]+' '*2+fragment1_info[2][1]+'\n'+' '*4+'
    End\n')
462     MESSFile.close()
463
464 # ------------------------------ WRITES THE BIMOLECULAR SECTION FOR A
    BF  ---------------------------------------- #
465 # 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 writen 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 frequecies section substracts 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 multplicity
    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')
```

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

C.4 writeMessFile.py

```
from messParsing import *
from geometryInfo import *
from get_energies import *
from os.path import basename

# Energies Dictionary, will contain all energies for each molecule to
   be added into energies spredsheet.
energiesDictionary = {}
all_molecules = []

# Condition to write excel spreadsheet
writeExcel = str(input("Do you want to create an Excel spreadsheet? (y/
   n): "))
if writeExcel == 'y':
    createExcel = True
else:
    createExcel = False

## -- Adds energies from m062x and high energy calcs into the
   energiesDictionary -- ##
def add_energies(pathway, FileList, non_ts_prods, non_ts,
   energiesDictionary, createExcel=False):
    num_fragments = len([file for file in FileList if file.endswith('
   _m062x.log') and not file.startswith('TS') and pathway.startswith('P
   ')])
    FileList = sorted(FileList)
    for filename in FileList:
        file = open(filename, 'r')
        filestring = file.read().replace('\n', '').replace(' ', '')
        file.close()
        if filename.endswith('E.log'):
            # gets energy from CCSD(T)
            E_ccsdt = filestring.split('\CCSD(T)')[1].split('\\')[0]
            E_ccsdt = float(re.findall(r'-?\d*\.\d*', E_ccsdt)[0])
            # gets T1 diagnostic
            t1diag = filestring.split('T1Diagnostic')[-1]
            t1diag = float(re.findall(r'-?\d*\.\d*', t1diag)[0])
        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
69      number_of_wells = sum('W' in path for path in pathways) - 1
70      lastParse = False
71      for pathway in pathways:
72          print('Working on: ', pathway)
73          if pathway == pathways[-1]:
74              lastParse = True
75          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
    filename.endswith("m062x.log")]
80          m062xFileName = m062xFileList[0]
81
82          # writes well section
83          if pathway.startswith('W'):
84              # adds energies from all fragment files into 'energies'
    dictionary
85              try:
86                  non_ts_prods, non_ts = add_energies(pathway, os.listdir
    (), non_ts_prods, non_ts, energiesDictionary, createExcel)
87              except PermissionError:
88                  pass
89
90              if len(m062xFileList)>1:
91                  # extracts Well's filename for Well Section
92                  m062xFileName   = [file for file in m062xFileList if
    file.startswith('W')]
93                  m062xFileName = m062xFileName[0]
94
95              # setting bond threshold for non-TS molecules
96              bond_thresh = 1.2
97              ## -- Topology Function Calls For Wells -- ##
98              # get xyz geometry and filename
99              W_xyz_geom = get_xyzGeom(m062xFileName)
100             # get frequencies from m062x file
101             W_freqs, W_charge_multiplicity = get_frequencies(
    m062xFileName)
102             # get rotors from geometry and get_geometry (rotors script)
     functions
103             W_rots = get_rotors(W_xyz_geom, m062xFileName, bond_thresh)
104             # finds corresponding z-matrix dihedral for each rotor
105             W_dihedrals = ['D'+str(max(rot)-3) for rot in W_rots]
106
107             print(W_dihedrals, m062xFileName)
108             rotorEnergies = get_peaks_valleys(W_dihedrals,
    m062xFileName)
109
110             # Change back to root directory and write in Mess input
    there!
111             os.chdir(root_directory)
112             write_Well(W_xyz_geom, W_freqs, W_charge_multiplicity,
    W_rots, rotorEnergies, path_dir, m062xFileName)
113
114             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_rots = 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_rots]
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_rots, 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_rots = 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' dicionary
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_rots = 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_rots]
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_rots, 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,
    fr1_rotorEnergies, fragment2_info, fr2_rotorEnergies, pathway,
    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('
    W')]
312 # print('dissociations: ', dissociations)
313 print(f"EnergiesDictionary {energiesDictionary}")
314
315
316 all_ts_molecules = [molecule for molecule in all_molecules if molecule
    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
    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
    +1], all_molecules[i+2]]
328                     else:
329                         ts_prods[all_molecules[i]] = [all_molecules[i
    +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,
      ts_prods, dissociations)
343 else:
344     pass
345
346 print('Seems like it worked!')
347 # end of program
```

Appendix D

Python scripts | Computational pipeline automation code

D.1 run_iter.py

```
import os

def fireIter():
    # finds directories ending in '_E', enters and runs the local 'run_all_gjfs.sh' file
    base_dir = os.getcwd()
    print(base_dir)
    os.chdir(base_dir)
    fire_m062x = 'sbatch run_all_gjfs.sh'
    os.system(fire_m062x)
    fire_rotors = 'nohup python start_rotor_run.py > log.out &'
    os.system(fire_rotors)

if __name__ == '__main__':
    fireIter()
```

D.2 searchLowConf.py

```
import os, re, numpy as np, shutil, get_input_gjf, run_iter, startHighEnergyCalcs
from get_geometry import get_gView_format

def low_conf():
    base_dir = os.getcwd()
    os.chdir(base_dir)
    # print(base_dir)

    curr_dir = base_dir
    # opens m062x log file to extract HF
```

```
    file_name=''
    files = os.listdir()
    for file in files:
        if file.endswith('.log'):
            file_name = file

    # print(file_name)
    file = open(curr_dir + '//' + file_name)
    flines = file.readlines()
    file.close

    HF_initial = 0
    for line in flines:
        if 'SCF Done' in line:
            HF_initial = float(line.split()[4])

    # print(HF_initial)

    # Open Rotor Directory
    files = os.listdir()
    # print(files)
    # print(curr_dir)
    for file in files:
        if 'Rotor' in file.split('_'):
            rotor_path = curr_dir + '//' + file
            # print(path)

    os.chdir(rotor_path)

    dihedrals = []

    for root, dirs, files in os.walk('.',topdown=True):
        # print(root)
        # for name in files:
        #   print(os.path.join(root, name))
        for name in dirs:
            dihedrals.append(os.path.join(root, name))

    # print(dihedrals)
    # os.chdir(dihedrals[0])
    # print(os.getcwd())

    normal_term_key = re.compile("Normal termination")
    file_name = ''
    error_files=[]
    allEnergies = []
    for dirs in dihedrals:
        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
    energy is the optimizes energy
78                      scanAngles.append(int(scanPoint))
79                  else:
80                      error_files.append(file)
81          scanEnergies.append(HF_initial)
82          scanAngles.append(0)
83          scanAngles,scanEnergies = zip(*sorted(zip(scanAngles,
    scanEnergies)))
84          allEnergies.append([scanAngles, scanEnergies])
85
86      allEnergies = np.array(allEnergies, dtype=object)
87      # print(allEnergies[0])
88
89      os.chdir(base_dir)
90
91      lowEnergy = 0
92      lowestAngle = 0
93      minDihedral = ''
94      minEnergy = []
95      minScanAngle = []
96      # minDihedrals = []
97      for i in range(0, len(allEnergies)):
98          startEnergy = allEnergies[i][1][0]
99          endEnergy = allEnergies[i][1][-1]
100         diff = (endEnergy - startEnergy)*627.5 # Convert energy
    difference from Hartrees to KCal/Mol
101         if diff > 0.01:
102             print("Start and End energy is not same")
103             exit()
```

```
104         else:
105             minEnergy.append(np.amin(allEnergies[i][1]))
106             minScanAngle.append(allEnergies[i][0][np.where(allEnergies[
    i][1] == np.amin(allEnergies[i][1]))[0][0]])
107             # minDihedrals.append(dihedrals[i])
108             # print(minDihedrals)
109             # print(minEnergy)
110             # print(minScanAngle)
111 
112     minEnergy = np.array(minEnergy)
113     minScanAngle = np.array(minScanAngle)
114     dihedrals = np.array(dihedrals)
115 
116     lowestEnergy = np.amin(minEnergy)
117     lowestAngle = minScanAngle[np.where(minEnergy == np.amin(minEnergy)
    )][0]
118     minDihedral = dihedrals[np.where(minEnergy == np.amin(minEnergy))
    ][0]
119     # print(lowestEnergy)
120     # print(lowestAngle)
121     # print(minDihedral)
122 
123     # it checks if the difference is within range to fire a lower
    conformer
124 
125     # print(allEnergies[np.where(minEnergy == np.amin(minEnergy))
    [0][0]][1][0])
126 
127     # os.chdir(base_dir)
128 
129     diff_range = lowestEnergy - allEnergies[np.where(minEnergy == np.
    amin(minEnergy))[0][0]][1][0]
130     # print(diff_range*627.5)
131 
132     if  diff_range*627.5 > -0.01:
133         # Call script to run higher energy calcs
134         print('No lower conformer found')
135         print("Sarting Higher Energy calculations!")
136         startHighEnergyCalcs.runHighECalcs()
137     else:
138         print('Lower Conformer Found!')
139         print('Starting next iteration')
140         # print(minDihedral[2:])
141         low_conf_path =os.path.join(curr_dir,rotor_path,minDihedral
    [2:])
142         print(low_conf_path)
143         files = os.listdir(low_conf_path)
144         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(
    int(fileNum)+1))
155         os.makedirs(nextIterPath)
156         print(os.path.dirname(base_dir))
157 
158         shutil.copy(f'{low_conf_path}/{lowerConfFileCHK}',f'{
    nextIterPath}/{lowerConfFileCHK}')
159         shutil.copy(f'{low_conf_path}/{lowerConfFileLOG}',f'{
    nextIterPath}/{lowerConfFileLOG}')
160         shutil.copy('geometryInfo.py', f'{nextIterPath}/geometryInfo.py
    ')
161         shutil.copy('get_geometry.py', f'{nextIterPath}/get_geometry.py
    ')
162         shutil.copy('get_rotors.py', f'{nextIterPath}/get_rotors.py')
163         shutil.copy('search_rotors.py', f'{nextIterPath}/search_rotors.
    py')
164         shutil.copy('start_rotor_run.py', f'{nextIterPath}/
    start_rotor_run.py')
165         shutil.copy('get_input_gjf.py', f'{nextIterPath}/get_input_gjf.
    py')
166         shutil.copy('newzmat.sh', f'{nextIterPath}/newzmat.sh')
167         shutil.copy('searchLowConf.py', f'{nextIterPath}/searchLowConf.
    py')
168         shutil.copy('startSearchLowConf.py',f'{nextIterPath}/
    startSearchLowConf.py')
169         shutil.copy('run_iter.py',f'{nextIterPath}/run_iter.py')
170         shutil.copy('startHighEnergyCalcs.py',f'{nextIterPath}/
    startHighEnergyCalcs.py')
171         shutil.copy('run_all_gjfs.sh', f'{nextIterPath}/run_all_gjfs.sh
    ')
172         shutil.copy('run_all_gjfs_array.sh', f'{nextIterPath}/
    run_all_gjfs_array.sh')
173 
174         os.chdir(nextIterPath)
175 
176         print(os.getcwd())
177 
178         files=os.listdir(nextIterPath)
179         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 '
       run_all_gjfs.sh' file
6      base_dir = os.getcwd()
7      for fileName in os.listdir():
8          if '_E' in fileName:
9              print(fileName)
10             os.chdir(f'{base_dir}/{fileName}/it1')
11             fire_iterations = 'nohup python run_iter.py > log.out &'
12             os.system(fire_iterations)
13             os.chdir(base_dir)
14 
15 if __name__ == '__main__':
16     main()
```

D.4 start_rotor_run.py

```
import get_rotors, get_input_gjf, time, os, sys, startSearchLowConf,
    startHighEnergyCalcs

def wait_for_file():
        """
        Wait for 'Finished' keyword in slurm file to fire. Checking
        in 10 minute intervals. First checks if job has started

        This method fires the rotor code once it detects that the
        m062x/cc-pVTZ run has completed. Script stops waiting when
        shell script job-time has been reached.

        """
        # checks job every five minutes if job has started by checking
    any slurm files in directory (times out after 1 day)
        timeout = 86400/300
        attempts = 0
        fileFound = False
        print('entering first loop...')
        while attempts < timeout:
            # print(os.listdir())
            for file in os.listdir():
                if file.endswith('.out') and file.startswith('slurm'):
                    slurmFile = file
                    fileFound = True
                    break
            if fileFound:
                break
            # Wait 5 minutes before trying again.
            time.sleep(300) # change to 300
            attempts += 1
            # time out, job still in queue after 24 hours
            if attempts == timeout:
                sys.exit()
        print('rotor script is running')
        # extracts job time from shell scirpt
        with open('run_all_gjfs.sh', 'r') as shellScript:
            shellLines = shellScript.readlines()
            shellScript.close()
        for line in shellLines:
            if 'time' in line:
                jobTimeLine = line
                break
        hrs, mins, secs = [int(time) for time in jobTimeLine.split('=')
    [-1].split(':')]
        timeout = round((hrs*3600)+(mins*60)+(secs)/600)

        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
     deletes unnecessary files)
62          # call rotor code
63          for logfile in os.listdir():
64              if logfile.endswith('.log'):
65                  gjfFile = get_input_gjf.main(logfile) # rename and save
     original .gjf somewhere else
66
67          rotor_dihedrals, rotors = get_rotors.get_rotors_from_rotorFile(
    rotorFile='rotors_found.txt')
68
69          if len(rotors) != 0:
70              print('script called rotor script')
71              get_rotors.main(rotorFile='rotors_found.txt')
72
73              # starts rotor jobs
74              # finds directories ending in '_E'>'D#', enters and runs
    the local 'run_all_gjfs_array.sh' file
75              base_dir = os.getcwd()
76              for fileName in os.listdir():
77                  # print(fileName)
78                  if 'Rotor' in fileName.split('_') and os.path.isdir(
    fileName):
79                      print('Rotor directory found!')
80                      print('Starting rotor jobs')
81                      os.chdir(f'{base_dir}/{fileName}')
82                      # inside molecule's Rotor_Files folder
83                      for file in os.listdir():
84                          if file.startswith('D') and os.path.isdir(file)
    :
85                              os.chdir(f'{file}')
86                              cmd = 'sbatch run_all_gjfs_array.sh'
87                              os.system(cmd)
```

```
                            os.chdir('./..')
                    os.chdir(base_dir)

            print('Starting startSearchLowConf.py')
            startSearchLowConf.wait_for_rotors()

        else:
            print('Starting startHighEnergyCalcs.py')
            startHighEnergyCalcs.runHighECalcs()


if __name__ == '__main__':
    wait_for_file()
```

D.5 startHighEnergyCalcs.py

```
import os, numpy as np, get_input_gjf,shutil, re
from get_geometry import  get_gView_format

def runHighECalcs():

    baseDir = os.getcwd()

    for file in os.listdir():
        if file.endswith('.log'):
            m062xLogFile = file
        if file.endswith('.chk'):
            m062xChkFile = file


    EFileLog = m062xLogFile.split('.')[0] + '_E.' + m062xLogFile.split('.')[-1]
    EFileChk = m062xChkFile.split('.')[0] + '_E.' + m062xChkFile.split('.')[-1]
    E1FileChk = m062xChkFile.split('.')[0] + '_E1.' + m062xChkFile.split('.')[-1]
    E1FileLog = m062xLogFile.split('.')[0] + '_E1.' + m062xLogFile.split('.')[-1]


    os.makedirs(f'HighEnergyCalcs')
    # highCalcsDir = os.makedirs(f'HighEnergyCalcs/{EFileLog}')
    # highCalcsDir = os.makedirs(f'HighEnergyCalcs/{EFileChk}')
    # highCalcsDir = os.makedirs(f'HighEnergyCalcs/{E1FileLog}')
    # highCalcsDir = os.makedirs(f'HighEnergyCalcs/{E1FileChk}')

    shutil.copy(f'{m062xLogFile}',f'HighEnergyCalcs/{EFileLog}')
    shutil.copy(f'{m062xChkFile}',f'HighEnergyCalcs/{EFileChk}')
```

```
    shutil.copy(f'{m062xLogFile}',f'HighEnergyCalcs/{E1FileLog}')
    shutil.copy(f'{m062xChkFile}',f'HighEnergyCalcs/{E1FileChk}')
    shutil.copy('newzmat.sh', f'HighEnergyCalcs/newzmat.sh')
    shutil.copy('get_input_gjf.py', f'HighEnergyCalcs/get_input_gjf.py')
    shutil.copy('get_geometry.py', f'HighEnergyCalcs/get_geometry.py')

    print(baseDir)

    higherCalcsPath = baseDir + '//HighEnergyCalcs'

    print(higherCalcsPath)

    os.chdir(higherCalcsPath)

    get_input_gjf.main(EFileLog,job='E')
    get_input_gjf.main(E1FileLog,job='E1')

    os.remove(EFileLog)
    os.remove(EFileChk)
    os.remove(E1FileLog)
    os.remove(E1FileChk)

    files=os.listdir(higherCalcsPath)
    print(files)
    for fileName in files:
        if fileName.endswith('.gjf'):
            file = open(fileName, 'r')
            flines = file.read()
            file.close()
            if 'Variables' in flines:
                get_gView_format(fileName)

    print(baseDir)
    print(os.getcwd())

    shutil.copy(f'{baseDir}/run_all_gjfs.sh', f'{higherCalcsPath}/run_all_gjfs.sh')

    # file = os.listdir(higherCalcsPath)

    # with open('run_all_gjf.sh', 'r') as sfile:
    #     slines = sfile.readlines()
    #     sfile.close()

    # keySearch = re.compile('job-name')
    # lineNum = 0
    # while lineNum < len(slines):
```

```
    #     line = slines[lineNum]
    #     strLine = str.strip(line)
    #     if keySearch.search(strLine):
    #         slines[lineNum] = strLine + 'E'
    #     lineNum += 1

    # with open('run_all_gjf.sh', 'w') as sfile:
    #     sfile.write(slines)
    #     sfile.close

    cmd = 'sbatch run_all_gjfs.sh'
    os.system(cmd)

if __name__ == '__main__':
    runHighECalcs()
```

D.6 startSearchLowConf.py

```
import searchLowConf, time, os, sys, numpy as np

def wait_for_rotors():
        """
        Wait for 'Finished' keyword in slurm file to fire. Checking
        in 10 minute intervals. First checks if job has started

        This method fires the search for lower conformer once it
    detects that the
        all 36 point of every rotor of the job has completed. Script
    stops waiting when
        shell script job-time has been reached.

        """
        # checks job every five minutes if job has started by checking
    any slurm files in directory (times out after 1 day)
        baseDir = os.getcwd()
        print(baseDir)
        timeout = 86400/300
        attempts = 0
        slurmCount = False
        print('entering first loop...')
        while attempts < timeout:
            # print(os.listdir())
            for file in os.listdir():
                # print(file)
                # rotrDir = ''
                # print(file.split())
                if 'Rotor' in file.split('_'):
                    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 scirpt
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
```

```
        finishFound = False
        while attempts < timeout:
            index = 0
            for dihedralDir in os.listdir(rotrDir):
                dihedralPath = os.path.join(rotrDir, dihedralDir)
                # count = 0
                for slurmFile in allSlurms[index]:
                    # print(slurmFile)
                    os.chdir(dihedralPath)
                    # print(dihedralPath)
                    with open(slurmFile, 'r') as sFile:
                        slurmFile_text = sFile.read()
                        sFile.close()
                        if 'Finished' in slurmFile_text:
                            finishFound = True
                        else:
                            finishFound = False
                            break
                    # count += 1
                # print(count)
                index += 1
                if finishFound == False:
                    break
            if finishFound:
                break

            os.chdir(baseDir)

            # Wait 10 minutes before trying again.
            time.sleep(600) # change to 600
            attempts += 1
            # time out, job didn't finish in time
            if attempts == timeout:
                sys.exit()

        print('script detected rotor jobs are finished')
        os.chdir(baseDir)
        # print(os.getcwd())
        searchLowConf.low_conf()

if __name__ == '__main__':
    wait_for_rotors()
```

Appendix E

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

E.1 DPM PIMS

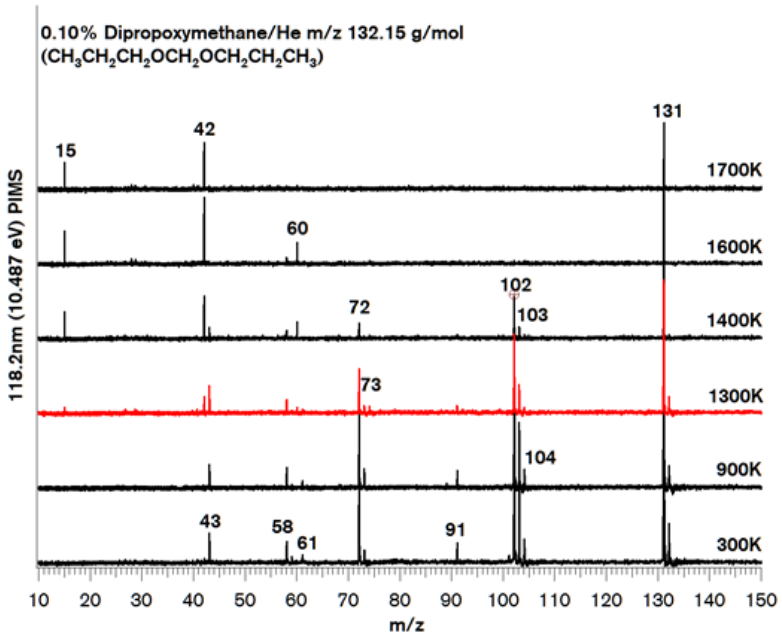

Fig. E.1 PIMS of 0.1% dipropoxymethane (P-1-P) in He in the micro reactor at 200 SCCM heated from 300 to 1700 L and ionized by 118.2 nm (10.487 eV) photons.

E.2 DEM

```
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
PressureList[atm]                        0.00001 0.001  0.01  0.1  3  10
     100.
!PressureList[bar]                        1.
EnergyStepOverTemperature   .2
ExcessEnergyOverTemperature   30
ModelEnergyLimit[kcal/mol]    400
CalculationMethod     direct
!CalculationMethod      low-eigenvalue !direct
WellCutoff        10
ChemicalEigenvalueMax     0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]      200  ! He
      Power                          .85
      ExponentCutoff                   15
    End
  CollisionFrequency
    LennardJones
        Epsilons[1/cm]            94.87   280.62  !Ar and CCOCOCC
  Sigmas[angstrom]    3.33    6.14
  Masses[amu]                     39.88   104.15
    End
  Well     W1 # CCOCOCC
    Species
    RRHO
      Geometry[angstrom]      19
        C                  2.87151100   -0.91974300   -0.14425500
   C                  1.71189100   -0.19908400    0.50247500
   O                  1.05453600    0.56382200   -0.49541600
   C                  0.00000000    1.32951900   -0.00000200
   O                 -1.05453600    0.56382200    0.49541400
   C                 -1.71188700   -0.19909100   -0.50247400
   C                 -2.87151500   -0.91973900    0.14425600
   H                  2.51206000   -1.58102500   -0.93147800
   H                  3.40769500   -1.51629500    0.59281000
   H                  3.56341500   -0.20463800   -0.58652600
   H                  1.01048100   -0.90733200    0.95176300
```

```
H                  2.06068700    0.47083600    1.29777000
H                  0.33204200    1.95229600    0.83602200
H                 -0.33204400    1.95229200   -0.83602800
H                 -2.06067500    0.47082300   -1.29777700
H                 -1.01047700   -0.90734600   -0.95174900
H                 -3.56341900   -0.20462600    0.58651500
H                 -3.40769600   -1.51629700   -0.59280600
H                 -2.51207200   -1.58101400    0.93148900
   Core                RigidRotor
     SymmetryFactor                          2
   End
   Rotor                      Hindered
       Group                        17 18 19
       Axis                         7 6
       Symmetry                     3
       Potential[kcal/mol]   2
 0. 3.05
   End
   Rotor                      Hindered
       Group                        7 15 16
       Axis                         6 5
       Symmetry                     1
       Potential[kcal/mol]          6
  0. 1.58  1.01 4.77 0.63 1.31
   End
   Rotor                      Hindered
        Group                   6
        Axis                 5 4
        Symmetry          1
        Potential[kcal/mol]  6
     0. 7.31 3.17 3.46 2.66 3.84
    End
    Rotor                       Hindered
     Group          2
     Axis           3 4
     Symmetry            1
     Potential[kcal/mol] 6
 0. 7.31 3.17 3.46 2.67 3.84
    End
    Rotor                       Hindered
           Group 1 11 12
           Axis  2 3
           Symmetry  1
           Potential[kcal/mol] 6
           0. 1.58 1.01 4.77 0.63 1.31
    End
    Rotor                       Hindered
     Group 8 9 10
```

```
       Axis  1 2
       Symmetry  3
       Potential[kcal/mol] 2
       0. 3.05
      End
      Frequencies[1/cm]      45
      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
      !50.73 57.89 74.4  176.16  235.73  258.31! Torsions
     ZeroEnergy[kcal/mol]          0
     ElectronicLevels[1/cm]      1
0 1
  End
End
Bimolecular   P1  # CCOC[O] + [CH2]C
 Fragment  CCOC[O]
    RRHO
Geometry[angstrom]  12
 O                 -0.03684500    0.62337700   -0.21626000
 C                  0.83914400   -0.35064900    0.32991000
 C                  2.23651200   -0.05572200   -0.16008200
 C                 -1.35876500    0.45047100    0.16929400
 H                 -1.92132100    1.31885200   -0.20159800
 H                 -1.45570300    0.44913100    1.27567500
 H                  0.79058300   -0.30540700    1.42548100
 O                 -1.96169300   -0.67772900   -0.24643500
 H                  0.51758500   -1.34807300    0.02010500
 H                  2.54400900    0.94186600    0.14942500
 H                  2.94105400   -0.78092800    0.24486200
 H                  2.27074200   -0.10522500   -1.24712500
Core                 RigidRotor
      SymmetryFactor                          1
    End
    Rotor                      Hindered
        Group                       5 6 8
        Axis                        4 1
        Symmetry                    1
        Potential[kcal/mol]   6
  0. 2.32 0.0 3.36 2.24 3.36
    End
    Rotor                      Hindered
        Group                       4
        Axis                        1 2
        Symmetry                    1
```

```
          Potential[kcal/mol]    8
  0. 1.74 0.99 4.51 1.166 1.178 1.072 1.41
      End
      Rotor                      Hindered
    Group                        10 11 12
    Axis                         3 2
    Symmetry                3
    Potential[kcal/mol] 2
        0. 3.088
       End
       Frequencies[1/cm]       27
       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
!70.21  146.84  248.71! Torsions
  ZeroEnergy[kcal/mol]      0.0
  ElectronicLevels[1/cm]      1
    0 2
      End
     Fragment  [CH2]C
            RRHO
     Geometry[angstrom]  7
      C                 -0.69222800    0.00000000   -0.00057700
      C                  0.79186100    0.00000000   -0.02396000
      H                 -1.10189400    0.88331200   -0.49094000
      H                 -1.08426500    0.00001300    1.02462600
      H                 -1.10189400   -0.88332500   -0.49091800
      H                  1.34512800    0.92312000    0.05222700
      H                  1.34512900   -0.92312000    0.05222700
    Core                 RigidRotor
        SymmetryFactor                          1
      End
      Rotor                      Hindered
          Group                       3 4 5
          Axis                        1 2
          Symmetry                    3
          Potential[kcal/mol]   4
    0. 0.07 0.0 0.08
      End
      Frequencies[1/cm]       14
      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
     !125.25! Torsions
     ZeroEnergy[kcal/mol]          0
      ElectronicLevels[1/cm]      1
        0 2
          End
```

```
        GroundEnergy[kcal/mol]    84.1
     End
     Bimolecular    P2  # CCO[CH2] + CC[O]
     Fragment  CCO[CH2]
           RRHO
     Geometry[angstrom]  11
      O                 -0.58408900   -0.46219100    0.00087000
      C                  0.44314400    0.51637400    0.04241600
      C                  1.77563600   -0.18931500   -0.02763400
      C                 -1.83740900    0.03341200    0.03858200
      H                 -2.60953400   -0.71258000   -0.05571200
      H                 -1.99460100    1.04964700   -0.30213200
      H                  0.31449400    1.20272600   -0.80109500
      H                  0.34725400    1.09386100    0.96636500
      H                  1.85215400   -0.76363100   -0.94943900
      H                  2.58809100    0.53547900    0.00078500
      H                  1.88662600   -0.87079400    0.81408600
      Core                 RigidRotor
        SymmetryFactor                          1
      End
      Rotor                      Hindered
          Group                        5 6
          Axis                         4 1
          Symmetry                     2
          Potential[kcal/mol]          2
    0. 5.5
    End
    Rotor                      Hindered
              Group                          4
              Axis                           1 2
              Symmetry                       1
              Potential[kcal/mol]            6
        0. 1.51 0.60 4.08 0.15 1.5
    End
    Rotor                      Hindered
                  Group                          9 10 11
                  Axis                           3 2
                  Symmetry                       3
                  Potential[kcal/mol]            2
            0. 3.0
    End
    Frequencies[1/cm]       24
       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
    !99.2 239.29 290.05! Torsions
    ZeroEnergy[kcal/mol]          0
      ElectronicLevels[1/cm]      1
```

```
      0 2
        End
   Fragment  CC[O]
       RRHO
   Geometry[angstrom]  8
C                  0.99339700   -0.58703400    0.00000000
C                  0.00000000    0.58827100    0.00000000
O                 -1.24967300    0.02452200    0.00000000
H                  2.00644500   -0.18921500    0.00000000
H                  0.84823600   -1.20028500    0.88617500
H                  0.84823600   -1.20028500   -0.88617500
H                  0.16704400    1.19309300    0.89813400
H                  0.16704400    1.19309300   -0.89813400
   Core                 RigidRotor
      SymmetryFactor                          1
    End
    Rotor                       Hindered
              Group                         4 5 6
              Axis                          1 2
              Symmetry                      3
              Potential[kcal/mol]           2
         0. 2.34
  End
  Frequencies[1/cm]       17
      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
  !244.47! Torsions
  ZeroEnergy[kcal/mol]              0
        ElectronicLevels[1/cm]      1
          0 2
        End
        GroundEnergy[kcal/mol]      92.7
   End
   Bimolecular    P3     # CCOCO[CH2] + [CH3]
   Fragment  CCOCO[CH2]
             RRHO
   Geometry[angstrom]  15
    C                  2.04184100    0.97940900   -0.23650800
    O                  1.63963800   -0.06987200    0.52169000
    C                  0.81124200   -0.99413900   -0.15113800
    O                 -0.38579500   -0.43724000   -0.56930300
    C                 -1.22597700   -0.02415200    0.49942400
    C                 -2.52515300    0.46978300   -0.09104300
    H                  2.63690400    1.70068700    0.29810600
    H                  1.43218100    1.25645300   -1.08472300
    H                  1.31526500   -1.35717500   -1.04817800
    H                  0.64903100   -1.80201100    0.56648700
```

```
     H                  -1.39588500   -0.87369500    1.17114100
     H                  -0.73109200    0.76294000    1.07386200
     H                  -3.00867800   -0.32169600   -0.66138000
     H                  -3.20073300    0.79539500    0.69883400
     H                  -2.33945300    1.31059200   -0.75764600
     Core                  RigidRotor
             SymmetryFactor                          1
     End
     Rotor                     Hindered
       Group                       13 14 15
       Axis                        6 5
       Symmetry                    3
       Potential[kcal/mol]         2
0. 3.05
  End
  Rotor                     Hindered
  Group                       6 11 12
  Axis                        5 4
  Symmetry                    1
  Potential[kcal/mol]         6
  0. 1.627 1.045 4.613 0.766 1.227
  End
  Rotor                     Hindered
      Group                       5
      Axis                        4 3
      Symmetry                    1
      Potential[kcal/mol]         6
  0. 6.906 2.099 4.464 3.800 4.790
  End
  Rotor                     Hindered
  Group                       1
  Axis                        2 3
  Symmetry                    1
  Potential[kcal/mol]         6
  0. 4.275 2.508 3.573 3.149 3.995
  End
  Rotor                     Hindered
      Group                       7 8
      Axis                        1 2
      Symmetry                    2
      Potential[kcal/mol]         2
0. 5.2
  End
  Frequencies[1/cm]       34
     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
```

```
   1536.64 3024.66 3057.19 3073.81 3076.5  3115.41 3150.44 3152.21
   3161.74 3302.14
    !57.06  80.74 172 241.97  273.48! Torsions
        ZeroEnergy[kcal/mol]              0
              ElectronicLevels[1/cm]      1
                0 2
          End
     Fragment [CH3]
           RRHO
      Geometry[angstrom]  4
            C                  0.00000000    0.00000000    0.00000000
            H                  0.00000000    0.00000000    1.07652900
            H                  0.93230200    0.00000000   -0.53826500
            H                 -0.93230200   -0.00000000   -0.53826500
      Core  RigidRotor
        SymmetryFactor  6
      End
      Frequencies[1/cm] 6
             409.94  1411.49  1412.56  3141.77  3320.20  3321.01
   !! torsion
        ZeroEnergy[kcal/mol]      0
        ElectronicLevels[1/cm]      1
        0 2
      End
      GroundEnergy[kcal/mol]            85.3
   End
   Bimolecular    P4     # CCO[CH]OCC + [H]
   Fragment H
          Atom
            Mass[amu]   1
            ElectronicLevels[1/cm]      1
               0     2
   End
   Fragment  CCO[CH]OCC
      RRHO
   Geometry[angstrom]  18
    C                  1.85123800    1.36692300   -0.11393900
    C                  1.96689700   -0.02829500    0.46760200
    O                  1.35369200   -1.01369700   -0.36424900
    C                  0.03415500   -0.85685700   -0.58928400
    O                 -0.69614700   -0.61826900    0.54142300
    C                 -2.06451100   -0.34257700    0.28446300
    C                 -2.27184300    1.06738700   -0.23360400
    H                  2.24378200    1.38817000   -1.12996300
    H                  2.41909800    2.06979700    0.49527800
    H                  0.81162300    1.69137600   -0.13652000
    H                  3.00777400   -0.33711600    0.53429500
    H                  1.52760000   -0.07194000    1.46460200
```

```
     H                  -0.36385800   -1.61659300   -1.26056200
     H                  -2.45580700   -1.07882900   -0.42562200
     H                  -2.57592300   -0.48826100    1.23398200
     H                  -1.74442300    1.20754600   -1.17653400
     H                  -3.33229600    1.26016800   -0.39476900
     H                  -1.89354200    1.79191800    0.48699300
     Core                  RigidRotor
     SymmetryFactor                          2
     End
           Rotor                       Hindered
             Group                         16 17 18
             Axis                          7 6
             Symmetry                      3
             Potential[kcal/mol]           2
       0. 3.025
  End
Rotor                       Hindered
      Group                          7 14 15
      Axis                           6 5
      Symmetry                       1
      Potential[kcal/mol]            6
0. 4.23 0.926 1.612 0.0435 1.442
  End
  Rotor                       Hindered
      Group                          6
      Axis                           5 4
      Symmetry                       1
      Potential[kcal/mol]            4
      0. 2.49 1.964 9.0
  End
  Rotor                       Hindered
          Group                            2
          Axis                             3 4
          Symmetry                         1
          Potential[kcal/mol]              4
  0. 2.49 1.964 9.0
  End
  Rotor                       Hindered
            Group                            1 11 12
      Axis                           2 3
      Symmetry                       1
      Potential[kcal/mol]            6
0. 4.23 0.926 1.612 0.0435 1.442
  End
  Rotor                       Hindered
            Group                            8 9 10
          Axis                             1 2
          Symmetry                         3
```

```
            Potential[kcal/mol]          2
        0. 3.025
    End
    Frequencies[1/cm]        42
       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
    !54.18 70.62 121.24 175.73  222.29  268.03!Torsions
    ZeroEnergy[kcal/mol]               0
            ElectronicLevels[1/cm]       1
            0 2
     End
     GroundEnergy[kcal/mol]                 97.3
    End
    Bimolecular    P5     # CCOCO[CH]C + [H]
    Fragment H
                Atom
                  Mass[amu]   1
                  ElectronicLevels[1/cm]       1
                     0     2
         End
    Fragment  CCOCO[CH]C
    RRHO
    Geometry[angstrom]  18
     C                 -1.75842200   -0.13403300   -0.46781200
     O                 -1.09509700    0.60904400    0.46548700
     C                 -0.01330100    1.35501300   -0.04090700
     C                 -2.85410500   -0.96514700    0.08007400
     O                  1.01893100    0.55641700   -0.51103000
     C                  1.65649100   -0.20390200    0.50439200
     C                  2.80557300   -0.95567500   -0.12445000
     H                 -2.47846600   -1.76188100    0.73417500
     H                 -3.41611000   -1.43101500   -0.72713700
     H                 -3.53683600   -0.35551300    0.67407300
     H                 -1.17785600   -0.44495900   -1.32790800
     H                 -0.34255100    1.96285200   -0.88525400
     H                  0.31673100    1.98162600    0.79154500
     H                  2.01218200    0.47292700    1.29023000
     H                  0.93781500   -0.89170300    0.95729300
     H                  3.51379600   -0.26075000   -0.57288800
     H                  3.32540300   -1.55052000    0.62546900
     H                  2.43780800   -1.62229200   -0.90303500
     Core                 RigidRotor
     SymmetryFactor                          1
     End
```

```
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
```

```
   3021.82 3055.1  3073.03 3075.09 3088.73 3113.75 3146.3  3149.87
   3151.12 3182.77
     !62.09 81.45 159.44  197.19  241.07  261.41!Torsions
     ZeroEnergy[kcal/mol]                 0
               ElectronicLevels[1/cm]      1
                 0 2
           End
           GroundEnergy[kcal/mol]               94.6
     End
     Bimolecular    P6     # CCOCOC[CH2] + [H]
          Fragment  H
                      Atom
                        Mass[amu]   1
                        ElectronicLevels[1/cm]      1
                           0     2
          End
     Fragment  CCOCOC[CH2]
         RRHO
     Geometry[angstrom]  18
      C                  2.94233500   -0.67034400   -0.14761700
      C                  1.78742600    0.14457100    0.38575300
      O                  0.80817900    0.24343000   -0.63524800
      C                 -0.28223800    1.03652700   -0.28368300
      O                 -1.03682300    0.49569300    0.76284600
      C                 -1.71162100   -0.70408300    0.40845000
      C                 -2.86279900   -0.45941400   -0.49590600
      H                  2.60356500   -1.66748400   -0.42538500
      H                  3.72126300   -0.76622200    0.60785300
      H                  3.36704400   -0.19434500   -1.03009700
      H                  1.35335100   -0.32249500    1.27350700
      H                  2.11614900    1.15201300    0.66825800
      H                  0.04724600    2.01712500    0.07145300
      H                 -0.88407800    1.13637100   -1.19045600
      H                 -1.00929200   -1.41413700   -0.03811800
      H                 -2.04480500   -1.13149900    1.36035400
      H                 -3.47587800    0.41624000   -0.34190400
      H                 -3.20403400   -1.22209400   -1.17822300
      Core                 RigidRotor
      SymmetryFactor                          1
      End
      Rotor                      Hindered
              Group                          8 9 10
              Axis                           1 2
              Symmetry                       3
              Potential[kcal/mol]            2
        0. 3.048
    End
    Rotor                      Hindered
```

```
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
```

```
Bimolecular                P7     # CCOCO + C=C
Fragment  CCOCO
        RRHO
     Geometry[angstrom]  13
      O                 -1.92826300   -0.68196600   -0.07973400
      O                  0.01015400    0.58970200   -0.30216800
      C                  0.89304700   -0.25879500    0.41481000
      C                  2.27188600   -0.12033700   -0.18641800
      C                 -1.30056300    0.54685900    0.16433400
      H                 -1.97484400   -0.80731600   -1.03181800
      H                 -1.81992400    1.36846600   -0.33161200
      H                 -1.33439300    0.68135600    1.24941000
      H                  0.89594800    0.03666700    1.47086500
      H                  0.54134800   -1.29155700    0.35888500
      H                  2.60988900    0.91307300   -0.12640900
      H                  2.98309100   -0.75247700    0.34381200
      H                  2.25753200   -0.41646200   -1.23427500
      Core                 RigidRotor
     SymmetryFactor                          1
      End
      Rotor                      Hindered
            Group                         11 12 13
            Axis                          4 3
            Symmetry                      3
            Potential[kcal/mol]           2
       0. 3.068
      End
      Rotor                      Hindered
       Group                         4 9 10
       Axis                          3 2
       Symmetry                      1
       Potential[kcal/mol]           6
            0. 1.515 0.886 4.604 0.988 1.276
      End
      Rotor                      Hindered
            Group                         1 7 8
            Axis                          5 2
            Symmetry                      1
            Potential[kcal/mol]           6
               0. 6.542 1.952 4.165 2.665 3.863
      End
      Rotor                      Hindered
       Group                         6
       Axis                          1 5
       Symmetry                      1
       Potential[kcal/mol]           4
     0. 3.883 1.92 3.614
      End
```

```
          Frequencies[1/cm]       29
          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
          !61.49 158.34 250.95 289.95! Torsions
        ZeroEnergy[kcal/mol]      0
        ElectronicLevels[1/cm]      1
        0 1
                  End
          Fragment  C=C
            RRHO
     Geometry[angstrom]  6
      C                  0.00000000    0.00000000    0.00000000
    H                   0.00000000    0.00000000    1.08216909
    H                   0.96588500    0.00000000   -0.48801240
    C                  -1.12558139   -0.00000000   -0.69239269
    H                  -1.12558139   -0.00000000   -1.77456178
        H                  -2.09146639   -0.00000000   -0.20438028
        Core   RigidRotor
     SymmetryFactor  2
        End
        Frequencies[1/cm]       12
        829.14 990.4 1002.92 1070.96 1243.08 1388.11 1473.77 1718.56
  3159.71 3175.83 3235.53 3261.92
        !!torsions
     ZeroEnergy[kcal/mol]          0
     ElectronicLevels[1/cm]      1
       0 1
          End
                 GroundEnergy[kcal/mol]            15.2
    End
    Bimolecular               P8     # CCOCC  + CH2O
    Fragment  CCOCC
      RRHO
 Geometry[angstrom]  15
  C                -2.36671500    0.40939100    0.00000000
  C                -1.17240100   -0.51689000    0.00000000
  O                 0.00000000    0.26250200    0.00000000
  C                 1.17240100   -0.51689000    0.00000000
  C                 2.36671500    0.40939100    0.00000000
  H                -2.34819700    1.04628100    0.88302400
  H                -3.29422700   -0.16193900    0.00000000
  H                -2.34819700    1.04628100   -0.88302400
  H                -1.18641200   -1.16781900    0.88393000
  H                -1.18641200   -1.16781900   -0.88392900
  H                 1.18641200   -1.16781900    0.88392900
  H                 1.18641200   -1.16781900   -0.88393000
```

```
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
```

```
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
```

```
   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
   !232.92 271.7! Torsions
   ZeroEnergy[kcal/mol]     0
      ElectronicLevels[1/cm]      1
        0 1
              End
  Fragment  CCO[[C]]
          RRHO
  Geometry[angstrom]  10
        C       0.2962234158    0.2799519783     0.0252389473
        O       0.1446716238   -0.1255305641     1.2720513805
        C       1.2944481399    0.0022054547     2.1303302756
        C       1.5788506213    1.4518618524     2.4536649072
        H       0.5351832549   -0.3751190301    -0.8093652333
        H       1.0437077815   -0.5660668847     3.0234590174
        H       2.1470686136   -0.4700165085     1.6370309882
        H       0.7134709961    1.9097143961     2.930397192
        H       2.431190729     1.5264741833     3.128390386
        H       1.8071838203    2.0032381221     1.5419321275
      Core                 RigidRotor
        SymmetryFactor                          1
      End
      Rotor                      Hindered
          Group                        8 9 10
          Axis                         4 3
          Symmetry                     3
          Potential[kcal/mol]          2
    0. 3.14
    End
    Rotor                       Hindered
                Group                        4 6 7
                Axis                         3 2
                Symmetry                     1
                Potential[kcal/mol]          6
           0. 0.59 0. 2.41 2.11 2.42
    End
    Frequencies[1/cm]       22
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
    !99.2 239.29 290.05! Torsions
    ZeroEnergy[kcal/mol]      0.0
      ElectronicLevels[1/cm]      1
        0 2
          End
      GroundEnergy[kcal/mol]      67.0
```

```
    End
Bimolecular                P10     # CCOH + CH2O + C=C approx as: CCOH
   + CH2O_C=C
    Fragment  CCOH
      RRHO
 Geometry[angstrom]  9
C                  0.08463800    0.54848000    0.00000000
H                  0.13973200    1.19166300   -0.88440500
H                  0.13973300    1.19166400    0.88440400
O                  1.14287200   -0.39509100   -0.00000100
H                  1.97961300    0.07336700    0.00000500
C                 -1.21571800   -0.22196200    0.00000000
H                 -1.27446800   -0.85670800    0.88299900
H                 -2.06664400    0.45834700   -0.00000100
H                 -1.27446600   -0.85671000   -0.88299700
  Core                 RigidRotor
         SymmetryFactor                          1
  End
  Rotor                     Hindered
       Group                      5
       Axis                       4 1
       Symmetry                   3
       Potential[kcal/mol]        2
 0. 1.12
  End
  Rotor                     Hindered
       Group                      7 8 9
       Axis                       6 1
       Symmetry                   3
       Potential[kcal/mol]        2
 0. 3.21
  End
  Frequencies[1/cm]       19
   421.70 825.30 920.25 1051.13 1139.97 1187.28 1273.09 1310.40
  1403.39 1463.29 1487.29
   1505.39 1539.06 3021.47 3052.30 3071.36 3148.12 3149.94 3901.98
  ! 232.91 271.69 ! Torsions
  ZeroEnergy[kcal/mol]     0
     ElectronicLevels[1/cm]      1
       0 1
 End
 Fragment  CH2O_C=C
          RRHO
 Geometry[angstrom]  10
C                 -2.22308600   -0.38804100    0.00000500
H                 -2.60698400   -0.80604300   -0.92177300
H                 -2.60697500   -0.80603000    0.92179200
C                  1.76407000   -0.62797700   -0.00000300
```

```
H                   2.68985700    -1.22874900     0.00000400
H                   0.80898100    -1.17966000    -0.00001600
C                  -1.33377900     0.59096200    -0.00000600
H                  -0.94409000     1.01086600     0.91791700
H                  -0.94409800     1.01085300    -0.91793800
O                   1.79501000     0.56863800     0.00000500
     Core                  RigidRotor
       SymmetryFactor                          1
     End
   Frequencies[1/cm]       24
   30.31 30.38 92.69 108.25 125.25 135.20 823.54 994.94 1017.54
  1075.60 1223.33 1238.35
   1282.56 1384.01 1471.90 1539.71 1713.08 1867.69 2945.393023.40
  3159.41 3177.82 3234.34 3262.56
   !  ! Torsions
   ZeroEnergy[kcal/mol]          0
     ElectronicLevels[1/cm]      1
       0 1
         End
     GroundEnergy[kcal/mol]      29.4
    End
    Barrier     B1   W1   P1    # CCOC[O] + [CH2]C = CCOCOCC
           RRHO
            Stoichiometry C5H12O2
             Core     PhaseSpaceTheory
          FragmentGeometry[angstrom]  12
       O                 -0.03684500     0.62337700    -0.21626000
       C                  0.83914400    -0.35064900     0.32991000
       C                  2.23651200    -0.05572200    -0.16008200
       C                 -1.35876500     0.45047100     0.16929400
       H                 -1.92132100     1.31885200    -0.20159800
       H                 -1.45570300     0.44913100     1.27567500
       H                  0.79058300    -0.30540700     1.42548100
       O                 -1.96169300    -0.67772900    -0.24643500
       H                  0.51758500    -1.34807300     0.02010500
       H                  2.54400900     0.94186600     0.14942500
       H                  2.94105400    -0.78092800     0.24486200
       H                  2.27074200    -0.10522500    -1.24712500
         FragmentGeometry[angstrom]  7
          C                 -0.69222800     0.00000000    -0.00057700
          C                  0.79186100     0.00000000    -0.02396000
          H                 -1.10189400     0.88331200    -0.49094000
          H                 -1.08426500     0.00001300     1.02462600
          H                 -1.10189400    -0.88332500    -0.49091800
          H                  1.34512800     0.92312000     0.05222700
          H                  1.34512900    -0.92312000     0.05222700
          SymmetryFactor               1
                PotentialPrefactor[au]       2.96  #3 4 4.5 4.8 5 5.5
```

```
                PotentialPowerExponent       6.63
        End
        Rotor                       Hindered
        Geometry[angstrom]  12
          O                  -0.03684500    0.62337700   -0.21626000
          C                   0.83914400   -0.35064900    0.32991000
          C                   2.23651200   -0.05572200   -0.16008200
          C                  -1.35876500    0.45047100    0.16929400
          H                  -1.92132100    1.31885200   -0.20159800
          H                  -1.45570300    0.44913100    1.27567500
          H                   0.79058300   -0.30540700    1.42548100
          O                  -1.96169300   -0.67772900   -0.24643500
          H                   0.51758500   -1.34807300    0.02010500
          H                   2.54400900    0.94186600    0.14942500
          H                   2.94105400   -0.78092800    0.24486200
                    H                  2.27074200   -0.10522500
-1.24712500
            Group                       5 6 8
            Axis                        4 1
            Symmetry                    1
            Potential[kcal/mol]   6
     0. 2.32 0.0 3.36 2.24 3.36
        End
        Rotor                       Hindered
        Geometry[angstrom]  12
          O                  -0.03684500    0.62337700   -0.21626000
          C                   0.83914400   -0.35064900    0.32991000
          C                   2.23651200   -0.05572200   -0.16008200
          C                  -1.35876500    0.45047100    0.16929400
          H                  -1.92132100    1.31885200   -0.20159800
          H                  -1.45570300    0.44913100    1.27567500
          H                   0.79058300   -0.30540700    1.42548100
          O                  -1.96169300   -0.67772900   -0.24643500
          H                   0.51758500   -1.34807300    0.02010500
          H                   2.54400900    0.94186600    0.14942500
          H                   2.94105400   -0.78092800    0.24486200
               H                  2.27074200   -0.10522500
-1.24712500
            Group                       4
            Axis                        1 2
            Symmetry                    1
            Potential[kcal/mol]    8
   0. 1.74 0.99 4.51 1.166 1.178 1.072 1.41
        End
        Rotor                       Hindered
        Geometry[angstrom]  12
          O                  -0.03684500    0.62337700   -0.21626000
          C                   0.83914400   -0.35064900    0.32991000
```

```
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
```

```
              ElectronicLevels[1/cm]         1
                   0    2
      End
      Barrier     B2   W1   P2    # CCO[CH2] + CC[O] = CCOCOCC
            RRHO
             Stoichiometry C5H12O2
            Core     PhaseSpaceTheory
            FragmentGeometry[angstrom]  11
            O                 -0.58408900   -0.46219100    0.00087000
            C                  0.44314400    0.51637400    0.04241600
            C                  1.77563600   -0.18931500   -0.02763400
            C                 -1.83740900    0.03341200    0.03858200
            H                 -2.60953400   -0.71258000   -0.05571200
            H                 -1.99460100    1.04964700   -0.30213200
            H                  0.31449400    1.20272600   -0.80109500
            H                  0.34725400    1.09386100    0.96636500
            H                  1.85215400   -0.76363100   -0.94943900
            H                  2.58809100    0.53547900    0.00078500
                  H                 1.88662600   -0.87079400
0.81408600
            FragmentGeometry[angstrom]  8
        C                  0.99339700   -0.58703400    0.00000000
        C                  0.00000000    0.58827100    0.00000000
        O                 -1.24967300    0.02452200    0.00000000
        H                  2.00644500   -0.18921500    0.00000000
        H                  0.84823600   -1.20028500    0.88617500
        H                  0.84823600   -1.20028500   -0.88617500
        H                  0.16704400    1.19309300    0.89813400
                H                 0.16704400    1.19309300
-0.89813400
                SymmetryFactor                  1
                 PotentialPrefactor[au]      3.91   #3 4 5 6
                PotentialPowerExponent       7.34
       End
       Rotor                      Hindered
       Geometry[angstrom]  11
              O                 -0.58408900   -0.46219100
0.00087000
              C                  0.44314400    0.51637400
0.04241600
              C                  1.77563600   -0.18931500
-0.02763400
              C                 -1.83740900    0.03341200
0.03858200
              H                 -2.60953400   -0.71258000
-0.05571200
              H                 -1.99460100    1.04964700
-0.30213200
```

```
                H                    0.31449400    1.20272600
-0.80109500
                H                    0.34725400    1.09386100
0.96636500
                H                    1.85215400   -0.76363100
-0.94943900
                H                    2.58809100    0.53547900
0.00078500
                  H                    1.88662600   -0.87079400
0.81408600
           Group                         5 6
           Axis                          4 1
           Symmetry                      2
           Potential[kcal/mol]           2
     0. 5.5
     End
     Rotor                       Hindered
     Geometry[angstrom]  11
                    O                   -0.58408900   -0.46219100
0.00087000
                    C                    0.44314400    0.51637400
0.04241600
                    C                    1.77563600   -0.18931500
-0.02763400
                    C                   -1.83740900    0.03341200
0.03858200
                    H                   -2.60953400   -0.71258000
-0.05571200
                    H                   -1.99460100    1.04964700
-0.30213200
                    H                    0.31449400    1.20272600
-0.80109500
                    H                    0.34725400    1.09386100
0.96636500
                    H                    1.85215400   -0.76363100
-0.94943900
                    H                    2.58809100    0.53547900
0.00078500
                  H                    1.88662600   -0.87079400
0.81408600
               Group                         4
               Axis                          1 2
               Symmetry                      1
               Potential[kcal/mol]           6
          0. 1.51 0.60 4.08 0.15 1.5
     End
     Rotor                       Hindered
     Geometry[angstrom]  11
```

```
                    O                  -0.58408900   -0.46219100
0.00087000
                    C                   0.44314400    0.51637400
0.04241600
                    C                   1.77563600   -0.18931500
-0.02763400
                    C                  -1.83740900    0.03341200
0.03858200
                    H                  -2.60953400   -0.71258000
-0.05571200
                    H                  -1.99460100    1.04964700
-0.30213200
                    H                   0.31449400    1.20272600
-0.80109500
                    H                   0.34725400    1.09386100
0.96636500
                    H                   1.85215400   -0.76363100
-0.94943900
                    H                   2.58809100    0.53547900
0.00078500
                  H                   1.88662600   -0.87079400
0.81408600
                    Group                        9 10 11
                    Axis                         3 2
                    Symmetry                     3
                    Potential[kcal/mol]          2
              0.  3.0
 End
 Rotor                       Hindered
 Geometry[angstrom]  8
             C                   0.99339700   -0.58703400
0.00000000
             C                   0.00000000    0.58827100
0.00000000
             O                  -1.24967300    0.02452200
0.00000000
             H                   2.00644500   -0.18921500
0.00000000
             H                   0.84823600   -1.20028500
0.88617500
             H                   0.84823600   -1.20028500
-0.88617500
             H                   0.16704400    1.19309300
0.89813400
                 H                   0.16704400    1.19309300
-0.89813400
                  Group                       4 5 6
                  Axis                        1 2
```

```
                    Symmetry                        3
                    Potential[kcal/mol]             2
              0. 2.34
    End
    Frequencies[1/cm]          41
          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
          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
          !99.2 239.29 290.05 244.47!
    ZeroEnergy[kcal/mol]                  92.7
         ElectronicLevels[1/cm]           1
              0    2
        End
     Barrier      B3   W1   P3    # CCOCO[CH2] + [CH3] = CCOCOCC
                  RRHO
                   Stoichiometry C5H12O2
              Core     PhaseSpaceTheory
              FragmentGeometry[angstrom]  15
              C                  2.04184100    0.97940900   -0.23650800
              O                  1.63963800   -0.06987200    0.52169000
              C                  0.81124200   -0.99413900   -0.15113800
              O                 -0.38579500   -0.43724000   -0.56930300
              C                 -1.22597700   -0.02415200    0.49942400
              C                 -2.52515300    0.46978300   -0.09104300
              H                  2.63690400    1.70068700    0.29810600
              H                  1.43218100    1.25645300   -1.08472300
              H                  1.31526500   -1.35717500   -1.04817800
              H                  0.64903100   -1.80201100    0.56648700
              H                 -1.39588500   -0.87369500    1.17114100
              H                 -0.73109200    0.76294000    1.07386200
              H                 -3.00867800   -0.32169600   -0.66138000
              H                 -3.20073300    0.79539500    0.69883400
              H                 -2.33945300    1.31059200   -0.75764600
               FragmentGeometry[angstrom] 4
      C                  0.00000000    0.00000000    0.00000000
      H                  0.00000000    0.00000000    1.07652900
      H                  0.93230200    0.00000000   -0.53826500
      H                 -0.93230200   -0.00000000   -0.53826500
               SymmetryFactor                          6
                   PotentialPrefactor[au]       4.68  #0.2 0.3
                   PotentialPowerExponent       6.31
         End
    Rotor                      Hindered
    Geometry[angstrom]  15
```

```
                C                     2.04184100    0.97940900
-0.23650800
                O                     1.63963800   -0.06987200
0.52169000
                C                     0.81124200   -0.99413900
-0.15113800
                O                    -0.38579500   -0.43724000
-0.56930300
                C                    -1.22597700   -0.02415200
0.49942400
                C                    -2.52515300    0.46978300
-0.09104300
                H                     2.63690400    1.70068700
0.29810600
                H                     1.43218100    1.25645300
-1.08472300
                H                     1.31526500   -1.35717500
-1.04817800
                H                     0.64903100   -1.80201100
0.56648700
                H                    -1.39588500   -0.87369500
1.17114100
                H                    -0.73109200    0.76294000
1.07386200
                H                    -3.00867800   -0.32169600
-0.66138000
                H                    -3.20073300    0.79539500
0.69883400
                                     H                  -2.33945300
1.31059200   -0.75764600
           Group                          13 14 15
           Axis                           6 5
           Symmetry                       3
           Potential[kcal/mol]            2
     0. 3.05
       End
       Rotor                        Hindered
       Geometry[angstrom]  15
         C                    2.04184100    0.97940900   -0.23650800
         O                    1.63963800   -0.06987200    0.52169000
         C                    0.81124200   -0.99413900   -0.15113800
         O                   -0.38579500   -0.43724000   -0.56930300
         C                   -1.22597700   -0.02415200    0.49942400
         C                   -2.52515300    0.46978300   -0.09104300
         H                    2.63690400    1.70068700    0.29810600
         H                    1.43218100    1.25645300   -1.08472300
         H                    1.31526500   -1.35717500   -1.04817800
         H                    0.64903100   -1.80201100    0.56648700
```

```
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
```

```
          H                  -1.39588500   -0.87369500    1.17114100
          H                  -0.73109200    0.76294000    1.07386200
          H                  -3.00867800   -0.32169600   -0.66138000
          H                  -3.20073300    0.79539500    0.69883400
                                   H                -2.33945300
1.31059200   -0.75764600
       Group                       1
       Axis                        2 3
       Symmetry                    1
       Potential[kcal/mol]         6
       0. 4.275 2.508 3.573 3.149 3.995
       End
       Rotor                       Hindered
       Geometry[angstrom]  15
         C                  2.04184100    0.97940900   -0.23650800
         O                  1.63963800   -0.06987200    0.52169000
         C                  0.81124200   -0.99413900   -0.15113800
         O                 -0.38579500   -0.43724000   -0.56930300
         C                 -1.22597700   -0.02415200    0.49942400
         C                 -2.52515300    0.46978300   -0.09104300
         H                  2.63690400    1.70068700    0.29810600
         H                  1.43218100    1.25645300   -1.08472300
         H                  1.31526500   -1.35717500   -1.04817800
         H                  0.64903100   -1.80201100    0.56648700
         H                 -1.39588500   -0.87369500    1.17114100
         H                 -0.73109200    0.76294000    1.07386200
         H                 -3.00867800   -0.32169600   -0.66138000
         H                 -3.20073300    0.79539500    0.69883400
                                   H                -2.33945300
1.31059200   -0.75764600
          Group                      7 8
          Axis                       1 2
          Symmetry                   2
          Potential[kcal/mol]        2
     0. 5.2
 End
 Frequencies[1/cm]         40
        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
1536.64 3024.66 3057.19 3073.81 3076.5  3115.41 3150.44 3152.21
3161.74 3302.14
        409.94  1411.49  1412.56  3141.77  3320.20  3321.01
        !57.06 80.74 172 241.97  273.48!
        ZeroEnergy[kcal/mol]               85.3
            ElectronicLevels[1/cm]         1
                 0    2
     End
```

```
        Barrier      B4    W1    P4     # CCO[CH]OCC + [H] = CCOCOCC
                     RRHO
                      Stoichiometry C5H12O2
              Core      PhaseSpaceTheory
               FragmentGeometry[angstrom]      1
        H                    0.000000    0.000000    0.000000
        FragmentGeometry[angstrom]  18
        C                   1.85123800    1.36692300   -0.11393900
        C                   1.96689700   -0.02829500    0.46760200
        O                   1.35369200   -1.01369700   -0.36424900
        C                   0.03415500   -0.85685700   -0.58928400
        O                  -0.69614700   -0.61826900    0.54142300
        C                  -2.06451100   -0.34257700    0.28446300
        C                  -2.27184300    1.06738700   -0.23360400
        H                   2.24378200    1.38817000   -1.12996300
        H                   2.41909800    2.06979700    0.49527800
        H                   0.81162300    1.69137600   -0.13652000
        H                   3.00777400   -0.33711600    0.53429500
        H                   1.52760000   -0.07194000    1.46460200
        H                  -0.36385800   -1.61659300   -1.26056200
        H                  -2.45580700   -1.07882900   -0.42562200
        H                  -2.57592300   -0.48826100    1.23398200
        H                  -1.74442300    1.20754600   -1.17653400
        H                  -3.33229600    1.26016800   -0.39476900
              H                  -1.89354200    1.79191800    0.48699300
           SymmetryFactor                2
                    PotentialPrefactor[au]      0.31  #0.01 0.007
                   PotentialPowerExponent       2.61
          End
              Rotor                       Hindered
              Geometry[angstrom]  18
                C                   1.85123800    1.36692300
    -0.11393900
                C                   1.96689700   -0.02829500
    0.46760200
                O                   1.35369200   -1.01369700
    -0.36424900
                C                   0.03415500   -0.85685700
    -0.58928400
                O                  -0.69614700   -0.61826900
    0.54142300
                C                  -2.06451100   -0.34257700
    0.28446300
                C                  -2.27184300    1.06738700
    -0.23360400
                H                   2.24378200    1.38817000
    -1.12996300
```

```
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
```

```
                Axis                          6 5
                Symmetry                      1
                Potential[kcal/mol]           6
          0.  4.23  0.926  1.612  0.0435  1.442
            End
            Rotor                       Hindered
            Geometry[angstrom]  18
          C                   1.85123800    1.36692300   -0.11393900
          C                   1.96689700   -0.02829500    0.46760200
          O                   1.35369200   -1.01369700   -0.36424900
          C                   0.03415500   -0.85685700   -0.58928400
          O                  -0.69614700   -0.61826900    0.54142300
          C                  -2.06451100   -0.34257700    0.28446300
          C                  -2.27184300    1.06738700   -0.23360400
          H                   2.24378200    1.38817000   -1.12996300
          H                   2.41909800    2.06979700    0.49527800
          H                   0.81162300    1.69137600   -0.13652000
          H                   3.00777400   -0.33711600    0.53429500
          H                   1.52760000   -0.07194000    1.46460200
          H                  -0.36385800   -1.61659300   -1.26056200
          H                  -2.45580700   -1.07882900   -0.42562200
          H                  -2.57592300   -0.48826100    1.23398200
          H                  -1.74442300    1.20754600   -1.17653400
          H                  -3.33229600    1.26016800   -0.39476900
                     H                 -1.89354200    1.79191800
  0.48699300
                Group                         6
                Axis                          5 4
                Symmetry                      1
                Potential[kcal/mol]           4
                0.  2.49  1.964  9.0
            End
            Rotor                       Hindered
            Geometry[angstrom]  18
          C                   1.85123800    1.36692300   -0.11393900
          C                   1.96689700   -0.02829500    0.46760200
          O                   1.35369200   -1.01369700   -0.36424900
          C                   0.03415500   -0.85685700   -0.58928400
          O                  -0.69614700   -0.61826900    0.54142300
          C                  -2.06451100   -0.34257700    0.28446300
          C                  -2.27184300    1.06738700   -0.23360400
          H                   2.24378200    1.38817000   -1.12996300
          H                   2.41909800    2.06979700    0.49527800
          H                   0.81162300    1.69137600   -0.13652000
          H                   3.00777400   -0.33711600    0.53429500
          H                   1.52760000   -0.07194000    1.46460200
          H                  -0.36385800   -1.61659300   -1.26056200
          H                  -2.45580700   -1.07882900   -0.42562200
```

```
        H                  -2.57592300   -0.48826100    1.23398200
        H                  -1.74442300    1.20754600   -1.17653400
        H                  -3.33229600    1.26016800   -0.39476900
                    H                -1.89354200    1.79191800
0.48699300
                Group                        2
                Axis                         3 4
                Symmetry                     1
                Potential[kcal/mol]          4
          0. 2.49 1.964 9.0
          End
          Rotor                      Hindered
          Geometry[angstrom]  18
        C                   1.85123800    1.36692300   -0.11393900
        C                   1.96689700   -0.02829500    0.46760200
        O                   1.35369200   -1.01369700   -0.36424900
        C                   0.03415500   -0.85685700   -0.58928400
        O                  -0.69614700   -0.61826900    0.54142300
        C                  -2.06451100   -0.34257700    0.28446300
        C                  -2.27184300    1.06738700   -0.23360400
        H                   2.24378200    1.38817000   -1.12996300
        H                   2.41909800    2.06979700    0.49527800
        H                   0.81162300    1.69137600   -0.13652000
        H                   3.00777400   -0.33711600    0.53429500
        H                   1.52760000   -0.07194000    1.46460200
        H                  -0.36385800   -1.61659300   -1.26056200
        H                  -2.45580700   -1.07882900   -0.42562200
        H                  -2.57592300   -0.48826100    1.23398200
        H                  -1.74442300    1.20754600   -1.17653400
        H                  -3.33229600    1.26016800   -0.39476900
                    H                -1.89354200    1.79191800
0.48699300
                    Group                        1 11 12
              Axis                         2 3
              Symmetry                     1
              Potential[kcal/mol]          6
       0. 4.23 0.926 1.612 0.0435 1.442
          End
          Rotor                      Hindered
          Geometry[angstrom]  18
        C                   1.85123800    1.36692300   -0.11393900
        C                   1.96689700   -0.02829500    0.46760200
        O                   1.35369200   -1.01369700   -0.36424900
        C                   0.03415500   -0.85685700   -0.58928400
        O                  -0.69614700   -0.61826900    0.54142300
        C                  -2.06451100   -0.34257700    0.28446300
        C                  -2.27184300    1.06738700   -0.23360400
        H                   2.24378200    1.38817000   -1.12996300
```

```
        H                   2.41909800    2.06979700    0.49527800
        H                   0.81162300    1.69137600   -0.13652000
        H                   3.00777400   -0.33711600    0.53429500
        H                   1.52760000   -0.07194000    1.46460200
        H                  -0.36385800   -1.61659300   -1.26056200
        H                  -2.45580700   -1.07882900   -0.42562200
        H                  -2.57592300   -0.48826100    1.23398200
        H                  -1.74442300    1.20754600   -1.17653400
        H                  -3.33229600    1.26016800   -0.39476900
                    H                 -1.89354200    1.79191800
0.48699300
                    Group                       8 9 10
                  Axis                        1 2
                  Symmetry                    3
                  Potential[kcal/mol]         2
              0. 3.025
 End
 Frequencies[1/cm] 42
        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
        !54.18 70.62 121.24  175.73  222.29  268.03!Torsions
  ZeroEnergy[kcal/mol]               97.3
       ElectronicLevels[1/cm]        1
            0    2
     End
     Barrier     B5   W1   P5    # CCOCO[CH]C + [H] = CCOCOCC
                   RRHO
                    Stoichiometry C5H12O2
             Core     PhaseSpaceTheory
      FragmentGeometry[angstrom]      1
     H                    0.000000    0.000000    0.000000
     FragmentGeometry[angstrom]  18
     C                  -1.75842200   -0.13403300   -0.46781200
     O                  -1.09509700    0.60904400    0.46548700
     C                  -0.01330100    1.35501300   -0.04090700
     C                  -2.85410500   -0.96514700    0.08007400
     O                   1.01893100    0.55641700   -0.51103000
     C                   1.65649100   -0.20390200    0.50439200
     C                   2.80557300   -0.95567500   -0.12445000
     H                  -2.47846600   -1.76188100    0.73417500
     H                  -3.41611000   -1.43101500   -0.72713700
     H                  -3.53683600   -0.35551300    0.67407300
     H                  -1.17785600   -0.44495900   -1.32790800
     H                  -0.34255100    1.96285200   -0.88525400
```

```
      H                  0.31673100    1.98162600    0.79154500
      H                  2.01218200    0.47292700    1.29023000
      H                  0.93781500   -0.89170300    0.95729300
      H                  3.51379600   -0.26075000   -0.57288800
      H                  3.32540300   -1.55052000    0.62546900
            H                 2.43780800   -1.62229200   -0.90303500
         SymmetryFactor                              2
                PotentialPrefactor[au]       0.31   #0.07 0.06
                PotentialPowerExponent       2.65
        End
             Rotor                      Hindered
             Geometry[angstrom]  18
              C                 -1.75842200   -0.13403300
   -0.46781200
              O                 -1.09509700    0.60904400
   0.46548700
              C                 -0.01330100    1.35501300
   -0.04090700
              C                 -2.85410500   -0.96514700
   0.08007400
              O                  1.01893100    0.55641700
   -0.51103000
              C                  1.65649100   -0.20390200
   0.50439200
              C                  2.80557300   -0.95567500
   -0.12445000
              H                 -2.47846600   -1.76188100
   0.73417500
              H                 -3.41611000   -1.43101500
   -0.72713700
              H                 -3.53683600   -0.35551300
   0.67407300
              H                 -1.17785600   -0.44495900
   -1.32790800
              H                 -0.34255100    1.96285200
   -0.88525400
              H                  0.31673100    1.98162600
   0.79154500
              H                  2.01218200    0.47292700
   1.29023000
              H                  0.93781500   -0.89170300
   0.95729300
              H                  3.51379600   -0.26075000
   -0.57288800
              H                  3.32540300   -1.55052000
   0.62546900
                    H                 2.43780800   -1.62229200
   -0.90303500
```

```
                    Group                          16 17 18
                    Axis                           7 6
                    Symmetry                       3
                    Potential[kcal/mol]            2
                0.  3.0522
            End
            Rotor                       Hindered
            Geometry[angstrom]  18
                    C                   -1.75842200    -0.13403300
-0.46781200
                    O                   -1.09509700     0.60904400
0.46548700
                    C                   -0.01330100     1.35501300
-0.04090700
                    C                   -2.85410500    -0.96514700
0.08007400
                    O                    1.01893100     0.55641700
-0.51103000
                    C                    1.65649100    -0.20390200
0.50439200
                    C                    2.80557300    -0.95567500
-0.12445000
                    H                   -2.47846600    -1.76188100
0.73417500
                    H                   -3.41611000    -1.43101500
-0.72713700
                    H                   -3.53683600    -0.35551300
0.67407300
                    H                   -1.17785600    -0.44495900
-1.32790800
                    H                   -0.34255100     1.96285200
-0.88525400
                    H                    0.31673100     1.98162600
0.79154500
                    H                    2.01218200     0.47292700
1.29023000
                    H                    0.93781500    -0.89170300
0.95729300
                    H                    3.51379600    -0.26075000
-0.57288800
                    H                    3.32540300    -1.55052000
0.62546900
                                        H                   2.43780800
-1.62229200    -0.90303500
                   Group                          7 14 15
                   Axis                           6 5
                   Symmetry                       1
                   Potential[kcal/mol]            8
```

```
             0.  1.627  1.032  1.115  1.063  4.677  0.586  1.190
               End
               Rotor                       Hindered
               Geometry[angstrom]  18
                         C                  -1.75842200   -0.13403300
   -0.46781200
                         O                  -1.09509700    0.60904400
    0.46548700
                         C                  -0.01330100    1.35501300
   -0.04090700
                         C                  -2.85410500   -0.96514700
    0.08007400
                         O                   1.01893100    0.55641700
   -0.51103000
                         C                   1.65649100   -0.20390200
    0.50439200
                         C                   2.80557300   -0.95567500
   -0.12445000
                         H                  -2.47846600   -1.76188100
    0.73417500
                         H                  -3.41611000   -1.43101500
   -0.72713700
                         H                  -3.53683600   -0.35551300
    0.67407300
                         H                  -1.17785600   -0.44495900
   -1.32790800
                         H                  -0.34255100    1.96285200
   -0.88525400
                         H                   0.31673100    1.98162600
    0.79154500
                         H                   2.01218200    0.47292700
    1.29023000
                         H                   0.93781500   -0.89170300
    0.95729300
                         H                   3.51379600   -0.26075000
   -0.57288800
                         H                   3.32540300   -1.55052000
    0.62546900
                                   H                   2.43780800
  -1.62229200   -0.90303500
                  Group                        6
                  Axis                         5 3
                  Symmetry                     1
                  Potential[kcal/mol]          6
            0.  6.63  2.07  3.64  2.99  4.09
               End
               Rotor                       Hindered
               Geometry[angstrom]  18
```

```
                        C                  -1.75842200   -0.13403300
   -0.46781200
                        O                  -1.09509700    0.60904400
    0.46548700
                        C                  -0.01330100    1.35501300
   -0.04090700
                        C                  -2.85410500   -0.96514700
    0.08007400
                        O                   1.01893100    0.55641700
   -0.51103000
                        C                   1.65649100   -0.20390200
    0.50439200
                        C                   2.80557300   -0.95567500
   -0.12445000
                        H                  -2.47846600   -1.76188100
    0.73417500
                        H                  -3.41611000   -1.43101500
   -0.72713700
                        H                  -3.53683600   -0.35551300
    0.67407300
                        H                  -1.17785600   -0.44495900
   -1.32790800
                        H                  -0.34255100    1.96285200
   -0.88525400
                        H                   0.31673100    1.98162600
    0.79154500
                        H                   2.01218200    0.47292700
    1.29023000
                        H                   0.93781500   -0.89170300
    0.95729300
                        H                   3.51379600   -0.26075000
   -0.57288800
                        H                   3.32540300   -1.55052000
    0.62546900
                                      H                  2.43780800
  -1.62229200   -0.90303500
             Group                        1
             Axis                         2 3
             Symmetry                     1
             Potential[kcal/mol]          6
       0. 9.97 1.65 2.70 2.29 2.93
             End
             Rotor                    Hindered
             Geometry[angstrom]  18
                        C                  -1.75842200   -0.13403300
   -0.46781200
                        O                  -1.09509700    0.60904400
    0.46548700
```

```
                        C                  -0.01330100    1.35501300
    -0.04090700
                        C                  -2.85410500   -0.96514700
     0.08007400
                        O                   1.01893100    0.55641700
    -0.51103000
                        C                   1.65649100   -0.20390200
     0.50439200
                        C                   2.80557300   -0.95567500
    -0.12445000
                        H                  -2.47846600   -1.76188100
     0.73417500
                        H                  -3.41611000   -1.43101500
    -0.72713700
                        H                  -3.53683600   -0.35551300
     0.67407300
                        H                  -1.17785600   -0.44495900
    -1.32790800
                        H                  -0.34255100    1.96285200
    -0.88525400
                        H                   0.31673100    1.98162600
     0.79154500
                        H                   2.01218200    0.47292700
     1.29023000
                        H                   0.93781500   -0.89170300
     0.95729300
                        H                   3.51379600   -0.26075000
    -0.57288800
                        H                   3.32540300   -1.55052000
     0.62546900
                                    H                   2.43780800
   -1.62229200   -0.90303500
                  Group                     4 11
                Axis                      1 2
                Symmetry                  1
                Potential[kcal/mol]       4
           0.  4.573  1.338  4.174
              End
              Rotor                    Hindered
              Geometry[angstrom]  18
                        C                 -1.75842200   -0.13403300
    -0.46781200
                        O                 -1.09509700    0.60904400
     0.46548700
                        C                 -0.01330100    1.35501300
    -0.04090700
                        C                 -2.85410500   -0.96514700
     0.08007400
```

```
                        O                   1.01893100    0.55641700
   -0.51103000
                        C                   1.65649100   -0.20390200
    0.50439200
                        C                   2.80557300   -0.95567500
   -0.12445000
                        H                  -2.47846600   -1.76188100
    0.73417500
                        H                  -3.41611000   -1.43101500
   -0.72713700
                        H                  -3.53683600   -0.35551300
    0.67407300
                        H                  -1.17785600   -0.44495900
   -1.32790800
                        H                  -0.34255100    1.96285200
   -0.88525400
                        H                   0.31673100    1.98162600
    0.79154500
                        H                   2.01218200    0.47292700
    1.29023000
                        H                   0.93781500   -0.89170300
    0.95729300
                        H                   3.51379600   -0.26075000
   -0.57288800
                        H                   3.32540300   -1.55052000
    0.62546900
                                    H                   2.43780800
  -1.62229200   -0.90303500
            Group                       8 9 10
            Axis                        4 1
            Symmetry                    3
            Potential[kcal/mol]         2
        0. 1.32
 End
 Frequencies[1/cm] 42
        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
        !62.09  81.45 159.44  197.19  241.07  261.41!Torsions
 ZeroEnergy[kcal/mol]               94.6
      ElectronicLevels[1/cm]        1
           0    2
    End
    Barrier     B6   W1   P6    # CCOCOC[CH2] + [H] = CCOCOCC
                    RRHO
```

```
                        Stoichiometry C5H12O2
                Core      PhaseSpaceTheory
          FragmentGeometry[angstrom]      1
       H                    0.000000    0.000000    0.000000
       FragmentGeometry[angstrom]  18
       C                   2.94233500   -0.67034400   -0.14761700
       C                   1.78742600    0.14457100    0.38575300
       O                   0.80817900    0.24343000   -0.63524800
       C                  -0.28223800    1.03652700   -0.28368300
       O                  -1.03682300    0.49569300    0.76284600
       C                  -1.71162100   -0.70408300    0.40845000
       C                  -2.86279900   -0.45941400   -0.49590600
       H                   2.60356500   -1.66748400   -0.42538500
       H                   3.72126300   -0.76622200    0.60785300
       H                   3.36704400   -0.19434500   -1.03009700
       H                   1.35335100   -0.32249500    1.27350700
       H                   2.11614900    1.15201300    0.66825800
       H                   0.04724600    2.01712500    0.07145300
       H                  -0.88407800    1.13637100   -1.19045600
       H                  -1.00929200   -1.41413700   -0.03811800
       H                  -2.04480500   -1.13149900    1.36035400
       H                  -3.47587800    0.41624000   -0.34190400
            H                 -3.20403400   -1.22209400   -1.17822300
         SymmetryFactor                                  2
                  PotentialPrefactor[au]       0.32  #0.07
                  PotentialPowerExponent       2.58
         End
             Rotor                       Hindered
             Geometry[angstrom]  18
               C                  2.94233500   -0.67034400
   -0.14761700
               C                  1.78742600    0.14457100
   0.38575300
               O                  0.80817900    0.24343000
   -0.63524800
               C                 -0.28223800    1.03652700
   -0.28368300
               O                 -1.03682300    0.49569300
   0.76284600
               C                 -1.71162100   -0.70408300
   0.40845000
               C                 -2.86279900   -0.45941400
   -0.49590600
               H                  2.60356500   -1.66748400
   -0.42538500
               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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                    H                    2.11614900    1.15201300
0.66825800
                    H                    0.04724600    2.01712500
0.07145300
                    H                   -0.88407800    1.13637100
-1.19045600
                    H                   -1.00929200   -1.41413700
-0.03811800
                    H                   -2.04480500   -1.13149900
1.36035400
                    H                   -3.47587800    0.41624000
-0.34190400
          H                  -3.20403400   -1.22209400   -1.17822300
                Group                       1 11 12
                Axis                        2 3
                Symmetry                    1
                Potential[kcal/mol]         8
          0. 1.525 0.954 1.108 1.077 4.728 0.771 1.294
            End
            Rotor                     Hindered
            Geometry[angstrom]  18
                        C                  2.94233500   -0.67034400
 -0.14761700
                        C                  1.78742600    0.14457100
  0.38575300
                        O                  0.80817900    0.24343000
 -0.63524800
                        C                 -0.28223800    1.03652700
 -0.28368300
                        O                 -1.03682300    0.49569300
  0.76284600
                        C                 -1.71162100   -0.70408300
  0.40845000
                        C                 -2.86279900   -0.45941400
 -0.49590600
                        H                  2.60356500   -1.66748400
 -0.42538500
                        H                  3.72126300   -0.76622200
  0.60785300
                        H                  3.36704400   -0.19434500
 -1.03009700
                        H                  1.35335100   -0.32249500
  1.27350700
                        H                  2.11614900    1.15201300
  0.66825800
                        H                  0.04724600    2.01712500
  0.07145300
```

```
                        H                  -0.88407800    1.13637100
    -1.19045600
                        H                  -1.00929200   -1.41413700
    -0.03811800
                        H                  -2.04480500   -1.13149900
     1.36035400
                        H                  -3.47587800    0.41624000
    -0.34190400
              H                  -3.20403400   -1.22209400   -1.17822300
                    Group                       2
                    Axis                        3 4
                    Symmetry                    1
                    Potential[kcal/mol]         6
            0.  7.39  3.02  3.07  2.66  3.95
                End
                Rotor                     Hindered
                Geometry[angstrom]  18
                          C                 2.94233500   -0.67034400
    -0.14761700
                          C                 1.78742600    0.14457100
     0.38575300
                          O                 0.80817900    0.24343000
    -0.63524800
                          C                -0.28223800    1.03652700
    -0.28368300
                          O                -1.03682300    0.49569300
     0.76284600
                          C                -1.71162100   -0.70408300
     0.40845000
                          C                -2.86279900   -0.45941400
    -0.49590600
                          H                 2.60356500   -1.66748400
    -0.42538500
                          H                 3.72126300   -0.76622200
     0.60785300
                          H                 3.36704400   -0.19434500
    -1.03009700
                          H                 1.35335100   -0.32249500
     1.27350700
                          H                 2.11614900    1.15201300
     0.66825800
                          H                 0.04724600    2.01712500
     0.07145300
                          H                -0.88407800    1.13637100
    -1.19045600
                          H                -1.00929200   -1.41413700
    -0.03811800
```

```
                          H                  -2.04480500   -1.13149900
    1.36035400
                          H                  -3.47587800    0.41624000
   -0.34190400
          H                  -3.20403400   -1.22209400   -1.17822300
                    Group                       6
                Axis                          5 4
                Symmetry                      1
                Potential[kcal/mol]           6
          0.  7.87  3.80  3.97  3.29  4.46
            End
            Rotor                     Hindered
            Geometry[angstrom]  18
                          C                   2.94233500   -0.67034400
   -0.14761700
                          C                   1.78742600    0.14457100
    0.38575300
                          O                   0.80817900    0.24343000
   -0.63524800
                          C                  -0.28223800    1.03652700
   -0.28368300
                          O                  -1.03682300    0.49569300
    0.76284600
                          C                  -1.71162100   -0.70408300
    0.40845000
                          C                  -2.86279900   -0.45941400
   -0.49590600
                          H                   2.60356500   -1.66748400
   -0.42538500
                          H                   3.72126300   -0.76622200
    0.60785300
                          H                   3.36704400   -0.19434500
   -1.03009700
                          H                   1.35335100   -0.32249500
    1.27350700
                          H                   2.11614900    1.15201300
    0.66825800
                          H                   0.04724600    2.01712500
    0.07145300
                          H                  -0.88407800    1.13637100
   -1.19045600
                          H                  -1.00929200   -1.41413700
   -0.03811800
                          H                  -2.04480500   -1.13149900
    1.36035400
                          H                  -3.47587800    0.41624000
   -0.34190400
          H                  -3.20403400   -1.22209400   -1.17822300
```

```
                Group                          7 15 16
                Axis                           6 5
                Symmetry                       1
                Potential[kcal/mol]            6
            0.  3.2  0.26  1.347  0.319  1.836
                End
                Rotor                       Hindered
                Geometry[angstrom]  18
                          C                   2.94233500    -0.67034400
    -0.14761700
                          C                   1.78742600     0.14457100
     0.38575300
                          O                   0.80817900     0.24343000
    -0.63524800
                          C                  -0.28223800     1.03652700
    -0.28368300
                          O                  -1.03682300     0.49569300
     0.76284600
                          C                  -1.71162100    -0.70408300
     0.40845000
                          C                  -2.86279900    -0.45941400
    -0.49590600
                          H                   2.60356500    -1.66748400
    -0.42538500
                          H                   3.72126300    -0.76622200
     0.60785300
                          H                   3.36704400    -0.19434500
    -1.03009700
                          H                   1.35335100    -0.32249500
     1.27350700
                          H                   2.11614900     1.15201300
     0.66825800
                          H                   0.04724600     2.01712500
     0.07145300
                          H                  -0.88407800     1.13637100
    -1.19045600
                          H                  -1.00929200    -1.41413700
    -0.03811800
                          H                  -2.04480500    -1.13149900
     1.36035400
                          H                  -3.47587800     0.41624000
    -0.34190400
              H                   -3.20403400    -1.22209400    -1.17822300
                Group                          17 18
                Axis                           7 6
                Symmetry                       2
                Potential[kcal/mol]            2
            0.  1.67
```

```
 End
 Frequencies[1/cm] 42
     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
     !58.76 93.4 190.21  194.44  239.52  287.32! Torsions
 ZeroEnergy[kcal/mol]                 101.7
       ElectronicLevels[1/cm]         1
            0    2
     End
  Barrier     B7   W1  P7    # CCOCO + C=C
        Variational
     RRHO
     Geometry[angstrom]                        19
      C                  1.86865600   -1.45276400   -0.31453300
C                  1.99044900   -0.44756700    0.66581100
O                  1.26508200    0.87588900   -0.40719600
C                  0.09293600    1.53443100   -0.03245800
O                 -0.88100900    0.67601300    0.48752700
C                 -1.56221900   -0.08691000   -0.49360500
C                 -2.57078700   -0.96542100    0.20899600
H                  1.29830200   -0.26031300   -0.88156200
H                  1.10214500   -2.20418100   -0.18020400
H                  2.75208400   -1.75617600   -0.85770000
H                  1.27823100   -0.38784500    1.47887900
H                  2.93441700    0.05024500    0.83885600
H                  0.32416900    2.24814600    0.75878600
H                 -0.29968900    2.06766900   -0.90719200
H                 -2.05815100    0.59095600   -1.19789500
H                 -0.85226800   -0.69772800   -1.06030800
H                 -3.26842100   -0.35617500    0.78153600
H                 -3.13188900   -1.55490100   -0.51496800
H                 -2.06572800   -1.64552100    0.89385000
Core RigidRotor
           SymmetryFactor              1
         End
  Rotor        Hindered
  Group                   17 18 19
  Axis                    7 6
       Symmetry                3
       Potential[kcal/mol]     2
   0. 3.058
      End
      Rotor        Hindered
 Group                   7 15 16
```

```
    Axis                    6 5
    Symmetry                1
    Potential[kcal/mol]     6
      0. 1.35 1.04 4.81 1.58 2.55
    End
    Rotor         Hindered
    Group                   6
    Axis                    5 4
    Symmetry                1
    Potential[kcal/mol]     6
      0. 6.72 2.04 3.04 1.23 2.59
    End
    Rotor         Hindered
    Group                   5 13 14
    Axis                    4 3
    Symmetry                1
    Potential[kcal/mol]     6
      0. 7.64 2.448 3.104 2.498 3.552
    End
    Frequencies[1/cm]       46
         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
   !33.09 57.13 115.63 257.80!
   ZeroEnergy[kcal/mol]                  69.1
             ElectronicLevels[1/cm]        1
                  0    1
           End
             Tunneling         Eckart
             ImaginaryFrequency[1/cm]      1895.98
             WellDepth[kcal/mol]           69.1
             WellDepth[kcal/mol]           54.0
           End
      End
      Barrier     B8   W1  P8    # CCOCOCC = CCOCC + CH2O
      Variational
              RRHO
        Geometry[angstrom]                        19
         C                 -2.39520700   -0.82724900   -0.51891400
  C                -1.39093000   -0.66063200    0.56249100
  O                -1.19657700    1.38141600    0.12043300
  C                 0.09893800    1.32827100   -0.02911100
  O                 0.35643600   -0.13510600   -0.17294400
  C                 1.53267100   -0.65605400    0.42368400
  C                 2.76857500   -0.25975500   -0.36094600
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H                  -3.07922600    0.01142000   -0.56095300
H                  -2.93786300   -1.76214600   -0.34070600
H                  -1.89178900   -0.92075700   -1.47998200
H                  -1.70306900   -0.17697700    1.47390300
H                  -0.81910900   -1.56486500    0.75466800
H                   0.49912000    1.78379300   -0.94929300
H                   0.71847700    1.64278600    0.83753600
H                   1.59917600   -0.30773100    1.46004800
H                   1.41783700   -1.74124200    0.43160200
H                   2.90422800    0.82086700   -0.34377600
H                   3.65513800   -0.72317000    0.07117700
H                   2.67392600   -0.57993700   -1.39737100
      Core RigidRotor
            SymmetryFactor               1
          End
     Rotor        Hindered
    Group                    17 18 19
    Axis                     7 6
          Symmetry                3
          Potential[kcal/mol]     2
     0. 3.35
       End
       Rotor        Hindered
        Group                   7 15 16
        Axis                    6 5
              Symmetry               1
              Potential[kcal/mol]    6
         0. 4.19 0.06 2.95 0.66 1.12
       End
       Rotor        Hindered
            Group                  8 9 10
            Axis                   1 2
                  Symmetry              3
                  Potential[kcal/mol]   2
             0. 2.13
       End
     Frequencies[1/cm]       47
     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
     !61.84 206.8 244.8! Torsions
     ZeroEnergy[kcal/mol]                    77.3
            ElectronicLevels[1/cm]       1
                  0    1
           End
```

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                Tunneling          Eckart
                ImaginaryFrequency[1/cm]       652.47
                WellDepth[kcal/mol]            77.4
                WellDepth[kcal/mol]            63.6
      End
    End
    Barrier     B9    W1   P9     # CCO + CCO[[C]]
    Variational
            RRHO
      Geometry[angstrom]                          19
C      0.0038259251     -0.0042530719     -0.0001336264
O      0.0017347903     -0.010888302       1.3998440961
C      1.9805950929      0.0071986858      2.0367355204
O      2.1150633304     -0.644072419       3.1420379586
C      1.5115774353     -0.0615116068      4.3182969376
H      0.8771096948      0.5513356318     -0.381102682
H     -0.8779935791      0.5380113494     -0.3595213374
H      0.9726964839      0.6786413733      1.7934304765
H      2.4340106877     -0.560885994       1.2226801616
H      2.2018398687     -0.2733256747      5.1319615639
H      1.4491435901      1.015395797       4.1612833391
C      0.0099014939     -1.4151833681     -0.5630102247
H     -0.8644159281     -1.9598265483     -0.2087409289
H     -0.0008499521     -1.4070883509     -1.653667084
H      0.8986331154     -1.9548624097     -0.2315695773
C      0.1532008337     -0.6830784574      4.5474241493
H     -0.2888191848     -0.2649151568      5.4513723677
H     -0.4972758232     -0.4825290689      3.6978352197
H      0.2467171625     -1.760558391       4.6735926872
    Core RigidRotor
           SymmetryFactor                1
         End
    Rotor        Hindered
          Group                    17 18 19
          Axis                     5 16
               Symmetry                 3
               Potential[kcal/mol]      2
      0. 3.25
    End
    Rotor        Hindered
          Group                    13 14 15
          Axis                     12 1
               Symmetry                 3
               Potential[kcal/mol]      2
      0. 3.06
    End
    Rotor        Hindered
          Group                    10 11 16
```

```
              Axis                      5 4
                    Symmetry                1
                    Potential[kcal/mol]     6
         0. 1.43 1.00 1.51 1.14 2.39
        End
        Rotor         Hindered
             Group                    6 7 12
             Axis                     1 2
                   Symmetry                1
                    Potential[kcal/mol]     6
         0. 1.63 0.26 1.83 1.79 2.27
        End
        Frequencies[1/cm]       46
        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
        ! 243.49 274.69 96.67 70.72! Torsions
        ZeroEnergy[kcal/mol]                 68.2
               ElectronicLevels[1/cm]        1
                    0    1
             End
               Tunneling          Eckart
               ImaginaryFrequency[1/cm]      1511.79
               WellDepth[kcal/mol]           68.16
               WellDepth[kcal/mol]           1.16
       End
     End
  Barrier     B10   W1  P10    # CCOH CH2O C=C
     Variational
             RRHO
       Geometry[angstrom]                        19
C                  1.09177900    1.60943000    0.14754200
C                 -1.75265200   -0.31317700    0.43254800
H                 -1.48855400    0.10686500    1.40821200
H                 -2.09281100   -1.33910800    0.58451200
O                 -0.58553800   -0.37529200   -0.38189600
H                  0.00309600    0.55017000   -0.25221400
H                  0.90385400    2.29978100   -0.66527500
H                  0.76921900    1.92764000    1.13099700
C                  0.63260000   -1.31249400    0.25698700
H                  0.20851400   -2.31508200    0.13578800
H                  0.56578400   -0.95256000    1.30060800
C                  2.18120200    0.75032100    0.04848500
H                  2.67436300    0.40555900    0.94922100
H                  2.81620200    0.77532800   -0.82543400
```

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 O                  1.68231100   -1.02848400   -0.40355700
 C                 -2.80708300    0.52572300   -0.25385800
 H                 -3.71065400    0.56748400    0.35316500
 H                 -2.44337000    1.54240400   -0.40061900
 H                 -3.05490500    0.10290000   -1.22555700
        Core RigidRotor
               SymmetryFactor              1
             End
        Rotor        Hindered
              Group                   17 18 19
              Axis                    16 2
                    Symmetry               3
                    Potential[kcal/mol]    2
          0. 3.26
        End
        Rotor        Hindered
              Group                   13 14 15
              Axis                    12 1
                     Symmetry               6
                     Potential[kcal/mol]    1
          0. 0.95 0.74 3.71 1.64 1.80
        End
         Frequencies[1/cm]       47
     107.03 142.06 196.62 244.83 289.90 396.15 457.92 515.76 584.59
   614.63 712.31 816.19 822.61
     917.22 1001.43 1065.57 1093.25 1100.82 1152.91 1166.80 1199.68
   1242.41 1249.24 1276.75 1327.38
     1357.11 1399.12 1407.76 1428.58 1457.49 1481.81 1493.80 1502.11
   1525.07 1536.95 1587.71 1774.83 2927.04
     3044.60 3048.35 3072.77 3096.84 3143.38 3147.90 3155.78 3157.36
   3221.79 3247.73
         ! 53.45 264.84 ! Torsions
         ZeroEnergy[kcal/mol]               67.9
                ElectronicLevels[1/cm]      1
                     0    1
              End
                Tunneling         Eckart
                ImaginaryFrequency[1/cm]    945.04
                WellDepth[kcal/mol]         67.87
                WellDepth[kcal/mol]         38.52
        End
      End
End
```

E.3 DPM

```
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
PressureList[atm]                        0.00001 0.001  0.01  0.1  1  10
     100.
!PressureList[bar]                       1.
EnergyStepOverTemperature   .2
ExcessEnergyOverTemperature   30
ModelEnergyLimit[kcal/mol]    400
CalculationMethod     direct
!CalculationMethod      low-eigenvalue !direct
WellCutoff                    10
ChemicalEigenvalueMax           0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]      200  ! He
      Power                  .85
      ExponentCutoff                 15
    End
  CollisionFrequency
    LennardJones
        Epsilons[1/cm]            94.87    304.8  !Ar and CCCOCOCCC
  Sigmas[angstrom]    3.33     6.77
  Masses[amu]                 39.88    132.23
    End
!------------------------------------------------------------------
!-------------------------WELLS------------------------------------
!------------------------------------------------------------------
  Well     W1 # CCCOCOCCC
    Species
    RRHO
      Geometry[angstrom] 25
 C                 2.32970600    1.53569100    0.76573700
 C                 2.73755600    0.55860200   -0.32975100
 C                 1.57284100   -0.28798700   -0.79697800
 O                 1.12566800   -1.07437300    0.29510000
 C                -0.00000500   -1.84236700   -0.00000200
 O                -1.12567500   -1.07436900   -0.29510400
 C                -1.57285800   -0.28799400    0.79697900
 C                -2.73755700    0.55861400    0.32974400
```

```
C                  -2.32967800    1.53571000   -0.76572800
H                   1.54040800    2.20205300    0.41193500
H                   3.17062500    2.15032600    1.08404300
H                   1.95159400    0.99742400    1.63357200
H                   3.13487700    1.09857800   -1.19132900
H                   3.52869200   -0.10177100    0.02980500
H                   0.75697300    0.35090900   -1.15184600
H                   1.86833500   -0.94812000   -1.62125300
H                   0.17313100   -2.46526300   -0.88268300
H                  -0.17314300   -2.46526500    0.88267700
H                  -1.86837200   -0.94813600    1.62124000
H                  -0.75699000    0.35089000    1.15187000
H                  -3.52869600   -0.10174600   -0.02983000
H                  -3.13488400    1.09858600    1.19132100
H                  -1.95156500    0.99744700   -1.63356500
H                  -3.17058200    2.15036300   -1.08403600
H                  -1.54037200    2.20205300   -0.41190800
     Core                    RigidRotor
       SymmetryFactor          2
     End
 Rotor                       Hindered
         Group                           10 11 12
         Axis                            1 2
         Symmetry                 3
         Potential[kcal/mol]      2
 0.00 2.90
 End
 Rotor                       Hindered
         Group                           1 13 14
         Axis                            2 3
         Symmetry                 1
         Potential[kcal/mol]      6
 0.00 5.12 0.31 3.88 0.64 3.73
 End
 Rotor                       Hindered
         Group                           2 15 16
         Axis                            3 4
         Symmetry                 1
         Potential[kcal/mol]      6
 0.00 1.93 1.21 7.68 2.64 3.41
 End
 Rotor                       Hindered
         Group                           6 17 18
         Axis                            5 4
         Symmetry                 1
         Potential[kcal/mol]      6
 0.00 7.57 3.33 4.00 3.16 4.33
 End
```

```
  Rotor                       Hindered
          Group                           4 17 18
          Axis                            5 6
          Symmetry                1
          Potential[kcal/mol]      6
  0.00 7.57 3.29 4.00 3.15 4.32
  End
  Rotor                       Hindered
          Group                           8 19 20
          Axis                            7 6
          Symmetry                1
          Potential[kcal/mol]      6
  0.00 1.93 1.21 7.68 2.64 3.41
  End
  Rotor                       Hindered
          Group                           9 21 22
          Axis                            8 7
          Symmetry                1
          Potential[kcal/mol]      6
  0.00 5.12 0.31 3.89 0.64 3.74
  End
  Rotor                       Hindered
          Group                           23 24 25
          Axis                            9 8
          Symmetry                3
          Potential[kcal/mol]      2
  0.00 2.90
  End
  Frequencies[1/cm] 61
  233.78 303.58 315.41 386.45
  444.32 515.04 672.04 768.66 770.64 900.46
  904.25 926.39 927.68 960.72 966.67 1085.49
  1088.04 1112.78 1133.11 1147.57 1179.54 1183.97
  1199.45 1221.82 1281.24 1283.9 1305.64 1313.55
  1344.72 1377.74 1378.51 1411.46 1411.69 1423.08
  1431.9 1458.37 1482.6 1484.77 1498.9 1499.35
  1512.28 1513.28 1515.67 1525.69 1534.92 3004.29
  3016.11 3036.47 3055.95 3059.11 3060.22 3064.04
  3070.79 3073.45 3087.11 3103.2 3104.93 3130.5
  3132.54 3147.43 3150.73
!30.0 38.88 58.9 109.75 138.41 186.7 204.83 276.38!Torsions
       ZeroEnergy[kcal/mol]         0
       ElectronicLevels[1/cm]       1
  0 1
    End
  End
!-------------------------------------------------------------
!------------------------FISSION PRODUCTS--------------------
```

```
!------------------------------------------------------------
  Bimolecular   P1  # [H] + CCCOCOCC[CH2]
    Fragment  H
       Atom
         Mass[amu]   1
         ElectronicLevels[1/cm]      1
            0     2
       End
    Fragment  CCCOCOCC[CH2]
      RRHO
  Geometry[angstrom]  24
  C  -0.0062476859  -0.02126965  -0.0163303857
  C  -0.0046988522  0.0014011342  1.4704960807
  C  1.4041056014  0.0136759017  2.0462213335
  O  2.060696304  -1.1706363361  1.6295849883
  C  3.4383611706  -1.1484599061  1.8579422363
  O  4.0951878338  -0.1699438712  1.1141734754
  C  4.0489889675  -0.3986242016  -0.2861167205
  C  4.4812144319  0.867036039  -0.9952777783
  C  3.5401618107  2.0291906974  -0.7020461274
  H  -0.6261609568  0.6500802134  -0.5891455735
  H  0.5056191706  -0.8166945049  -0.5349501258
  H  -0.5403403289  0.8736463849  1.8460697671
  H  -0.5159089877  -0.8847071884  1.8665583753
  H  1.9476627341  0.8886559429  1.6808343383
  H  1.3758863213  0.050086519  3.1416401568
  H  3.6571391054  -0.9233885893  2.905845261
  H  3.7969874586  -2.1486946742  1.598074315
  H  4.705459439  -1.2400328027  -0.5363514022
  H  3.0278640037  -0.6582734506  -0.5815536658
  H  5.4984206731  1.1171482707  -0.6882601899
  H  4.5097186941  0.6618989089  -2.0672042196
  H  3.5691956753  2.2831478998  0.3565701398
  H  3.8122455928  2.9160652485  -1.2728612302
  H  2.5104868528  1.7629559594  -0.9537030583
      Core                  RigidRotor
        SymmetryFactor            1
      End
  Rotor                     Hindered
          Group                          10 11
          Axis                           1 2
          Symmetry               1
          Potential[kcal/mol]     4
0.00 0.81 0.00 0.80
  End
  Rotor                     Hindered
          Group                          1 12 13
          Axis                           2 3
```

```
          Symmetry                1
          Potential[kcal/mol]     6
0.00 5.63 0.87 4.34 1.16 4.08
  End
  Rotor                     Hindered
          Group                         5
          Axis                          4 3
          Symmetry                1
          Potential[kcal/mol]     6
0.00 2.28 0.91 5.36 1.89 2.44
  End
  Rotor                     Hindered
          Group                         6 16 17
          Axis                          5 4
          Symmetry                1
          Potential[kcal/mol]     6
0.00 8.05 3.64 4.70 3.74 4.70
  End
  Rotor                     Hindered
          Group                         7
          Axis                          6 5
          Symmetry                1
          Potential[kcal/mol]     6
0.00 7.90 3.42 4.59 3.70 4.70
  End
  Rotor                     Hindered
          Group                         8 18 19
          Axis                          7 6
          Symmetry                1
          Potential[kcal/mol]     6
0.00 2.24 1.37 7.84 2.73 3.54
  End
  Rotor                     Hindered
          Group                         9 20 21
          Axis                          8 7
          Symmetry                1
          Potential[kcal/mol]     6
0.00 5.32 0.85 4.20 1.06 4.29
  End
  Rotor                     Hindered
          Group                         22 23 24
          Axis                          9 8
          Symmetry                3
          Potential[kcal/mol]     2
0.00 2.79
  End
  Frequencies[1/cm] 58
41.37 237.47 318.42 373.23
```

```
443.87 488.4  532.66 670.51 755.06 771.66
900.01 917.39 928.04 954.97 965.94 1067.61
1085.12 1088.44 1112.25 1131.49 1149.18 1184.65
1194.56 1219.39 1249.07 1287.29 1298.87 1309.31
1343.03 1360.57 1377.17 1411.46 1415.86 1430.01
1452.39 1462.74 1475.89 1483.54 1497.04 1511.03
1519.85 1525.76 1528.06 3012.83 3021.14 3022.77
3040.32 3055.78 3063.68 3076.35 3086.22 3091.2
3104.47 3108.24 3127.85 3145.69 3180.95 3286.5
!49.7 63.84  96.04  120.38 162.38 213.89 260.19 301.91!Torsions
  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    100.8
  End
! ------------------------------------------------------------
     Barrier     B1   W1   P1    # [H] + CCCOCOCC[CH2]
       RRHO
        Stoichiometry C7H16O2
         Core     PhaseSpaceTheory
           FragmentGeometry[angstrom]      1
        H                  0.000000    0.000000    0.000000
           FragmentGeometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
H  0.5056191706  -0.8166945049  -0.5349501258
H  -0.5403403289  0.8736463849  1.8460697671
H  -0.5159089877  -0.8847071884  1.8665583753
H  1.9476627341  0.8886559429  1.6808343383
H  1.3758863213  0.050086519  3.1416401568
H  3.6571391054  -0.9233885893  2.905845261
H  3.7969874586  -2.1486946742  1.598074315
H  4.705459439  -1.2400328027  -0.5363514022
H  3.0278640037  -0.6582734506  -0.5815536658
H  5.4984206731  1.1171482707  -0.6882601899
H  4.5097186941  0.6618989089  -2.0672042196
H  3.5691956753  2.2831478998  0.3565701398
H  3.8122455928  2.9160652485  -1.2728612302
H  2.5104868528  1.7629559594  -0.9537030583
```

```
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   3.8122455928   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
```

```
H   0.5056191706   -0.8166945049   -0.5349501258
H   -0.5403403289   0.8736463849   1.8460697671
H   -0.5159089877   -0.8847071884   1.8665583753
H   1.9476627341   0.8886559429   1.6808343383
H   1.3758863213   0.050086519   3.1416401568
H   3.6571391054   -0.9233885893   2.905845261
H   3.7969874586   -2.1486946742   1.598074315
H   4.705459439   -1.2400328027   -0.5363514022
H   3.0278640037   -0.6582734506   -0.5815536658
H   5.4984206731   1.1171482707   -0.6882601899
H   4.5097186941   0.6618989089   -2.0672042196
H   3.5691956753   2.2831478998   0.3565701398
H   3.8122455928   2.9160652485   -1.2728612302
H   2.5104868528   1.7629559594   -0.9537030583
           Group                          1 12 13
           Axis                           2 3
           Symmetry                       1
           Potential[kcal/mol]     6
0.00 5.63 0.87 4.34 1.16 4.08
  End
  Rotor                       Hindered
                 Geometry[angstrom]      24
C   -0.0062476859   -0.02126965   -0.0163303857
C   -0.0046988522   0.0014011342   1.4704960807
C   1.4041056014   0.0136759017   2.0462213335
O   2.060696304   -1.1706363361   1.6295849883
C   3.4383611706   -1.1484599061   1.8579422363
O   4.0951878338   -0.1699438712   1.1141734754
C   4.0489889675   -0.3986242016   -0.2861167205
C   4.4812144319   0.867036039   -0.9952777783
C   3.5401618107   2.0291906974   -0.7020461274
H   -0.6261609568   0.6500802134   -0.5891455735
H   0.5056191706   -0.8166945049   -0.5349501258
H   -0.5403403289   0.8736463849   1.8460697671
H   -0.5159089877   -0.8847071884   1.8665583753
H   1.9476627341   0.8886559429   1.6808343383
H   1.3758863213   0.050086519   3.1416401568
H   3.6571391054   -0.9233885893   2.905845261
H   3.7969874586   -2.1486946742   1.598074315
H   4.705459439   -1.2400328027   -0.5363514022
H   3.0278640037   -0.6582734506   -0.5815536658
H   5.4984206731   1.1171482707   -0.6882601899
H   4.5097186941   0.6618989089   -2.0672042196
H   3.5691956753   2.2831478998   0.3565701398
H   3.8122455928   2.9160652485   -1.2728612302
H   2.5104868528   1.7629559594   -0.9537030583
           Group                          5
           Axis                           4 3
```

```
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 2.28 0.91 5.36 1.89 2.44
  End
  Rotor                       Hindered
               Geometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
H  0.5056191706  -0.8166945049  -0.5349501258
H  -0.5403403289  0.8736463849  1.8460697671
H  -0.5159089877  -0.8847071884  1.8665583753
H  1.9476627341  0.8886559429  1.6808343383
H  1.3758863213  0.050086519  3.1416401568
H  3.6571391054  -0.9233885893  2.905845261
H  3.7969874586  -2.1486946742  1.598074315
H  4.705459439  -1.2400328027  -0.5363514022
H  3.0278640037  -0.6582734506  -0.5815536658
H  5.4984206731  1.1171482707  -0.6882601899
H  4.5097186941  0.6618989089  -2.0672042196
H  3.5691956753  2.2831478998  0.3565701398
H  3.8122455928  2.9160652485  -1.2728612302
H  2.5104868528  1.7629559594  -0.9537030583
          Group                           6 16 17
          Axis                            5 4
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 8.05 3.64 4.70 3.74 4.70
  End
  Rotor                       Hindered
               Geometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
```

```
H  0.5056191706  -0.8166945049  -0.5349501258
H  -0.5403403289  0.8736463849  1.8460697671
H  -0.5159089877  -0.8847071884  1.8665583753
H  1.9476627341  0.8886559429  1.6808343383
H  1.3758863213  0.050086519  3.1416401568
H  3.6571391054  -0.9233885893  2.905845261
H  3.7969874586  -2.1486946742  1.598074315
H  4.705459439  -1.2400328027  -0.5363514022
H  3.0278640037  -0.6582734506  -0.5815536658
H  5.4984206731  1.1171482707  -0.6882601899
H  4.5097186941  0.6618989089  -2.0672042196
H  3.5691956753  2.2831478998  0.3565701398
H  3.8122455928  2.9160652485  -1.2728612302
H  2.5104868528  1.7629559594  -0.9537030583
          Group                          7
          Axis                           6 5
          Symmetry                       1
          Potential[kcal/mol]     6
0.00 7.90 3.42 4.59 3.70 4.70
  End
  Rotor                       Hindered
              Geometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
H  0.5056191706  -0.8166945049  -0.5349501258
H  -0.5403403289  0.8736463849  1.8460697671
H  -0.5159089877  -0.8847071884  1.8665583753
H  1.9476627341  0.8886559429  1.6808343383
H  1.3758863213  0.050086519  3.1416401568
H  3.6571391054  -0.9233885893  2.905845261
H  3.7969874586  -2.1486946742  1.598074315
H  4.705459439  -1.2400328027  -0.5363514022
H  3.0278640037  -0.6582734506  -0.5815536658
H  5.4984206731  1.1171482707  -0.6882601899
H  4.5097186941  0.6618989089  -2.0672042196
H  3.5691956753  2.2831478998  0.3565701398
H  3.8122455928  2.9160652485  -1.2728612302
H  2.5104868528  1.7629559594  -0.9537030583
          Group                          8 18 19
          Axis                           7 6
```

```
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 2.24 1.37 7.84 2.73 3.54
  End
  Rotor                       Hindered
              Geometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
H  0.5056191706  -0.8166945049  -0.5349501258
H  -0.5403403289  0.8736463849  1.8460697671
H  -0.5159089877  -0.8847071884  1.8665583753
H  1.9476627341  0.8886559429  1.6808343383
H  1.3758863213  0.050086519  3.1416401568
H  3.6571391054  -0.9233885893  2.905845261
H  3.7969874586  -2.1486946742  1.598074315
H  4.705459439  -1.2400328027  -0.5363514022
H  3.0278640037  -0.6582734506  -0.5815536658
H  5.4984206731  1.1171482707  -0.6882601899
H  4.5097186941  0.6618989089  -2.0672042196
H  3.5691956753  2.2831478998  0.3565701398
H  3.8122455928  2.9160652485  -1.2728612302
H  2.5104868528  1.7629559594  -0.9537030583
          Group                           9 20 21
          Axis                            8 7
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 5.32 0.85 4.20 1.06 4.29
  End
  Rotor                       Hindered
              Geometry[angstrom]      24
C  -0.0062476859  -0.02126965  -0.0163303857
C  -0.0046988522  0.0014011342  1.4704960807
C  1.4041056014  0.0136759017  2.0462213335
O  2.060696304  -1.1706363361  1.6295849883
C  3.4383611706  -1.1484599061  1.8579422363
O  4.0951878338  -0.1699438712  1.1141734754
C  4.0489889675  -0.3986242016  -0.2861167205
C  4.4812144319  0.867036039  -0.9952777783
C  3.5401618107  2.0291906974  -0.7020461274
H  -0.6261609568  0.6500802134  -0.5891455735
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519 H  0.5056191706  -0.8166945049  -0.5349501258
520 H  -0.5403403289  0.8736463849  1.8460697671
521 H  -0.5159089877  -0.8847071884  1.8665583753
522 H  1.9476627341  0.8886559429  1.6808343383
523 H  1.3758863213  0.050086519  3.1416401568
524 H  3.6571391054  -0.9233885893  2.905845261
525 H  3.7969874586  -2.1486946742  1.598074315
526 H  4.705459439  -1.2400328027  -0.5363514022
527 H  3.0278640037  -0.6582734506  -0.5815536658
528 H  5.4984206731  1.1171482707  -0.6882601899
529 H  4.5097186941  0.6618989089  -2.0672042196
530 H  3.5691956753  2.2831478998  0.3565701398
531 H  3.8122455928  2.9160652485  -1.2728612302
532 H  2.5104868528  1.7629559594  -0.9537030583
533          Group                          22 23 24
534          Axis                           9 8
535          Symmetry                       3
536          Potential[kcal/mol]     2
537 0.00 2.79
538   End
539   Frequencies[1/cm] 58
540 41.37 237.47 318.42 373.23
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
543 1085.12 1088.44 1112.25 1131.49 1149.18 1184.65
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
549 3104.47 3108.24 3127.85 3145.69 3180.95 3286.5
550 !49.7 63.84  96.04  120.38 162.38 213.89 260.19 301.91!Torsions
551          ZeroEnergy[kcal/mol]        100.8
552          ElectronicLevels[1/cm]      1
553               0   2
554        End
555 !---------------------------------------------------------------
556 !---------------------------------------------------------------
557 !---------------------------------------------------------------
558   Bimolecular   P2  # [H] + CCCOCOC[CH]C
559     Fragment  H
560       Atom
561         Mass[amu]   1
562         ElectronicLevels[1/cm]      1
563            0     2
564       End
565     Fragment  CCCOCOC[CH]C
566       RRHO
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  Geometry[angstrom]  24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
     Core                  RigidRotor
       SymmetryFactor      1
     End
  Rotor                    Hindered
          Group                          10 11 12
          Axis                           1 2
          Symmetry               3
          Potential[kcal/mol]     2
0.00 0.25
  End
  Rotor                    Hindered
          Group                          1 13
          Axis                           2 3
          Symmetry               1
          Potential[kcal/mol]     4
0.00 4.80 0.49 2.53
  End
  Rotor                    Hindered
          Group                          2 14 15
          Axis                           3 4
          Symmetry               1
          Potential[kcal/mol]     4
0.00 5.88 0.62 2.23
```

```
  End
  Rotor                       Hindered
          Group                           6 16 17
          Axis                            5 4
          Symmetry                1
          Potential[kcal/mol]     6
0.00 7.77 2.30 4.03 2.83 3.68
  End
  Rotor                       Hindered
          Group                           7
          Axis                            6 5
          Symmetry                1
          Potential[kcal/mol]     6
0.00 7.57 3.14 3.53 2.97 4.16
  End
  Rotor                       Hindered
          Group                           8 18 19
          Axis                            7 6
          Symmetry                1
          Potential[kcal/mol]     6
0.00 1.71 1.13 7.53 3.02 3.40
  End
  Rotor                       Hindered
          Group                           9 20 21
          Axis                            8 7
          Symmetry                1
          Potential[kcal/mol]     6
0.00 5.03 0.22 3.79 0.54 3.73
  End
  Rotor                       Hindered
          Group                           22 23 24
          Axis                            9 8
          Symmetry                3
          Potential[kcal/mol]     2
0.00 2.91
  End
  Frequencies[1/cm] 58
181.99 247.59 327.06 362.73
395.1 478.22 605.07 653.6 771.5 885.42
902.25 923.94 931.35 953.92 966.19 995.33
1087.27 1104.36 1112.34 1136.3 1158.69 1181.11
1189.53 1212.98 1284.04 1301.89 1315.95 1346.1
1377.09 1378.89 1394.61 1410.91 1417.38 1428.94
1454.92 1480.78 1484.24 1488.38 1493.96 1499.43
1513.27 1515.11 1531.56 3001.21 3018.12 3022.75
3043.63 3058.1 3060.67 3071.72 3081.17 3090.51
3095.81 3105.5 3130.5 3136.87 3146.79 3209.61
!30.02 38.37 54.99 70.59 100.17 148.23 224.5 308.22!Torsions
```

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  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    98.7
  End
! ------------------------------------------------------------
     Barrier     B2   W1   P2    # [H] + CCCOCOC[CH]C
       RRHO
        Stoichiometry C7H16O2
         Core     PhaseSpaceTheory
           FragmentGeometry[angstrom]      1
        H                   0.0000000   0.000000    0.000000
           FragmentGeometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
           SymmetryFactor              2
           PotentialPrefactor[au]      0.31 #0.05 0.07
           PotentialPowerExponent      2.6
         End
  Rotor                     Hindered
              Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
```

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C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          10 11 12
          Axis                           1 2
          Symmetry                       3
          Potential[kcal/mol]     2
0.00 0.25
  End
  Rotor                      Hindered
                 Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703  -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
```

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H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          1 13
          Axis                           2 3
          Symmetry                       1
          Potential[kcal/mol]     4
0.00 4.80 0.49 2.53
  End
  Rotor                      Hindered
                 Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          2 14 15
          Axis                           3 4
          Symmetry                1
          Potential[kcal/mol]     4
0.00 5.88 0.62 2.23
  End
  Rotor                      Hindered
               Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
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C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          6 16 17
          Axis                           5 4
          Symmetry                       1
          Potential[kcal/mol]     6
0.00 7.77 2.30 4.03 2.83 3.68
  End
  Rotor                       Hindered
               Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703  -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
```

```
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          7
          Axis                           6 5
          Symmetry                       1
          Potential[kcal/mol]     6
0.00 7.57 3.14 3.53 2.79 4.16
  End
  Rotor                      Hindered
               Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          8 18 19
          Axis                           7 6
          Symmetry                       1
          Potential[kcal/mol]     6
0.00 1.71 1.13 7.53 3.02 3.40
  End
  Rotor                      Hindered
               Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703   -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
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C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          9 20 21
          Axis                           8 7
          Symmetry                       1
          Potential[kcal/mol]     6
0.00 5.03 0.22 3.79 0.54 3.73
  End
  Rotor                      Hindered
               Geometry[angstrom]      24
C  -0.0036417969  -0.0113165538  0.0009621034
C  -0.009071703  -0.0175444756  1.4870498268
C  1.274613024  -0.003526504  2.241472572
O  2.1921274451  -1.0002392887  1.7946641173
C  1.7687409483  -2.30684524  2.0582618428
O  1.6444406178  -2.575977837  3.4198554709
C  2.8757189889  -2.5286225567  4.1216760662
C  2.5996301779  -2.7898591305  5.5871006631
C  1.7034666186  -1.7215015966  6.2007485082
H  0.8211932724  -0.6105888564  -0.3865122561
H  0.1303127427  1.0042713586  -0.3942202372
H  -0.9380836718  -0.3922607998  -0.4093885349
H  -0.9241205215  0.196415055  2.0203125821
H  1.8095489902  0.9403769374  2.0876089519
H  1.0940579811  -0.1149164068  3.3134731075
H  0.7821534067  -2.4962738099  1.6276553872
H  2.5222182054  -2.9530710846  1.5983871464
H  3.5565064933  -3.2822796728  3.7082972904
H  3.340682038  -1.5462983146  3.9891569651
H  2.1346569793  -3.7724325656  5.6853591049
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H  3.555532423  -2.8314433237  6.112775321
H  0.7422166319  -1.6928402958  5.6898518498
H  1.5234064585  -1.9129674615  7.2577232161
H  2.1631571936  -0.7353835483  6.1109080277
          Group                          22 23 24
          Axis                           9 8
          Symmetry                       3
          Potential[kcal/mol]     2
0.00 2.91
  End
  Frequencies[1/cm] 58
181.99 247.59 327.06 362.73
395.1 478.22 605.07 653.6 771.5 885.42
902.25 923.94 931.35 953.92 966.19 995.33
1087.27 1104.36 1112.34 1136.3 1158.69 1181.11
1189.53 1212.98 1284.04 1301.89 1315.95 1346.1
1377.09 1378.89 1394.61 1410.91 1417.38 1428.94
1454.92 1480.78 1484.24 1488.38 1493.96 1499.43
1513.27 1515.11 1531.56 3001.21 3018.12 3022.75
3043.63 3058.1 3060.67 3071.72 3081.17 3090.51
3095.81 3105.5 3130.5 3136.87 3146.79 3209.61
!30.02 38.37 54.99 70.59 100.17 148.23 224.5 308.22!Torsions
          ZeroEnergy[kcal/mol]        98.7
          ElectronicLevels[1/cm]      1
                0    2
      End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
  Bimolecular   P3  # [H] + CCCOCO[CH]CC
    Fragment  H
       Atom
         Mass[amu]   1
         ElectronicLevels[1/cm]      1
            0     2
       End
    Fragment  CCCOCO[CH]CC
      RRHO
  Geometry[angstrom]  24
C  -0.0170347954  -0.042787223  -0.0096479289
C  -0.0103493905  -0.00574936  1.5254452795
C  1.3609626603  0.0134329938  2.0910962383
O  2.0717771554  -1.1296747497  1.8665190464
C  3.424495751  -1.0712574673  2.2548318118
O  4.1386275867  -0.105293047  1.5617498313
C  4.2288852372  -0.3546645325  0.1665566211
C  4.9296949737  0.820108021  -0.4808277032
C  4.1394862671  2.1130109891  -0.3224175239
```

```
H  0.4738905145  0.8419861727  -0.4168027131
H  -1.0338721144  -0.0807139299  -0.4001200724
H  0.5196748539  -0.9224174817  -0.3638284901
H  -0.5464190356  0.8748536578  1.8803139529
H  -0.5400203646  -0.8828377721  1.9061604744
H  1.9372196587  0.9288054062  2.1626848698
H  3.4992399408  -0.810304153  3.3118909895
H  3.8188275083  -2.0731744067  2.0670764988
H  4.7803217317  -1.2876011437  0.002034374
H  3.2238435373  -0.4733227786  -0.2517504526
H  5.9208529181  0.9258975795  -0.036222829
H  5.0736048782  0.5900423737  -1.5381794198
H  4.0168531139  2.357841837  0.731459885
H  4.640589712  2.9472041973  -0.8114061524
H  3.1450686243  2.0117248472  -0.7614365875
      Core                  RigidRotor
        SymmetryFactor      1
      End
  Rotor                     Hindered
         Group                          10 11 12
         Axis                           1 2
         Symmetry               3
         Potential[kcal/mol]     2
0.00 3.11
  End
  Rotor                     Hindered
         Group                          1 13 14
         Axis                           2 3
         Symmetry               1
         Potential[kcal/mol]     6
0.00 2.36 0.37 1.85 0.49 1.62
  End
  Rotor                     Hindered
         Group                          2 15
         Axis                           3 4
         Symmetry               1
         Potential[kcal/mol]     6
0.00 4.99 1.51 4.63 3.19 5.89
  End
  Rotor                     Hindered
         Group                          3
         Axis                           4 5
         Symmetry               1
         Potential[kcal/mol]     6
0.00 12.0 2.41 3.32 2.98 3.55
  End
  Rotor                     Hindered
         Group                          7
```

```
          Axis                            6 5
          Symmetry                1
          Potential[kcal/mol]     6
0.00 6.99 2.23 4.18 3.47 4.48
  End
  Rotor                       Hindered
          Group                           8 18 19
          Axis                            7 6
          Symmetry                1
          Potential[kcal/mol]     6
0.00 2.02 1.24 7.74 2.66 3.57
  End
  Rotor                       Hindered
          Group                           9 20 21
          Axis                            8 7
          Symmetry                1
          Potential[kcal/mol]     6
0.00 5.15 0.35 3.91 0.66 3.72
  End
  Rotor                       Hindered
          Group                           22 23 24
          Axis                            9 8
          Symmetry                3
          Potential[kcal/mol]     2
0.00 2.64
  End
    Frequencies[1/cm] 58
103.35 302.11 309.99 366.51
436.0 508.65 600.36 675.99 770.37 779.5
902.17 911.37 925.92 963.07 972.59 1058.48
1088.4 1099.05 1118.58 1145.5 1171.55 1188.38
1210.08 1247.04 1285.29 1296.06 1309.92 1334.78
1350.45 1377.37 1392.11 1411.87 1418.4 1432.69
1469.48 1475.81 1483.67 1495.88 1498.28 1507.02
1510.3 1520.54 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 53.63 138.98 193.1 212.95 223.84 273.48!Torsions
  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    94.8
  End
! ------------------------------------------------------
    Barrier     B3   W1   P3    [H] + CCCOCO[CH]CC
      RRHO
       Stoichiometry C7H16O2
```

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          Core     PhaseSpaceTheory
                FragmentGeometry[angstrom]      1
        H                    0.000000    0.000000    0.000000
           FragmentGeometry[angstrom]      24
C  -0.0170347954  -0.042787223  -0.0096479289
C  -0.0103493905  -0.00574936  1.5254452795
C  1.3609626603  0.0134329938  2.0910962383
O  2.0717771554  -1.1296747497  1.8665190464
C  3.424495751  -1.0712574673  2.2548318118
O  4.1386275867  -0.105293047  1.5617498313
C  4.2288852372  -0.3546645325  0.1665566211
C  4.9296949737  0.820108021  -0.4808277032
C  4.1394862671  2.1130109891  -0.3224175239
H  0.4738905145  0.8419861727  -0.4168027131
H  -1.0338721144  -0.0807139299  -0.4001200724
H  0.5196748539  -0.9224174817  -0.3638284901
H  -0.5464190356  0.8748536578  1.8803139529
H  -0.5400203646  -0.8828377721  1.9061604744
H  1.9372196587  0.9288054062  2.1626848698
H  3.4992399408  -0.810304153  3.3118909895
H  3.8188275083  -2.0731744067  2.0670764988
H  4.7803217317  -1.2876011437  0.002034374
H  3.2238435373  -0.4733227786  -0.2517504526
H  5.9208529181  0.9258975795  -0.036222829
H  5.0736048782  0.5900423737  -1.5381794198
H  4.0168531139  2.357841837  0.731459885
H  4.640589712  2.9472041973  -0.8114061524
H  3.1450686243  2.0117248472  -0.7614365875
           SymmetryFactor               2
           PotentialPrefactor[au]       0.31 #0.05 0.07
           PotentialPowerExponent       2.66
         End
  Rotor                      Hindered
            Geometry[angstrom]      24
C  -0.0170347954  -0.042787223  -0.0096479289
C  -0.0103493905  -0.00574936  1.5254452795
C  1.3609626603  0.0134329938  2.0910962383
O  2.0717771554  -1.1296747497  1.8665190464
C  3.424495751  -1.0712574673  2.2548318118
O  4.1386275867  -0.105293047  1.5617498313
C  4.2288852372  -0.3546645325  0.1665566211
C  4.9296949737  0.820108021  -0.4808277032
C  4.1394862671  2.1130109891  -0.3224175239
H  0.4738905145  0.8419861727  -0.4168027131
H  -1.0338721144  -0.0807139299  -0.4001200724
H  0.5196748539  -0.9224174817  -0.3638284901
H  -0.5464190356  0.8748536578  1.8803139529
H  -0.5400203646  -0.8828377721  1.9061604744
```

```
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          10 11 12
          Axis                           1 2
          Symmetry                       3
          Potential[kcal/mol]      2
0.00 3.11
  End
  Rotor                       Hindered
             Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          1 13 14
          Axis                           2 3
          Symmetry                       1
          Potential[kcal/mol]      6
0.00 2.36 0.37 1.85 0.49 1.62
  End
```

```
  Rotor                        Hindered
              Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
           Group                          2 15
           Axis                           3 4
           Symmetry                       1
           Potential[kcal/mol]     6
0.00 4.99 1.51 4.63 3.19 5.89
  End
  Rotor                        Hindered
              Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
```

```
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          3
          Axis                           4 5
          Symmetry                       1
          Potential[kcal/mol]      6
0.00 12.0 2.41 3.32 2.98 3.55
  End
  Rotor                       Hindered
             Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          7
          Axis                           6 5
          Symmetry                       1
          Potential[kcal/mol]      6
0.00 6.99 2.23 4.18 3.47 4.48
  End
```

```
  Rotor                        Hindered
              Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
           Group                          8 18 19
           Axis                           7 6
           Symmetry                       1
           Potential[kcal/mol]     6
0.00 2.02 1.24 7.74 2.66 3.57
  End
  Rotor                        Hindered
              Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
```

```
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          9 20 21
          Axis                           8 7
          Symmetry                       1
          Potential[kcal/mol]      6
0.00 5.15 0.35 3.91 0.66 3.72
  End
  Rotor                       Hindered
               Geometry[angstrom]      24
C   -0.0170347954   -0.042787223   -0.0096479289
C   -0.0103493905   -0.00574936   1.5254452795
C   1.3609626603   0.0134329938   2.0910962383
O   2.0717771554   -1.1296747497   1.8665190464
C   3.424495751   -1.0712574673   2.2548318118
O   4.1386275867   -0.105293047   1.5617498313
C   4.2288852372   -0.3546645325   0.1665566211
C   4.9296949737   0.820108021   -0.4808277032
C   4.1394862671   2.1130109891   -0.3224175239
H   0.4738905145   0.8419861727   -0.4168027131
H   -1.0338721144   -0.0807139299   -0.4001200724
H   0.5196748539   -0.9224174817   -0.3638284901
H   -0.5464190356   0.8748536578   1.8803139529
H   -0.5400203646   -0.8828377721   1.9061604744
H   1.9372196587   0.9288054062   2.1626848698
H   3.4992399408   -0.810304153   3.3118909895
H   3.8188275083   -2.0731744067   2.0670764988
H   4.7803217317   -1.2876011437   0.002034374
H   3.2238435373   -0.4733227786   -0.2517504526
H   5.9208529181   0.9258975795   -0.036222829
H   5.0736048782   0.5900423737   -1.5381794198
H   4.0168531139   2.357841837   0.731459885
H   4.640589712   2.9472041973   -0.8114061524
H   3.1450686243   2.0117248472   -0.7614365875
          Group                          22 23 24
          Axis                           9 8
          Symmetry                       3
          Potential[kcal/mol]      2
0.00 2.64
  End
```

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    Frequencies[1/cm] 58
103.35 302.11 309.99 366.51
436.0 508.65 600.36 675.99 770.37 779.5
902.17 911.37 925.92 963.07 972.59 1058.48
1088.4 1099.05 1118.58 1145.5 1171.55 1188.38
1210.08 1247.04 1285.29 1296.06 1309.92 1334.78
1350.45 1377.37 1392.11 1411.87 1418.4 1432.69
1469.48 1475.81 1483.67 1495.88 1498.28 1507.02
1510.3 1520.54 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 53.63 138.98 193.1 212.95 223.84 273.48!Torsions
          ZeroEnergy[kcal/mol]        94.8
          ElectronicLevels[1/cm]      1
                0    2
      End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
  Bimolecular   P4  # [H] + CCCO[CH]OCCC
    Fragment  H
       Atom
         Mass[amu]   1
         ElectronicLevels[1/cm]      1
            0     2
       End
    Fragment  CCCO[CH]OCCC
      RRHO
  Geometry[angstrom]  24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
```

```
H   6.2351251895   1.0149296251   5.4429878715
H   4.6126339337   1.5896450659   5.7897467152
H   5.3203591415   -1.2709566824   4.9367779445
H   4.8905822352   -0.7744307183   6.57384944
H   3.6923498108   -0.689415   5.2803319621
      Core                    RigidRotor
        SymmetryFactor        2
      End
  Rotor                       Hindered
          Group                             10 11 12
          Axis                              1 2
          Symmetry                  3
          Potential[kcal/mol]      2
0.00 2.69
  End
  Rotor                       Hindered
          Group                             1 13 14
          Axis                              2 3
          Symmetry                  1
          Potential[kcal/mol]      6
0.00 3.61 0.32 3.59 0.04 4.68
  End
  Rotor                       Hindered
          Group                             2 15 16
          Axis                              3 4
          Symmetry                  1
          Potential[kcal/mol]      6
0.00 0.75 0.44 6.06 0.74 1.48
  End
  Rotor                       Hindered
          Group                             3
          Axis                              4 5
          Symmetry                  1
          Potential[kcal/mol]      4
0.00 1.96 1.51 8.93
  End
  Rotor                       Hindered
          Group                             7
          Axis                              6 5
          Symmetry                  1
          Potential[kcal/mol]      4
0.00 1.96 1.51 8.93
  End
  Rotor                       Hindered
          Group                             8 18 19
          Axis                              7 6
          Symmetry                  1
          Potential[kcal/mol]      6
```

```
0.00 0.75 0.44 6.06 0.74 1.48
  End
  Rotor                       Hindered
          Group                            9 20 21
          Axis                             8 7
          Symmetry                 1
          Potential[kcal/mol]      6
0.00 3.61 0.32 3.59 0.04 4.68
  End
  Rotor                       Hindered
          Group                            22 23 24
          Axis                             9 8
          Symmetry                 3
          Potential[kcal/mol]      2
0.00 2.69
  End
    Frequencies[1/cm] 58
185.29 296.31 326.5 334.78
437.29 506.85 634.41 768.03 783.95 889.91
907.31 920.0 928.19 940.92 970.58 1013.01 1091.4
1104.51 1134.75 1160.39 1178.64 1181.03 1230.14
1279.62 1284.11 1291.42 1311.01 1315.82 1368.48
1381.21 1390.65 1412.81 1414.18 1426.27 1450.29
1481.74 1484.33 1499.48 1500.22 1512.21 1512.42
1524.13 1526.13 3022.11 3034.86 3056.98 3064.67
3065.22 3067.43 3073.44 3101.05 3106.31 3107.2
3108.57 3134.29 3135.48 3148.14 3150.9
!26.47 42.12 54.62 112.86 131.44 149.62 214.02 257.6!Torsions
  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    97.0
  End
! ------------------------------------------------------------
     Barrier     B4   W1   P4    # [H] + CCCO[CH]OCCC
       RRHO
        Stoichiometry C7H16O2
         Core     PhaseSpaceTheory
           FragmentGeometry[angstrom]      1
        H                    0.0000000   0.000000    0.000000
           FragmentGeometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
```

```
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
            SymmetryFactor              2
            PotentialPrefactor[au]      0.31    #0.009 0.0007
            PotentialPowerExponent      2.62
          End
  Rotor                     Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
```

```
          Group                          10 11 12
          Axis                           1 2
          Symmetry                       3
          Potential[kcal/mol]            2
0.00 2.69
  End
  Rotor                      Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
          Group                          1 13 14
          Axis                           2 3
          Symmetry                       1
          Potential[kcal/mol]            6
0.00 3.61 0.32 3.59 0.04 4.68
  End
  Rotor                      Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
```

```
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
          Group                          2 15 16
          Axis                           3 4
          Symmetry                       1
          Potential[kcal/mol]            6
0.00 0.75 0.44 6.06 0.74 1.48
  End
  Rotor                      Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
```

```
          Group                           3
          Axis                            4 5
          Symmetry                  1
          Potential[kcal/mol]     4
0.00 1.96 1.51 8.93
  End
  Rotor                       Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
          Group                           7
          Axis                            6 5
          Symmetry                  1
          Potential[kcal/mol]     4
0.00 1.96 1.51 8.93
  End
  Rotor                       Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
```

```
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
          Group                          8 18 19
          Axis                           7 6
          Symmetry                       1
          Potential[kcal/mol]            6
0.00 0.75 0.44 6.06 0.74 1.48
  End
  Rotor                      Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
```

```
          Group                          9 20 21
          Axis                           8 7
          Symmetry                       1
          Potential[kcal/mol]            6
0.00 3.61 0.32 3.59 0.04 4.68
  End
  Rotor                      Hindered
             Geometry[angstrom]      24
C  0.1272836176  -0.0980909414  0.0670793598
C  0.0279854388  0.0213509486  1.5821135859
C  1.3835889491  0.0984857464  2.2500008907
O  2.0269096879  1.2916311462  1.8039833799
C  3.3337453847  1.3952720573  2.1124981028
O  3.6166046274  1.1274510121  3.4189133337
C  4.9980333045  1.2117165474  3.7299873392
C  5.1817389474  0.8741978383  5.1936050221
C  4.7454822632  -0.5486370162  5.5184559671
H  0.6529940289  0.759264736  -0.34960684
H  -0.8595000208  -0.1501063095  -0.390892139
H  0.6769159573  -0.9978869925  -0.2138784206
H  -0.5423450774 0.9113322552  1.8545255462
H  -0.5030175413 -0.8373060581  1.9976095994
H  1.2897134088  0.1217870336  3.3364092777
H  2.007070188  -0.7597531465  1.976608288
H  3.7899351263  2.2930571471  1.6975225622
H  5.5518159502  0.5108555694  3.0962923662
H  5.3562597864  2.2239785098  3.5130684671
H  6.2351251895  1.0149296251  5.4429878715
H  4.6126339337  1.5896450659  5.7897467152
H  5.3203591415  -1.2709566824  4.9367779445
H  4.8905822352  -0.7744307183  6.57384944
H  3.6923498108  -0.689415  5.2803319621
          Group                          22 23 24
          Axis                           9 8
          Symmetry                       3
          Potential[kcal/mol]            2
0.00 2.69
  End
    Frequencies[1/cm] 58
185.29 296.31 326.5 334.78
437.29 506.85 634.41 768.03 783.95 889.91
907.31 920.0 928.19 940.92 970.58 1013.01 1091.4
1104.51 1134.75 1160.39 1178.64 1181.03 1230.14
1279.62 1284.11 1291.42 1311.01 1315.82 1368.48
1381.21 1390.65 1412.81 1414.18 1426.27 1450.29
1481.74 1484.33 1499.48 1500.22 1512.21 1512.42
1524.13 1526.13 3022.11 3034.86 3056.98 3064.67
3065.22 3067.43 3073.44 3101.05 3106.31 3107.2
```

```
3108.57 3134.29 3135.48 3148.14 3150.9
!26.47 42.12 54.62 112.86 131.44 149.62 214.02 257.6!Torsions
          ZeroEnergy[kcal/mol]        97.0
          ElectronicLevels[1/cm]      1
                0      2
      End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
Bimolecular    P5 # CCCOCOC[CH2] + [CH3]
  Fragment              CCCOCOC[CH2]
    RRHO
    Geometry[angstrom]          21
     C                  2.94549700    0.92678700   -0.45160800
     C                  1.84415100    0.74209600    0.52595900
     O                  1.48912200   -0.62395300    0.69534100
     C                  0.83562100   -1.17091700   -0.41422000
     O                 -0.40255000   -0.58162700   -0.66138000
     C                 -1.35570300   -0.81254900    0.36315700
     C                 -2.63212200   -0.08378500    0.00049200
     C                 -2.42929700    1.42415200   -0.07699400
     H                  3.75871800    0.21627200   -0.46940300
     H                  3.04011300    1.84184700   -1.01486800
     H                  2.14619600    1.07740400    1.52396900
     H                  0.96565900    1.32775900    0.23851900
     H                  1.42091700   -1.02695200   -1.32577100
     H                  0.72509500   -2.23564300   -0.18974000
     H                 -1.53063000   -1.89090300    0.45706800
     H                 -0.96662600   -0.44966600    1.31991300
     H                 -2.99193000   -0.46443100   -0.95708400
     H                 -3.38866300   -0.32715600    0.74897400
     H                 -1.69080500    1.66948600   -0.83872700
     H                 -3.35763300    1.93776800   -0.32321700
     H                 -2.07187800    1.81413800    0.87795600
    Core    RigidRotor
      SymmetryFactor          1
    End
    Rotor                     Hindered
            Group                       4
            Axis                        3 2
            Symmetry                    1
            Potential[kcal/mol]         6
        0. 3.31 0.06 0.83 0.25 1.81
    End
    Rotor                     Hindered
            Group                       6
            Axis                        5 4
            Symmetry                    1
```

```
        Potential[kcal/mol]         6
    0.  7.54  2.92  3.22  2.77  4.12
End
Rotor                       Hindered
        Group                       7 15 16
        Axis                        6 5
        Symmetry                    1
        Potential[kcal/mol]         6
    0.  1.67  1.19  7.50  2.97  3.36
End
Rotor                       Hindered
        Group                       8 17 18
        Axis                        7 6
        Symmetry                    1
        Potential[kcal/mol]         6
    0.  5.03  0.19  3.76  0.51  3.71
End
Rotor                       Hindered
        Group                       9 10
        Axis                        1 2
        Symmetry                    2
        Potential[kcal/mol]         2
    0.  1.69
End
Rotor                       Hindered
        Group                       5 13 14
        Axis                        4 3
        Symmetry                    1
        Potential[kcal/mol]         4
    0.  7.29  3.13  3.82
End
Rotor                       Hindered
        Group                       19 20 21
        Axis                        8 7
        Symmetry                    3
        Potential[kcal/mol]         2
    0.  2.87
End
Frequencies[1/cm]    50
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
```

```
    !37.25  169.21  224.22  84.79  44.83  144.36  196.42! Torsions
  ZeroEnergy[kcal/mol]      0
  ElectronicLevels[1/cm]    1
    0    2
    End
   Fragment [CH3]
           RRHO
      Geometry[angstrom]  4
            C                  0.00000000    0.00000000    0.00000000
            H                  0.00000000    0.00000000    1.07652900
            H                  0.93230200    0.00000000   -0.53826500
            H                 -0.93230200   -0.00000000   -0.53826500
      Core  RigidRotor
        SymmetryFactor  6
      End
      Frequencies[1/cm] 6
             409.94  1411.49  1412.56  3141.77  3320.20  3321.01
     !  ! torsion
        ZeroEnergy[kcal/mol]        0
        ElectronicLevels[1/cm]      1
        0 2
      End
    GroundEnergy[kcal/mol]          88.0
End
!----------------------------------------------------------------------
Barrier    B5  W1  P5  # CCCOCOC[CH2] + [CH3]
  RRHO
  Stoichiometry  C7H16O2
  Core           PhaseSpaceTheory
    FragmentGeometry[angstrom]  21
     C  2.94549700    0.92678700   -0.45160800
     C  1.84415100    0.74209600    0.52595900
     O  1.48912200   -0.62395300    0.69534100
     C  0.83562100   -1.17091700   -0.41422000
     O  -0.40255000   -0.58162700   -0.66138000
     C  -1.35570300   -0.81254900    0.36315700
     C  -2.63212200   -0.08378500    0.00049200
     C  -2.42929700    1.42415200   -0.07699400
     H  3.75871800    0.21627200   -0.46940300
     H  3.04011300    1.84184700   -1.01486800
     H  2.14619600    1.07740400    1.52396900
     H  0.96565900    1.32775900    0.23851900
     H  1.42091700   -1.02695200   -1.32577100
     H  0.72509500   -2.23564300   -0.18974000
     H  -1.53063000   -1.89090300    0.45706800
     H  -0.96662600   -0.44966600    1.31991300
     H  -2.99193000   -0.46443100   -0.95708400
     H  -3.38866300   -0.32715600    0.74897400
```

```
 H   -1.69080500    1.66948600   -0.83872700
 H   -3.35763300    1.93776800   -0.32321700
 H   -2.07187800    1.81413800    0.87795600
FragmentGeometry[angstrom]  4
 C                  0.000000    0.000000    0.000000
 H                  0.000000    0.000000    1.076529
 H                  0.932302    0.000000   -0.538265
 H                 -0.932302   -0.000000   -0.538265
SymmetryFactor             6
  PotentialPrefactor[au]   5.96 #0.3 0.5
  PotentialPowerExponent   6.64
End
Rotor Hindered
  Geometry[angstrom]          21
   C                  2.94549700    0.92678700   -0.45160800
   C                  1.84415100    0.74209600    0.52595900
   O                  1.48912200   -0.62395300    0.69534100
   C                  0.83562100   -1.17091700   -0.41422000
   O                 -0.40255000   -0.58162700   -0.66138000
   C                 -1.35570300   -0.81254900    0.36315700
   C                 -2.63212200   -0.08378500    0.00049200
   C                 -2.42929700    1.42415200   -0.07699400
   H                  3.75871800    0.21627200   -0.46940300
   H                  3.04011300    1.84184700   -1.01486800
   H                  2.14619600    1.07740400    1.52396900
   H                  0.96565900    1.32775900    0.23851900
   H                  1.42091700   -1.02695200   -1.32577100
   H                  0.72509500   -2.23564300   -0.18974000
   H                 -1.53063000   -1.89090300    0.45706800
   H                 -0.96662600   -0.44966600    1.31991300
   H                 -2.99193000   -0.46443100   -0.95708400
   H                 -3.38866300   -0.32715600    0.74897400
   H                 -1.69080500    1.66948600   -0.83872700
   H                 -3.35763300    1.93776800   -0.32321700
   H                 -2.07187800    1.81413800    0.87795600
  Group                       4
  Axis                        3 2
  Symmetry                    1
  Potential[kcal/mol]         6
    0.  3.31  0.06  0.83  0.25  1.81
End
Rotor Hindered
  Geometry[angstrom]          21
   C                  2.94549700    0.92678700   -0.45160800
   C                  1.84415100    0.74209600    0.52595900
   O                  1.48912200   -0.62395300    0.69534100
   C                  0.83562100   -1.17091700   -0.41422000
   O                 -0.40255000   -0.58162700   -0.66138000
```

```
      C                  -1.35570300   -0.81254900    0.36315700
      C                  -2.63212200   -0.08378500    0.00049200
      C                  -2.42929700    1.42415200   -0.07699400
      H                   3.75871800    0.21627200   -0.46940300
      H                   3.04011300    1.84184700   -1.01486800
      H                   2.14619600    1.07740400    1.52396900
      H                   0.96565900    1.32775900    0.23851900
      H                   1.42091700   -1.02695200   -1.32577100
      H                   0.72509500   -2.23564300   -0.18974000
      H                  -1.53063000   -1.89090300    0.45706800
      H                  -0.96662600   -0.44966600    1.31991300
      H                  -2.99193000   -0.46443100   -0.95708400
      H                  -3.38866300   -0.32715600    0.74897400
      H                  -1.69080500    1.66948600   -0.83872700
      H                  -3.35763300    1.93776800   -0.32321700
      H                  -2.07187800    1.81413800    0.87795600
    Group                        6
    Axis                         5 4
    Symmetry                     1
    Potential[kcal/mol]          6
      0.  7.54  2.92  3.22  2.77  4.12
  End
  Rotor Hindered
    Geometry[angstrom]           21
      C                   2.94549700    0.92678700   -0.45160800
      C                   1.84415100    0.74209600    0.52595900
      O                   1.48912200   -0.62395300    0.69534100
      C                   0.83562100   -1.17091700   -0.41422000
      O                  -0.40255000   -0.58162700   -0.66138000
      C                  -1.35570300   -0.81254900    0.36315700
      C                  -2.63212200   -0.08378500    0.00049200
      C                  -2.42929700    1.42415200   -0.07699400
      H                   3.75871800    0.21627200   -0.46940300
      H                   3.04011300    1.84184700   -1.01486800
      H                   2.14619600    1.07740400    1.52396900
      H                   0.96565900    1.32775900    0.23851900
      H                   1.42091700   -1.02695200   -1.32577100
      H                   0.72509500   -2.23564300   -0.18974000
      H                  -1.53063000   -1.89090300    0.45706800
      H                  -0.96662600   -0.44966600    1.31991300
      H                  -2.99193000   -0.46443100   -0.95708400
      H                  -3.38866300   -0.32715600    0.74897400
      H                  -1.69080500    1.66948600   -0.83872700
      H                  -3.35763300    1.93776800   -0.32321700
      H                  -2.07187800    1.81413800    0.87795600
    Group                        7 15 16
    Axis                         6 5
    Symmetry                     1
```

```
    Potential[kcal/mol]          6
      0.  1.67  1.19  7.50  2.97  3.36
  End
  Rotor Hindered
    Geometry[angstrom]           21
     C                   2.94549700    0.92678700   -0.45160800
     C                   1.84415100    0.74209600    0.52595900
     O                   1.48912200   -0.62395300    0.69534100
     C                   0.83562100   -1.17091700   -0.41422000
     O                  -0.40255000   -0.58162700   -0.66138000
     C                  -1.35570300   -0.81254900    0.36315700
     C                  -2.63212200   -0.08378500    0.00049200
     C                  -2.42929700    1.42415200   -0.07699400
     H                   3.75871800    0.21627200   -0.46940300
     H                   3.04011300    1.84184700   -1.01486800
     H                   2.14619600    1.07740400    1.52396900
     H                   0.96565900    1.32775900    0.23851900
     H                   1.42091700   -1.02695200   -1.32577100
     H                   0.72509500   -2.23564300   -0.18974000
     H                  -1.53063000   -1.89090300    0.45706800
     H                  -0.96662600   -0.44966600    1.31991300
     H                  -2.99193000   -0.46443100   -0.95708400
     H                  -3.38866300   -0.32715600    0.74897400
     H                  -1.69080500    1.66948600   -0.83872700
     H                  -3.35763300    1.93776800   -0.32321700
     H                  -2.07187800    1.81413800    0.87795600
    Group                        8 17 18
    Axis                         7 6
    Symmetry                     1
    Potential[kcal/mol]          6
      0.  5.03  0.19  3.76  0.51  3.71
  End
  Rotor Hindered
    Geometry[angstrom]           21
     C                   2.94549700    0.92678700   -0.45160800
     C                   1.84415100    0.74209600    0.52595900
     O                   1.48912200   -0.62395300    0.69534100
     C                   0.83562100   -1.17091700   -0.41422000
     O                  -0.40255000   -0.58162700   -0.66138000
     C                  -1.35570300   -0.81254900    0.36315700
     C                  -2.63212200   -0.08378500    0.00049200
     C                  -2.42929700    1.42415200   -0.07699400
     H                   3.75871800    0.21627200   -0.46940300
     H                   3.04011300    1.84184700   -1.01486800
     H                   2.14619600    1.07740400    1.52396900
     H                   0.96565900    1.32775900    0.23851900
     H                   1.42091700   -1.02695200   -1.32577100
     H                   0.72509500   -2.23564300   -0.18974000
```

```
      H                  -1.53063000   -1.89090300    0.45706800
      H                  -0.96662600   -0.44966600    1.31991300
      H                  -2.99193000   -0.46443100   -0.95708400
      H                  -3.38866300   -0.32715600    0.74897400
      H                  -1.69080500    1.66948600   -0.83872700
      H                  -3.35763300    1.93776800   -0.32321700
      H                  -2.07187800    1.81413800    0.87795600
    Group                        9 10
    Axis                         1 2
    Symmetry                     2
    Potential[kcal/mol]          2
      0. 1.69
  End
  Rotor Hindered
    Geometry[angstrom]           21
      C                   2.94549700    0.92678700   -0.45160800
      C                   1.84415100    0.74209600    0.52595900
      O                   1.48912200   -0.62395300    0.69534100
      C                   0.83562100   -1.17091700   -0.41422000
      O                  -0.40255000   -0.58162700   -0.66138000
      C                  -1.35570300   -0.81254900    0.36315700
      C                  -2.63212200   -0.08378500    0.00049200
      C                  -2.42929700    1.42415200   -0.07699400
      H                   3.75871800    0.21627200   -0.46940300
      H                   3.04011300    1.84184700   -1.01486800
      H                   2.14619600    1.07740400    1.52396900
      H                   0.96565900    1.32775900    0.23851900
      H                   1.42091700   -1.02695200   -1.32577100
      H                   0.72509500   -2.23564300   -0.18974000
      H                  -1.53063000   -1.89090300    0.45706800
      H                  -0.96662600   -0.44966600    1.31991300
      H                  -2.99193000   -0.46443100   -0.95708400
      H                  -3.38866300   -0.32715600    0.74897400
      H                  -1.69080500    1.66948600   -0.83872700
      H                  -3.35763300    1.93776800   -0.32321700
      H                  -2.07187800    1.81413800    0.87795600
    Group                        5 13 14
    Axis                         4 3
    Symmetry                     1
    Potential[kcal/mol]          4
      0. 7.29 3.13 3.82
  End
  Rotor Hindered
    Geometry[angstrom]           21
      C                   2.94549700    0.92678700   -0.45160800
      C                   1.84415100    0.74209600    0.52595900
      O                   1.48912200   -0.62395300    0.69534100
      C                   0.83562100   -1.17091700   -0.41422000
```

```
       O                   -0.40255000   -0.58162700   -0.66138000
       C                   -1.35570300   -0.81254900    0.36315700
       C                   -2.63212200   -0.08378500    0.00049200
       C                   -2.42929700    1.42415200   -0.07699400
       H                    3.75871800    0.21627200   -0.46940300
       H                    3.04011300    1.84184700   -1.01486800
       H                    2.14619600    1.07740400    1.52396900
       H                    0.96565900    1.32775900    0.23851900
       H                    1.42091700   -1.02695200   -1.32577100
       H                    0.72509500   -2.23564300   -0.18974000
       H                   -1.53063000   -1.89090300    0.45706800
       H                   -0.96662600   -0.44966600    1.31991300
       H                   -2.99193000   -0.46443100   -0.95708400
       H                   -3.38866300   -0.32715600    0.74897400
       H                   -1.69080500    1.66948600   -0.83872700
       H                   -3.35763300    1.93776800   -0.32321700
       H                   -2.07187800    1.81413800    0.87795600
     Group                          19 20 21
     Axis                           8 7
     Symmetry                       3
     Potential[kcal/mol]            2
       0. 2.87
   End
   Frequencies[1/cm]        56
     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
     436.03 1412.64 1412.73 3144.41 3323.11 3323.14
     ! 37.25 169.21 224.22 84.79 44.83 144.36 196.42 ! Torsions
   ZeroEnergy[kcal/mol]       88.0
   ElectronicLevels[1/cm]     1
     0   2
End
!---------------------------------------------------------------------
!---------------------------------------------------------------------
!---------------------------------------------------------------------
Bimolecular    P6 # CCCOCO[CH2] + [CH2]C
   Fragment  CCCOCO[CH2]
   RRHO
   Geometry[angstrom]          18
    C                  -1.94844600    1.34603200   -0.02364300
    O                  -1.99833800    0.06676400   -0.46784100
    C                  -1.41208600   -0.87943300    0.40124300
    O                  -0.06725200   -0.63706500    0.62513000
    C                   0.73962300   -0.78301800   -0.53591100
```

```
     C                    2.14983100   -0.35591100   -0.19139900
     C                    2.21952600    1.11138500    0.21269100
     H                   -2.35406300    2.06443900   -0.71594300
     H                   -1.18632700    1.60835200    0.69589600
     H                   -1.90151500   -0.83911200    1.37566500
     H                   -1.57359700   -1.84552000   -0.08305400
     H                    0.70918100   -1.82783200   -0.86507900
     H                    0.34005100   -0.15831600   -1.34085300
     H                    2.52131800   -0.98859100    0.61666900
     H                    2.78217300   -0.54090700   -1.06178200
     H                    1.62193200    1.28976200    1.10520000
     H                    3.24385200    1.41700900    0.42091500
     H                    1.83102700    1.74879000   -0.58383900
   Core    RigidRotor
     SymmetryFactor           1
   End
   Rotor                    Hindered
     Group                       8 9
     Axis                        1 2
     Symmetry                    1
     Potential[kcal/mol]         4
       0.  4.95  0.  4.58
   End
   Rotor                      Hindered
     Group                       1
     Axis                        2 3
     Symmetry                    1
     Potential[kcal/mol]         6
       0.  4.27  2.05  2.88  2.49  3.23
   End
   Rotor                      Hindered
     Group                       5
     Axis                        4 3
     Symmetry                    1
     Potential[kcal/mol]         6
       0.  7.10  2.12  4.66  3.93  4.87
   End
   Rotor                      Hindered
     Group                       6 12 13
     Axis                        5 4
     Symmetry                    1
     Potential[kcal/mol]         6
       0.  1.83  1.19  7.28  2.94  3.12
   End
   Rotor                      Hindered
     Group                       7 14 15
     Axis                        6 5
     Symmetry                    1
```

```
      Potential[kcal/mol]          6
        0.  5.06  0.26  3.81  0.55  3.72
    End
    Rotor                       Hindered
      Group                          16 17 18
      Axis                           7 6
      Symmetry                       3
      Potential[kcal/mol]          6
        0.  2.65  0.  2.65  0.  2.65
  End
  Frequencies[1/cm]    42
    302.98 320.40 403.53 484.76 547.99 651.91
    771.94 901.65 924.85 964.05 992.83 1089.89
    1113.29 1146.62 1185.12 1193.40 1241.81 1269.08
    1286.98 1309.09 1347.55 1378.42 1412.76 1430.59
    1447.63 1484.95 1492.60 1497.44 1511.48 1521.44
    1528.95 3024.07 3057.90 3061.28 3063.87 3075.38
    3106.52 3116.50 3132.47 3148.95 3164.17 3304.07
    !    38.26  72.94  136.42  190.27  212.06  270.86    ! Torsions
  ZeroEnergy[kcal/mol]       0
  ElectronicLevels[1/cm]    1
    0    2
  End
  Fragment  [CH2]C
              RRHO
       Geometry[angstrom]  7
C                  0.00000000    0.00000000    0.00000000
H                  0.00000000    0.00000000    1.07891861
H                  0.95569277    0.00000000   -0.50071618
C                 -1.25516714    0.22579375   -0.75938703
H                 -2.11691855   -0.20402144   -0.24834925
H                 -1.46763143    1.29494164   -0.88792976
H                 -1.20242708   -0.20402144   -1.75988369
      Core                  RigidRotor
          SymmetryFactor                          1
        End
        Rotor                       Hindered
            Group                         5 6 7
            Axis                          4 1
            Symmetry                      3
            Potential[kcal/mol]    2
      0.  0.08
        End
        Frequencies[1/cm]        14
        445.30   810.67  983.05  1081.37   1195.61  1403.88   1471.54
    1487.47
        1489.48  3004.42   3085.31  3128.78  3174.30  3275.74
      !126.44! Torsions
```

```
      ZeroEnergy[kcal/mol]          0
        ElectronicLevels[1/cm]      1
          0 2
          End
    GroundEnergy[kcal/mol]          85.2
End
!----------------------------------------------------------------------
Barrier    B6   W1   P6   # CCCOCO[CH2] + [CH2]C
  RRHO
  Stoichiometry  C7H16O2
  Core           PhaseSpaceTheory
    FragmentGeometry[angstrom]  18
     C                 -1.94844600    1.34603200   -0.02364300
     O                 -1.99833800    0.06676400   -0.46784100
     C                 -1.41208600   -0.87943300    0.40124300
     O                 -0.06725200   -0.63706500    0.62513000
     C                  0.73962300   -0.78301800   -0.53591100
     C                  2.14983100   -0.35591100   -0.19139900
     C                  2.21952600    1.11138500    0.21269100
     H                 -2.35406300    2.06443900   -0.71594300
     H                 -1.18632700    1.60835200    0.69589600
     H                 -1.90151500   -0.83911200    1.37566500
     H                 -1.57359700   -1.84552000   -0.08305400
     H                  0.70918100   -1.82783200   -0.86507900
     H                  0.34005100   -0.15831600   -1.34085300
     H                  2.52131800   -0.98859100    0.61666900
     H                  2.78217300   -0.54090700   -1.06178200
     H                  1.62193200    1.28976200    1.10520000
     H                  3.24385200    1.41700900    0.42091500
     H                  1.83102700    1.74879000   -0.58383900
    FragmentGeometry[angstrom]  7
     C                   0.000000    0.000000    0.000000
     H                   0.000000    0.000000    1.078919
     H                   0.955693    0.000000   -0.500716
     C                  -1.255167    0.225794   -0.759387
     H                  -2.116919   -0.204021   -0.248349
     H                  -1.467631    1.294942   -0.887930
     H                  -1.202427   -0.204021   -1.759884
    SymmetryFactor             1
      PotentialPrefactor[au]   26.33 #5.5 6.3
      PotentialPowerExponent   9.67
    End
    Rotor Hindered
      Geometry[angstrom]          18
       C                 -1.94844600    1.34603200   -0.02364300
       O                 -1.99833800    0.06676400   -0.46784100
       C                 -1.41208600   -0.87943300    0.40124300
       O                 -0.06725200   -0.63706500    0.62513000
```

```
      C                    0.73962300   -0.78301800   -0.53591100
      C                    2.14983100   -0.35591100   -0.19139900
      C                    2.21952600    1.11138500    0.21269100
      H                   -2.35406300    2.06443900   -0.71594300
      H                   -1.18632700    1.60835200    0.69589600
      H                   -1.90151500   -0.83911200    1.37566500
      H                   -1.57359700   -1.84552000   -0.08305400
      H                    0.70918100   -1.82783200   -0.86507900
      H                    0.34005100   -0.15831600   -1.34085300
      H                    2.52131800   -0.98859100    0.61666900
      H                    2.78217300   -0.54090700   -1.06178200
      H                    1.62193200    1.28976200    1.10520000
      H                    3.24385200    1.41700900    0.42091500
      H                    1.83102700    1.74879000   -0.58383900
    Group                          8 9
    Axis                           1 2
    Symmetry                       1
    Potential[kcal/mol]            4
      0. 4.95 0. 4.58
  End
  Rotor Hindered
    Geometry[angstrom]             18
      C                   -1.94844600    1.34603200   -0.02364300
      O                   -1.99833800    0.06676400   -0.46784100
      C                   -1.41208600   -0.87943300    0.40124300
      O                   -0.06725200   -0.63706500    0.62513000
      C                    0.73962300   -0.78301800   -0.53591100
      C                    2.14983100   -0.35591100   -0.19139900
      C                    2.21952600    1.11138500    0.21269100
      H                   -2.35406300    2.06443900   -0.71594300
      H                   -1.18632700    1.60835200    0.69589600
      H                   -1.90151500   -0.83911200    1.37566500
      H                   -1.57359700   -1.84552000   -0.08305400
      H                    0.70918100   -1.82783200   -0.86507900
      H                    0.34005100   -0.15831600   -1.34085300
      H                    2.52131800   -0.98859100    0.61666900
      H                    2.78217300   -0.54090700   -1.06178200
      H                    1.62193200    1.28976200    1.10520000
      H                    3.24385200    1.41700900    0.42091500
      H                    1.83102700    1.74879000   -0.58383900
    Group                          1
    Axis                           2 3
    Symmetry                       1
    Potential[kcal/mol]            6
      0. 4.27 2.05 2.88 2.49 3.23
  End
  Rotor Hindered
    Geometry[angstrom]             18
```

```
      C                  -1.94844600    1.34603200   -0.02364300
      O                  -1.99833800    0.06676400   -0.46784100
      C                  -1.41208600   -0.87943300    0.40124300
      O                  -0.06725200   -0.63706500    0.62513000
      C                   0.73962300   -0.78301800   -0.53591100
      C                   2.14983100   -0.35591100   -0.19139900
      C                   2.21952600    1.11138500    0.21269100
      H                  -2.35406300    2.06443900   -0.71594300
      H                  -1.18632700    1.60835200    0.69589600
      H                  -1.90151500   -0.83911200    1.37566500
      H                  -1.57359700   -1.84552000   -0.08305400
      H                   0.70918100   -1.82783200   -0.86507900
      H                   0.34005100   -0.15831600   -1.34085300
      H                   2.52131800   -0.98859100    0.61666900
      H                   2.78217300   -0.54090700   -1.06178200
      H                   1.62193200    1.28976200    1.10520000
      H                   3.24385200    1.41700900    0.42091500
      H                   1.83102700    1.74879000   -0.58383900
    Group                         5
    Axis                          4 3
    Symmetry                      1
    Potential[kcal/mol]           6
      0.  7.10  2.12  4.66  3.93  4.87
  End
  Rotor Hindered
    Geometry[angstrom]           18
      C                  -1.94844600    1.34603200   -0.02364300
      O                  -1.99833800    0.06676400   -0.46784100
      C                  -1.41208600   -0.87943300    0.40124300
      O                  -0.06725200   -0.63706500    0.62513000
      C                   0.73962300   -0.78301800   -0.53591100
      C                   2.14983100   -0.35591100   -0.19139900
      C                   2.21952600    1.11138500    0.21269100
      H                  -2.35406300    2.06443900   -0.71594300
      H                  -1.18632700    1.60835200    0.69589600
      H                  -1.90151500   -0.83911200    1.37566500
      H                  -1.57359700   -1.84552000   -0.08305400
      H                   0.70918100   -1.82783200   -0.86507900
      H                   0.34005100   -0.15831600   -1.34085300
      H                   2.52131800   -0.98859100    0.61666900
      H                   2.78217300   -0.54090700   -1.06178200
      H                   1.62193200    1.28976200    1.10520000
      H                   3.24385200    1.41700900    0.42091500
      H                   1.83102700    1.74879000   -0.58383900
    Group                         6 12 13
    Axis                          5 4
    Symmetry                      1
    Potential[kcal/mol]           6
```

```
        0.  1.83  1.19  7.28  2.94  3.12
    End
    Rotor Hindered
      Geometry[angstrom]          18
       C                 -1.94844600    1.34603200   -0.02364300
       O                 -1.99833800    0.06676400   -0.46784100
       C                 -1.41208600   -0.87943300    0.40124300
       O                 -0.06725200   -0.63706500    0.62513000
       C                  0.73962300   -0.78301800   -0.53591100
       C                  2.14983100   -0.35591100   -0.19139900
       C                  2.21952600    1.11138500    0.21269100
       H                 -2.35406300    2.06443900   -0.71594300
       H                 -1.18632700    1.60835200    0.69589600
       H                 -1.90151500   -0.83911200    1.37566500
       H                 -1.57359700   -1.84552000   -0.08305400
       H                  0.70918100   -1.82783200   -0.86507900
       H                  0.34005100   -0.15831600   -1.34085300
       H                  2.52131800   -0.98859100    0.61666900
       H                  2.78217300   -0.54090700   -1.06178200
       H                  1.62193200    1.28976200    1.10520000
       H                  3.24385200    1.41700900    0.42091500
       H                  1.83102700    1.74879000   -0.58383900
      Group                       7 14 15
      Axis                        6 5
      Symmetry                    1
      Potential[kcal/mol]         6
        0.  5.06  0.26  3.81  0.55  3.72
    End
    Rotor Hindered
      Geometry[angstrom]          18
       C                 -1.94844600    1.34603200   -0.02364300
       O                 -1.99833800    0.06676400   -0.46784100
       C                 -1.41208600   -0.87943300    0.40124300
       O                 -0.06725200   -0.63706500    0.62513000
       C                  0.73962300   -0.78301800   -0.53591100
       C                  2.14983100   -0.35591100   -0.19139900
       C                  2.21952600    1.11138500    0.21269100
       H                 -2.35406300    2.06443900   -0.71594300
       H                 -1.18632700    1.60835200    0.69589600
       H                 -1.90151500   -0.83911200    1.37566500
       H                 -1.57359700   -1.84552000   -0.08305400
       H                  0.70918100   -1.82783200   -0.86507900
       H                  0.34005100   -0.15831600   -1.34085300
       H                  2.52131800   -0.98859100    0.61666900
       H                  2.78217300   -0.54090700   -1.06178200
       H                  1.62193200    1.28976200    1.10520000
       H                  3.24385200    1.41700900    0.42091500
       H                  1.83102700    1.74879000   -0.58383900
```

```
      Group                          16 17 18
      Axis                           7 6
      Symmetry                       3
      Potential[kcal/mol]            6
        0. 2.65 0. 2.65 0. 2.65
  End
    Rotor Hindered
      Geometry[angstrom]             7
       C                    0.000000    0.000000    0.000000
       H                    0.000000    0.000000    1.078919
       H                    0.955693    0.000000   -0.500716
       C                   -1.255167    0.225794   -0.759387
       H                   -2.116919   -0.204021   -0.248349
       H                   -1.467631    1.294942   -0.887930
       H                   -1.202427   -0.204021   -1.759884
            Group                        5 6 7
            Axis                         4 1
            Symmetry                     3
            Potential[kcal/mol]    2
      0. 0.08
    End
    Frequencies[1/cm]     56
      302.98  320.40  403.53  484.76  547.99  651.91  771.94  901.65
   924.85  964.05  992.83  1089.89  1113.29  1146.62  1185.12  1193.40
    1241.81  1269.08  1286.98  1309.09  1347.55  1378.42  1412.76
   1430.59  1447.63  1484.95  1492.60  1497.44  1511.48  1521.44
   1528.95  3024.07  3057.90  3061.28  3063.87  3075.38  3106.52
   3116.50  3132.47  3148.95  3164.17  3304.07
      445.30   810.68   983.06   1081.38   1195.62   1403.89   1471.54
     1487.48  1489.48   3004.42   3085.31   3128.78   3174.29   3275.74
      !    126.45 38.26  72.94  136.42  190.27  212.06  270.86    !
   Torsions
    ZeroEnergy[kcal/mol]       85.2
    ElectronicLevels[1/cm]     1
      0    2
End
!---------------------------------------------------------------
!---------------------------------------------------------------
!---------------------------------------------------------------
Bimolecular    P7     # CCCO[CH2] + CCC[O]
    Fragment  CCCO[CH2]
    RRHO
    Geometry[angstrom]          14
     C                 -1.78045700   -0.57633100    0.40428300
     O                 -1.06456400   -0.06010800   -0.61593800
     C                 -0.13758000    0.95064700   -0.24518600
     C                  1.02666700    0.39769000    0.56030500
     C                  1.76281900   -0.71079000   -0.17947000
```

```
 H                  -2.49993900   -1.32000100    0.10195800
 H                  -1.96045200    0.05427900    1.26775200
 H                   0.21562100    1.37685500   -1.18381500
 H                  -0.66451900    1.73033500    0.31502500
 H                   1.70201500    1.22640500    0.78328400
 H                   0.65353000    0.02475100    1.51629800
 H                   2.14744800   -0.35155400   -1.13523500
 H                   2.60297800   -1.08342900    0.40445300
 H                   1.09113200   -1.54406600   -0.38180700
Core    RigidRotor
  SymmetryFactor           1
End
Rotor                      Hindered
  Group                        6 7
  Axis                         1 2
  Symmetry                     1
  Potential[kcal/mol]          4
    0. 5.10 0. 5.37
End
Rotor                      Hindered
  Group                        1
  Axis                         2 3
  Symmetry                     1
  Potential[kcal/mol]          6
    0. 1.60 0.12 1.17 1.10 5.99
End
Rotor                      Hindered
  Group                        5 10 11
  Axis                         4 3
  Symmetry                     1
  Potential[kcal/mol]          6
    0. 3.74 0.47 3.46 0.73 4.79
End
Rotor                      Hindered
  Group                        12 13 14
  Axis                         5 4
  Symmetry                     3
  Potential[kcal/mol]          2
    0. 2.78
End
Frequencies[1/cm]    32
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
!     70.31  168.24  232.84  307.28    ! Torsions
```

```
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
    0    2
    End
    Fragment  CCC[O]
    RRHO
      Geometry[angstrom]          11
     C                 -1.49590800   -0.48329300    0.10802900
     C                 -0.56831200    0.66534600   -0.26144700
     C                  0.84087600    0.44659000    0.27076000
     O                  1.45814100   -0.68198500   -0.19676600
     H                 -1.08741200   -1.42684200   -0.25185400
     H                 -2.48614800   -0.35213400   -0.32501100
     H                 -1.60940000   -0.55763200    1.19092100
     H                 -0.51218700    0.77212100   -1.34631700
     H                 -0.94736500    1.61106700    0.13180500
     H                  1.49493800    1.31421200    0.10098500
     H                  0.82251400    0.32322800    1.36955000
      Core    RigidRotor
      SymmetryFactor           1
    End
    Rotor                     Hindered
      Group                       4 10 11
      Axis                        3 2
      Symmetry                    1
      Potential[kcal/mol]         6
        0.  3.15  0.44  3.15  0.  3.29
    End
    Rotor                     Hindered
      Group                       5 6 7
      Axis                        1 2
      Symmetry                    3
      Potential[kcal/mol]         2
        0.  2.78
  End
  Frequencies[1/cm]   25
    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
    !    141.59  231.1    ! Torsions
  ZeroEnergy[kcal/mol]      0
  ElectronicLevels[1/cm]    1
        0 2
    End
    GroundEnergy[kcal/mol]  89.1
End
!---------------------------------------------------------------
```

```
Barrier    B7   W1   P7   # CCCO[CH2] + CCC[O]
  RRHO
  Stoichiometry   C7H16O2
  Core            PhaseSpaceTheory
    FragmentGeometry[angstrom]  14
     C                 -1.78045700   -0.57633100    0.40428300
     O                 -1.06456400   -0.06010800   -0.61593800
     C                 -0.13758000    0.95064700   -0.24518600
     C                  1.02666700    0.39769000    0.56030500
     C                  1.76281900   -0.71079000   -0.17947000
     H                 -2.49993900   -1.32000100    0.10195800
     H                 -1.96045200    0.05427900    1.26775200
     H                  0.21562100    1.37685500   -1.18381500
     H                 -0.66451900    1.73033500    0.31502500
     H                  1.70201500    1.22640500    0.78328400
     H                  0.65353000    0.02475100    1.51629800
     H                  2.14744800   -0.35155400   -1.13523500
     H                  2.60297800   -1.08342900    0.40445300
     H                  1.09113200   -1.54406600   -0.38180700
    FragmentGeometry[angstrom]  11
     C                 -1.49590800   -0.48329300    0.10802900
     C                 -0.56831200    0.66534600   -0.26144700
     C                  0.84087600    0.44659000    0.27076000
     O                  1.45814100   -0.68198500   -0.19676600
     H                 -1.08741200   -1.42684200   -0.25185400
     H                 -2.48614800   -0.35213400   -0.32501100
     H                 -1.60940000   -0.55763200    1.19092100
     H                 -0.51218700    0.77212100   -1.34631700
     H                 -0.94736500    1.61106700    0.13180500
     H                  1.49493800    1.31421200    0.10098500
     H                  0.82251400    0.32322800    1.36955000
      SymmetryFactor              1
      PotentialPrefactor[au]      10.07 #0.5 0.75
      PotentialPowerExponent      9.18
    End
    Rotor Hindered
      Geometry[angstrom]          14
       C                  -1.78045700   -0.57633100    0.40428300
       O                  -1.06456400   -0.06010800   -0.61593800
       C                  -0.13758000    0.95064700   -0.24518600
       C                   1.02666700    0.39769000    0.56030500
       C                   1.76281900   -0.71079000   -0.17947000
       H                  -2.49993900   -1.32000100    0.10195800
       H                  -1.96045200    0.05427900    1.26775200
       H                   0.21562100    1.37685500   -1.18381500
       H                  -0.66451900    1.73033500    0.31502500
       H                   1.70201500    1.22640500    0.78328400
       H                   0.65353000    0.02475100    1.51629800
```

```
      H                    2.14744800   -0.35155400   -1.13523500
      H                    2.60297800   -1.08342900    0.40445300
      H                    1.09113200   -1.54406600   -0.38180700
    Group                          6 7
    Axis                           1 2
    Symmetry                       1
    Potential[kcal/mol]            4
      0. 5.10 0. 5.37
  End
  Rotor Hindered
    Geometry[angstrom]             14
     C                   -1.78045700   -0.57633100    0.40428300
     O                   -1.06456400   -0.06010800   -0.61593800
     C                   -0.13758000    0.95064700   -0.24518600
     C                    1.02666700    0.39769000    0.56030500
     C                    1.76281900   -0.71079000   -0.17947000
     H                   -2.49993900   -1.32000100    0.10195800
     H                   -1.96045200    0.05427900    1.26775200
     H                    0.21562100    1.37685500   -1.18381500
     H                   -0.66451900    1.73033500    0.31502500
     H                    1.70201500    1.22640500    0.78328400
     H                    0.65353000    0.02475100    1.51629800
     H                    2.14744800   -0.35155400   -1.13523500
     H                    2.60297800   -1.08342900    0.40445300
     H                    1.09113200   -1.54406600   -0.38180700
    Group                          1
    Axis                           2 3
    Symmetry                       1
    Potential[kcal/mol]            6
      0. 1.60 0.12 1.17 1.10 5.99
  End
  Rotor Hindered
    Geometry[angstrom]             14
     C                   -1.78045700   -0.57633100    0.40428300
     O                   -1.06456400   -0.06010800   -0.61593800
     C                   -0.13758000    0.95064700   -0.24518600
     C                    1.02666700    0.39769000    0.56030500
     C                    1.76281900   -0.71079000   -0.17947000
     H                   -2.49993900   -1.32000100    0.10195800
     H                   -1.96045200    0.05427900    1.26775200
     H                    0.21562100    1.37685500   -1.18381500
     H                   -0.66451900    1.73033500    0.31502500
     H                    1.70201500    1.22640500    0.78328400
     H                    0.65353000    0.02475100    1.51629800
     H                    2.14744800   -0.35155400   -1.13523500
     H                    2.60297800   -1.08342900    0.40445300
     H                    1.09113200   -1.54406600   -0.38180700
    Group                          5 10 11
```

```
    Axis                          4 3
    Symmetry                      1
    Potential[kcal/mol]           6
      0. 3.74 0.47 3.46 0.73 4.79
  End
  Rotor Hindered
    Geometry[angstrom]            14
     C                  -1.78045700   -0.57633100    0.40428300
     O                  -1.06456400   -0.06010800   -0.61593800
     C                  -0.13758000    0.95064700   -0.24518600
     C                   1.02666700    0.39769000    0.56030500
     C                   1.76281900   -0.71079000   -0.17947000
     H                  -2.49993900   -1.32000100    0.10195800
     H                  -1.96045200    0.05427900    1.26775200
     H                   0.21562100    1.37685500   -1.18381500
     H                  -0.66451900    1.73033500    0.31502500
     H                   1.70201500    1.22640500    0.78328400
     H                   0.65353000    0.02475100    1.51629800
     H                   2.14744800   -0.35155400   -1.13523500
     H                   2.60297800   -1.08342900    0.40445300
     H                   1.09113200   -1.54406600   -0.38180700
    Group                         12 13 14
    Axis                          5 4
    Symmetry                      3
    Potential[kcal/mol]           2
      0. 2.78
  End
  Rotor Hindered
    Geometry[angstrom]            11
     C                  -1.49590800   -0.48329300    0.10802900
     C                  -0.56831200    0.66534600   -0.26144700
     C                   0.84087600    0.44659000    0.27076000
     O                   1.45814100   -0.68198500   -0.19676600
     H                  -1.08741200   -1.42684200   -0.25185400
     H                  -2.48614800   -0.35213400   -0.32501100
     H                  -1.60940000   -0.55763200    1.19092100
     H                  -0.51218700    0.77212100   -1.34631700
     H                  -0.94736500    1.61106700    0.13180500
     H                   1.49493800    1.31421200    0.10098500
     H                   0.82251400    0.32322800    1.36955000
    Group                         4 10 11
    Axis                          3 2
    Symmetry                      1
    Potential[kcal/mol]           6
      0. 3.15 0.44 3.15 0. 3.29
  End
  Rotor Hindered
    Geometry[angstrom]            11
```

```
       C                  -1.49590800   -0.48329300    0.10802900
       C                  -0.56831200    0.66534600   -0.26144700
       C                   0.84087600    0.44659000    0.27076000
       O                   1.45814100   -0.68198500   -0.19676600
       H                  -1.08741200   -1.42684200   -0.25185400
       H                  -2.48614800   -0.35213400   -0.32501100
       H                  -1.60940000   -0.55763200    1.19092100
       H                  -0.51218700    0.77212100   -1.34631700
       H                  -0.94736500    1.61106700    0.13180500
       H                   1.49493800    1.31421200    0.10098500
       H                   0.82251400    0.32322800    1.36955000
     Group                         5 6 7
     Axis                          1 2
     Symmetry                      3
     Potential[kcal/mol]           2
       0. 2.78
   End
   Frequencies[1/cm]    57
     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
     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
     !    70.31  168.24  232.84  307.28  141.59  231.1    ! Torsions
   ZeroEnergy[kcal/mol]      89.1
   ElectronicLevels[1/cm]    1
     0    2
End
!---------------------------------------------------------------------
!---------------------------------------------------------------------
!---------------------------------------------------------------------
Bimolecular    P8    # CCCOC[O] + CC[CH2]
   Fragment  CCCOC[O]
   RRHO
   Geometry[angstrom]          15
    O                  2.57240700    0.43032500   -0.10693800
    C                  1.72881400   -0.59369500    0.11318800
    O                  0.42531800   -0.42837200   -0.33341500
    C                 -0.26608100    0.62485100    0.32084700
    C                 -1.68092200    0.67656700   -0.21398300
    C                 -2.45912000   -0.60124900    0.07111200
    H                  2.12524600   -1.49827000   -0.36931500
    H                  1.75566100   -0.77135500    1.20909800
    H                 -0.27299600    0.43272400    1.40317600
    H                  0.25430800    1.56959100    0.14634100
    H                 -2.18189500    1.53591200    0.23563800
```

```
    H                  -1.63463300    0.85888200   -1.28891600
    H                  -2.52631100   -0.78110400    1.14548000
    H                  -3.47263500   -0.54255300   -0.32298300
    H                  -1.96468300   -1.45829900   -0.38268200
  Core    RigidRotor
    SymmetryFactor           1
  End
      Rotor                      Hindered
    Group                        1 7 8
    Axis                         2 3
    Symmetry                     1
    Potential[kcal/mol]          6
      0. 2.35 0.05 3.26 2.17 3.36
  End
  Rotor                      Hindered
    Group                        2
    Axis                         3 4
    Symmetry                     1
    Potential[kcal/mol]          4
      0. 7.19 0.78 1.44
  End
  Rotor                      Hindered
    Group                        6 11 12
    Axis                         5 4
    Symmetry                     1
    Potential[kcal/mol]          6
      0. 3.64 0.35 3.58 0.10 4.82
  End
  Rotor                      Hindered
    Group                        13 14 15
    Axis                         6 5
    Symmetry                     3
    Potential[kcal/mol]          2
      0. 2.74
End
  Frequencies[1/cm]    35
  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
  !    49.19  109.4  212.14  164.27    ! Torsions
  ZeroEnergy[kcal/mol]    0
ElectronicLevels[1/cm]    1
  0    2
End
  Fragment  CC[CH2]
```

```
    RRHO
    Geometry[angstrom]          10
     C                 -1.21576400   -0.24393400   -0.03513100
     C                  0.07906700    0.55925200    0.04786100
     C                  1.29106100   -0.29615900   -0.03188100
     H                 -1.27316400   -0.78426700   -0.98002700
     H                 -2.09049500    0.40029700    0.04349600
     H                 -1.26327100   -0.97710700    0.77093600
     H                  0.10443800    1.31177800   -0.74483100
     H                  0.08395300    1.13114900    0.98641300
     H                  2.25628600    0.12468300   -0.26877100
     H                  1.25606300   -1.32148700    0.30769100
    Core    RigidRotor
      SymmetryFactor           1
    End
    Rotor                       Hindered
      Group                         4 5 6
      Axis                          1 2
      Symmetry                      3
      Potential[kcal/mol]           6
        0.  3.0  0.  3.0  0.  3.0
    End
    Rotor                       Hindered
      Group                         9 10
      Axis                          3 2
      Symmetry                      2
      Potential[kcal/mol]           2
        0.  0.26
  End
    Frequencies[1/cm]    22
    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
    ! 93.61 253.67 ! Torsions
  ZeroEnergy[kcal/mol]      0
  ElectronicLevels[1/cm]    1
        0 2
  End
    GroundEnergy[kcal/mol]  85.7
End
!----------------------------------------------------------------
Barrier    B8 W1 P8  # CCCOC[O] + CC[CH2]
  RRHO
  Stoichiometry  C7H16O2
  Core           PhaseSpaceTheory
    FragmentGeometry[angstrom]  15
     O                  2.57240700    0.43032500   -0.10693800
```

```
    C                    1.72881400   -0.59369500    0.11318800
    O                    0.42531800   -0.42837200   -0.33341500
    C                   -0.26608100    0.62485100    0.32084700
    C                   -1.68092200    0.67656700   -0.21398300
    C                   -2.45912000   -0.60124900    0.07111200
    H                    2.12524600   -1.49827000   -0.36931500
    H                    1.75566100   -0.77135500    1.20909800
    H                   -0.27299600    0.43272400    1.40317600
    H                    0.25430800    1.56959100    0.14634100
    H                   -2.18189500    1.53591200    0.23563800
    H                   -1.63463300    0.85888200   -1.28891600
    H                   -2.52631100   -0.78110400    1.14548000
    H                   -3.47263500   -0.54255300   -0.32298300
    H                   -1.96468300   -1.45829900   -0.38268200
  FragmentGeometry[angstrom]  10
    C                   -1.21576400   -0.24393400   -0.03513100
    C                    0.07906700    0.55925200    0.04786100
    C                    1.29106100   -0.29615900   -0.03188100
    H                   -1.27316400   -0.78426700   -0.98002700
    H                   -2.09049500    0.40029700    0.04349600
    H                   -1.26327100   -0.97710700    0.77093600
    H                    0.10443800    1.31177800   -0.74483100
    H                    0.08395300    1.13114900    0.98641300
    H                    2.25628600    0.12468300   -0.26877100
    H                    1.25606300   -1.32148700    0.30769100
     SymmetryFactor             1
     PotentialPrefactor[au]     11.02 #1
     PotentialPowerExponent     9.12
  End
  Rotor Hindered
    Geometry[angstrom]          15
     O                   2.57240700    0.43032500   -0.10693800
     C                   1.72881400   -0.59369500    0.11318800
     O                   0.42531800   -0.42837200   -0.33341500
     C                  -0.26608100    0.62485100    0.32084700
     C                  -1.68092200    0.67656700   -0.21398300
     C                  -2.45912000   -0.60124900    0.07111200
     H                   2.12524600   -1.49827000   -0.36931500
     H                   1.75566100   -0.77135500    1.20909800
     H                  -0.27299600    0.43272400    1.40317600
     H                   0.25430800    1.56959100    0.14634100
     H                  -2.18189500    1.53591200    0.23563800
     H                  -1.63463300    0.85888200   -1.28891600
     H                  -2.52631100   -0.78110400    1.14548000
     H                  -3.47263500   -0.54255300   -0.32298300
     H                  -1.96468300   -1.45829900   -0.38268200
    Group                        1 7 8
    Axis                         2 3
```

```
    Symmetry                      1
    Potential[kcal/mol]           6
      0.  2.35  0.05  3.26  2.17  3.36
  End
  Rotor Hindered
    Geometry[angstrom]            15
     O                   2.57240700    0.43032500   -0.10693800
     C                   1.72881400   -0.59369500    0.11318800
     O                   0.42531800   -0.42837200   -0.33341500
     C                  -0.26608100    0.62485100    0.32084700
     C                  -1.68092200    0.67656700   -0.21398300
     C                  -2.45912000   -0.60124900    0.07111200
     H                   2.12524600   -1.49827000   -0.36931500
     H                   1.75566100   -0.77135500    1.20909800
     H                  -0.27299600    0.43272400    1.40317600
     H                   0.25430800    1.56959100    0.14634100
     H                  -2.18189500    1.53591200    0.23563800
     H                  -1.63463300    0.85888200   -1.28891600
     H                  -2.52631100   -0.78110400    1.14548000
     H                  -3.47263500   -0.54255300   -0.32298300
     H                  -1.96468300   -1.45829900   -0.38268200
    Group                         2
    Axis                          3 4
    Symmetry                      1
    Potential[kcal/mol]           4
      0.  7.19  0.78  1.44
  End
  Rotor Hindered
    Geometry[angstrom]            15
     O                   2.57240700    0.43032500   -0.10693800
     C                   1.72881400   -0.59369500    0.11318800
     O                   0.42531800   -0.42837200   -0.33341500
     C                  -0.26608100    0.62485100    0.32084700
     C                  -1.68092200    0.67656700   -0.21398300
     C                  -2.45912000   -0.60124900    0.07111200
     H                   2.12524600   -1.49827000   -0.36931500
     H                   1.75566100   -0.77135500    1.20909800
     H                  -0.27299600    0.43272400    1.40317600
     H                   0.25430800    1.56959100    0.14634100
     H                  -2.18189500    1.53591200    0.23563800
     H                  -1.63463300    0.85888200   -1.28891600
     H                  -2.52631100   -0.78110400    1.14548000
     H                  -3.47263500   -0.54255300   -0.32298300
     H                  -1.96468300   -1.45829900   -0.38268200
    Group                         6 11 12
    Axis                          5 4
    Symmetry                      1
    Potential[kcal/mol]           6
```

```
        0.  3.64  0.35  3.58  0.10  4.82
    End
    Rotor Hindered
      Geometry[angstrom]          15
       O                  2.57240700    0.43032500   -0.10693800
       C                  1.72881400   -0.59369500    0.11318800
       O                  0.42531800   -0.42837200   -0.33341500
       C                 -0.26608100    0.62485100    0.32084700
       C                 -1.68092200    0.67656700   -0.21398300
       C                 -2.45912000   -0.60124900    0.07111200
       H                  2.12524600   -1.49827000   -0.36931500
       H                  1.75566100   -0.77135500    1.20909800
       H                 -0.27299600    0.43272400    1.40317600
       H                  0.25430800    1.56959100    0.14634100
       H                 -2.18189500    1.53591200    0.23563800
       H                 -1.63463300    0.85888200   -1.28891600
       H                 -2.52631100   -0.78110400    1.14548000
       H                 -3.47263500   -0.54255300   -0.32298300
       H                 -1.96468300   -1.45829900   -0.38268200
      Group                       13 14 15
      Axis                        6 5
      Symmetry                    3
      Potential[kcal/mol]         2
        0.  2.74
    End
    Rotor Hindered
      Geometry[angstrom]          10
       C                 -1.21576400   -0.24393400   -0.03513100
       C                  0.07906700    0.55925200    0.04786100
       C                  1.29106100   -0.29615900   -0.03188100
       H                 -1.27316400   -0.78426700   -0.98002700
       H                 -2.09049500    0.40029700    0.04349600
       H                 -1.26327100   -0.97710700    0.77093600
       H                  0.10443800    1.31177800   -0.74483100
       H                  0.08395300    1.13114900    0.98641300
       H                  2.25628600    0.12468300   -0.26877100
       H                  1.25606300   -1.32148700    0.30769100
      Group                       4 5 6
      Axis                        1 2
      Symmetry                    3
      Potential[kcal/mol]         6
        0.  3.0  0.  3.0  0.  3.0
    End
    Rotor Hindered
      Geometry[angstrom]          10
       C                 -1.21576400   -0.24393400   -0.03513100
       C                  0.07906700    0.55925200    0.04786100
       C                  1.29106100   -0.29615900   -0.03188100
```

```
       H                  -1.27316400   -0.78426700   -0.98002700
       H                  -2.09049500    0.40029700    0.04349600
       H                  -1.26327100   -0.97710700    0.77093600
       H                   0.10443800    1.31177800   -0.74483100
       H                   0.08395300    1.13114900    0.98641300
       H                   2.25628600    0.12468300   -0.26877100
       H                   1.25606300   -1.32148700    0.30769100
     Group                         9 10
     Axis                          3 2
     Symmetry                      2
     Potential[kcal/mol]           2
       0. 0.26
   End
   Frequencies[1/cm]    57
     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
     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
     !    93.61  253.67  49.19  109.4  212.14  164.27    ! Torsions
   ZeroEnergy[kcal/mol]      85.7
   ElectronicLevels[1/cm]    1
     0    2
End
!------------------------------------------------
!-----------------TS PRODUCTS--------------------
!------------------------------------------------
Bimolecular   P9 # CC=C + CCCOCO
   Fragment  CC=C
     RRHO
  Geometry[angstrom]  9
C  0.0036214937  -0.0000114327  0.0051615123
C  -0.0039889758  -0.0000394546  1.500892564
C  1.07912644  0.0000345476  2.2615817567
H  -0.5150658471  -0.8766640488  -0.3868397296
H  1.0214524858  0.0000723263  -0.3822168897
H  -0.515197614  0.876577764  -0.3868072993
H  -0.9797651506  -0.0001270642  1.9768345388
H  1.0142061682  0.0000099149  3.34096794
H  2.0713279302  0.0001224921  1.8258035873
     Core                  RigidRotor
       SymmetryFactor      1
     End
  Rotor                    Hindered
         Group                          4 5 6
```

```
          Axis                            1 2
          Symmetry                3
          Potential[kcal/mol]     2
0.00 2.01
  End
    Frequencies[1/cm] 21
206.03 430.51 596.0 938.41 947.42 967.29
1036.32 1079.5 1195.46 1330.57 1407.13 1454.25
1484.54 1497.22 1742.34 3056.62 3111.88 3138.7
3159.03 3168.59 3248.77
!206.03!Torsions
  ZeroEnergy[kcal/mol]      0
  ElectronicLevels[1/cm]      1
    0 2
      End
    Fragment  CCCOCO
      RRHO
  Geometry[angstrom]  16
O  -0.0070840343  0.0074935394  0.002485829
C  -0.0052295361  -0.0011633336  1.4035402734
O  1.2769173339  -0.0001760102  1.9450189173
C  1.994960368  -1.2008949833  1.7067639473
C  3.3454734353  -1.0953810921  2.3828006609
C  3.2308461484  -0.9453409113  3.8941177227
H  0.4089591955  0.8234248166  -0.289985711
H  -0.5011758121  0.8812907321  1.8112104507
H  -0.5498680154  -0.9051527654  1.6908158425
H  1.4266005788  -2.0458507992  2.1184037593
H  2.1043805809  -1.3603307372  0.6317282107
H  3.9219367639  -1.987850797  2.131735042
H  3.8776483113  -0.2417971891  1.9587696541
H  2.7189686338  -1.8054470792  4.3291377946
H  4.212257742  -0.8680061494  4.360045638
H  2.6601503483  -0.0533242743  4.1461459727
      Core                    RigidRotor
        SymmetryFactor        1
      End
  Rotor                       Hindered
          Group                           7
          Axis                            1 2
          Symmetry                1
          Potential[kcal/mol]     4
0.00 3.88 1.85 3.60
  End
  Rotor                       Hindered
          Group                           4
          Axis                            3 2
          Symmetry                1
```

```
          Potential[kcal/mol]     6
0.00 6.53 1.96 3.99 2.66 3.89
  End
  Rotor                       Hindered
          Group                           2
          Axis                            3 4
          Symmetry                1
          Potential[kcal/mol]     4
0.00 6.72 0.96 1.31
  End
  Rotor                       Hindered
          Group                           6 12 13
          Axis                            5 4
          Symmetry                1
          Potential[kcal/mol]     6
0.00 3.61 0.36 3.58 0.07 4.86
  End
  Rotor                       Hindered
          Group                           14 15 16
          Axis                            6 5
          Symmetry                3
          Potential[kcal/mol]     2
0.00 2.73
  End
    Frequencies[1/cm] 37
293.77 334.78 469.42 626.34 768.17 900.63 928.85
963.33 1055.02 1088.72 1106.95 1143.48 1178.74
1194.09 1279.38 1297.37 1321.49 1379.31 1391.74
1412.62 1427.11 1460.64 1482.68 1499.38 1512.17
1527.51 1535.37 3005.84 3050.91 3063.51 3066.07
3086.26 3104.39 3104.79 3133.09 3151.04 3871.0
!42.97 107.33 170.94 209.45 367.96!Torsions
  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    13.1
  End
!-------------------------------------------------
     Barrier     B9   W1   P9    # TS: CC=C + CCCOCO
      Variational
        RRHO
          Geometry[angstrom] 25
C  0.0167726852  -0.0011656826  -0.0035102651
C  0.0050199859  -0.0005832888  1.5082116449
C  1.2058640161  0.0031095776  2.2370221966
O  1.1111527393  1.8707111927  2.5899211208
C  1.1863728083  2.4302655822  3.8585419819
```

```
O   0.5849188541   1.6409484035   4.8504368591
C   -0.8275027078   1.6204621347   4.7898140631
C   -1.342595167   0.6898593028   5.8679389065
C   -0.8622466294   -0.741321895   5.6625784546
H   0.0752455206   -1.0102750682   -0.416901552
H   0.8719190593   0.5629254617   -0.3783498515
H   -0.881532865   0.4645912054   -0.4071348115
H   0.1324629328   1.2927113328   2.0239015209
H   -0.8468723042   -0.4635136453   1.9944328146
H   1.22596035   -0.3252898892   3.2682721279
H   2.1647934139   0.0489156797   1.7374416323
H   2.2312749378   2.5301979991   4.1560727257
H   0.7152573048   3.4221665032   3.8339527379
H   -1.2148365536   2.6367321713   4.929587707
H   -1.1606494527   1.2666009614   3.8064688709
H   -1.0118845242   1.061919829   6.839153618
H   -2.4335519639   0.7287619893   5.8613338879
H   0.2243675556   -0.7886870892   5.716390056
H   -1.270022524   -1.4110766954   6.4184127455
H   -1.1692604021   -1.1142360472   4.6827847884
          Core RigidRotor
            SymmetryFactor                0.5
          End
  Rotor                      Hindered
          Group                           10 11 12
          Axis                            1 2
          Symmetry                        3
          Potential[kcal/mol]     2
0.00 1.55
  End
  Rotor                      Hindered
          Group                           6 17 18
          Axis                            5 4
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 7.51 2.82 3.28 3.24 3.91
  End
  Rotor                      Hindered
          Group                           7
          Axis                            6 5
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 6.67 2.40 3.28 1.29 2.66
  End
  Rotor                      Hindered
          Group                           8 19 20
          Axis                            7 6
          Symmetry                        1
```

```
          Potential[kcal/mol]     6
0.00 1.70 1.58 9.16 8.41 13.97
  End
  Rotor                       Hindered
          Group                           9 21 22
          Axis                            8 7
          Symmetry                        1
          Potential[kcal/mol]     6
0.00 5.25 0.37 3.94 0.71 3.75
  End
  Rotor                       Hindered
          Group                           23 24 25
          Axis                            9 8
          Symmetry                        3
          Potential[kcal/mol]     2
0.00 2.80
  End
          Frequencies[1/cm]         62
117.89 166.0 205.77 308.01 350.84
387.2 426.71 463.37 529.01 637.25 755.43
771.58 897.19 904.66 926.24 929.31 962.19
984.85 1025.75 1078.29 1083.07 1114.62 1143.68
1156.61 1180.53 1185.64 1200.42 1258.67 1284.35
1295.17 1315.26 1328.51 1377.35 1408.82 1410.08
1422.36 1435.99 1444.9 1484.45 1492.03 1499.11
1508.48 1511.17 1513.6 1527.96 1549.25 1601.1
3002.19 3013.38 3045.91 3050.17 3057.33 3070.77
3096.41 3106.08 3108.47 3128.7 3128.99 3146.59
3160.97 3167.5 3252.96
!47.77 59.97 85.73 151.33 184.1 235.42!Torsions
          ZeroEnergy[kcal/mol]          67.1
          ElectronicLevels[1/cm]        1
               0    1
        End
          Tunneling         Eckart
          ImaginaryFrequency[1/cm]      1858.51
          WellDepth[kcal/mol]           67.1
          WellDepth[kcal/mol]           54.0
      End
  End
!---------------------------------------------------------------
!---------------------------------------------------------------
!---------------------------------------------------------------
Bimolecular   P10 # CH2O + CCCOCCC
    Fragment  CH2O
              RRHO
       Geometry[angstrom] 4
              O                 -0.67047700    0.00000100    0.00000200
```

```
              C                   0.52488300    -0.00000200    -0.00000900
              H                   1.10726700     0.93752700     0.00001900
              H                   1.10725400    -0.93752400     0.00001900
       Core   RigidRotor
       SymmetryFactor 2
       End
       Frequencies[1/cm]  6
                1218.60              1279.77              1546.46
                1877.07              2943.65              3014.58
       !!torsions
          ZeroEnergy[kcal/mol]      0
          ElectronicLevels[1/cm]      1
          0 1
      End
    Fragment  CCCOCCC
      RRHO
  Geometry[angstrom]  21
C -0.0091120319 0.0318976555 0.0140270155
C 0.0076480544 0.003019928 1.5368771873
C 1.4151072597 -0.0090342913 2.0966049439
O 2.068631021 1.1789261673 1.7166217725
C 3.4018293127 1.23950968 2.1656681858
C 4.0037317542 2.563633421 1.7428293813
C 3.2867148829 3.7518655262 2.3706660009
H 0.5084579275 0.9154998431 -0.3549639519
H -1.0279584179 0.0441753618 -0.3709015659
H 0.4939225903 -0.846615849  -0.3937450685
H -0.5143122593 0.8746125952 1.936064385
H -0.5152872461 -0.8813245007 1.9063228173
H 1.3969864114 -0.0890275817 3.1910289633
H 1.9690435532 -0.8767794906 1.7103091638
H 3.4289443256 1.1434600255  3.2606981916
H 3.9732870959 0.4016860188 1.7461700967
H 5.0590355738  2.5649384134 2.0227372361
H 3.9604134115 2.6296732015 0.6541471454
H 3.3421192777 3.7040928395 3.45959027
H 3.729606735 4.6949223832 2.0530826932
H 2.2354096682 3.7535686208 2.0886371151
      Core  RigidRotor
    SymmetryFactor  2.0
      End
  Rotor                     Hindered
          Group                         19 20 21
          Axis                          7 6
          Symmetry              3
          Potential[kcal/mol]     2
0.00 2.73
  End
```

```
  Rotor                       Hindered
          Group                           7 17 18
          Axis                            6 5
          Symmetry                1
          Potential[kcal/mol]     6
0.00 3.54 0.36 3.54 0.07 4.74
  End
  Rotor                       Hindered
          Group                           6 15 16
          Axis                            5 4
          Symmetry                1
          Potential[kcal/mol]     6
0.00 3.42 3.37 7.91 0.74 2.34
  End
    Frequencies[1/cm] 54
115.58 163.28 228.07
272.32 326.16 338.86 488.35 504.21 757.79
789.06 895.97 916.73 926.55 939.76 971.08
1037.51 1103.93 1116.99 1156.21 1185.33 1190.88
1207.0 1278.86 1288.61 1309.22 1316.9 1376.06
1379.61 1401.47 1412.08 1414.32 1457.87 1482.7
1482.76 1498.57 1499.34 1511.95 1513.54 1518.02
1536.54 2984.22 2992.11 3022.48 3025.59 3062.71
3062.89 3067.72 3067.86 3103.4 3103.59 3131.32
3131.32 3150.44 3150.56
!43.43 79.47 161.64!Torsions
  ZeroEnergy[kcal/mol]        0
  ElectronicLevels[1/cm]      1
    0 2
      End
    GroundEnergy[kcal/mol]    14.6
  End
!-----------------------------------------------------------
Barrier    B10   W1   P10     # CH2O + CCCOCCC
  Variational
    RRHO
    Geometry[angstrom]   25
     C                 -1.78945300    1.71595700   -0.46761900
     C                 -2.48127800    0.63506400    0.35516100
     C                 -1.52914000   -0.31559200    0.99265800
     O                 -1.37808000   -1.40439300   -0.79603800
     C                 -0.07342300   -1.35704300   -0.84946000
     O                  0.25556500   -0.31485000    0.16080800
     C                  1.43294100   -0.46536600    0.93495800
     C                  2.67383700   -0.11636300    0.12793200
     C                  2.61632800    1.29790700   -0.43307200
     H                  3.51485000    1.53307800   -1.00114300
     H                  1.75495900    1.41532400   -1.08961700
```

```
     H                   2.52461900    2.03008900    0.37102600
     H                   2.78191700   -0.84059200   -0.68216400
     H                   3.54392600   -0.23744200    0.77662400
     H                   1.33100400    0.22155100    1.77941100
     H                   1.48885000   -1.48837800    1.32103800
     H                   0.35743700   -0.98816900   -1.79691500
     H                   0.47752100   -2.26327400   -0.52220200
     H                  -0.93734500    0.15270900    1.77679500
     H                  -1.89957800   -1.28630900    1.28060200
     H                  -3.19190100    0.08967900   -0.25711500
     H                  -3.01885500    1.10714000    1.18930300
     H                  -2.51283900    2.44918300   -0.82013200
     H                  -1.03007500    2.23356000    0.12020700
     H                  -1.30324000    1.25842400   -1.32722000
   Core    RigidRotor
      SymmetryFactor          1
   End
   Rotor         Hindered
     Group                   23 24 25
     Axis                    1 2
     Symmetry                3
     Potential[kcal/mol]     2
       0. 3.64
   End
   Rotor         Hindered
     Group                   1 21 22
     Axis                    2 3
     Symmetry          1
     Potential[kcal/mol]     6
       0. 4.12 0.95 2.99 1.45 2.84
   End
   Rotor         Hindered
     Group                   9 13 14
     Axis                    8 7
     Symmetry                1
     Potential[kcal/mol]     6
       0. 4.15 0.59 4.02 0.67 4.74
   End
   Rotor         Hindered
     Group                   10 11 12
     Axis                    9 8
     Symmetry                3
     Potential[kcal/mol]     2
       0. 2.78
   End
   Rotor         Hindered
     Group                   8 15 16
     Axis                    7 6
```

```
      Symmetry                1
      Potential[kcal/mol]     4
        0.  2.29  0.84  5.12
    End
    Frequencies[1/cm]       63
    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
    !    41.87  52.66  105.97  229.73  259.97    ! Torsions
    ZeroEnergy[kcal/mol]      75.2
    ElectronicLevels[1/cm]    1
      0    1
    End
    Tunneling         Eckart
    ImaginaryFrequency[1/cm]      623.59
    WellDepth[kcal/mol]           75.2 #forward
    WellDepth[kcal/mol]           60.6 #reverse
    End
  End
!---------------------------------------------------------------------
!---------------------------------------------------------------------
!---------------------------------------------------------------------
Bimolecular   P11 # CCCOH + CH2O + CC=C
    Fragment  CCCOH
              RRHO
       Geometry[angstrom] 12
     C                 -0.76638800    0.54197400    0.30744200
     H                 -0.68989900    0.51309800    1.39542400
     H                 -1.36276700    1.42058700    0.04122900
     C                  0.62135600    0.64084800   -0.30584300
     H                  1.05982000    1.60005700   -0.02116000
     H                  0.52455700    0.65729100   -1.39608100
     O                 -1.44103100   -0.64976500   -0.05727000
     H                 -1.55616700   -0.65245600   -1.01069500
     C                  1.52716500   -0.50623100    0.12172300
     H                  2.50265700   -0.44583100   -0.35880500
     H                  1.68152400   -0.49044800    1.20162500
     H                  1.07572600   -1.46372900   -0.13330500
        Core    RigidRotor
      SymmetryFactor  1
        End
      Rotor                     Hindered
          Group                         5 6 9
```

```
        Axis                            4 1
        Symmetry                        1
        Potential[kcal/mol]             6
    0.00 4.73 0.12 3.99 0.27 3.93
  End
  Rotor                     Hindered
        Group                           8
        Axis                            7 1
        Symmetry                        1
        Potential[kcal/mol]             6
    0.00 1.47 0.08 0.81 0.03 1.09
  End
  Rotor                     Hindered
        Group                           10 11 12
        Axis                            9 4
        Symmetry                        3
        Potential[kcal/mol]             2
    0.00 2.66
  End
     Frequencies[1/cm]  27
  1329.10 495.74 779.30 883.17 912.08 999.97 1093.35 1110.10 1148.02
  1245.92 1305.74 1373.34 1385.96 1411.18 1428.30 1486.33 1499.45
 1511.53 1520.86 3032.45
  3043.64 3065.99 3085.67 3103.59 3133.63 3148.78 3878.55
     ! 47.01 229.69 284.50  !torsions
        ZeroEnergy[kcal/mol]      0
        ElectronicLevels[1/cm]      1
        0 1
    End
  Fragment  CH2O_CC=C # modeled as CH2O + CC=C
    RRHO
  Geometry[angstrom]  13
   C                  1.70393900   -0.12689800    0.23836200
   H                  2.57483300   -0.15398600    0.88629100
   C                 -1.98376900    0.00019000    0.58412100
   H                 -2.90175000    0.08135500    1.19082100
   H                 -1.02704000   -0.07059400    1.12848700
   C                  1.16542700   -1.26763200   -0.16706300
   H                  1.57530000   -2.22323800    0.13102200
   H                  0.29691800   -1.27299300   -0.81623300
   O                 -2.02562200   -0.01450500   -0.61272400
   C                  1.19425200    1.22791100   -0.14115700
   H                  0.32159800    1.14774400   -0.78804000
   H                  0.92205600    1.80586300    0.74551600
   H                  1.96396200    1.80045800   -0.66165800
  Core  RigidRotor
    SymmetryFactor  1
  End
```

```
      Rotor                        Hindered
          Group                            11 12 13
          Axis                             10 1
          Symmetry                         3
          Potential[kcal/mol]              2
          0.00 2.01
      End
      Frequencies[1/cm] 32
       61.05 78.27 95.02 123.94 133.22 155.46 436.53 603.91 937.86
   952.87 983.07 1042.88
       1080.88 1200.43 1224.88 1284.84 1333.58 1406.81 1452.74 1491.58
   1497.85 1541.85 1736.70
       1864.43 2951.87 3031.61 3049.39 3102.84 3140.69 3154.12 3165.17
   3246.78
    !  232.59 !Torsions
      ZeroEnergy[kcal/mol]         0
      ElectronicLevels[1/cm]       1
      0 1
        End
      GroundEnergy[kcal/mol]     27.6
End
!-----------------------------------------------------------------
Barrier    B11   W1   P11      # CCCOH + CH2O + CC=C
  Variational
    RRHO
    Geometry[angstrom]   25
   C                 -1.15807200    1.29059800   -0.38172200
   H                 -0.78736100    1.73132700   -1.30274100
   C                  1.39742900   -0.83047300    0.68158000
   H                  1.50068200   -1.82065100    1.13227300
   H                  1.15649800   -0.11662100    1.47664100
   C                  2.66408000   -0.42827900   -0.04587800
   H                  2.86197200   -1.16543800   -0.82532900
   H                  3.49196100   -0.47897000    0.66399800
   C                 -0.85269300    2.05336000    0.89384300
   H                  0.21912300    2.14833500    1.08012500
   H                 -1.28684300    1.54888200    1.75941800
   H                 -0.20094700    0.09411200   -0.38166300
   H                 -1.25734600    3.06862800    0.87423500
   C                 -2.30967600    0.52112300   -0.49959900
   H                 -2.76941400    0.36952100   -1.46500300
   H                 -2.98852900    0.44265700    0.34272100
   O                 -1.98261700   -1.37267600   -0.43165500
   C                 -1.04554700   -1.57175000    0.41036100
   H                 -1.07440800   -1.00109600    1.35839800
   H                 -0.71689600   -2.60588000    0.57152900
   O                  0.30876900   -0.90274100   -0.23533700
   C                  2.57138700    0.96739600   -0.64870700
```

```
 H                  3.48765400    1.22849200   -1.17557100
 H                  1.74739100    1.03183000   -1.35957900
 H                  2.40579800    1.71636100    0.12721500
  Core    RigidRotor
     SymmetryFactor          0.5
  End
Rotor        Hindered
    Group                   23 24 25
    Axis                    22 6
    Symmetry                3
    Potential[kcal/mol]     2
      0. 2.89
  End
  Rotor        Hindered
    Group                   10 11 13
    Axis                    9 1
    Symmetry                3
    Potential[kcal/mol]     2
      0. 1.17
  End
  Rotor        Hindered
    Group                   7 8 22
    Axis                    6 3
    Symmetry                1
    Potential[kcal/mol]     6
      0. 4.11 0.38 3.84 0.24 4.37
  End
  Rotor        Hindered
    Group                   4 5 6
    Axis                    3 21
    Symmetry                1
    Potential[kcal/mol]     8
      0. 4.94 3.27 5.02 4.41 5.63 0.87 1.42
  End
  Frequencies[1/cm]       63
 91.98 150.04 161.68 205.78 248.33 289.90  383.54 439.86 493.91
 519.38 591.21
 716.18 778.73 846.60 894.86 903.59 922.90 958.99 1008.28 1041.82
 1079.35 1106.40 1110.76 1146.64 1160.20
 1180.17 1186.74 1244.10 1270.02 1285.45 1310.77 1360.34 1378.65
 1390.55 1403.97 1411.75 1417.79 1425.30
 1462.26 1481.42 1487.09 1501.37 1507.80 1513.25 1520.71 1541.09
 1581.48 1697.82 2916.52 3027.19 3036.79
 3038.53 3063.77 3068.92 3085.13 3088.73 3107.70 3109.32 3136.16
 3143.67 3145.57 3146.38 3244.05
  !   49.10 82.08 175.57 262.15  ! Torsions
  ZeroEnergy[kcal/mol]      69.3
  ElectronicLevels[1/cm]    1
```

```
      0    1
    End
    Tunneling          Eckart
    ImaginaryFrequency[1/cm]       945.04
    WellDepth[kcal/mol]            69.3 #forward
    WellDepth[kcal/mol]            41.7 #reverse
    End
  End
End
```

E.4 CCOCO[CH]C

```
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
PressureList[atm]                  0.00001 0.001  0.01  0.1  1  10  100.
!PressureList[bar]                 1.
EnergyStepOverTemperature          .2
ExcessEnergyOverTemperature        30
ModelEnergyLimit[kcal/mol]         400
CalculationMethod                  direct
!CalculationMethod                 low-eigenvalue !direct
WellCutoff                         10
ChemicalEigenvalueMax              0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                 200
      Power                        .85
      ExponentCutoff               15
    End
  CollisionFrequency
    LennardJones
      Epsilons[1/cm]     94.87    280.62  !Ar and parent
  Sigmas[angstrom]       3.33     6.14
  Masses[amu]            39.88    103.14
    End
!-------------------------------------------------------
!-------------------------WELL 1 to Products ------------
```

```
!------------------------------------------------------
Well         W1         # W_CCOCO[CH]C_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         0.0018769997     0.0094064935     0.0012941865
     O         0.0039309591     0.0072602134     1.3662849761
     C         1.2855525506     0.0024860843     1.9499037665
     C         -1.346396422     -0.0499286474     -0.6070549333
     O         1.9906696984     -1.1640472244     1.6924437196
     C         1.4124285819     -2.3190617661     2.2817038138
     C         2.3182091531     -3.4937477233     1.997679624
     H         -1.8440152607     -1.0080384834     -0.411761856
     H         -1.2813663239     0.0804784422     -1.68558997
     H         -1.9856104581     0.7344173299     -0.1986214421
     H         0.8664421701     -0.4358868633     -0.4759230566
     H         1.8829927666     0.82040967     1.5438726681
     H         1.1126468079     0.1339867918     3.0210491031
     H         1.3053534229     -2.1566238159     3.3607326044
     H         0.4138671779     -2.4839512655     1.8689428887
     H         3.3095168826     -3.3177320862     2.4123189612
     H         1.910371308     -4.4025224742     2.438405425
     H         2.4160899446     -3.6421806901     0.9233374842
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      4 11
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   4.57   1.34   4.17
    End
    Rotor         Hindered
        Group                      8 9 10
        Axis                       4 1
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   1.32
    End
    Rotor         Hindered
        Group                      1
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   9.97   1.65   2.7   2.29   2.93
    End
    Rotor         Hindered
```

```
        Group                       6
        Axis                        5 3
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   6.63   2.07   3.63   2.99   4.09
    End
    Rotor         Hindered
        Group                       7 14 15
        Axis                        6 5
        Symmetry                     1
        Potential[kcal/mol]          8
         0.0   1.63   1.03   1.11   1.06   4.68   0.59   1.19
    End
    Rotor         Hindered
        Group                       16 17 18
        Axis                        7 6
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   3.05
    End
    Frequencies[1/cm]    42
           261.41       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
     !51.91       62.09       81.45       159.44       197.19       241.07!
   Torsions
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
End
Well         W2         # W_CCOCOC[CH2]_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         0.0178514596     0.001513644     0.0015050088
     C         0.0061733634     0.0060023634     1.5122092312
     O         1.3503838993     -0.000462482     1.9640903547
     C         1.4695606045     -0.0679502667     3.350760128
     O         0.9724288929     1.0682112413     3.9981565554
     C         1.7359894587     2.2399023396     3.7441343836
     C         3.0431599872     2.2264259073     4.4470251509
```

```
 H         0.5328050795    0.884658872    -0.3741076412
 H         -0.9999152244    0.0016478828    -0.3868338208
 H         0.5348524908    -0.8813260579    -0.3713600265
 H         -0.5120122208    0.887265821    1.898910857
 H         -0.5093275874    -0.8797487016    1.9027366081
 H         0.8932370681    -0.9068222381    3.7512582343
 H         2.5353928321    -0.1999953512    3.5532013909
 H         1.8739990233    2.3741461536    2.6671959717
 H         1.1095824236    3.0662606886    4.0970698107
 H         3.1000482125    1.8153779981    5.4440992415
 H         3.886509222    2.7768942041    4.0604685335
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    8 9 10
    Axis                     1 2
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  3.05  0.0  3.05  0.0  3.05
End
Rotor        Hindered
    Group                    4
    Axis                     3 2
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  1.53  0.95  1.11  1.08  4.73  0.77  1.29
End
Rotor        Hindered
    Group                    5 13 14
    Axis                     4 3
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  7.38  2.68  3.06  2.66  3.95
End
Rotor        Hindered
    Group                    6
    Axis                     5 4
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  7.87  2.85  4.21  2.88  3.57
End
Rotor        Hindered
    Group                    7 15 16
    Axis                     6 5
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  3.2  0.26  1.35  0.32  1.84
```

```
    End
    Rotor         Hindered
        Group                      17 18
        Axis                       7 6
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   1.66   0.0   1.68
    End
    Frequencies[1/cm]     42
           287.32       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
           1453.0       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
     !47.2       58.76       93.4       190.21       194.44       239.52!
   Torsions
    ZeroEnergy[kcal/mol]       7.1
    ElectronicLevels[1/cm]     1
        0  2
    End
End
Barrier         B1   W1   W2     # W_CCOCOC[CH2]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0291534613     0.0291135435     0.0022248553
     C         0.038909059     -0.0467305797     1.5024767004
     O         1.3550074629     -0.0195272448     2.0368748677
     C         2.0689992934     -1.211207772     1.9703022812
     O         2.6482348505     -1.4726275816     0.7200596194
     C         1.7666050564     -1.966393255     -0.2376049469
     H         1.2435806975     -2.86345737     0.1138572717
     C         2.4498442264     -2.1153028938     -1.5628419875
     H         0.8353289444     -1.0703216507     -0.3428760312
     H         0.5690676587     0.8767044645     -0.4094115617
     H         -0.9333338235     -0.1523638473     -0.4666688809
     H         -0.4752898278     0.8051347715     1.9524766809
     H         -0.473912245     -0.9560926026     1.8419010164
     H         2.8958259828     -1.114174801     2.6685115874
     H         1.4205179652     -2.0541464319     2.2538600376
     H         1.7518555396     -2.4892115905     -2.3104466087
     H         2.8380420199     -1.1526416087     -1.894097549
     H         3.2881549995     -2.8112755004     -1.4894884615
    Core RigidRotor
```

```
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      16 17 18
        Axis                       8 6
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.37   0.0   2.37   0.0   2.37
    End
    Frequencies[1/cm]    46
           89.45       142.21       181.39       282.88       382.76
   416.56       443.98       548.41       563.69
           654.2       845.13       871.55       897.26       911.27
   1021.65       1079.68       1100.39       1119.97       1135.27
           1163.4       1177.85       1188.43       1257.09       1314.52
       1351.23       1365.47       1400.73       1410.19       1438.87
           1441.94       1457.12       1478.95       1489.43       1498.62
        1510.27       1518.36       2986.4       3012.57       3031.02
           3057.06       3078.69       3117.27       3124.59       3150.17
        3153.01       3205.56
     !220.24! Torsions
    ZeroEnergy[kcal/mol]       21.3
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1713.1882
    WellDepth[kcal/mol]         21.3
    WellDepth[kcal/mol]         14.2
    End
End
Well         W3         # W_CCO[CH]OCC_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         0.0416232376     -0.37750273     0.1259507271
     C         0.064858533     0.0468264808     1.5811502014
     O         1.3885661895     0.0727441412     2.1160722767
     C         2.0530796439     -1.0997084414     2.1021605902
     O         1.3283383836     -2.1530229094     2.585939944
     C         1.9923620462     -3.4014452666     2.4635967907
     C         1.9486900981     -3.9307345213     1.0432721483
     H         0.7082422586     0.2512444402     -0.4632387071
     H         -0.9691159014     -0.2836520477     -0.2705842106
     H         0.3588097986     -1.4142493039     0.0204649586
     H         -0.2952907809     1.0669209536     1.6949190779
     H         -0.5581205202     -0.6106713951     2.1881833486
     H         3.0676123132     -1.004417402     2.4866981573
```

```
 H         3.0268268166    -3.2974090352     2.8077760606
 H         1.4781808821    -4.074807134     3.1466442951
 H         2.4530598175    -3.2429740763     0.36538534
 H         2.4402670067    -4.9016395637     0.985008223
 H         0.9155186867    -4.0452846885     0.7165437614
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                     8 9 10
    Axis                      1 2
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   3.02   0.0   3.02   0.0   3.03
End
Rotor        Hindered
    Group                     1 11 12
    Axis                      2 3
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   4.23   0.93   1.61   0.04   1.44
End
Rotor        Hindered
    Group                     2
    Axis                      3 4
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0   2.5   1.96   9.0
End
Rotor        Hindered
    Group                     6
    Axis                      5 4
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0   2.5   1.96   9.0
End
Rotor        Hindered
    Group                     7 14 15
    Axis                      6 5
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   4.23   0.93   1.61   0.04   1.44
End
Rotor        Hindered
    Group                     16 17 18
    Axis                      7 6
    Symmetry                   1
    Potential[kcal/mol]        6
```

```
          0.0   3.02   0.0   3.02   0.0   3.03
    End
    Frequencies[1/cm]     42
           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
     !54.18       70.62       121.24       175.73       222.29       268.03!
    Torsions
    ZeroEnergy[kcal/mol]       2.7
    ElectronicLevels[1/cm]     1
        0   2
    End
End
Barrier         B2   W1   W3     # W_CCO[CH]OCC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.0001323234     0.0040976776     0.0000333068
     C         -0.0003628155     -0.009351158     1.509667851
     O         1.3551114327     -0.0090822941     1.945193012
     C         1.543344293     -0.0426376655     3.2851818521
     O         0.8775227636     0.9447772638     4.0265274903
     C         0.2360601518     0.0517182754     4.9264202216
     H         0.6994755055     0.0506549958     5.9117511448
     C         -1.2574101633     0.1052606438     4.8932331708
     H         0.5025521372     0.8969743284     -0.36801236
     H         -1.0221607345     -0.0001680744     -0.3764885573
     H         0.5195807861     -0.8699718527     -0.3887851191
     H         -0.5127909119     0.8638706009     1.9160624459
     H         -0.4910694374     -0.9085554011     1.8989031303
     H         0.8407830213     -0.9318754718     4.1040192214
     H         2.6082196165     -0.1105900382     3.5036621271
     H         -1.6053474201     1.1071095764     5.1617779016
     H         -1.6420003491     -0.1238584055     3.8995075006
     H         -1.6776505615     -0.6054570187     5.6032856661
    Core RigidRotor
        SymmetryFactor    0.25
    End
    Rotor         Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    3
```

```
        Potential[kcal/mol]        2
         0.0   3.07
    End
    Rotor        Hindered
        Group                     4
        Axis                      3 2
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.26   0.35   6.59   0.96   1.86
    End
    Rotor        Hindered
        Group                     2
        Axis                      3 4
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.61   2.03   3.43   1.39   4.57
    End
    Rotor        Hindered
        Group                     16 17 18
        Axis                      8 6
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0   2.18
    End
    Frequencies[1/cm]    43
           94.89      187.93      316.31      394.98      408.77
   563.9
           640.54      831.94      836.82      879.62      901.05
   989.32      1062.74      1104.36      1121.92      1137.78
           1143.97      1172.89      1192.35      1251.41      1304.64
        1325.1      1351.42      1394.99      1399.15      1421.29
           1434.74      1476.98      1488.76      1490.12      1506.59
        1536.24      1886.48      3027.53      3042.39      3075.08
           3098.21      3108.59      3114.0      3117.46      3148.95
       3152.18      3154.33
     !83.35   134.62    207.6      255.72! Torsions
    ZeroEnergy[kcal/mol]      39.0
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1969.1996
    WellDepth[kcal/mol]         39.0
    WellDepth[kcal/mol]         36.3
    End
End
Bimolecular         P1    # CC=O  +  [CH2]OCC
    Fragment  CC=O
```

```
        RRHO
    Geometry[angstrom]        7
     O         -0.0087358454    0.0000127436    0.0277268521
     C         -0.0047280904    -0.0000001382    1.2269625046
     H         0.9544802472    -0.0000142081    1.780404527
     C         -1.2396838276    0.0000000246    2.0771909663
     H         -1.2332835064    0.8770130299    2.7268240198
     H         -2.128706571    0.0000295926    1.4528082197
     H         -1.2333121081    -0.8770468713    2.7267788357
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    5 6 7
        Axis                     4 2
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   1.2   0.0   1.2   0.01   1.2
    End
    Frequencies[1/cm]    14
           513.29       776.08       900.41       1138.06       1146.18
     1379.69       1433.6       1464.85       1474.9
           1874.29       2942.78       3063.51       3127.31       3180.67
     !157.82! Torsions
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH2]OCC
        RRHO
    Geometry[angstrom]        11
     C         -0.000713851    -0.00468289    -0.0013813868
     C         0.0020061486    0.0195391378    1.5078714749
     O         1.3497803524    0.0331924413    1.9526669773
     C         1.5016858874    0.0729897102    3.2917698434
     H         0.6942750287    0.4852982544    3.8847448002
     H         2.5265617388    0.1454538458    3.6172715885
     H         0.5074620339    0.8739651182    -0.3952754403
     H         -1.0231776684    -0.0142928625    -0.3764715017
     H         0.5127457376    -0.8928926347    -0.3656189069
     H         -0.5073568477    0.910485179    1.8898447205
     H         -0.4999305632    -0.8603473004    1.9204598359
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    7 8 9
        Axis                     1 2
```

```
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   3.0
    End
    Rotor         Hindered
        Group                     4
        Axis                      3 2
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.5   0.15   4.08   0.6   1.51
    End
    Rotor         Hindered
        Group                     5 6
        Axis                      4 3
        Symmetry                   1
        Potential[kcal/mol]        5
         0.0   0.28   5.33   0.00   5.24
    End
    Frequencies[1/cm]     24
           303.35       487.19       593.21       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
     !99.2       239.29       290.05!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   2
    End
    GroundEnergy[kcal/mol]          9.1
End
Barrier         B3   W1   P1     # TS_[CH2]OCC+CC=O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.2892651787     0.4355725263     0.2088041375
     C         0.1927708311     0.0615880561     1.6670646364
     O         1.5121356891     0.0411313718     2.2109818852
     C         1.5520378285    -0.0884728634     3.5405629387
     O         1.097182838     1.7193582988     4.1683940128
     C         1.3822917157     2.5869799751     3.3121857974
     H         0.6097213073     2.9416751252     2.6191935408
     C         2.7854760811     3.059080859     3.1116660598
     H         0.7292004905     1.4264507089     0.1036484217
     H        -0.7011420089     0.4429844687    -0.2439589688
     H         0.912116916     -0.2789594862    -0.3269247623
     H        -0.4058473849     0.780817811     2.231058101
```

```
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
```

```
           1124.1       1186.28       1247.34       1257.1       1308.18
      1352.76       1389.27       1400.27       1436.73       1464.75
           1475.55       1487.53       1503.43       1509.23       1523.01
        1532.74       3024.03       3028.46       3040.3       3073.77
           3088.22       3102.98       3145.2       3150.32       3151.06
       3153.66       3280.87
     !50.87       82.89       94.79       148.6       223.25! Torsions
    ZeroEnergy[kcal/mol]       22.9
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    650.5068
    WellDepth[kcal/mol]         22.9
    WellDepth[kcal/mol]         13.8
    End
End
Bimolecular         P2    # CCOCOC=C  +  [H]
    Fragment  CCOCOC=C
        RRHO
    Geometry[angstrom]         17
     C         0.003704926    0.011003447    0.0030123498
     C         -0.0001753209    -0.0111612222    1.5130392284
     O         1.3488412493    -0.0083458226    1.955267626
     C         1.4878789917    -0.1344914621    3.3275401745
     O         0.9230283265    0.9327964379    4.0527734254
     C         1.5431702152    2.1388556198    3.9627766339
     H         1.1098293717    2.831767739    4.671955592
     C         2.5376446081    2.4852391641    3.1576906268
     H         0.5090017066    0.9058488399    -0.3570470834
     H         -1.0164850284    0.0106347429    -0.3785648335
     H         0.5246846344    -0.8610772423    -0.3890182473
     H         -0.5216245523    0.860217875    1.9161358018
     H         -0.5017897138    -0.9090694755    1.893455498
     H         0.967953537    -1.022596122    3.6958681857
     H         2.5587067785    -0.1923572933    3.5305549059
     H         2.9360332044    3.4847561322    3.2368289234
     H         2.9503070969    1.823094593    2.4125811985
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0  3.09  0.0  3.09  0.0  3.09
    End
```

```
    Rotor        Hindered
        Group                    4
        Axis                     3 2
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0   1.64   1.12   1.16   1.02   4.7   0.84   1.26
    End
    Rotor        Hindered
        Group                    5 14 15
        Axis                     4 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   6.87   3.44   5.47   3.25   4.03
    End
    Rotor        Hindered
        Group                    6
        Axis                     5 4
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   23.03   3.72   4.13   1.66   4.79
    End
    Rotor        Hindered
        Group                    7 8
        Axis                     6 5
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   4.7   1.02   4.96
    End
    Frequencies[1/cm]    40
           273.28       348.3       410.48       552.88       688.35
           737.64       822.64       883.78       892.23       925.25
   1017.82       1043.59       1066.7       1127.76       1179.8
           1197.15       1218.88       1249.45       1310.9       1347.59
      1364.99       1401.33       1429.33       1437.29       1470.8
           1488.78       1505.54       1517.99       1536.78       1724.01
        3021.8       3056.71       3073.83       3079.92       3116.01
           3151.19       3152.23       3198.53       3215.5       3293.31
     !56.52       65.51       143.41       204.74       250.54!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment    H
            Atom
              Mass[amu]   1
              ElectronicLevels[1/cm]      1
                 0     2
     End
```

```
    GroundEnergy[kcal/mol]          36.55
End
Barrier         B4   W1   P2    # TS_C=COCOCC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.003339935     -0.0115834043     -0.0019916556
     C         0.000670349     0.0145241132     1.5073403092
     O         1.3550375237     0.009660827     1.9372520714
     C         1.5166431385     -0.0500381398     3.3085996248
     O         0.9145734104     1.0267276745     3.9986818365
     C         1.3926716581     2.2683265972     3.7611522479
     H         0.9087287007     2.9889856141     4.4061700562
     C         2.2797242445     2.6375093145     2.8276780537
     H         0.5083370338     0.8708380929     -0.3855730689
     H         -1.0257037015     -0.0124343291     -0.3777330978
     H         0.5076460713     -0.8997097623     -0.370581228
     H         -0.4980362421     0.9135898245     1.8785066299
     H         -0.5138139625     -0.8585438393     1.9261117955
     H         1.0406638583     -0.9384704813     3.7307823632
     H         2.5917871545     -0.0520820292     3.4978769955
     H         1.162346159     2.8131745513     1.2162993637
     H         2.5929135647     3.6697659297     2.8059041199
     H         2.8036329387     1.9310264618     2.2039335003
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.14   0.0   3.14   0.0   3.14
    End
    Rotor         Hindered
        Group                      4
        Axis                       3 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.22   1.58   5.28   1.56   1.99
    End
    Rotor         Hindered
        Group                      5 14 15
        Axis                       4 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   8.15   3.98   5.58   4.05   5.24
    End
```

```
    Rotor        Hindered
        Group                      6
        Axis                       5 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   24.63   5.03   5.6   3.04   6.12
    End
    Rotor        Hindered
        Group                      7 8
        Axis                       6 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   6.38   2.14   6.12
    End
    Frequencies[1/cm]    42
           276.98       330.53       353.86       398.78       422.7
           543.97       692.59       783.27       818.61       881.51
   920.98       933.1       997.88       1035.27       1065.48
           1126.75       1179.1       1197.59       1211.35       1250.88
       1310.07       1339.63       1351.08       1397.93       1423.17
           1435.51       1467.77       1486.38       1501.79       1516.52
        1532.3       1667.4       3021.67       3056.12       3070.8
           3077.62       3112.22       3147.36       3151.59       3200.07
        3218.32       3295.43
     !89.02       98.37       144.96       213.47       251.97!
    ZeroEnergy[kcal/mol]    38.9
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    629.6205
    WellDepth[kcal/mol]         38.9
    WellDepth[kcal/mol]         2.4
    End
End
!------------------------------------------------------------
!-------------------------WELL 2 to Products -------------
!------------------------------------------------------------
Bimolecular         P3    # CCOC[O]  +  C=C
    Fragment  CCOC[O]
        RRHO
    Geometry[angstrom]        12
     O         -0.0000136479     -0.0158947662     0.0001300488
     C         0.0003804679     -0.0116558615     1.4194515571
     C         1.4348826083     0.0041591029     1.8907607535
     C         -1.2747334222     -0.0278957055     -0.5487163989
     H         -1.1614851697     0.0929277806     -1.6352880151
     H         -1.8740917079     0.8342817878     -0.1867784254
```

```
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
```

```
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[O]+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
```

```
    End
    Rotor        Hindered
        Group                    4
        Axis                     3 2
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   1.63   0.8   5.06   0.8   1.35
    End
    Rotor        Hindered
        Group                    5 15 16
        Axis                     4 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   6.35   3.0   5.25   2.67   4.22
    End
    Rotor        Hindered
        Group                    3 15 16
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   16.44   3.51   8.29
    End
    Rotor        Hindered
        Group                    7 17 18
        Axis                     6 5
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   2.94   0.38   1.27
    End
    Frequencies[1/cm]    41
           214.09       228.48       318.68       393.07       428.54
           650.27       819.15       825.8       878.14       941.23
   972.79       1018.36       1046.09       1057.11       1115.82
           1160.6       1185.05       1190.48       1242.04       1274.31
       1307.79       1327.36       1395.24       1405.95       1432.51
           1454.84       1475.57       1487.87       1504.68       1536.22
        1602.5       2922.05       3012.29       3044.71       3071.06
           3080.18       3145.55       3150.05       3171.2       3183.07
       3255.7       3281.22
     !49.16       61.81       68.6       257.07     150.33! Torsions
    ZeroEnergy[kcal/mol]       29.9
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    495.1418
    WellDepth[kcal/mol]         22.84
    WellDepth[kcal/mol]         4.77
```

```
    End
End
!-------------------------------------------------------
!-------------------------WELL 3 to Products ------------
!-------------------------------------------------------
Barrier         B6   W3   W2    # W_CCOCOC[CH2]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.0025244205     0.0056905039     0.0052114419
     C         0.0030527174     -0.0070677518     1.5090603793
     O         1.3796096603     -0.0095103862     1.9572710314
     C         2.2339392713     0.4519195532     0.9790537239
     H         3.0789473393     -0.2099321694     0.8103696197
     O         2.7018876774     1.7263190923     1.1428348699
     C         1.7096452024     2.7048316387     1.416327854
     C         2.3853118982     4.0548511916     1.4577190352
     H         1.3606983305     0.3816927582     -0.020673918
     H         -0.6003474534     0.7580464504     -0.4941259996
     H         -0.0107417894     -0.9585264976     -0.4908480508
     H         -0.4981074459     0.8727012819     1.9187671598
     H         -0.456862618     -0.8969717152     1.9355598297
     H         0.9458016159     2.6706793556     0.6303318064
     H         1.2278545449     2.4762966345     2.3696364095
     H         2.858895726     4.2727578019     0.5019572329
     H         1.6576047964     4.8357324475     1.6745821379
     H         3.150385874     4.0667948224     2.2322734199
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      7
        Axis                       6 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.69   1.28   2.58   0.82   3.77
    End
    Rotor         Hindered
        Group                      4
        Axis                       6 7
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.42   1.08   7.13   0.91   2.2
    End
    Rotor         Hindered
        Group                      16 17 18
        Axis                       8 7
        Symmetry                    3
```

```
        Potential[kcal/mol]        2
         0.0  3.07
    End
    Frequencies[1/cm]    44
           111.53      175.99      274.74      378.86      473.57
   602.13      661.31
           696.85      831.34      846.41      875.2      900.46
   994.2      1033.52      1068.27      1089.15      1126.45
           1170.31      1186.51      1197.56      1233.26      1265.54
        1309.85      1362.5      1388.19      1398.34      1420.17
           1436.48      1465.32      1488.71      1506.19      1526.38
        1538.53      1706.91      3022.82      3062.76      3074.46
           3083.48      3118.64      3140.66      3146.84      3151.4
       3153.67      3226.26
     !84.26      139.63      245.26!
    ZeroEnergy[kcal/mol]      26.5
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1761.9442
    WellDepth[kcal/mol]         23.8
    WellDepth[kcal/mol]         19.4
    End
End
Bimolecular         P4    # CCOC=O  +  [CH2]C
    Fragment  CCOC=O
        RRHO
    Geometry[angstrom]        11
     O         0.0003751914    0.0195019996    0.0000937786
     C         0.0001265563    -0.004345369    1.1953307137
     H         0.9004012035    -0.0400753727    1.8192029238
     O         -1.0829367177    0.0082212829    1.9688922103
     C         -2.3404949867    0.0546247319    1.2732313729
     C         -3.4329185306    0.0620891264    2.3131654086
     H         -2.3591827021    0.9480385077    0.6494872714
     H         -2.4046538937    -0.8110246448    0.6143470667
     H         -3.3385498744    0.9308923884    2.9624082139
     H         -4.406482661    0.0969837863    1.8264015124
     H         -3.3842195937    -0.835651434    2.9271125409
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    1 3
        Axis                     2 4
        Symmetry                  1
        Potential[kcal/mol]       4
```

```
        0.0   12.99   5.27   12.99
    End
    Rotor        Hindered
        Group                    2
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   1.12   0.01   6.55   0.01   1.12
    End
    Rotor        Hindered
        Group                    4 7 8
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   3.12   0.0   3.12   0.0   3.12
    End
    Frequencies[1/cm]    24
           237.16       389.93       806.77       814.71       883.19
   1062.71       1063.87
           1145.7       1187.56       1261.98       1310.78       1399.55
       1413.17       1434.43       1490.84       1503.7       1528.65
           1852.53       3076.3       3081.04       3086.08       3124.94
       3153.11       3158.28
     !77.65       236.19       344.76!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0   1
    End
    Fragment   [CH2]C
        RRHO
    Geometry[angstrom]        7
     C         0.0002983383     -0.0005389889     0.0004031088
     C         0.0047388604     -0.0084680438     1.4846485597
     H         1.0125028336     -0.0004449026     -0.404522378
     H         -0.4985399523     0.8907396606     -0.4014899118
     H         -0.5291032253     -0.8632636678     -0.4045194797
     H         0.770457535     0.5135203684     2.0371553306
     H         -0.8406008348     -0.3881967978     2.037158663
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    3 4 5
        Axis                     1 2
        Symmetry                  1
        Potential[kcal/mol]       12
         0.0   0.07   0.0   0.08   0.0   0.07   0.0   0.08   0.0   0.07   0.0
   0.08
```

```
    End
    Frequencies[1/cm]    14
           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
     !125.25!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]    -8.5
End
Barrier         B7   W3   P4    # TS_C[CH2]+CCOC=O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0000195605     -0.0472638199     0.0287198103
     C         0.0253434927     0.0201317747     1.5145228557
     O         1.8045050035     0.0142911779     1.97451411
     C         2.6013087674     -0.5546067834     1.1882554509
     H         3.0243833619     -0.0810173971     0.3075481595
     O         2.8037819939     -1.8908717469     1.1832014256
     C         2.4403675918     -2.5917469208     2.3744674322
     C         3.4092207332     -2.3034915987     3.5033852905
     H         0.4692349885     0.8336524478     -0.4098914219
     H         -1.0218082174     -0.1096374114     -0.3521629558
     H         0.5343335661     -0.9315341625     -0.3271200146
     H         -0.2441638626     0.9599688676     1.9745973978
     H         -0.3393537     -0.8484228916     2.0483515014
     H         1.4228411211     -2.3267702314     2.6604706734
     H         2.4614024225     -3.6424383173     2.0941214856
     H         3.3684133116     -1.2508251925     3.7778586308
     H         3.1517304806     -2.9001370543     4.378179816
     H         4.4258033717     -2.5507087124     3.2005793676
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.11   0.0   1.1   0.0   1.12
    End
    Rotor         Hindered
        Group                      1 12 13
        Axis                       2 3
        Symmetry                    1
```

```
        Potential[kcal/mol]        4
         0.0   2.09   0.85   1.59
    End
    Rotor        Hindered
        Group                     7
        Axis                      6 4
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   8.86   2.26   7.04
    End
    Rotor        Hindered
        Group                     4
        Axis                      6 7
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   5.78   0.7   0.9   0.0   0.98
    End
    Rotor        Hindered
        Group                     6 14 15
        Axis                      7 8
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.94   0.05   2.94   0.05   2.94
    End
    Frequencies[1/cm]    42
           144.97      282.94      325.2      413.68      467.65
           696.67      723.0      771.55      816.7      856.27
   874.57      917.8      1028.03      1065.06      1103.71
           1121.54      1186.7      1203.7      1226.51      1329.54
      1353.19      1388.78      1400.19      1416.66      1475.84
           1486.32      1488.27      1490.43      1495.06      1503.39
        1525.26      3045.62      3072.17      3092.69      3102.55
           3126.25      3136.2      3147.05      3152.95      3161.51
       3164.69      3244.26
     !27.96      67.63      106.01      173.43      221.36!
    ZeroEnergy[kcal/mol]      16.5
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    791.7485
    WellDepth[kcal/mol]    13.8
    WellDepth[kcal/mol]    25.0
    End
End
End
```

E.5 CCCOCO[CH]CC

```
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
PressureList[atm]                 0.00001 0.001  0.01  0.1  1  10  100.
!PressureList[bar]                1.
EnergyStepOverTemperature         .2
ExcessEnergyOverTemperature       30
ModelEnergyLimit[kcal/mol]        400
CalculationMethod                 direct
!CalculationMethod                low-eigenvalue !direct
WellCutoff                        10
ChemicalEigenvalueMax             0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                200
      Power                       .85
      ExponentCutoff              15
    End
  CollisionFrequency
    LennardJones
      Epsilons[1/cm]     94.87   304.79  !Ar and parent
  Sigmas[angstrom]       3.33    6.77
  Masses[amu]            39.88   131.19
    End
!-------------------------------------------------------------
!-------------------------WELL 1 to Products ---------------
!-------------------------------------------------------------
Well        W1        # W_CCCOCO[CH]CC_m062x.log
    Species
        RRHO
    Geometry[angstrom]        24
     C         -0.0170347954     -0.042787223     -0.0096479289
     C         -0.0103493905     -0.00574936     1.5254452795
     C         1.3609626603     0.0134329938     2.0910962383
     O         2.0717771554     -1.1296747497     1.8665190464
     C         3.424495751     -1.0712574673     2.2548318118
```

```
     O         4.1386275867    -0.105293047    1.5617498313
     C         4.2288852372    -0.3546645325    0.1665566211
     C         4.9296949737    0.820108021    -0.4808277032
     C         4.1394862671    2.1130109891    -0.3224175239
     H         0.4738905145    0.8419861727    -0.4168027131
     H         -1.0338721144    -0.0807139299    -0.4001200724
     H         0.5196748539    -0.9224174817    -0.3638284901
     H         -0.5464190356    0.8748536578    1.8803139529
     H         -0.5400203646    -0.8828377721    1.9061604744
     H         1.9372196587    0.9288054062    2.1626848698
     H         3.4992399408    -0.810304153    3.3118909895
     H         3.8188275083    -2.0731744067    2.0670764988
     H         4.7803217317    -1.2876011437    0.002034374
     H         3.2238435373    -0.4733227786    -0.2517504526
     H         5.9208529181    0.9258975795    -0.036222829
     H         5.0736048782    0.5900423737    -1.5381794198
     H         4.0168531139    2.357841837    0.731459885
     H         4.640589712    2.9472041973    -0.8114061524
     H         3.1450686243    2.0117248472    -0.7614365875
  Core RigidRotor
      SymmetryFactor    1.0
  End
  Rotor        Hindered
      Group                    10 11 12
      Axis                     1 2
      Symmetry                  3
      Potential[kcal/mol]       2
       0.0  3.11
  End
  Rotor        Hindered
      Group                    1 13 14
      Axis                     2 3
      Symmetry                  1
      Potential[kcal/mol]       6
       0.0  2.36  0.37  1.85  0.49  1.62
  End
  Rotor        Hindered
      Group                    2 15
      Axis                     3 4
      Symmetry                  1
      Potential[kcal/mol]       6
       0.0  4.88  2.4  3.2  2.81  3.46
  End
  Rotor        Hindered
      Group                    3
      Axis                     4 5
      Symmetry                  1
      Potential[kcal/mol]       6
```

```
        0.0   6.99   2.23   4.18   3.47   4.48
    End
    Rotor        Hindered
        Group                    4 16 17
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   6.99   2.23   4.18   3.47   4.48
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   2.02   1.24   7.62   2.66   3.57
    End
    Rotor        Hindered
        Group                    6 18 19
        Axis                     7 8
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   5.15   0.35   3.91   0.66   3.72
    End
    Rotor        Hindered
        Group                    7 20 21
        Axis                     8 9
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0   2.64
    End
    Frequencies[1/cm]    58
           223.84      302.11
           309.99      366.51      436.0      508.65      600.36
   675.99      770.37      779.5      902.17      911.37
           925.92      963.07      972.59      1058.48      1088.4
    1099.05      1118.58      1145.5      1171.55      1188.38
           1210.08      1247.04      1285.29      1296.06      1309.92
        1334.78      1350.45      1377.37      1392.11      1411.87
           1418.4      1432.69      1469.48      1475.81      1483.67
       1495.88      1498.28      1507.02      1510.3      1520.54
           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!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
```

```
        0  2
    End
End
Well         W2         # W_CCCOCOC[CH]C_m062x.log
    Species
        RRHO
    Geometry[angstrom]         24
     C         -0.0036417969     -0.0113165538     0.0009621034
     C         -0.009071703     -0.0175444756     1.4870498268
     C         1.274613024     -0.003526504     2.241472572
     O         2.1921274451     -1.0002392887     1.7946641173
     C         1.7687409483     -2.30684524     2.0582618428
     O         1.6444406178     -2.575977837     3.4198554709
     C         2.8757189889     -2.5286225567     4.1216760662
     C         2.5996301779     -2.7898591305     5.5871006631
     C         1.7034666186     -1.7215015966     6.2007485082
     H         0.8211932724     -0.6105888564     -0.3865122561
     H         0.1303127427     1.0042713586     -0.3942202372
     H         -0.9380836718     -0.3922607998     -0.4093885349
     H         -0.9241205215     0.196415055     2.0203125821
     H         1.8095489902     0.9403769374     2.0876089519
     H         1.0940579811     -0.1149164068     3.3134731075
     H         0.7821534067     -2.4962738099     1.6276553872
     H         2.5222182054     -2.9530710846     1.5983871464
     H         3.5565064933     -3.2822796728     3.7082972904
     H         3.340682038     -1.5462983146     3.9891569651
     H         2.1346569793     -3.7724325656     5.6853591049
     H         3.555532423     -2.8314433237     6.112775321
     H         0.7422166319     -1.6928402958     5.6898518498
     H         1.5234064585     -1.9129674615     7.2577232161
     H         2.1631571936     -0.7353835483     6.1109080277
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      10 11 12
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  0.25
    End
    Rotor         Hindered
        Group                      1 13
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0  4.8  0.5  2.64
    End
```

```
    Rotor        Hindered
        Group                    2 14 15
        Axis                     3 4
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  2.23  0.62  5.88
    End
    Rotor        Hindered
        Group                    3
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  7.77  2.3  4.03  2.83  3.68
    End
    Rotor        Hindered
        Group                    4 16 17
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0  7.57  3.14  3.54  2.98  4.7  2.8  4.17
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0  1.71  1.2  1.24  1.13  7.43  3.02  3.4
    End
    Rotor        Hindered
        Group                    6 18 19
        Axis                     7 8
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  5.03  0.22  3.79  0.54  3.73
    End
    Rotor        Hindered
        Group                    7 20 21
        Axis                     8 9
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.91
    End
    Frequencies[1/cm]    58
           224.5      308.22
           327.06      362.73      395.1      478.22      605.07
  653.6      771.5      885.42      902.25      923.94
           931.35      953.92      966.19      995.33      1087.27
   1104.36      1112.34      1136.3      1158.69      1181.11
```

```
           1189.53       1212.98       1284.04       1301.89       1315.95
        1346.1       1377.09       1378.89       1394.61       1410.91
           1417.38       1428.94       1454.92       1480.78       1484.24
        1488.38       1493.96       1499.43       1513.27       1515.11
           1531.56       3001.21       3018.12       3022.75       3043.63
        3058.1       3060.67       3071.72       3081.17       3090.51
           3095.81       3105.5       3130.5       3136.87       3146.79
      3209.61
     !30.02       38.37       54.99       70.59       100.17       148.23
      181.99       247.59!
    ZeroEnergy[kcal/mol]       3.9
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Barrier         B1   W1   W2    # W_CCCOCOC[CH]C_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         -0.0207083008    -0.0126520428    0.019198108
     C         -0.0074282377    0.0010512106    1.5228137321
     C         1.3558663108    0.0012382675    2.1588911755
     O         1.3067359434    0.1896964903    3.5640914783
     C         1.1325606473    1.4997075837    3.9995119502
     O         -0.1882225199    1.9646510375    3.9344602013
     C         -0.6163406432    2.3310787694    2.6599928303
     C         -2.062896585    2.735256129    2.6714114145
     C         -2.9845391525    1.5902964936    3.0796994587
     H         -0.4827063908    1.2307723528    1.9361611207
     H         0.5379803445    0.8347916488    -0.3846354525
     H         -1.0363412701    0.0381124971    -0.3715570058
     H         0.4394084244    -0.9219860005    -0.3822158264
     H         -0.6893352468    -0.6978220382    2.0034616972
     H         1.8668438114    -0.9529185809    2.0027343545
     H         1.979241558    0.7837762186    1.702322423
     H         1.4033606154    1.5130072446    5.0516481238
     H         1.7833517417    2.175135642    3.4236772201
     H         0.061967466    3.0563936602    2.196023778
     H         -2.1871468137    3.5756453356    3.3623757707
     H         -2.3244713636    3.0997923496    1.6765070001
     H         -2.6970677475    1.201684531    4.05518868
     H         -4.0212292066    1.9196629426    3.1311730144
     H         -2.9235804145    0.7726032529    2.3604327746
    Core RigidRotor
        SymmetryFactor    0.25
    End
    Rotor         Hindered
        Group                      11 12 13
```

```
        Axis                        1 2
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   1.87
    End
    Rotor         Hindered
        Group                       9 20 21
        Axis                        8 7
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   3.81   0.27   2.96   0.16   2.66
    End
    Rotor         Hindered
        Group                       22 23 24
        Axis                        9 8
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   2.69
    End
    Frequencies[1/cm]     62
           71.33       128.93       137.84       202.02       290.37
   295.32       338.54
           413.49       447.92       510.42       560.9       637.61
   774.04       844.63       903.02       908.9       936.16
           955.42       982.37       997.35       1089.16       1102.07
     1119.57       1135.34       1146.03       1150.12       1179.69
           1188.45       1247.85       1293.5       1306.76       1332.36
      1348.7       1366.8       1371.44       1409.71       1412.48
           1416.34       1441.05       1456.87       1474.2       1487.92
      1494.61       1495.37       1502.37       1509.11       1513.08
           1515.58       2984.03       2994.53       3026.77       3027.99
       3039.77       3064.72       3067.63       3084.6       3095.15
           3121.84       3133.56       3136.05       3151.07       3153.07
     !56.02       166.58       217.62!
    ZeroEnergy[kcal/mol]       19.1
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1671.6942
    WellDepth[kcal/mol]          19.1
    WellDepth[kcal/mol]          15.2
    End
End
Well         W3         # W_CCCOCOCC[CH2]_m062x.log
    Species
        RRHO
    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
```

```
    Rotor        Hindered
        Group                    3
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   8.05   3.64   5.32   3.75   4.7
    End
    Rotor        Hindered
        Group                    4 16 17
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   7.93   3.43   5.11   3.78   4.75
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   3.57   2.73   7.84   1.37   2.24
    End
    Rotor        Hindered
        Group                    6 18 19
        Axis                     7 8
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   5.32   0.85   4.2   1.06   4.33
    End
    Rotor        Hindered
        Group                    22 23 24
        Axis                     9 8
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   2.79   -0.0   2.79   0.0   2.79
    End
    Frequencies[1/cm]    58
           237.47       301.91
           318.42       373.23       443.87       488.4       532.66
      670.51       755.06       771.66       900.01       917.39
           928.04       954.97       965.94       1067.61       1085.12
      1088.44       1112.25       1131.49       1149.18       1184.65
           1194.56       1219.39       1249.07       1287.29       1298.87
        1309.31       1343.03       1360.57       1377.17       1411.46
           1415.86       1430.01       1452.39       1462.74       1475.89
        1483.54       1497.04       1511.03       1519.85       1525.76
           1528.06       3012.83       3021.14       3022.77       3040.32
        3055.78       3063.68       3076.35       3086.22       3091.2
```

```
            3104.47       3108.24       3127.85       3145.69       3180.95
        3286.5
     !41.37       49.7       63.84       96.04       120.38       162.38
     213.89       260.19!
    ZeroEnergy[kcal/mol]       6.0
    ElectronicLevels[1/cm]     1
        0  2
    End
End
Barrier         B2   W1   W3     # W_CCCOCOCC[CH2]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.0063543956     -0.0023067813     -0.009240457
     C         0.0019448391     -0.0070882557     1.4963992392
     C         1.4170199035     -0.0032029093     2.071907247
     O         2.3112648134     0.8716905792     1.4015546517
     C         2.1603037574     2.2224258141     1.6812036117
     O         0.9695016282     2.7748629251     1.1862883584
     C         0.7696687124     2.5676685475     -0.1787911088
     C         -0.3606511164     3.4194843895     -0.687755721
     C         -1.6598632965     3.1829504735     0.0756986393
     H         0.4137232661     1.3078419703     -0.2986678061
     H         -0.9676179331     -0.1004014325     -0.4799890318
     H         0.7686806983     -0.6189372635     -0.4789970045
     H         -0.556333731     0.8573084462     1.8634481656
     H         -0.5064125715     -0.894146489     1.8912520574
     H         1.3983244014     0.2383454879     3.1406205333
     H         1.8596756828     -0.9923469733     1.9547119308
     H         2.1396039138     2.407035973     2.7590983958
     H         3.0206622184     2.7150156725     1.2195074101
     H         1.7013924987     2.6506777982     -0.7468202552
     H         -0.07821961     4.4745760147     -0.6154430797
     H         -0.4977984812     3.1990619833     -1.7481004931
     H         -1.5299686282     3.416884835     1.1311029482
     H         -2.4632037121     3.8049527895     -0.316393649
     H         -1.9698077205     2.1400664509     -0.0024515451
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      9 20 21
        Axis                       8 7
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.94   0.19   3.09   0.19   3.27
    End
    Rotor         Hindered
```

```
        Group                       22 23 24
        Axis                        9 8
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0  2.89
    End
    Frequencies[1/cm]    63
           72.39      138.46      228.26      250.15      273.61
   291.36      308.78      418.13
           474.22      480.12      525.85      632.22      678.42
   778.26      803.87      888.13      904.72      920.43
           953.59      965.69      979.37      1059.49      1090.35
     1113.25      1117.62      1138.29      1163.36      1174.06
           1202.93      1213.79      1257.9      1294.38      1321.95
      1345.28      1366.27      1368.89      1384.02      1408.54
           1415.09      1427.63      1450.78      1461.77      1477.33
       1480.21      1491.54      1501.28      1503.47      1512.11
           1520.68      3023.9      3034.68      3036.91      3039.37
      3057.04      3069.18      3075.81      3090.86      3093.29
           3107.34      3112.93      3136.91      3148.75      3188.9
     !100.09      209.83!
    ZeroEnergy[kcal/mol]      20.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1721.6105
    WellDepth[kcal/mol]    20.2
    WellDepth[kcal/mol]    14.2
    End
End
Bimolecular         P1    # CCC=O  +  CCCO[CH2]
    Fragment  CCC=O
        RRHO
    Geometry[angstrom]        10
     O         -0.0016887113    0.0713256657    0.0025329724
     C         -0.0002866444    -0.0006238542    1.2003000648
     C         1.2414214573    0.0044649469    2.0474156978
     C         2.5200956405    0.1108944722    1.2367087341
     H         -0.9548921268    -0.0771166876    1.7562509656
     H         1.1389672739    0.8283859718    2.7607751845
     H         1.2171547154    -0.9046876655    2.6565767532
     H         2.5240120839    1.0254852172    0.6465567594
     H         3.3931207594    0.1112190273    1.8863927315
     H         2.6028715485    -0.7225020952    0.5414611314
    Core RigidRotor
        SymmetryFactor    1.0
    End
```

```
    Rotor        Hindered
        Group                    1 5
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   2.34   1.42   2.11   1.42   2.34
    End
    Rotor        Hindered
        Group                    2 6 7
        Axis                     3 4
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0   2.12
    End
    Frequencies[1/cm]    22
           266.82       673.44       677.86       873.63       908.86
   1008.52       1121.87       1156.86
           1283.92       1372.83       1414.21       1430.39       1457.55
        1497.45       1504.72       1866.92       2945.02       3050.32
           3077.74       3081.28       3153.86       3156.87
     !148.66       238.11!
    ZeroEnergy[kcal/mol]    0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  CCCO[CH2]
        RRHO
    Geometry[angstrom]        14
     C         -0.0002301642    0.000779469    0.0007852634
     O         -0.0001081683    0.0004484355    1.3498002998
     C         1.2885083909    -0.0002312539    1.9480065736
     C         2.0188320424    1.317189872    1.7453369611
     C         1.2223868513    2.5031840503    2.2716522358
     H         -0.9849359431    -0.0292074563    -0.4368838879
     H         0.8486696718    -0.4436878423    -0.5066231056
     H         1.1144973047    -0.1812898889    3.008368478
     H         1.8698582902    -0.8352511245    1.5428034104
     H         2.9835329869    1.2456869418    2.2521128773
     H         2.2268062162    1.4495464457    0.6816326348
     H         1.0116874266    2.3884900839    3.3360426458
     H         1.7671144817    3.4358545839    2.1334849946
     H         0.2698405869    2.5833486777    1.7494626238
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    6 7
        Axis                     1 2
```

```
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   5.1   0.6   0.64   0.0   5.38
    End
    Rotor         Hindered
        Group                     1
        Axis                      2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.6   0.12   1.17   1.1   6.0
    End
    Rotor         Hindered
        Group                     2 8 9
        Axis                      3 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.74   0.47   3.46   0.73   4.79
    End
    Rotor         Hindered
        Group                     3 10 11
        Axis                      4 5
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.78
    End
    Frequencies[1/cm]     32
            307.28       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
     !70.31       168.24       232.84       282.38!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   2
    End
    GroundEnergy[kcal/mol]          9.5
End
Barrier         B3   W1   P1     # TS_CCCO[CH2]+CCC=O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         -0.2977681986     0.94025752     0.8446553582
     C         0.1345516785     0.4902163595     2.2341817319
     C         1.612520992     0.1805370586     2.3106014925
```

```
     O         2.3467930225    1.3534164845    1.9556663001
     C         3.6540944494    1.2804246792    2.2207925747
     O         3.723757381    1.6164224058    4.1452532961
     C         2.6981502122    2.2131502993    4.5471971612
     C         2.4881515167    3.6868660087    4.3764743717
     C         1.0882137659    4.0202016809    3.8639592068
     H         1.8780524693    1.6403748438    5.0029426516
     H         0.2294018983    1.8473883809    0.5533276482
     H         -1.3673587317    1.1417114752    0.8123393733
     H         -0.0768059314    0.1716479838    0.1023175605
     H         -0.0961881588    1.2616417561    2.9716031475
     H         -0.410020693    -0.4085226587    2.5297545558
     H         1.9078903675    -0.1257763242    3.3168831347
     H         1.8825529155    -0.6174235008    1.6095127526
     H         4.1165552432    0.3016821579    2.2380222626
     H         4.2174383309    2.1227981881    1.8515345924
     H         2.6502498328    4.1850174504    5.3389556655
     H         3.2576868637    4.0585191799    3.698005871
     H         0.3271514924    3.5993325677    4.5234840544
     H         0.9288440207    5.0968689204    3.817686415
     H         0.9381220209    3.6029894988    2.8682926818
   Core RigidRotor
       SymmetryFactor    1.0
   End
   Rotor        Hindered
       Group                    11 12 13
       Axis                     1 2
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  2.69  0.0  2.69  0.0  2.69
   End
   Rotor        Hindered
       Group                    1 14 15
       Axis                     2 3
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  3.66  0.38  3.03  0.02  4.88
   End
   Rotor        Hindered
       Group                    2 16 17
       Axis                     3 4
       Symmetry                  1
       Potential[kcal/mol]       8
        0.0  1.98  1.46  5.18  4.64  4.98  1.61  2.59
   End
   Rotor        Hindered
       Group                    3
       Axis                     4 5
```

```
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   11.39   4.1   9.46   4.95   6.37
    End
    Rotor         Hindered
        Group                      4 18 19
        Axis                       5 6
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   5.97   4.14   5.0
    End
    Rotor         Hindered
        Group                      9 20 21
        Axis                       8 7
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.15   0.13   0.29   0.1   0.65
    End
    Rotor         Hindered
        Group                      22 23 24
        Axis                       9 8
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.6   0.0   2.58   0.0   2.59
    End
    Frequencies[1/cm]     58
           152.94       233.67       313.2
           345.69       360.72       434.28       507.08       541.99
   679.16       704.22       768.89       810.18       899.99
           900.65       925.81       927.53       967.0       1036.16
   1075.67       1095.3       1124.28       1151.33       1176.49
           1237.97       1247.27       1269.82       1287.81       1315.15
        1324.19       1357.34       1381.27       1405.59       1414.59
           1430.78       1469.12       1481.39       1498.45       1500.33
        1505.73       1510.43       1512.28       1522.18       1525.34
           3005.76       3025.5       3028.73       3058.13       3064.35
       3068.22       3088.05       3098.49       3105.82       3127.58
           3135.33       3139.66       3145.03       3149.89       3280.03
     !210.4       259.02       32.87       48.26       71.65       95.18
     108.25!
    ZeroEnergy[kcal/mol]       23.6
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    647.1787
    WellDepth[kcal/mol]     23.6
    WellDepth[kcal/mol]     14.1
```

```
    End
End
Bimolecular         P2    # CCCOCOC=C  +  [CH3]
    Fragment  CCCOCOC=C
        RRHO
    Geometry[angstrom]         20
     C         0.0001382433     -0.0042677269     0.0055963329
     C         0.0018443352     0.0017509637     1.528540548
     C         1.400333565     0.0063919074     2.1076951505
     O         2.0475617435     1.2037105878     1.7031038956
     C         3.3910291673     1.2560592444     2.0352317372
     O         3.6310626296     1.2176727007     3.4224893201
     C         3.2690818581     2.310765694     4.1444291626
     C         2.5790248539     3.3658213201     3.7348073567
     H         3.6345993458     2.2217755539     5.1589825489
     H         0.5163644521     0.8731188284     -0.3800549883
     H         -1.0150749421     -0.0046672329     -0.3886280278
     H         0.5095981989     -0.8900693394     -0.3777073386
     H         -0.5277834175     0.8791114413     1.9041948029
     H         -0.5211061595     -0.8757819161     1.9134154853
     H         1.3730271055     -0.0464079383     3.1985401456
     H         1.973598099     -0.8547461925     1.738816927
     H         3.927533483     0.3900420857     1.6394459287
     H         3.7817614552     2.1861815387     1.61863812
     H         2.1669871371     3.4514358534     2.7414719831
     H         2.4024308441     4.1659116531     4.4367228655
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      10 11 12
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  2.71
    End
    Rotor         Hindered
        Group                      1 13 14
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0  3.65  0.35  3.49  0.0  4.81
    End
    Rotor         Hindered
        Group                      2 15 16
        Axis                       3 4
        Symmetry                    1
        Potential[kcal/mol]         8
```

```
        0.0  3.52  3.03  6.97  0.59  0.7  0.58  1.19
    End
    Rotor        Hindered
        Group                    3
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  6.85  3.41  5.08  2.8  4.0
    End
    Rotor        Hindered
        Group                    4 17 18
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  4.76  1.58  4.01  3.56  11.44
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  4.69  1.02  4.94
    End
    Frequencies[1/cm]    48
           276.08      307.46      387.49      452.62
           560.19      689.39      738.11      772.27      892.16
   901.6      924.56      930.59      965.2      1020.18
           1047.31      1090.63      1128.87      1162.0      1198.88
       1214.23      1250.34      1283.71      1313.25      1347.86
           1365.54      1381.67      1414.26      1428.86      1433.66
        1471.77      1484.62      1500.81      1513.37      1517.23
           1531.15      1724.3      3007.79      3057.25      3063.12
       3066.36      3084.36      3105.76      3115.98      3132.8
           3150.14      3199.42      3216.04      3294.21
     !37.64      63.89      113.28      150.74      203.16      237.51!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH3]
        RRHO
    Geometry[angstrom]        3
     C        0.    0.    0.
     H        0.    0.    1.0765291468
     H        0.9323015891    0.    -0.5382645734
    Core RigidRotor
        SymmetryFactor    6.0
    End
```

```
    Frequencies[1/cm]     6
           436.03       1412.64       1412.73       3144.41       3323.11
       3323.14
     !   !
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          22.9
End
Barrier         B4   W1   P2     # TS_CCCOCOC=C+[CH3]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         -0.0040543148     -0.0386425229     0.0073857711
     C         -0.0048900436      0.0061823278     1.5300622428
     C          1.3972642581     -0.0005551268     2.0992571791
     O          2.0019545826     -1.2476422451     1.7814371128
     C          3.3405752059     -1.3215358129     2.1296132728
     O          4.1497648813     -0.4681681052     1.3544114536
     C          4.1970245146     -0.7790732066     0.0295259382
     C          4.8053156527      0.0419774673    -0.8476695298
     H          3.6418436109     -1.6607272095     -0.2683773973
     C          3.30287806     1.6405400101    -1.4838550463
     H          0.5014610447      0.8374302655    -0.4020192743
     H         -1.0180307632      -0.0594446642     -0.3895728613
     H          0.5209480037     -0.9246238244     -0.3475336323
     H         -0.5120967721      0.9062976302     1.8823791475
     H         -0.5479161416      -0.849017135     1.9363981832
     H          1.9879766946      0.8139750743     1.6685141958
     H          1.3846335149      0.1222871611     3.1881314955
     H          3.5073948986     -1.010131902     3.1635375573
     H          3.6410234428     -2.3609769182     1.9844596142
     H          5.4455036203      0.8321233846    -0.4835767967
     H          4.9409763173     -0.293059714     -1.8635607
     H          3.9212887789      2.2751443976    -2.1030833855
     H          2.5615966951      1.0390754015    -1.9884097552
     H          3.0386283274      2.0213352419    -0.5080937686
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      11 12 13
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.52
    End
```

```
    Rotor        Hindered
        Group                    1 14 15
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   4.82   0.31   3.82   0.54   3.57
    End
    Rotor        Hindered
        Group                    2 16 17
        Axis                     3 4
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0   3.16   2.62   7.24   1.21   1.46   1.43   1.93
    End
    Rotor        Hindered
        Group                    3
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   6.49   1.74   4.07   3.43   4.38
    End
    Rotor        Hindered
        Group                    4 18 19
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   13.23   3.02   3.38   3.29   3.87
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   4.1   -0.04   3.2
    End
    Rotor        Hindered
        Group                    22 23 24
        Axis                     10 8
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0   2.52
    End
    Frequencies[1/cm]    58
           194.66       260.63       285.58
           316.67       363.32       422.86       473.51       514.17
   521.71       674.69       743.54       771.03       782.35
           886.53       902.56       911.83       927.61       958.77
   964.71       1088.46       1113.65       1123.94       1143.86
```

```
           1185.27       1202.85       1242.57       1284.17       1309.25
        1313.56       1349.05       1378.21       1412.87       1416.53
           1422.86       1425.36       1433.42       1460.04       1483.77
        1499.09       1510.98       1521.47       1527.85       1621.17
           3023.61       3055.62       3061.41       3064.01       3074.88
        3105.83       3108.44       3111.05       3134.06       3145.59
           3184.98       3192.37       3266.32       3276.08       3286.21
     !33.53       34.63       50.72       84.92       116.06       134.24
      199.9!
    ZeroEnergy[kcal/mol]       30.2
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    589.1433
    WellDepth[kcal/mol]    30.2
    WellDepth[kcal/mol]    7.3
    End
End
!------------------------------------------------------------
!-------------------------WELL 2 to Products ----------------
!------------------------------------------------------------
Well         W4         # W_CCCO[CH]OCCC_m062x.log
    Species
        RRHO
    Geometry[angstrom]         24
     C         0.1272836176     -0.0980909414     0.0670793598
     C         0.0279854388     0.0213509486     1.5821135859
     C         1.3835889491     0.0984857464     2.2500008907
     O         2.0269096879     1.2916311462     1.8039833799
     C         3.3337453847     1.3952720573     2.1124981028
     O         3.6166046274     1.1274510121     3.4189133337
     C         4.9980333045     1.2117165474     3.7299873392
     C         5.1817389474     0.8741978383     5.1936050221
     C         4.7454822632     -0.5486370162     5.5184559671
     H         0.6529940289     0.759264736     -0.34960684
     H         -0.8595000208     -0.1501063095     -0.390892139
     H         0.6769159573     -0.9978869925     -0.2138784206
     H         -0.5423450774     0.9113322552     1.8545255462
     H         -0.5030175413     -0.8373060581     1.9976095994
     H         1.2897134088     0.1217870336     3.3364092777
     H         2.007070188     -0.7597531465     1.976608288
     H         3.7899351263     2.2930571471     1.6975225622
     H         5.5518159502     0.5108555694     3.0962923662
     H         5.3562597864     2.2239785098     3.5130684671
     H         6.2351251895     1.0149296251     5.4429878715
     H         4.6126339337     1.5896450659     5.7897467152
     H         5.3203591415     -1.2709566824     4.9367779445
```

```
 H         4.8905822352    -0.7744307183    6.57384944
 H         3.6923498108    -0.689415    5.2803319621
Core RigidRotor
    SymmetryFactor    1.0
End
Rotor         Hindered
    Group                      10 11 12
    Axis                       1 2
    Symmetry                    3
    Potential[kcal/mol]         2
     0.0   2.69
End
Rotor         Hindered
    Group                      1 13 14
    Axis                       2 3
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0   3.61   0.32   3.59   0.04   4.68
End
Rotor         Hindered
    Group                      2 15 16
    Axis                       3 4
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0   0.75   0.44   6.06   0.74   1.48
End
Rotor         Hindered
    Group                      3
    Axis                       4 5
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0   1.96   1.51   8.93   8.18   8.19
End
Rotor         Hindered
    Group                      4 17
    Axis                       5 6
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0   1.96   1.51   8.93   8.18   8.19
End
Rotor         Hindered
    Group                      5
    Axis                       6 7
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0   0.75   0.44   6.06   0.74   1.48
End
Rotor         Hindered
```

```
        Group                       6 18 19
        Axis                        7 8
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   3.61   0.32   3.59   0.04   4.68
    End
    Rotor         Hindered
        Group                       22 23 24
        Axis                        9 8
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   2.69
    End
    Frequencies[1/cm]    58
           257.6       296.31
           326.5       334.78       437.29       506.85       634.41
   768.03       783.95       889.91       907.31       920.0
           928.19       940.92       970.58       1013.01       1091.44
     1104.51       1134.75       1160.39       1178.64       1181.03
           1230.14       1279.62       1284.11       1291.42       1311.01
        1315.82       1368.48       1381.21       1390.65       1412.81
           1414.18       1426.27       1450.29       1481.74       1484.33
        1499.48       1500.22       1512.21       1512.42       1524.13
           1526.13       3022.11       3034.86       3056.98       3064.67
        3065.22       3067.43       3073.44       3101.05       3106.31
           3107.2       3108.57       3134.29       3135.48       3148.14
       3150.9
     !26.47       42.12       54.62       112.86       131.44       149.62
       185.29       214.02!
    ZeroEnergy[kcal/mol]       2.2
    ElectronicLevels[1/cm]     1
        0  2
    End
End
Barrier         B5   W2   W4    # W_CCCO[CH]OCCC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.0016775365     0.0477152333     -0.0034631646
     C         0.0026649258     -0.0256681971     1.5178652057
     C         1.403121516     -0.005228173     2.0924647062
     O         2.099587898     -1.1462140199     1.6274264448
     C         3.3846321181     -1.2348630967     2.1268126407
     O         4.0806145508     -2.254386116     1.5556922408
     C         4.5252960266     -1.8223027733     0.2491909212
     C         4.7809132083     -0.33349828     0.3225025926
     H         5.7987233467     -0.0532500445     0.5794113327
     C         4.1012534193     0.5488097629     -0.6849562218
```

```
     H         0.4797604706    0.967547668    -0.3456305395
     H         -1.0126640121    0.0298785788    -0.3994240787
     H         0.5479655371    -0.7944303945    -0.4261361282
     H         -0.5503421534    0.8158802524    1.9392453926
     H         -0.4948325043    -0.9376159465    1.8519324494
     H         1.9371939708    0.9000023164    1.7735328143
     H         1.3759178398    -0.0110981967    3.1881151352
     H         4.0759551745    -0.2463853519    1.532564733
     H         3.4321593742    -1.2498734644    3.217168969
     H         5.4089388495    -2.4132423448    0.0180552664
     H         3.7437988297    -2.0437864837    -0.4819741207
     H         4.5019642315    0.4025597862    -1.6934805311
     H         3.0329682556    0.3240354192    -0.7251056543
     H         4.2219536079    1.6039159716    -0.4391453916
   Core RigidRotor
       SymmetryFactor    0.25
   End
   Rotor        Hindered
       Group                    11 12 13
       Axis                     1 2
       Symmetry                  3
       Potential[kcal/mol]       2
        0.0  3.09
   End
   Rotor        Hindered
       Group                    1 14 15
       Axis                     2 3
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  4.9  0.26  3.83  0.6  3.73
   End
   Rotor        Hindered
       Group                    2 16 17
       Axis                     3 4
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  2.18  1.27  7.3  1.76  2.22
   End
   Rotor        Hindered
       Group                    3
       Axis                     4 5
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  3.65  0.32  3.23  0.7  2.19
   End
   Rotor        Hindered
       Group                    22 23 24
       Axis                     10 8
```

```
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.12
    End
    Frequencies[1/cm]     60
           137.68       147.89       252.32       288.74       339.3
           389.72       478.33       541.11       564.44       698.93
   778.63       815.57       906.93       913.28       928.84
           932.87       957.4       1004.99       1081.56       1091.81
     1110.75       1128.19       1154.1       1167.76       1181.89
           1183.17       1191.33       1265.51       1286.29       1313.15
        1334.27       1352.75       1379.64       1401.23       1409.22
           1412.48       1426.78       1453.29       1482.98       1488.42
        1497.31       1499.67       1511.9       1519.99       1526.03
           1706.99       3000.88       3027.45       3041.46       3059.87
        3060.49       3071.73       3086.46       3088.99       3106.76
           3122.01       3131.53       3131.6       3146.11       3149.38
     !49.56       61.62       79.17       203.38       208.68!
    ZeroEnergy[kcal/mol]       24.5
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1778.2786
    WellDepth[kcal/mol]     20.6
    WellDepth[kcal/mol]     22.3
    End
End
Bimolecular         P3     # CC=C_E_11-7  +  CCCOC[O]
    Fragment  CC=C_E_11-7
        RRHO
    Geometry[angstrom]         9
     C         -0.0044412043     -0.0000110914     0.0103255099
     C         0.0031104224     0.0000305649     1.3338548948
     H         0.9563842389     0.0000683216     1.853401758
     C         -1.2203917251     0.0000297128     2.1942686299
     H         0.9129247895     -0.0000084902     -0.5621505225
     H         -0.9344963126     -0.0000493071     -0.5458794081
     H         -2.1258482562     -0.0000066241     1.589131927
     H         -1.2392978378     -0.8765730159     2.8442160417
     H         -1.2393345334     0.8766687931     2.8441658868
    Core RigidRotor
        SymmetryFactor     1.0
    End
    Rotor         Hindered
        Group                      1 3
        Axis                       2 4
        Symmetry                    3
```

```
        Potential[kcal/mol]        2
         0.0   2.01
    End
    Frequencies[1/cm]    20
           430.51       596.0       938.41       947.42       967.29
   1036.32       1079.5       1195.46       1330.57
           1407.13       1454.25       1484.54       1497.22       1742.34
        3056.62       3111.88       3138.7       3159.03       3168.59
           3248.77
     !206.03!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  CCCOC[O]
        RRHO
    Geometry[angstrom]         15
     O         0.0533340676     0.0524975625     0.0276926138
     C         0.0247111721     -0.0115849308     1.3707476695
     O         1.2527276949     0.0015027426     2.0170390537
     C         2.059460825     -1.1279289307     1.7188172707
     C         3.3438158934     -1.0246840295     2.5127091364
     C         3.1029266468     -1.0437506459     4.0164691369
     H         -0.5565050223     0.83610001     1.7604186659
     H         -0.5438276209     -0.9343351991     1.6128169707
     H         1.5133966609     -2.0420950005     1.9917873502
     H         2.2628029419     -1.1606993273     0.6457993422
     H         3.9906011024     -1.8539256038     2.220074996
     H         3.8526904915     -0.1037539302     2.2232315106
     H         2.6109166569     -1.9703669905     4.3171943809
     H         4.039235916     -0.9672944128     4.567330343
     H         2.4638926709     -0.2131978417     4.3110017184
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      1 7 8
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.35   0.05   3.26   2.17   3.36
    End
    Rotor         Hindered
        Group                      2
        Axis                       3 4
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   7.19   0.78   1.44
```

```
    End
    Rotor        Hindered
        Group                      3 9 10
        Axis                       4 5
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.64   0.35   3.58   0.1   4.82
    End
    Rotor        Hindered
        Group                      4 11 12
        Axis                       5 6
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.74   -0.0   2.74   0.0   2.74
    End
    Frequencies[1/cm]    35
           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
     !49.19       109.4       164.27       212.14!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          23.3
End
Barrier         B6   W2   P3    # TS_CCCOC[O]_CC=C_E13-7_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.0082367959     -0.0441869379     0.0059753787
     C         0.0012877635     0.0306977027     1.5276564619
     C         1.3995290604     0.0035233363     2.1090445907
     O         2.000275203     -1.2316015084     1.7680579448
     C         3.2993977733     -1.3895120171     2.2797726508
     O         4.1804097252     -0.4146294666     1.9419627494
     C         4.8200580787     -0.6441453994     -0.0147294509
     C         3.7072363984     -1.0766386767     -0.6515460266
     H         2.9919662703     -0.3432056057     -1.0065766931
     C         3.3410784044     -2.5088225406     -0.8185420501
     H         0.566036095     0.7934312755     -0.4174054118
     H         -1.0024653667     -0.0129944282     -0.3989466214
     H         0.4809803916     -0.9671891022     -0.3284430408
```

```
     H         -0.488657736     0.9489828608     1.8571969313
     H         -0.5671407972     -0.8040723505     1.9416660668
     H         1.9978045     0.828587059     1.7110081865
     H         1.3703792048     0.1059840066     3.201199007
     H         3.2651149706     -1.3719602705     3.3857032028
     H         3.6150581184     -2.3895680606     1.9606427061
     H         5.0838060522     0.401660595     -0.0052685865
     H         5.5896713594     -1.3458815357     0.2781676554
     H         4.1483605596     -3.1665604552     -0.4986618142
     H         2.4483879763     -2.7334815374     -0.2279657349
     H         3.1024872558     -2.7323448973     -1.8602750799
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                     11 12 13
        Axis                      1 2
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0  2.99
    End
    Rotor        Hindered
        Group                     1 14 15
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  4.99  0.42  4.06  0.69  3.95
    End
    Rotor        Hindered
        Group                     2 16 17
        Axis                      3 4
        Symmetry                   1
        Potential[kcal/mol]        8
         0.0  1.98  0.94  7.86  3.59  3.82  1.83  1.86
    End
    Rotor        Hindered
        Group                     3
        Axis                      4 5
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  6.47  4.42  6.47  3.72  4.46
    End
    Rotor        Hindered
        Group                     4 18 19
        Axis                      5 6
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0  16.0  5.47  9.75
```

```
    End
    Rotor        Hindered
        Group                      5
        Axis                       6 7
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.34   1.47   1.47   1.37   1.74
    End
    Rotor        Hindered
        Group                      22 23 24
        Axis                       10 8
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   1.93
    End
    Frequencies[1/cm]    57
           211.42       245.7       265.01
           311.54       363.73       435.34       463.02       652.32
   705.05       769.87       900.58       924.49       931.81
           944.29       955.93       968.47       998.52       1048.93
    1050.97       1080.33       1121.56       1147.49       1174.74
           1186.75       1200.64       1269.22       1283.75       1305.03
        1314.91       1375.91       1391.16       1402.91       1408.47
           1427.94       1443.65       1461.93       1480.35       1484.63
        1496.43       1498.46       1510.64       1529.65       1615.23
           2924.46       3011.69       3036.8       3045.37       3058.69
       3061.69       3072.12       3102.14       3104.4       3129.94
           3136.02       3142.1       3176.1       3180.81       3273.09
     !44.32       60.31       72.75       125.79       168.04       181.92
       191.09!
    ZeroEnergy[kcal/mol]       25.0
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    434.7994
    WellDepth[kcal/mol]    21.1
    WellDepth[kcal/mol]    1.7
    End
End
!------------------------------------------------------
!-------------------------WELL 3 to Products -----------
!------------------------------------------------------
Barrier         B7   W3   W4    # W_CCCO[CH]OCCC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.1780002918     -0.0671964137     0.0377491709
```

```
     C         0.0625996808     -0.026879569     1.5558361128
     C         1.4092024243     0.0720476868     2.2393226673
     O         2.0116446525     1.3042283496     1.8553917044
     C         3.3205628785     1.4315392093     2.2084321593
     O         3.5022032271     1.3118379731     3.5821058089
     C         4.8375183462     0.9928689799     3.9300034208
     C         5.2085701788     -0.4082407631     3.4415165854
     C         5.1217751399     -0.4808865627     1.9389899405
     H         4.8035600824     -1.4238844924     1.5077075823
     H         5.9535672543     -0.0296245513     1.4040602193
     H         0.6693493058     0.8313782968     -0.3312629133
     H         -0.8021099066     -0.1384305458     -0.4318238069
     H         0.7676303094     -0.9281026129     -0.281967393
     H         -0.5439021771     0.825959277     1.866015847
     H         -0.4375275206     -0.9248458084     1.9238112198
     H         1.3067483951     0.0390699892     3.3247048039
     H         2.0626795425     -0.7535775503     1.9306137283
     H         4.0813909092     0.4554992998     1.7427890339
     H         3.7135197703     2.3725141047     1.8121507511
     H         5.523375463     1.7350671718     3.5016190493
     H         4.8922781457     1.0621015232     5.0141151076
     H         6.2112169049     -0.6453724711     3.8112202498
     H         4.5178381471     -1.1170472943     3.9012237673
   Core RigidRotor
       SymmetryFactor    0.5
   End
   Rotor        Hindered
       Group                     12 13 14
       Axis                      1 2
       Symmetry                   3
       Potential[kcal/mol]        2
        0.0  2.67
   End
   Rotor        Hindered
       Group                     1 15 16
       Axis                      2 3
       Symmetry                   1
       Potential[kcal/mol]        6
        0.0  3.65  0.35  3.58  0.11  4.85
   End
   Rotor        Hindered
       Group                     2 17 18
       Axis                      3 4
       Symmetry                   1
       Potential[kcal/mol]        6
        0.0  3.62  3.52  7.16  2.3  4.35
   End
   Rotor        Hindered
```

```
        Group                       3
        Axis                        4 5
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   4.34   1.96   3.49   2.51   4.26
    End
    Frequencies[1/cm]    61
           137.43       213.77       281.84       312.2       325.01
   398.84
           439.85       453.7       491.96       625.21       645.82
   768.75       835.27       892.8       901.75       926.95
           933.8       964.43       983.42       1045.88       1086.19
    1091.89       1117.92       1142.79       1169.43       1180.56
           1198.71       1249.45       1257.22       1281.48       1303.56
        1313.76       1360.67       1366.41       1382.13       1407.28
           1412.88       1424.63       1451.48       1456.04       1480.58
        1482.44       1499.74       1511.8       1512.2       1526.22
           1584.42       3013.39       3020.91       3037.01       3055.89
        3063.9       3067.95       3097.22       3101.18       3106.34
           3112.89       3133.5       3134.98       3150.67       3198.43
     !29.75       65.87       78.98       178.46!
    ZeroEnergy[kcal/mol]       21.8
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    1763.4704
    WellDepth[kcal/mol]    15.8
    WellDepth[kcal/mol]    19.6
    End
End
Bimolecular         P4    # CCCOCO[CH2]  +  C=C
    Fragment  CCCOCO[CH2]
        RRHO
    Geometry[angstrom]         18
     C         0.0311661217     0.0273945471     -0.0073920717
     O         0.0008726024     -0.0003344328     1.3470971999
     C         1.2718969625     -0.0010868223     1.9625522936
     O         2.0371738652     -1.0984453087     1.6053349774
     C         1.5046898095     -2.3365310186     2.0569645026
     C         2.3492102059     -3.4541398315     1.4846601166
     C         2.3025725506     -3.4829732554     -0.0378694179
     H         -0.9417292694     -0.0219034321     -0.4666927815
     H         0.9209060385     -0.3283557532     -0.5065696589
     H         1.8325501568     0.8825769852     1.6535709655
     H         1.0659106826     0.0161076734     3.0355048638
     H         1.5127942182     -2.3523341223     3.1526831659
     H         0.4678291934     -2.4341429204     1.7204628624
```

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 H         3.3773835247    -3.3296150904     1.8290629402
 H         1.9846590054    -4.3981463638     1.8940489802
 H         2.7040927723    -2.5582183692    -0.4491108344
 H         2.8824681573    -4.3140906107    -0.4365831457
 H         1.2744294983    -3.5876778898    -0.389485947
Core RigidRotor
    SymmetryFactor    1.0
End
Rotor        Hindered
    Group                     8 9
    Axis                      1 2
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  4.95  0.1  0.21  0.02  4.6
End
Rotor        Hindered
    Group                     1
    Axis                      2 3
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  4.26  2.5  2.86  2.44  3.18
End
Rotor        Hindered
    Group                     2 10 11
    Axis                      3 4
    Symmetry                   1
    Potential[kcal/mol]        8
     0.0  7.1  2.28  2.38  2.11  4.66  3.93  4.87
End
Rotor        Hindered
    Group                     3
    Axis                      4 5
    Symmetry                   1
    Potential[kcal/mol]        8
     0.0  1.83  1.29  1.32  1.19  7.27  2.94  3.12
End
Rotor        Hindered
    Group                     4 12 13
    Axis                      5 6
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  4.98  0.13  3.74  0.48  3.62
End
Rotor        Hindered
    Group                     5 14 15
    Axis                      6 7
    Symmetry                   1
    Potential[kcal/mol]        6
```

```
          0.0   2.64   0.0   2.64   0.0   2.64
    End
    Frequencies[1/cm]     42
           302.98       320.4       403.52       484.76
           547.99       651.91       771.94       901.65       924.85
   964.05       992.83       1089.89       1113.29       1146.62
           1185.12       1193.4       1241.82       1269.08       1286.98
       1309.09       1347.55       1378.42       1412.76       1430.59
           1447.63       1484.95       1492.6       1497.44       1511.48
       1521.44       1528.95       3024.07       3057.9       3061.28
           3063.87       3075.38       3106.52       3116.5       3132.47
       3148.95       3164.17       3304.07
     !38.26       72.94       136.42       190.27       212.06       270.87!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
  Fragment  C=C
    RRHO
    Geometry[angstrom]         6
   C                  0.00000000     0.00000000     0.00000000
   H                  0.00000000     0.00000000     1.08216909
   H                  0.96588500     0.00000000    -0.48801240
   C                 -1.12558139    -0.00000000    -0.69239269
   H                 -1.12558139    -0.00000000    -1.77456178
   H                 -2.09146639    -0.00000000    -0.20438028
  Core    RigidRotor
      SymmetryFactor         2
    End
    Frequencies[1/cm]        12
    829.14  990.4  1002.92  1070.96  1243.08  1388.11  1473.77  1718.56
     3159.71  3175.83  3235.53  3261.92
     !!torsions
    ZeroEnergy[kcal/mol]       0
  ElectronicLevels[1/cm]       1
    0 1
  End
    GroundEnergy[kcal/mol]       26.0
End
Barrier         B8   W3   P4     # TS_C=C_CCCOCO[CH2]_E26_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.0015933747     0.0000014138     0.0035392005
     C         0.0006558822     0.0009953422     1.5266282417
     C         1.3979507206     -0.0028765102     2.1081622597
     O         2.0667982075     1.1782752931     1.6855191368
     C         3.3851282544     1.2524974518     2.1063561057
```

```
     O         3.5147016605    1.4139628202    3.4981727382
     C         3.1056148385    2.6218344363    3.9824718183
     C         0.9121834886    2.5883630207    4.4226582797
     C         0.5295685905    3.7148319043    5.065368704
     H         0.2236691434    4.5975545296    4.5208540968
     H         0.5716947109    3.7932301797    6.1430771723
     H         0.5157791633    0.879755479    -0.3792566823
     H         -1.0133258758    -0.0021895913    -0.3912219649
     H         0.514014336    -0.8831926412    -0.3817301337
     H         -0.530918643    0.8765707059    1.9045591329
     H         -0.5244552338    -0.8768906286    1.907739157
     H         1.368017764    -0.0384697763    3.1998972061
     H         1.9603260063    -0.8763831273    1.7533708186
     H         3.9272656625    0.3326564034    1.8729997662
     H         3.8266894116    2.1087168353    1.5918247277
     H         3.4629732991    2.8007843444    4.986176226
     H         3.1333689348    3.4497521014    3.279753961
     H         0.7423325661    2.4719377359    3.3602548392
     H         1.0841678559    1.6743592897    4.97824026
   Core RigidRotor
       SymmetryFactor    1.0
   End
   Rotor        Hindered
       Group                    12 13 14
       Axis                     1 2
       Symmetry                  3
       Potential[kcal/mol]       2
        0.0  2.73
   End
   Rotor        Hindered
       Group                    1 15 16
       Axis                     2 3
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0  3.48  0.29  3.21  0.14  4.69
   End
   Rotor        Hindered
       Group                    2 17 18
       Axis                     3 4
       Symmetry                  1
       Potential[kcal/mol]       8
        0.0  4.12  3.52  6.61  2.3  2.8  2.22  2.44
   End
   Rotor        Hindered
       Group                    3
       Axis                     4 5
       Symmetry                  1
       Potential[kcal/mol]       6
```

```
         0.0   11.0   4.74   5.24   3.41   4.25
    End
    Rotor        Hindered
        Group                     4 19 20
        Axis                      5 6
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   8.67   2.89   3.11   2.97   3.73
    End
    Rotor        Hindered
        Group                     5
        Axis                      6 7
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   4.85   0.87   6.02
    End
    Rotor        Hindered
        Group                     6 21 22
        Axis                      7 8
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.13   0.48   2.39   0.11   1.59
    End
    Frequencies[1/cm]    58
           220.08       286.59       296.93
           320.08       391.21       431.29       497.65       578.89
   654.7       768.85       826.38       846.57       888.05
           899.47       927.95       961.77       997.18       1001.26
    1040.6       1090.6       1113.09       1143.18       1180.12
           1193.27       1238.41       1240.52       1263.17       1283.32
        1308.6       1313.88       1350.93       1381.36       1414.34
           1427.66       1450.58       1469.31       1482.91       1487.48
        1499.89       1512.1       1519.84       1529.01       1591.18
           3011.61       3053.0       3063.52       3066.83       3085.34
       3104.75       3107.32       3109.68       3133.64       3149.64
           3151.14       3167.6       3232.3       3250.11       3260.29
     !41.33       60.43       81.11       84.5       117.8       136.51
    187.67!
    ZeroEnergy[kcal/mol]      33.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    493.4911
    WellDepth[kcal/mol]    27.2
    WellDepth[kcal/mol]    7.2
    End
End
```

```
!-------------------------------------------------------------
!-------------------------WELL 4 to Products -----------------
!-------------------------------------------------------------
Bimolecular         P5    # Bi_CCCOC=O_E4-4  +  CC[CH2]_E6-5
    Fragment  Bi_CCCOC=O_E4-4
        RRHO
    Geometry[angstrom]        14
     C         0.0240964182    0.0095221715    0.0177319524
     C         -0.0030425293    -0.0039903355    1.5406932512
     C         1.3810526487    0.0075489273    2.1477852797
     O         2.0145018277    1.2430203364    1.7720768004
     C         3.2624172943    1.4051392265    2.20525629
     O         3.8765204621    0.6198108646    2.8648746235
     H         0.5240548293    0.9039028938    -0.3506417673
     H         -0.9838521124    -0.009648659    -0.3935102324
     H         0.5610273437    -0.858905151    -0.3666945599
     H         -0.5595170156    0.8555979426    1.9180905613
     H         -0.514632694    -0.8978448249    1.9021761279
     H         1.3548784005    -0.0512964009    3.2356710446
     H         1.9904306763    -0.8198792418    1.7803288283
     H         3.6490536234    2.3730992117    1.8666815551
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    7 8 9
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.75
    End
    Rotor        Hindered
        Group                    1 10 11
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  3.6  0.28  3.6  0.03  4.82
    End
    Rotor        Hindered
        Group                    2 12 13
        Axis                     3 4
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
    End
    Rotor        Hindered
        Group                    3
        Axis                     4 5
```

```
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   12.84   5.12   12.83
    End
    Frequencies[1/cm]     32
           299.37       351.0       467.28       768.7       797.8
   912.78
           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
           3076.24       3084.0       3107.9       3126.48       3138.05
      3150.08
     !55.58       128.77       199.8       261.94!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   1
    End
    Fragment  CC[CH2]_E6-5
        RRHO
    Geometry[angstrom]         10
     C         0.0039810468     -0.0002188188     0.0092042733
     C         -0.0088483198     0.0002930088     1.5351197712
     C         1.3565534595     0.0092394493     2.1204521286
     H         0.5040514096     0.8903711756     -0.371400763
     H         -1.00586973     -0.025183384     -0.398163844
     H         0.541628334     -0.8708029617     -0.3683706538
     H         -0.575496772     0.8591900883     1.9045845297
     H         -0.5626721837     -0.881435076     1.8869769385
     H         1.5205634067     0.2906855121     3.1494183006
     H         2.1839808894     -0.4237198291     1.5766300632
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      4 5 6
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   3.01
    End
    Rotor         Hindered
        Group                      1 7 8
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         12
         0.0   0.05   0.01   0.28   0.26   0.28   0.0   0.05   0.01   0.28   0.26
     0.28
```

```
    End
    Frequencies[1/cm]    22
           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
     !93.61       253.67!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]          -7.9
End
Barrier         B9   W4   P5    # TS_CCCOC=O_CC[CH2]_E10-8_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         24
     C         0.0355582487     -0.0169682364     -0.024441075
     C         -0.0174643074     0.0319156001     1.497679403
     C         1.3377549595     0.0133839198     2.1127552365
     O         1.9675796799     -1.6870469738     1.851598868
     C         1.1303926374     -2.6232702254     1.8742289959
     H         0.5340194479     -2.9258124172     1.0182470626
     O         0.6903709664     -3.1886318632     3.0181647772
     C         1.4805170906     -2.9522444514     4.1838711104
     C         0.9669881192     -3.8564485148     5.2832694929
     C         1.1387818653     -5.3333553412     4.9531277396
     H         0.5329320481     0.8703898738     -0.4176804113
     H         -0.9617894819     -0.0664137513     -0.4588386977
     H         0.6018424877     -0.8863596783     -0.3590532796
     H         -0.5646478328     0.9191540018     1.8302386245
     H         -0.587727851     -0.8235792453     1.881647916
     H         2.1236143005     0.5424004711     1.5895613189
     H         1.3915417151     0.0993418245     3.1908928274
     H         2.527795135     -3.163351405     3.9520223574
     H         1.4045370614     -1.9018504516     4.4687781353
     H         1.5052610019     -3.6074484959     6.1998255835
     H         -0.0858183929     -3.6284183895     5.4596076675
     H         2.1914264139     -5.5735874229     4.7960334853
     H         0.7667981359     -5.9635921894     5.7595732225
     H         0.5973224969     -5.5876727571     4.0435866402
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                        11 12 13
        Axis                         1 2
```

```
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.74
    End
    Rotor         Hindered
        Group                     1 14 15
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   6.53   0.79   2.22   1.17   2.7
    End
    Rotor         Hindered
        Group                     2 16 17
        Axis                      3 4
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.15   2.32   4.61   1.01   2.11
    End
    Rotor         Hindered
        Group                     8
        Axis                      7 5
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   6.95   1.32   6.28
    End
    Rotor         Hindered
        Group                     9 18 19
        Axis                      8 7
        Symmetry                   1
        Potential[kcal/mol]        8
         0.0   0.52   0.28   7.45   0.76   0.93   0.62   0.8
    End
    Rotor         Hindered
        Group                     10 20 21
        Axis                      9 8
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.68   0.32   3.63   0.05   4.9
    End
    Rotor         Hindered
        Group                     22 23 24
        Axis                      10 9
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.7   -0.0   2.7   0.0   2.7
    End
    Frequencies[1/cm]    58
           224.92       262.22       303.5
```

```
            313.96       380.55       456.05       466.63       710.75
    722.51       759.25       767.72       811.04       904.7
            909.15       922.5       941.85       956.95       979.1
    1085.43       1092.72       1113.51       1133.89       1178.57
            1194.17       1199.12       1282.74       1283.18       1310.55
         1349.7       1375.0       1380.35       1412.83       1414.96
            1423.73       1473.8       1481.74       1482.86       1485.4
       1500.04       1501.16       1511.52       1512.35       1523.2
            3016.66       3055.65       3055.94       3063.73       3064.7
         3067.62       3100.64       3108.27       3130.6       3135.24
            3141.82       3145.03       3151.0       3160.53       3233.34
      !30.49       35.17       67.64       114.45       125.63       168.78
        194.4!
     ZeroEnergy[kcal/mol]       15.8
     ElectronicLevels[1/cm]     1
         0  2
     End
     Tunneling                  Eckart
     ImaginaryFrequency[1/cm]    777.0171
     WellDepth[kcal/mol]     13.6
     WellDepth[kcal/mol]     23.7
     End
End
End
```

E.6 CCOC[O]

```
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
PressureList[atm]                  0.00001 0.001  0.01  0.1  1  10  100.
!PressureList[bar]                 1.
EnergyStepOverTemperature          .2
ExcessEnergyOverTemperature        30
ModelEnergyLimit[kcal/mol]         400
CalculationMethod                  direct
!CalculationMethod                 low-eigenvalue !direct
WellCutoff                         10
ChemicalEigenvalueMax              0.2
```

```
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                 200
      Power                        .85
      ExponentCutoff               15
    End
  CollisionFrequency
    LennardJones
        Epsilons[1/cm]     94.87   292.09  !Ar and CCOC[O]
    Sigmas[angstrom]       3.33    6.03
    Masses[amu]            39.88   75.09
    End
!------------------------------------------------------
!-------------------------WELL 1 to Products ------------
!------------------------------------------------------
Well         W1         # W_CCOC[O]_m062x.log
    Species
        RRHO
    Geometry[angstrom]         12
     O         -0.0000136479     -0.0158947662     0.0001300488
     C         0.0003804679     -0.0116558615     1.4194515571
     C         1.4348826083     0.0041591029     1.8907607535
     C         -1.2747334222     -0.0278957055     -0.5487163989
     H         -1.1614851697     0.0929277806     -1.6352880151
     H         -1.8740917079     0.8342817878     -0.1867784254
     H         -0.5391724883     0.8746145099     1.7772187915
     O         -2.0241910818     -1.1168828411     -0.3006299029
     H         -0.5240324399     -0.896234416     1.7892024768
     H         1.948419974     0.8871976315     1.5138163786
     H         1.4763606257     0.0127262847     2.9791096444
     H         1.9577182949     -0.8794154994     1.528544097
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      4
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         8
         0.0   1.74   0.99   4.51   1.17   1.18   1.07   1.41
    End
    Rotor         Hindered
        Group                      5 6 8
        Axis                       4 1
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.32   0.0   3.36   2.24   3.36
```

```
    End
    Rotor        Hindered
        Group                      10 11 12
        Axis                       3 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  3.09
    End
    Frequencies[1/cm]    27
           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

     !70.21      146.84      248.71! Torsions
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Well         W2         # W_CCO[CH]O_m062x.log
    Species
        RRHO
    Geometry[angstrom]        12
     C         0.0000433788    0.0024700771    -0.0001972596
     C         0.0000555856    -0.0060724026    1.5095492025
     O         1.3609586911    -0.0100016927    1.9407270439
     C         1.5529542565    0.1873578303    3.2577024765
     O         0.7754147405    -0.6270805274    4.0474432603
     H         0.5027965156    0.8916338309    -0.3770671566
     H         -1.0222238956    -0.0077779008    -0.3761901143
     H         0.5193106247    -0.8752249686    -0.3821236336
     H         -0.4942982298    0.8805352656    1.9164680211
     H         -0.508055467    -0.8872933108    1.901618396
     H         0.8746968719    -0.3531018135    4.9619264266
     H         2.6096999086    0.2443476066    3.5075233557
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                      6 7 8
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  3.1
    End
```

```
    Rotor        Hindered
        Group                     4
        Axis                      3 2
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.05   0.43   3.78   0.05   1.21
    End
    Rotor        Hindered
        Group                     5 12
        Axis                      4 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.12   1.53   2.78   2.13   2.67
    End
    Rotor        Hindered
        Group                     11
        Axis                      5 4
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   0.91   0.64   1.57   1.55   1.56
    End
    Frequencies[1/cm]    26
           295.7      388.13      632.61      818.14      868.85
   956.6
           1061.23      1129.08      1139.35      1185.94      1203.81
        1306.09      1325.06      1392.69      1417.9      1443.11
           1487.63      1505.16      1533.66      3050.46      3073.56
        3104.54      3122.4      3150.03      3153.21      3906.57

     !61.97      154.12      229.46      246.96!
    ZeroEnergy[kcal/mol]      -8.0
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Barrier        B1   W1   W2    # W_CCO[CH]O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]        12
     C        -0.000495912    -0.0129654119    -0.001674686
     C        0.0016077345    0.0396372445    1.5064494001
     O        1.3644538144    0.0385229135    1.9358970487
     C        1.5650231361    0.1847645992    3.2573361323
     O        0.6563462207    -0.3015643612    4.1463779212
     H        0.5197404715    0.8487322661    -0.4163625889
     H        -1.0242354078    -0.0151333828    -0.3731718261
     H        0.4966091561    -0.9170525219    -0.3494129069
     H        -0.4803039534    0.9497488699    1.8775900663
```

```
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
```

```
Geometry[angstrom]        12
 C        0.0004564886    -0.0000249976    -0.000991796
 C        -0.000737671    0.0130950412    1.4790860616
 O        1.2433878871    -0.0123497744    2.0435730865
 C        1.2481614968    -0.0486442093    3.4482040185
 O        0.754882183    -1.2515320109    3.9529452249
 H        0.6357579886    0.7967984946    -0.3909132844
 H        -1.0092294668    0.1421233641    -0.3814256615
 H        0.383274109    -0.9462746894    -0.4027243023
 H        1.3381403125    -1.9616079289    3.6698040167
 H        -0.7901844682    -0.4555533757    2.0539256901
 H        2.2848377266    0.1242307419    3.7374850965
 H        0.6013924262    0.7346113427    3.8465078376
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    6 7 8
    Axis                     1 2
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0   1.35   0.0   1.35   0.0   1.35
End
Rotor        Hindered
    Group                    4
    Axis                     3 2
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0   3.98   1.7   2.57   1.45   4.53
End
Rotor        Hindered
    Group                    5 11 12
    Axis                     4 3
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0   2.92   2.25   3.03   0.88   5.82
End
Rotor        Hindered
    Group                    9
    Axis                     5 4
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0   3.79   1.87   3.45
End
Frequencies[1/cm]    26
       192.58      412.79      581.44      643.53      900.2
1023.24
```

```
           1054.01       1105.96       1115.94       1165.06       1233.43
        1315.86       1382.36       1394.78       1429.31       1465.7
           1470.31       1495.98       1533.53       3008.62       3072.48
        3090.17       3127.17       3146.72       3183.56       3870.29

     !81.75       136.16   278.45       371.56! Torsions
    ZeroEnergy[kcal/mol]       -9.8
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Barrier         B2  W1  W3    # W_C[CH]OCO_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         -0.0028669845    0.0124688762    0.0329675519
     C         0.0296622093    0.0145978304    1.524947518
     O         1.3231640274    0.0322625014    2.0472670249
     C         1.1651753608    0.7495049941    3.2565127917
     O         0.3086696827    1.8090378537    2.9743251821
     H         0.5451798726    0.8683853881    -0.3560561568
     H         -1.027316072    0.0357601353    -0.3337583574
     H         0.4765682159    -0.8963906411    -0.3391791118
     H         -0.3450618306    1.098537956    2.0202827976
     H         -0.6152742937    -0.7238595711    2.0162037757
     H         0.7459317725    0.0796102228    4.0201803272
     H         2.1325603922    1.1377591664    3.5798597608
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      6 7 8
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  2.36
    End
    Frequencies[1/cm]    28
           138.51       266.44       425.96       548.14       712.57
   841.13       900.44       1007.32       1097.43
           1114.53       1144.01       1160.76       1173.86       1258.84
        1305.05       1373.9       1410.55       1426.9       1478.35
           1488.98       1541.2       1888.35       2993.62       3036.13
       3056.7       3098.98       3129.49       3162.73
     !206.95! Torsions
    ZeroEnergy[kcal/mol]       20.3
    ElectronicLevels[1/cm]    1
        0  2
```

```
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1776.8973
    WellDepth[kcal/mol]    20.3
    WellDepth[kcal/mol]    30.1
    End
End
Well        W4        # W_[CH2]COCO_m062x.log
    Species
        RRHO
    Geometry[angstrom]        12
     C         0.0020189982    0.0160214494    0.0079808931
     C         -0.0011068789    -0.0107611031    1.491695066
     O         1.3138665327    -0.0044799478    2.0340728911
     C         1.9504732489    1.2341013732    1.9297213108
     O         1.3752386068    2.2050155801    2.7591146397
     H         1.4665801644    1.9092547911    3.6694630063
     H         -0.8305830737    0.4279129436    -0.5405010272
     H         0.7545916178    -0.5440867673    -0.5269618518
     H         -0.5787944972    0.8243553346    1.8972422432
     H         -0.4567196771    -0.9333686733    1.8667518137
     H         2.9943151448    1.0495217498    2.1874254768
     H         1.8770537949    1.6324342886    0.9147145292
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    7 8
        Axis                     1 2
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   1.66   0.0   1.66
    End
    Rotor        Hindered
        Group                    4
        Axis                     3 2
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   1.89   0.52   1.89   1.03   3.18
    End
    Rotor        Hindered
        Group                    5 11 12
        Axis                     4 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   3.75   3.08   3.82   1.25   7.35
    End
    Rotor        Hindered
```

```
        Group                       6
        Axis                        5 4
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   3.8   1.97   4.01
    End
    Frequencies[1/cm]    26
           197.85       461.35       526.27       597.23       848.63
   942.06
           1053.71       1061.06       1104.25       1133.55       1168.91
        1279.69       1325.05       1390.63       1393.54       1453.75
           1459.94       1493.77       1531.99       3027.43       3060.81
        3073.6       3111.96       3173.81       3283.94       3869.91

     !79.29       187.13    313.1       359.39!
    ZeroEnergy[kcal/mol]      -3.0
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Barrier         B3   W1   W4    # W_[CH2]COCO_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C              0.0330815491         -0.0299443728
   0.0032413357
     C              0.0505711386         -0.0132639494
   1.5137513189
     O              1.3822464438          0.0067349515        1.998019554
     C              2.0678044661         -1.1106234354
   1.5006877424
     O              2.226632952          -1.0574978407
   0.1250709843
     H              1.0539801123         -0.7130359604
   -0.2491314131
     H              0.2848761441          0.9186162715
   -0.4624067274
     H             -0.8201809608         -0.5218149587
   -0.4546175024
     H             -0.4337242566          0.878778394
   1.9119831239
     H             -0.4694162922         -0.8932364273
   1.9095650939
     H              3.0707064228         -1.0985879864        1.935888386
     H              1.5384364757         -2.0243473483
   1.8090746643
    Core RigidRotor
        SymmetryFactor    1
```

```
    End
    Frequencies[1/cm]    29
           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
     ! !
    ZeroEnergy[kcal/mol]      16.7
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1627.79
    WellDepth[kcal/mol]    16.70
    WellDepth[kcal/mol]    19.7
    End
End
Bimolecular         P1    # C=O  +  CC[O]
    Fragment  C=O
        RRHO
    Geometry[angstrom]        4
     O         -0.000000016    -0.0000022088    0.0061054213
     C         -0.0000000144    0.0000068137    1.2014608526
     H         0.9375275336    -0.0000022726    1.7838372267
     H         -0.9375275608    0.0000246367    1.7838372291
    Core RigidRotor
        SymmetryFactor    2
    End
    Frequencies[1/cm]    6
           1216.69      1279.34      1545.84      1876.79      2940.94
        3011.91
     !!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  CC[O]
        RRHO
    Geometry[angstrom]        6
     C         0.0155365932    -0.0000000007    0.0171987239
     C         0.0029660543    0.000000002    1.5560358386
     O         1.3181854365    -0.0000000006    1.942937121
     H         -1.0120743165    0.0000000013    -0.3413302391
     H         0.5253156863    0.8861747108    -0.3533063308
     H         -0.5179168516    0.8981336306    1.9058855675
    Core RigidRotor
        SymmetryFactor    1
    End
```

```
    Rotor         Hindered
        Group                      4 5 6
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.34   0.0   2.35   0.0   2.34
    End
    Frequencies[1/cm]     17
           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
     !244.47! Torsions
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          18.5
End
Barrier         B4   W1   P1     # TS_CC[O]+C=O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         -0.0036292853     -0.0069715059     -0.004787059
     C         0.0055451657     0.0052156433     1.5095753484
     O         1.2868547532     0.0024082279     2.0619025642
     C         1.8908586856     1.6659620251     2.4563858684
     O         1.8277593448     2.1202822645     1.3025123835
     H         0.4085951259     0.9309296114     -0.3722360157
     H         -1.0208202027     -0.1248729846     -0.3780202194
     H         0.6062373243     -0.8280072188     -0.3778300604
     H         -0.5884670004     0.8292628686     1.9170835203
     H         -0.4257465282     -0.9279039418     1.9043200986
     H         1.1205153644     1.9238811198     3.1964227131
     H         2.8458432615     1.3250549017     2.8724518577
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      6 7 8
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.91
    End
    Rotor         Hindered
        Group                      1 9 10
        Axis                       2 3
```

```
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.91   1.32   2.23   0.59   4.2
    End
    Rotor         Hindered
        Group                      5 11 12
        Axis                       4 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0  2.25  0.60  6.68  4.68  6.26
    End
    Frequencies[1/cm]     26
           281.54       375.03       464.19       776.99       846.6
   906.94       1029.11
           1107.66       1156.08       1220.65       1244.06       1270.16
        1389.17       1407.08       1426.16       1466.48       1483.8
           1503.12       1609.99       2981.16       2984.81       3057.7
       3068.11       3071.94       3150.02       3161.37
     !109.15       130.6       213.03!
    ZeroEnergy[kcal/mol]       22.9
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    620.8219
    WellDepth[kcal/mol]    22.88
    WellDepth[kcal/mol]    4.41
    End
End
Bimolecular         P2     # CCOC=O  +  [H]
    Fragment  CCOC=O
        RRHO
    Geometry[angstrom]         11
     O         0.0001875982    0.0001810121    -0.0000045809
     C         0.0000360448    0.0001495603    1.1954700817
     H         0.9006620095    0.000133797    1.8198581397
     O         -1.0833263564    0.0001288025    1.9687150237
     C         -2.3413617547    0.0001474237    1.272369565
     C         -3.4340641981    0.0001156125    2.3120371537
     H         -2.3828528182    0.8801670343    0.6309353146
     H         -2.3828502516    -0.8798347151    0.6308837924
     H         -3.3624530972    0.8838386974    2.9438172999
     H         -4.407993839    0.0001325389    1.8247539829
     H         -3.3624553661    -0.8836477651    2.9437612352
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
```

```
        Group                       5
        Axis                        4 2
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   12.99   5.27   12.99
    End
    Rotor         Hindered
        Group                       6 7 8
        Axis                        5 4
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   1.12   0.01   6.55   0.01   1.12
    End
    Rotor         Hindered
        Group                       9 10 11
        Axis                        6 5
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   3.12   0.0   3.12   0.0   3.12
    End
    Frequencies[1/cm]    24
           237.16       389.93       806.77       814.71       883.19
   1062.71       1063.87
           1145.7       1187.56       1261.98       1310.78       1399.55
       1413.17       1434.43       1490.84       1503.7       1528.65
           1852.53       3076.3       3081.04       3086.08       3124.94
       3153.11       3158.28
     !77.65       236.19       344.76!
    ZeroEnergy[kcal/mol]       18.5
    ElectronicLevels[1/cm]     1
        0   1
    End
    Fragment    H
      Atom
        Mass[amu]     1
        ElectronicLevels[1/cm]     1
          0   2
    End
    GroundEnergy[kcal/mol]          1.9
End
Barrier         B5   W1   P2     # TS_CCOC=O+[H]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0099622992     -0.0195631625     0.0098023554
     C         -0.005631246     0.0063995797     1.5246746767
     O         1.3250247148     -0.0080232284     2.0606508365
     C         1.9729632713     -1.1867030096     1.9862101831
```

```
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
```

```
    End
End
!-----------------------------------------------------
!-------------------------WELL 2 to Products --------
!-----------------------------------------------------
Barrier         B6   W2   W3    # W_C[CH]OCO_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0355619539     0.0416762584     0.0370615052
     C         -0.0112738058     -0.0235741654     1.5299232092
     O         1.2746920873     -0.0285172415     2.144631517
     C         1.1666856207     1.2438026194     2.7128464394
     H         1.0608141319     1.248147706     3.7975014404
     O         2.1422278535     2.1159992294     2.3288013842
     H         0.5660877945     0.9357401208     -0.2969715773
     H         -0.9714225967     0.0654336357     -0.376635257
     H         0.5582300261     -0.8279853245     -0.3709708399
     H         -0.0867205469     1.2589641504     2.1246090392
     H         -0.6878632551     -0.7490294149     1.975811977
     H         2.4073981864     1.8885376401     1.4312247248
    Core RigidRotor
        SymmetryFactor             0.25
    End
    Rotor         Hindered
        Group                      7 8 9
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   2.71
    End
    Rotor         Hindered
        Group                      12
        Axis                       6 4
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.91   2.05   3.08
    End
    Frequencies[1/cm]     27
           89.62         245.02        409.31       514.2       617.48
    832.84       899.1       993.24
           1059.28       1121.72       1137.12       1150.17       1196.6
       1265.11       1347.5       1368.8       1403.45       1433.0
           1478.84       1489.73       1911.77       3039.58       3096.91
        3105.99       3128.46       3146.25       3858.27
     !214.06       320.78!
    ZeroEnergy[kcal/mol]       29.1
    ElectronicLevels[1/cm]     1
```

```
        0  2
    End
    Tunneling                Eckart
    ImaginaryFrequency[1/cm]    1975.6035
    WellDepth[kcal/mol]         37.1
    WellDepth[kcal/mol]         38.9
    End
End
Barrier         B7   W2   W4    # W_[CH2]COCO_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0101776697    0.0085592581    0.0040915509
     C         0.0135812119    -0.0105137826    1.5083146517
     O         1.3886575449    0.04579091    1.9380873378
     C         2.1751066387    -0.6325188378    1.026749986
     H         2.3048699515    -1.6981934462    1.228032958
     O         3.3948688613    -0.0457908878    0.8575557741
     H         1.3356924844    -0.5167646673    0.0074371442
     H         0.0973026982    0.9818291601    -0.4677619359
     H         -0.6492832335    -0.676208698    -0.5136874113
     H         -0.4813661762    0.8405189596    1.9722707519
     H         -0.4438887183    -0.9283885377    1.8858389625
     H         3.2669830792    0.9083526515    0.8944641679
    Core RigidRotor
        SymmetryFactor            0.5
    End
    Rotor         Hindered
        Group                      12
        Axis                       6 4
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   3.67   3.16   5.22
    End
    Frequencies[1/cm]    28
           120.85       182.09         424.93       542.35       577.84
     683.07       850.5       904.33       996.03
           1036.57       1079.59       1118.15       1172.02       1213.2
       1268.71       1305.3       1373.28       1416.37       1445.65
           1461.81       1527.09       1726.22       3057.82       3079.46
        3124.06       3136.64       3227.07       3854.3
     !360.0!
    ZeroEnergy[kcal/mol]       16.3
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                Eckart
    ImaginaryFrequency[1/cm]    1817.3507
```

```
    WellDepth[kcal/mol]          24.3
    WellDepth[kcal/mol]          19.3
    End
End
Barrier         B8   W2   P2    # TS_CCOC=O_[H]_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
   O                  1.42029000   -0.82782200   -0.43457200
   C                  1.25749600    0.16903000    0.25069700
   O                  0.18028600    0.97564900    0.19040600
   C                 -0.95394600    0.44887800   -0.51255500
   C                 -1.65739900   -0.62019100    0.29861700
   H                  0.97604100   -0.57931100    1.63917400
   H                  2.07872400    0.69940000    0.75225700
   H                 -1.59624300    1.31068100   -0.67415200
   H                 -0.62478300    0.05951500   -1.47490300
   H                 -2.57392700   -0.92257000   -0.20667000
   H                 -1.02460400   -1.49875600    0.41151600
   H                 -1.91672200   -0.23788700    1.28556000
    Core RigidRotor
        SymmetryFactor             0.5
    End
    Rotor         Hindered
        Group                       4
        Axis                        3 2
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   11.1   4.59   10.83
    End
    Rotor         Hindered
        Group                       5 8 9
        Axis                        4 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.56   0.20   1.64   0.43   6.81
    End
    Rotor         Hindered
        Group                       10 11 12
        Axis                        5 4
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   3.15
    End
    Frequencies[1/cm]     26
           323.87       440.07       545.76       630.86       760.87
   829.12       872.74
```

```
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
```

```
     H         -0.4985399523     0.8907396606     -0.4014899118
     H         -0.5291032253     -0.8632636678     -0.4045194797
     H         0.770457535     0.5135203684     2.0371553306
     H         -0.8406008348     -0.3881967978     2.037158663
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor        Hindered
        Group                      3 4 5
        Axis                       1 2
        Symmetry                   1
        Potential[kcal/mol]        12
         0.0   0.07   0.0   0.08   0.0   0.07   0.0   0.08   0.0   0.07   0.0
   0.08
    End
    Frequencies[1/cm]    14
           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
     !125.25!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]    -18.6
End
Barrier         B9   W2   P3     # TS_C[CH2]_O=CO_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0044939866     0.0131629173     0.0042243499
     C         -0.0033355631     -0.0061896502     1.4908118003
     O         1.7705109138     0.0083192681     1.9801088228
     C         2.5414097919     0.6942424321     1.2688222001
     H         3.0337831409     0.3375640884     0.3698523993
     O         2.6088583844     2.0424052828     1.3982386482
     H         0.5636645464     0.876656145     -0.3659586897
     H         -1.006845848     0.0875954588     -0.4017265142
     H         0.4650166474     -0.8897463421     -0.3962904458
     H         -0.3747230679     0.8809636764     1.9884967752
     H         -0.2801187622     -0.9293183723     1.9788268854
     H         2.1638178298     2.2741450956     2.2222467686
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor        Hindered
        Group                      7 8 9
        Axis                       1 2
```

```
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.23   0.0   1.21   0.0   1.23
    End
    Rotor         Hindered
        Group                       1 10 11
        Axis                        2 3
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   1.76   1.23   1.81
    End
    Rotor         Hindered
        Group                       12
        Axis                        4 6
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   6.8   2.7   8.07
    End
    Frequencies[1/cm]     26
           127.36       263.95        380.69        606.61       715.3
    767.1       859.18
           915.31       1046.43       1096.98       1113.96       1225.87
       1294.76       1338.56       1400.42       1484.91       1488.61
           1493.35       1512.97       3043.68       3098.61       3130.06
        3154.48       3174.28       3246.86       3838.56
     !52.74     175.38     509.41!
    ZeroEnergy[kcal/mol]       5.8
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     786.3561
    WellDepth[kcal/mol]          13.8
    WellDepth[kcal/mol]          24.4
    End
End
!------------------------------------------------------------
!-------------------------WELL 3 to Products ------------
!------------------------------------------------------------
Bimolecular         P4     # CC=O_E4-80  +  [CH2]O_E4-80
    Fragment  CC=O_E4-80
        RRHO
    Geometry[angstrom]         7
     C         0.0018814559     0.0000017976     -0.0001381206
     C         0.0031292531     0.0000006426     1.4991972767
     H         1.0033145885     0.0000269684     1.9745983086
     O         -0.9863570005     -0.0000264084     2.1767693385
     H         -1.0168597697     -0.0000237514     -0.377470613
```

```
 H         0.540287054    -0.8770154643    -0.3636967341
 H         0.5402427993    0.8770466646    -0.3636956282
Core RigidRotor
    SymmetryFactor             1.0
End
Rotor        Hindered
    Group                      5 6 7
    Axis                       1 2
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  1.2
End
Frequencies[1/cm]    14
       513.29      776.08      900.41      1138.06      1146.18
 1379.68      1433.59      1464.85      1474.9
       1874.28      2942.79      3063.52      3127.31      3180.67
 !157.82!
ZeroEnergy[kcal/mol]      0
ElectronicLevels[1/cm]    1
    0  1
End
Fragment  [CH2]O_E4-80
    RRHO
Geometry[angstrom]        5
 C         0.0017120689    0.0006775385    0.0060328527
 O         0.0003046754    -0.0110369781    1.3662657057
 H         0.9891031273    0.0055497388    -0.425004445
 H         -0.8280009474    0.4619203835    -0.510815411
 H         -0.8993933768    0.068252049    1.6902446555
Core RigidRotor
    SymmetryFactor             1.0
End
Rotor        Hindered
    Group                      3 4
    Axis                       1 2
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0  4.31  0.0  5.13
End
Frequencies[1/cm]    8
       605.38      1066.47      1240.91      1364.7      1496.89
  3154.31      3293.73      3901.11
 !413.46!
ZeroEnergy[kcal/mol]      0
ElectronicLevels[1/cm]    1
    0  2
End
GroundEnergy[kcal/mol]    0.4
```

```
End
Barrier         B10   W3   P4     # TS_CC=O_[CH2]O_E19-08_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0012282983     0.000171847     -0.0002578412
     C         -0.0009891069     0.0001393909     1.494070945
     H         0.9645484119     -0.0011986766     2.0135991487
     O         -1.0598667002     0.1071190181     2.1520400767
     C         -1.6682358888     1.9662294404     2.2833975279
     O         -0.569364828     2.6892587847     1.9845829764
     H         0.8931279391     -0.4787582699     -0.4017622807
     H         -0.019107577     1.0324996439     -0.3667585382
     H         -0.8880767949     -0.5052235063     -0.375762331
     H         -2.4136621759     1.9966557738     1.5054523068
     H         -1.989066137     1.9180641157     3.31385606
     H         0.0546685291     2.6513114473     2.7153229607
    Core RigidRotor
        SymmetryFactor              1.0
    End
    Rotor         Hindered
        Group                       7 8 9
        Axis                        1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   0.33
    End
    Rotor         Hindered
        Group                       6 10 11
        Axis                        5 4
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.93   3.21   3.59
    End
    Rotor         Hindered
        Group                       12
        Axis                        6 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.39   0.63   5.6
    End
    Frequencies[1/cm]     26
            108.25       217.63       436.15       504.11       664.94
   702.63       911.23
            941.51       1026.42       1086.7       1122.55       1216.47
      1343.08       1382.52       1390.42       1464.18       1476.47
            1513.43       1526.66       3028.89       3034.39       3105.66
        3150.49       3159.62       3291.15       3869.05
```

```
     !81.32      91.28      317.16!
    ZeroEnergy[kcal/mol]      15.1
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    656.9909
    WellDepth[kcal/mol]         24.9
    WellDepth[kcal/mol]         14.7
    End
End
!------------------------------------------------------------
!-------------------------WELL 4 to Products ----------------
!------------------------------------------------------------
Bimolecular         P5    # C=C  +  OC[O]_E10-83
    Fragment  C=C
        RRHO
    Geometry[angstrom]        6
     C         0.0000005934    -0.0000013257    0.005740686
     C         -0.00000068    0.0000017949    1.3272371407
     H         0.9217469077    -0.0000000153    -0.5612441874
     H         -0.9217446282    -0.0000053139    -0.5612459638
     H         0.9217445416    0.000005783    1.8942237904
     H         -0.9217469943    0.0000004844    1.894222014
    Core RigidRotor
        SymmetryFactor        4
    End
    Frequencies[1/cm]    12
           829.14      990.39      1002.91      1070.95      1243.09
      1388.1      1473.76      1718.54      3159.72      3175.83
           3235.55      3261.94
     !   !
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  OC[O]_E10-83
        RRHO
    Geometry[angstrom]        6
     O         -0.0179552501    0.0302415143    -0.006361056
     C         0.0041382763    0.0110589374    1.3314866849
     O         1.2589086436    0.0840212439    1.9357400001
     H         -0.5947076421    0.8417540232    1.7323338284
     H         -0.5341035012    -0.9194312946    1.6108216799
     H         1.8532698239    -0.5108496864    1.4687292972
    Core RigidRotor
        SymmetryFactor            1.0
    End
```

```
    Rotor        Hindered
        Group                       1 4 5
        Axis                        2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   0.34   0.0   2.89   2.85   2.89
    End
    Frequencies[1/cm]    11
           558.99       759.52       1020.09       1132.89       1167.89
      1315.09       1364.87       1423.56       2878.54
           3001.58       3871.87
     !222.92!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   2
    End
    GroundEnergy[kcal/mol]     14.7
End
Barrier         B11   W4   P5     # TS_OC[O]C=C_E14-13_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         12
     C         0.0017283294     0.0009604065     -0.0042823292
     H         0.0085101916     0.0061042776     1.0766073696
     H         0.9610513573     -0.0026343736     -0.5015232257
     C         -1.155823243     0.0864589269     -0.6950038853
     O         -1.4137172979     2.1264059571     -0.7865721885
     C         -0.30084044     2.7030378402     -1.3076505758
     O         0.7494328262     2.8881078541     -0.3913913128
     H         -1.1679294103     -0.007854312     -1.7715198108
     H         -2.1085252448     0.0060969228     -0.1941930089
     H         0.1305888705     2.1416967919     -2.1437788387
     H         -0.6517027368     3.6756368555     -1.6973913782
     H         0.3557108433     3.2130938657     0.4240661984
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                       1 8 9
        Axis                        4 5
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   2.94   0.35   1.25
    End
    Rotor        Hindered
        Group                       7 10 11
        Axis                        6 5
        Symmetry                     1
```

```
        Potential[kcal/mol]        4
         0.0   10.88   3.32   8.11
    End
    Rotor        Hindered
        Group                      12
        Axis                       7 6
        Symmetry                    1
        Potential[kcal/mol]        6
         0.0   2.0   2.0   3.92   3.56   3.82
    End
    Frequencies[1/cm]    25
           205.02       309.72       409.5       574.59       826.52
   938.49       972.05
           1008.55       1028.23       1056.41       1138.11       1233.16
        1242.7       1319.63       1336.84       1422.04       1469.26
           1476.69       1604.51       2937.27       3041.72       3174.9
       3182.94       3257.42       3281.89       3866.28
     !83.87       132.89       265.51!
    ZeroEnergy[kcal/mol]       20.1
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    486.1776
    WellDepth[kcal/mol]         23.1
    WellDepth[kcal/mol]         5.4
    End
End
End
```

E.7 CCCOC[O]

```
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
PressureList[atm]                           0.00001 0.001  0.01  0.1  1  10
     100.
!PressureList[bar]                           1.
EnergyStepOverTemperature           .2
```

```
ExcessEnergyOverTemperature           30
ModelEnergyLimit[kcal/mol]            400
CalculationMethod                   direct
!CalculationMethod                    low-eigenvalue !direct
WellCutoff                          10
ChemicalEigenvalueMax               0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                    200  ! He
      Power                          .85
      ExponentCutoff                    15
    End
  CollisionFrequency
    LennardJones
        Epsilons[1/cm]    94.87   304.14  !Ar and CCCOC[O]
  Sigmas[angstrom]    3.33    6.34
  Masses[amu]         39.88   89.11
    End
!------------------------------------------------------------
!-------------------------WELL 1 to Products ----------------
!------------------------------------------------------------
Well        W1        # W_CCCOC[O]
    Species
        RRHO
    Geometry[angstrom]        15
     O        0.0533340676    0.0524975625    0.0276926138
     C        0.0247111721    -0.0115849308    1.3707476695
     O        1.2527276949    0.0015027426    2.0170390537
     C        2.059460825    -1.1279289307    1.7188172707
     C        3.3438158934    -1.0246840295    2.5127091364
     C        3.1029266468    -1.0437506459    4.0164691369
     H        -0.5565050223    0.83610001    1.7604186659
     H        -0.5438276209    -0.9343351991    1.6128169707
     H        1.5133966609    -2.0420950005    1.9917873502
     H        2.2628029419    -1.1606993273    0.6457993422
     H        3.9906011024    -1.8539256038    2.220074996
     H        3.8526904915    -0.1037539302    2.2232315106
     H        2.6109166569    -1.9703669905    4.3171943809
     H        4.039235916    -0.9672944128    4.567330343
     H        2.4638926709    -0.2131978417    4.3110017184
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    1 7 8
        Axis                     2 3
        Symmetry                  1
```

```
        Potential[kcal/mol]        6
         0.0   2.35   0.05   3.26   2.17   3.36
    End
    Rotor        Hindered
        Group                      2
        Axis                       3 4
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   7.19   0.78   1.44
    End
    Rotor        Hindered
        Group                      3 9 10
        Axis                       4 5
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.64   0.35   3.58   0.1   4.82
    End
    Rotor        Hindered
        Group                      4 11 12
        Axis                       5 6
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.74   -0.0   2.74   0.0   2.74
    End
    Frequencies[1/cm]    35
           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
     !49.19       109.4       164.27       212.14!
    ZeroEnergy[kcal/mol]    0.0
    ElectronicLevels[1/cm]    1
        0  2
    End
End
!------------------------------------------------
!-------------------------WELLS 2----------------
!------------------------------------------------
Well         W2         # W_[CH2]CCOCO
    Species
        RRHO
    Geometry[angstrom]         15
     C         -0.0007888382     0.0423351303     -0.0027660947
     C         -0.0026569732     -0.0222994013     1.4810808463
```

```
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
```

```
        Potential[kcal/mol]        4
         0.0   3.57   1.84   3.98
    End
    Frequencies[1/cm]    34
           263.15       335.9       450.62       499.73       628.5
           770.23       922.4       962.66       1041.24       1062.12
    1093.67       1113.58       1144.89       1192.39       1230.52
           1295.08       1310.03       1375.66       1391.93       1419.38
        1455.23       1459.56       1470.97       1526.03       1534.85
           2993.96       3018.46       3052.46       3083.16       3088.24
        3106.21       3179.01       3285.1       3870.83
     !45.45       116.55       167.27       189.57       368.88!
    ZeroEnergy[kcal/mol]    -4.9
    ElectronicLevels[1/cm]    1
        0  2
    End
End
#------------------------------------------------------------
Barrier         B1   W1   W2    # W_[CH2]CCOCO
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0471343566     0.0165551784     -0.0037644318
     C         0.0143163212     0.0215167537     1.5041082537
     C         1.4070205885     -0.0018369492     2.1286099
     O         2.1419884307     1.1888159482     1.9336824731
     C         2.5605925246     1.4075881583     0.6181389723
     O         1.5883114589     1.9334120307     -0.210638619
     H         0.7218224199     1.0045839168     -0.3284352832
     H         -0.9096865757     0.1880381388     -0.4899977536
     H         0.5819506228     -0.8266423538     -0.4399525816
     H         -0.5134895133     0.9059060495     1.8635778249
     H         -0.5357006684     -0.8534508264     1.8648079513
     H         1.3271917484     -0.1244099688     3.2072444451
     H         1.9757431805     -0.8544703514     1.7324844702
     H         3.3502343755     2.163312085     0.6536722189
     H         2.9728092338     0.4739652581     0.2070155769
    Core RigidRotor
        SymmetryFactor    1
    End
    Frequencies[1/cm]    38
           150.65       195.29       324.56       402.01       458.63
   519.39       609.89       642.63       819.0       893.89
           927.38       965.0       1057.26       1076.35       1112.23
     1127.87       1167.28       1199.69       1254.36       1275.52
           1303.63       1338.71       1384.58       1405.58       1430.72
        1455.87       1468.0       1471.78       1480.91       1510.03
```

```
           2984.38       3005.03       3046.28       3075.74       3092.16
        3108.67       3125.24       3176.81
     ! !
    ZeroEnergy[kcal/mol]       11.3
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]     1560.3939
    WellDepth[kcal/mol]          11.3
    WellDepth[kcal/mol]          16.2
    End
End
!------------------------------------------------------------
!-------------------------WELLS 3----------------------------
!------------------------------------------------------------
Well         W3         # W_C[CH]COCO
    Species
        RRHO
    Geometry[angstrom]         15
     C         -0.0003548893     0.0015419689     -0.0003085236
     C         -0.0003519064     -0.0015829022     1.485736156
     C         1.2853762052     -0.0007448143     2.2369764143
     O         2.1932106763     -1.0002631954     1.7745101317
     C         1.8021159842     -2.2998574132     2.101286603
     O         1.8711999495     -2.5530635343     3.4772671151
     H         0.1728201785     1.0104926277     -0.3975719067
     H         -0.9507456963     -0.3425494202     -0.4060523454
     H         0.7985240253     -0.630387483     -0.3899414723
     H         2.7864767578     -2.4467754168     3.7520998739
     H         -0.9084173895     0.2366524593     2.02092318
     H         1.8237677586     0.9425862606     2.0921971333
     H         1.1100414512     -0.1243678831     3.3075349303
     H         0.7619123612     -2.4832727158     1.8203793749
     H         2.4665305229     -2.9558125592     1.5365383229
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      7 8 9
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   0.26
    End
    Rotor         Hindered
        Group                       1 11
        Axis                       2 3
```

```
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   4.68   0.46   2.58
    End
    Rotor         Hindered
        Group                     2 12 13
        Axis                      3 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   4.14   0.93   1.93   0.91   2.26
    End
    Rotor         Hindered
        Group                     3
        Axis                      4 5
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   7.06   0.58   3.74   2.99   3.6
    End
    Rotor         Hindered
        Group                     4 14 15
        Axis                      5 6
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.97   1.6   3.8
    End
    Frequencies[1/cm]     34
           237.15       368.23       386.92       596.38       607.18
           885.64       924.94       956.34       993.99       1056.17
    1105.09       1112.35       1155.8       1169.94       1283.64
           1327.65       1378.38       1390.04       1392.22       1416.91
        1455.72       1480.35       1489.04       1495.43       1529.74
           3000.91       3023.66       3057.71       3089.36       3091.45
        3108.18       3138.14       3207.15       3870.55
     !46.38       67.34       98.83       201.97       347.27!
    ZeroEnergy[kcal/mol]      -6.6
    ElectronicLevels[1/cm]    1
        0  2
    End
End
!-----------------------------------------------------
Barrier         B2   W1   W3     # W_C[CH]COCO
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0122708786     0.00904156     0.0152456969
     C         -0.0176660359     0.0293530846     1.5212246116
     C         1.3294933784     0.0056425315     2.2138303234
     O         1.2595198607     0.598212452     3.4955347899
```

```
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
    498.74       672.23       794.02       909.59
301             935.35       992.94       1069.32       1084.26       1119.49
       1129.39       1153.87       1191.83       1261.85       1317.19
302             1330.58       1334.55       1393.86       1410.87       1429.67
         1488.72       1491.85       1495.96       1508.06       1593.35
303             2976.52       3005.04       3043.31       3073.39       3096.18
         3108.28       3121.59       3150.93
304      !186.49!
305     ZeroEnergy[kcal/mol]      12.0
306     ElectronicLevels[1/cm]    1
307         0  2
308     End
309     Tunneling                 Eckart
310     ImaginaryFrequency[1/cm]    1417.0484
311     WellDepth[kcal/mol]         12.0
312     WellDepth[kcal/mol]         18.6
313     End
314 End
315 !------------------------------------------------
316 !-------------------------WELLS 4-----------------
317 !------------------------------------------------
318 Well         W4         # W_CC[CH]OCO
319     Species
320         RRHO
321     Geometry[angstrom]        15
```

```
     C         0.0003569795    0.0020586305    0.0003532474
     C         -0.0000298536    -0.0013546711    1.5292935205
     C         1.368719835    -0.0010106197    2.1027893036
     O         2.1506353068    1.0450770468    1.7012980214
     C         3.4406480251    1.0619505147    2.2586316308
     O         3.4258183243    1.309410035    3.6307438825
     H         0.5278495072    0.8762239886    -0.3773509146
     H         -1.0163329842    0.0189901444    -0.390203997
     H         0.5033199421    -0.8856916341    -0.3830183079
     H         -0.5559868679    0.8759228805    1.8876066363
     H         -0.5267887786    -0.8781230132    1.9070473059
     H         3.0674900423    2.1896109788    3.7771400448
     H         1.5768027316    -0.3939030689    3.0905834202
     H         3.9166456622    0.0885998471    2.131110015
     H         3.9825981532    1.830899958    1.7078931773
  Core RigidRotor
      SymmetryFactor    1
  End
  Rotor        Hindered
      Group                    7 8 9
      Axis                     1 2
      Symmetry                  3
      Potential[kcal/mol]       2
       0.0  2.84
  End
  Rotor        Hindered
      Group                    1 10 11
      Axis                     2 3
      Symmetry                  1
      Potential[kcal/mol]       6
       0.0  1.53  0.17  1.59  0.04  2.12
  End
  Rotor        Hindered
      Group                    2 13
      Axis                     3 4
      Symmetry                  1
      Potential[kcal/mol]       4
       0.0  5.8  2.28  4.14
  End
  Rotor        Hindered
      Group                    3
      Axis                     4 5
      Symmetry                  1
      Potential[kcal/mol]       6
       0.0  5.81  0.75  2.96  2.23  2.91
  End
  Rotor        Hindered
      Group                    4 14 15
```

```
        Axis                         5 6
        Symmetry                      1
        Potential[kcal/mol]           4
         0.0   3.45   1.86   3.8
    End
    Frequencies[1/cm]     33
           327.62       472.64       589.3       675.71
           775.22       910.43       983.75       1055.26       1076.55
     1110.85       1122.4       1146.52       1227.15       1284.83
           1320.79       1362.25       1394.1       1399.34       1416.8
      1468.32       1471.53       1499.37       1512.4       1532.3
           2990.97       3067.85       3072.11       3101.26       3126.88
        3138.16       3149.54       3180.26       3871.17
     !367.29     47.81       93.71       163.29       207.29       282.77!
    ZeroEnergy[kcal/mol]     -10.0
    ElectronicLevels[1/cm]     1
        0  2
    End
End
!------------------------------------------------
Barrier         B3   W1   W4     # W_CC[CH]OCO
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0013116439     -0.004451816     0.0000690726
     C         -0.000217632     0.002330939     1.5242335275
     C         1.3814142069     -0.0022082611     2.1004753635
     O         2.1562470771     -1.0872420571     1.6849885304
     C         3.4600221698     -0.5439539344     1.6141043987
     O         3.3279866905     0.7246958295     1.056657381
     H         0.5135272532     0.8767503475     -0.3863999681
     H         -1.0152543703      -0.010298084     -0.3889946521
     H         0.5217990909     -0.8831937267     -0.3747997253
     H         -0.5352385545      0.8696607525     1.9137020088
     H         -0.5183648753      -0.8848788045     1.9048234022
     H         2.0948501239     0.8934918743     1.5985683708
     H         1.4497073146     0.1780675686     3.1794924553
     H         3.8875743281     -0.5009232226     2.6252713189
     H         4.0798745582     -1.164546411     0.9643835043
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                        7 8 9
        Axis                         1 2
        Symmetry                      3
        Potential[kcal/mol]           2
         0.0   2.4
```

```
    End
    Rotor         Hindered
        Group                      1 10 11
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.7   0.47   3.19   0.62   2.99
    End
    Frequencies[1/cm]     36
            113.04       282.95       304.96       519.57       554.96
   711.73       771.82       899.54
            927.55       982.71       1017.61       1098.87       1119.24
      1141.3       1150.3       1171.48       1251.33       1280.55
            1308.25       1369.55       1380.66       1414.52       1425.16
        1467.09       1499.96       1510.33       1541.72       1878.0
            2994.55       3033.33       3042.61       3073.82       3099.53
        3102.45       3144.04       3159.46
     !79.88       203.61!
    ZeroEnergy[kcal/mol]       19.4
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1741.1981
    WellDepth[kcal/mol]          19.4
    WellDepth[kcal/mol]          29.4
    End
End
!---------------------------------------------------------------------
!------------------------------W1 - > P1-------------------------
!---------------------------------------------------------------------
Bimolecular         P1     # CCCOC=O  +  [H]
    Fragment  CCCOC=O
        RRHO
    Geometry[angstrom]         14
     C         0.0240964182     0.0095221715     0.0177319524
     C         -0.0030425293     -0.0039903355     1.5406932512
     C         1.3810526487     0.0075489273     2.1477852797
     O         2.0145018277     1.2430203364     1.7720768004
     C         3.2624172943     1.4051392265     2.20525629
     O         3.8765204621     0.6198108646     2.8648746235
     H         0.5240548293     0.9039028938     -0.3506417673
     H         -0.9838521124     -0.009648659     -0.3935102324
     H         0.5610273437     -0.858905151     -0.3666945599
     H         -0.5595170156     0.8555979426     1.9180905613
     H         -0.514632694     -0.8978448249     1.9021761279
     H         1.3548784005     -0.0512964009     3.2356710446
     H         1.9904306763     -0.8198792418     1.7803288283
```

```
 H         3.6490536234    2.3730992117    1.8666815551
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    7 8 9
    Axis                     1 2
    Symmetry                  3
    Potential[kcal/mol]       2
     0.0  2.75
End
Rotor        Hindered
    Group                    1 10 11
    Axis                     2 3
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  3.6  0.28  3.6  0.03  4.82
End
Rotor        Hindered
    Group                    2 12 13
    Axis                     3 4
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
End
Rotor        Hindered
    Group                    3
    Axis                     4 5
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0  12.84  4.65  12.83
End
Frequencies[1/cm]    32
       261.94      351.0      467.28      768.7      797.8
912.78
       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
       3076.24      3084.0      3107.9      3126.48      3138.05
  3150.08
 !55.58      128.77      199.8      299.37!
ZeroEnergy[kcal/mol]      0
ElectronicLevels[1/cm]    1
    0  1
End
Fragment    H
  Atom
```

```
        Mass[amu]    1
        ElectronicLevels[1/cm]    1
          0  2
    End
    GroundEnergy[kcal/mol]        1.5
End
!------------------------------------------------------------
Barrier        B4  W1  P1    # TS_CCCOC=O_H
    Variational
        RRHO
    Geometry[angstrom]        15
     C        0.054140414    0.0251811368    0.0206005523
     C        0.0015816414    -0.0114492624    1.5424551698
     C        1.3759153991    0.0213345372    2.1715115793
     O        1.9884433581    1.2686744176    1.8227636788
     C        3.2710567471    1.4026456716    2.2072578252
     O        3.8285066051    0.6831939706    3.0197304403
     H        0.5415419008    0.935245658    -0.3255241915
     H        -0.9456428412    -0.0092894826    -0.4092685592
     H        0.6163087432    -0.8260350729    -0.3666515369
     H        -0.5782248599    0.8312629162    1.9228256059
     H        -0.4973300195    -0.9205463655    1.8829044693
     H        1.3352763899    -0.062192662    3.2573400932
     H        2.0070473244    -0.7897996943    1.7960411102
     H        4.0062334779    0.8124679712    0.8971036043
     H        3.6341465541    2.4022383547    1.9321667243
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor        Hindered
        Group                    7 8 9
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.62
    End
    Rotor        Hindered
        Group                    1 10 11
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  3.65  0.34  3.63  0.1  4.85
    End
    Rotor        Hindered
        Group                    2 12 13
        Axis                     3 4
        Symmetry                  1
        Potential[kcal/mol]       4
```

```
         0.0   7.73   0.42   1.54
    End
    Rotor         Hindered
        Group                      3
        Axis                       4 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   10.33   3.83   10.24
    End
    Frequencies[1/cm]    34
           259.39       317.29       465.42       544.73       603.91
   767.92
           789.84       909.72       921.95       958.58       1089.28
    1119.08       1136.9       1179.25       1225.21       1286.86
           1311.4       1373.29       1380.5       1414.81       1427.41
      1484.01       1500.91       1512.09       1519.11       1676.16
           3035.67       3053.24       3065.2       3070.85       3107.34
       3116.84       3136.44       3149.44
     !52.03       116.3       187.2       221.67!
    ZeroEnergy[kcal/mol]       11.6
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1073.8059
    WellDepth[kcal/mol]          11.6
    WellDepth[kcal/mol]          10.1
    End
End
!------------------------------------------------------------
!-------------------------------W1 - > P2--------------------
!------------------------------------------------------------
Bimolecular         P2     # CCC[O]  +  CH2O
    Fragment  CCC[O]
        RRHO
    Geometry[angstrom]         11
     C         0.0123289889     0.0008284765     0.0157060082
     C         -0.0102318725     -0.0063326812     1.5374674503
     C         1.3947992388     -0.0037428312     2.122950554
     O         2.1545760773     1.0809214006     1.7772294789
     H         0.5824550629     0.8549966456     -0.3476429006
     H         -0.9928461086     0.0595956019     -0.3983845671
     H         0.4825717163     -0.9054375589     -0.369798953
     H         -0.5391724294     0.8719988963     1.911966076
     H         -0.5434565335     -0.8824344933     1.9127449196
     H         1.3956084458     -0.1128711697     3.2172441153
     H         1.966221157     -0.8766033662     1.7562262415
    Core  RigidRotor
```

```
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                     5 6 7
        Axis                      1 2
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0  2.78
    End
    Rotor        Hindered
        Group                     1 8 9
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  3.15  0.44  3.15  0.0  3.29
    End
    Frequencies[1/cm]    25
           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
     !141.59      231.1!
    ZeroEnergy[kcal/mol]    0
    ElectronicLevels[1/cm]    1
        0  2
    End
    Fragment  CH2O
        RRHO
    Geometry[angstrom]        4
     O        -0.000000016    -0.0000022088    0.0061054213
     C        -0.0000000144    0.0000068137    1.2014608526
     H        0.9375275336    -0.0000022726    1.7838372267
     H        -0.9375275608    0.0000246367    1.7838372291
    Core RigidRotor
        SymmetryFactor    2
    End
    Frequencies[1/cm]    6
           1216.69      1279.34      1545.84      1876.79      2940.94
        3011.91
     !  !
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    GroundEnergy[kcal/mol]    13.6
End
```

```
!-----------------------------------------------------------
Barrier         B5   W1   P2     # TS_CH2O_CCC[O]
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0019699561     -0.0000919431     -0.0015719815
     C         -0.0015799842     0.0002768644     1.5195420225
     C         1.4022922402     0.0001829883     2.1046037522
     O         2.236333603     0.993185311     1.5957294832
     C         2.1914332554     2.5287451669     2.5611079796
     O         0.9863306899     2.7757680319     2.3925327458
     H         0.5031151667     0.8893064065     -0.3790237071
     H         -1.0138939147     -0.0117409793     -0.3930313354
     H         0.5239991516     -0.8748858761     -0.3938569219
     H         -0.5132216713     0.8858378107     1.8979762609
     H         -0.5247471892     -0.8773730621     1.9055139309
     H         1.3891032127     0.0242382859     3.1990624291
     H         1.9269066352     -0.9211440386     1.8006808972
     H         2.5429046081     2.1056754089     3.512581186
     H         2.9558292389     3.0379776351     1.9629972382
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      7 8 9
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.71   0.0   2.71   0.0   2.71
    End
    Rotor         Hindered
        Group                      1 10 11
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.63   0.46   2.75   0.82   4.23
    End
    Rotor         Hindered
        Group                      2 12 13
        Axis                       3 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.24   1.76   3.76   2.5   5.82
    End
    Rotor         Hindered
        Group                      3
        Axis                       4 5
        Symmetry                    1
```

```
        Potential[kcal/mol]        6
         0.0   2.41   0.83   7.7   5.7   8.11
    End
    Frequencies[1/cm]    34
           265.59       304.52       400.22       522.65       772.25
   848.85
           874.11       889.61       983.63       1067.44       1115.95
     1154.97       1221.77       1246.04       1250.84       1301.38
           1349.54       1387.6       1419.44       1425.44       1467.39
       1484.01       1500.09       1510.43       1612.22       2964.83
           2984.8       3053.74       3063.19       3070.24       3071.36
       3115.5       3135.64       3153.42
     !47.67       111.45       152.89       230.11!
    ZeroEnergy[kcal/mol]       22.1
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    605.8983
    WellDepth[kcal/mol]         22.1
    WellDepth[kcal/mol]         8.5
    End
End
!------------------------------------------------------------
!-------------------------WELL 2 to Products ----------------
!------------------------------------------------------------
Well        W5        # W_CCCO[CH]OH
    Species
        RRHO
    Geometry[angstrom]        15
     C         -0.1409798046    -0.0341013083    0.0763015037
     C         0.0121541307    0.0370002934    1.5891725723
     H         1.0676670275    0.0848289751    1.8652901911
     C         -0.6738050233    1.2582768935    2.1805893645
     O         -2.0438012216    1.3562875298    1.8149918464
     C         -2.826007979    0.3625459895    2.3247248681
     O         -4.1216274451    0.4735529442    1.9401598926
     H         0.2459142346    0.869209414    -0.3980264374
     H         -1.1912815929    -0.130879985    -0.196474374
     H         0.3954301383    -0.888254189    -0.3338765581
     H         -0.5926792487    1.2570308265    3.2729237666
     H         -0.2147890825    2.1721592248    1.8052571425
     H         -0.3974944842    -0.8647860678    2.0472240876
     H         -2.7195578926    0.1620168852    3.3909299896
     H         -4.1358407166    0.8273336402    1.0444402337
    Core RigidRotor
        SymmetryFactor    1
    End
```

```
    Rotor        Hindered
        Group                    8 9 10
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.72
    End
    Rotor        Hindered
        Group                    1 3 13
        Axis                     2 4
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  3.61  0.44  3.17  0.7  4.61
    End
    Rotor        Hindered
        Group                    2 11 12
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  1.5  0.03  4.93
    End
    Rotor        Hindered
        Group                    4
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  5.27 2.1 2.33
    End
    Rotor        Hindered
        Group                    5 14
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  2.87  2.39  3.44
    End
    Frequencies[1/cm]    34
           297.55      363.93      468.2      577.42      777.93
           883.61      917.35      947.38      992.2      1067.71
  1116.61      1173.66      1193.27      1222.05      1300.26
           1310.77      1351.42      1378.19      1398.57      1414.36
        1441.83      1483.23      1499.12      1507.57      1515.9
           3036.05      3063.11      3068.6      3093.88      3100.04
       3122.51      3134.95      3145.13      3859.58
     !60.69      79.12      158.53      248.41      251.0!
    ZeroEnergy[kcal/mol]      -9.0
    ElectronicLevels[1/cm]    1
        0  2
    End
```

```
End
!------------------------------------------------------------
Barrier         B6   W2   W5     # W_CCCO[CH]OH
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0004933203     -0.0002683619     -0.0001444953
     H         0.0001392167     -0.0001247247     1.0865831687
     H         0.9970944499     -0.0021910808     -0.428201126
     C         -1.0172736301     -0.9076612767     -0.6429719458
     C         -2.422275895     -0.3302877511     -0.4886880841
     O         -2.5000774019     0.9524249394     -1.1069066509
     C         -1.6903956588     1.8922113716     -0.5049469765
     O         -2.0856510568     2.2492305485     0.7758052609
     H         -0.8079291931     -1.0218908243     -1.7074629191
     H         -1.0098692701     -1.9088611765     -0.1998149958
     H         -3.1632020894     -0.9483688706     -0.9899781151
     H         -2.6870358301     -0.2459274728     0.5687789542
     H         -0.5624784656     1.2171508409     -0.288941986
     H         -1.5563190952     2.7321128059     -1.1856237846
     H         -2.9676353604     2.6368580963     0.7351987235
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      15
        Axis                       8 7
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   1.76   0.53   1.65
    End
    Frequencies[1/cm]    37
            139.07       160.34       303.61       417.14       491.46
   542.82       602.58       650.19       826.84
            899.43       929.61       948.53       1032.08       1047.44
     1095.0       1129.62       1171.6       1191.24       1242.94
            1285.39       1307.39       1362.64       1374.81       1410.46
        1449.76       1455.31       1479.01       1511.56       1578.88
            3036.76       3059.91       3100.98       3108.23       3117.09
        3143.74       3202.16       3811.26
     !273.86!
    ZeroEnergy[kcal/mol]       11.0
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1734.3756
    WellDepth[kcal/mol]          15.9
```

```
    WellDepth[kcal/mol]          18.0
    End
End
!-----------------------------------------------------
!-----------------------------------------------------
!-----------------------------------------------------
Bimolecular         P3    # [CH2]OCOH  +  C=C
    Fragment  [CH2]OCOH
        RRHO
    Geometry[angstrom]         9
     C         0.0004242915     -0.0000363321     0.0000815993
     O         0.0001503754     0.0000678304     1.3573274535
     C         1.2812584108     0.00041206     1.9419188129
     O         1.9858635589     -1.1721603274     1.6812220126
     H         0.8587661489     -0.420451383     -0.5044915023
     H         -0.9848098531     -0.0361202249     -0.433865058
     H         1.8794068052     0.8132560077     1.5276025639
     H         1.1083169825     0.1519565878     3.0072090351
     H         1.5181302731     -1.9071692222     2.0883780825
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      5 6
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   4.96   0.0   4.87   0.47   0.51
    End
    Rotor         Hindered
        Group                      1
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         8
         0.0   3.94   3.78   3.91   1.94   2.97   2.16   3.24
    End
    Rotor         Hindered
        Group                      2 7 8
        Axis                       3 4
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.41   1.08   4.54
    End
    Frequencies[1/cm]    18
           396.61       601.46       613.01       991.83       1063.89
    1122.38       1199.26
           1269.0       1316.15       1395.84       1447.11       1494.35
       1533.68       3074.17       3129.72       3160.7       3300.39
```

```
           3869.46
     !162.73      260.33      372.97!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  2
    End
  Fragment  C=C
    RRHO
      Geometry[angstrom]  6
       C                  0.00000000    0.00000000    0.00000000
     H                   0.00000000    0.00000000    1.08216909
     H                   0.96588500    0.00000000   -0.48801240
     C                  -1.12558139   -0.00000000   -0.69239269
     H                  -1.12558139   -0.00000000   -1.77456178
         H                 -2.09146639   -0.00000000   -0.20438028
        Core    RigidRotor
      SymmetryFactor     4
        End
        Frequencies[1/cm]       12
         829.14 990.4 1002.92 1070.96 1243.08 1388.11 1473.77 1718.56
   3159.71 3175.83 3235.53 3261.92
         !!torsions
      ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]      1
        0 1
     End
    GroundEnergy[kcal/mol]         15.6
End
!------------------------------------------------------------
Barrier         B7   W2   P3    # TS_[CH2]OCOH_C=C
    Variational
        RRHO
    Geometry[angstrom]        15
     C        0.0263795788    0.1012610411    -0.0777414441
     H        0.1067962175    0.1356612    1.0003690486
     H        0.9494112323    0.1045374881    -0.6412513109
     C        -1.174588009    0.1223070847    -0.6986384714
     C        -1.8284554476    2.2225386781    -1.1381741645
     O        -0.7722865345    2.8318913691    -1.7448325637
     C        0.1435479081    3.4248112457    -0.8546338498
     O        -0.3892741708    4.5472130136    -0.2215425078
     H        -1.2346087326    -0.0609839998    -1.7632377594
     H        -2.0866571114    -0.0322884042    -0.1360904856
     H        -2.6291578774    2.0024961307    -1.8310536181
     H        -2.0979077326    2.5990179807    -0.1576281188
     H        0.4058991384    2.721218317    -0.0645154199
     H        1.0162116121    3.6678058856    -1.4609383166
     H        -0.5809850679    5.2116296398    -0.8896757886
```

```
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    1 9 10
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  1.02  0.62  1.54  0.23  0.37
    End
    Rotor        Hindered
        Group                    4 11 12
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  6.7  0.22  4.78
    End
    Rotor        Hindered
        Group                    5
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  5.29  0.33  2.7
    End
    Rotor        Hindered
        Group                    6 13 14
        Axis                     7 8
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  3.56  1.95  3.94
    End
    Frequencies[1/cm]    34
           122.64       193.09       383.87       443.33       560.22
   606.09
           819.05       850.99       876.81       982.01       1001.63
    1034.51       1065.84       1115.05       1197.19       1243.92
           1250.5       1308.34       1318.91       1392.68       1444.17
       1461.68       1497.03       1537.08       1589.01       3079.85
           3120.6       3138.88       3150.01       3165.81       3229.19
       3245.24       3258.58       3869.91
     !55.3       75.24       262.59       369.26!
    ZeroEnergy[kcal/mol]       23.1
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                Eckart
    ImaginaryFrequency[1/cm]    509.5638
    WellDepth[kcal/mol]         28.0
```

```
    WellDepth[kcal/mol]          7.5
    End
End
!------------------------------------------------------------
!-------------------------WELL 3 to Products -------------
!------------------------------------------------------------
Barrier         B8   W3   W5    # TS C[CH]COCO <=> CCCO[CH]OH
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0028356065     -0.0028728929     0.0131504744
     C         0.0027164622     0.0079084147     1.51414265
     H         0.9884947858     0.0120013202     1.9748118025
     C         -1.0104892599     -0.8378853967     2.2438728701
     O         -1.4785688727     -0.0787009194     3.3712565412
     C         -1.529620761     1.2592975236     3.0219733813
     O         -1.2041609063     2.078099782     4.0648173566
     H         0.3329372683     -0.9662367512     -0.3897051759
     H         0.6693072016     0.759342913     -0.3892208251
     H         -0.9990249146     0.1825244209     -0.3785067698
     H         -1.8536180925     -1.0681980694     1.583466329
     H         -0.6203964274     -1.7718560672     2.6457770228
     H         -0.6119584216     1.1592060097     2.041310814
     H         -2.4739842082     1.584252324     2.5799903955
     H         -0.4897976077     1.6561383996     4.5541550108
    Core RigidRotor
        SymmetryFactor    0.25
    End
    Rotor         Hindered
        Group                      8 9 10
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   1.87
    End
    Rotor         Hindered
        Group                      15
        Axis                       7 6
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   4.91   3.12   3.44   0.62   0.67
    End
    Frequencies[1/cm]    36
           99.34       128.44       177.22       377.94       496.87
   551.33       624.97       810.21
           913.28       946.24       988.83       1052.37       1089.73
     1118.9       1137.08       1164.86       1210.88       1262.26
```

```
            1305.58       1335.16       1399.26       1410.13       1418.36
         1450.42       1486.86       1497.76       1524.17       1724.44
            3027.0       3032.9       3079.87       3089.08       3113.87
       3124.89       3136.99       3855.45
     !185.34       338.46!
    ZeroEnergy[kcal/mol]       14.3
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]     1794.304
    WellDepth[kcal/mol]          20.9
    WellDepth[kcal/mol]          23.3
    End
End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
Bimolecular         P4     # C=CC  +  [O]COH
    Fragment  C=CC
        RRHO
    Geometry[angstrom]         9
     C         -0.0036173945     -0.0000157516     0.0051672399
     C         0.0040011912     -0.000049678     1.5008982519
     H         0.9797799476     -0.000127773     1.9768349341
     C         -1.079110104     0.0000087324     2.2615933185
     H         0.5151885421     0.876581567     -0.3868008481
     H         -1.0214504945     0.000056787     -0.3822056223
     H         0.5150788396     -0.8766602561     -0.3868403603
     H         -1.0141839757     -0.0000194025     3.3409791477
     H         -2.0713139546     0.0000868059     1.8258205252
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                       5 6 7
        Axis                        1 2
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0  2.01
    End
    Frequencies[1/cm]     20
            430.51       596.0       938.41       947.42       967.29
    1036.32       1079.5       1195.46       1330.57
            1407.13       1454.25       1484.54       1497.22       1742.34
         3056.62       3111.88       3138.7       3159.03       3168.59
            3248.77
     !206.03!
```

```
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  1
    End
    Fragment   [O]COH
        RRHO
    Geometry[angstrom]         6
     O         -0.0179086386     0.0302114826     -0.0063445877
     C         0.0041353263     0.011029922     1.3315040021
     O         1.2588889626     0.0839062173     1.9358024239
     H         -0.5946672698     0.8417674225     1.7323279478
     H         -0.5341812063     -0.9194223458     1.6108213777
     H         1.8532254387     -0.5110076245     1.4688149448
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      1 4 5
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   0.34   0.0   2.89   2.85   2.89
    End
    Frequencies[1/cm]     11
           558.99       759.52       1020.09       1132.89       1167.89
      1315.09       1364.87       1423.56       2878.54
           3001.58       3871.87
     !222.92!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]     11.7
End
!------------------------------------------------------------
Barrier         B9   W3   P4     # TS_[O]COH_CC=C
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0185437987     -0.1312956575     0.0796816176
     C         -0.0145806727     -0.0520296972     1.5645188906
     H         0.9412851349     -0.0685416726     2.075478971
     C         -1.15048733     -0.0556461536     2.2963676225
     O         -1.5119003381     -2.1054989383     2.4029249915
     C         -0.4053491109     -2.739054531     2.8666078844
     O         0.5897574347     -2.9690387118     1.8948216374
     H         0.5678736959     -1.021775022     -0.2320220895
     H         0.5407905317     0.7283577276     -0.3460757619
```

```
 H         -0.9861651356    -0.1728916396    -0.337196289
 H         -1.1220846839     0.0639226529    3.3696630475
 H         -2.1141344899     0.0486063206    1.8187621407
 H         0.0974982749     -2.1996285978    3.6765420067
 H         -0.7745278226     -3.6967487099    3.2736131566
 H         0.1477506622     -3.3405279549    1.1251076998
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    8 9 10
    Axis                     1 2
    Symmetry                  3
    Potential[kcal/mol]       2
     0.0  1.4
End
Rotor        Hindered
    Group                    2 11 12
    Axis                     4 5
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0  3.13  0.0  1.32
End
Rotor        Hindered
    Group                    4
    Axis                     5 6
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0  11.03  3.7  8.28
End
Rotor        Hindered
    Group                    5 13 14
    Axis                     6 7
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  2.84  2.68  3.53  3.05  3.24
End
Frequencies[1/cm]    33
       136.85      228.45      303.06      432.61      578.3
688.5
       935.51      946.74      960.36      994.49      1016.92
 1047.88      1051.54      1132.09      1201.74      1232.7
       1307.15      1337.66      1394.7      1417.95      1445.82
    1471.01      1475.92      1494.9      1624.27      2945.59
       3043.31      3052.88      3107.01      3144.97      3177.09
     3184.41      3268.64      3862.44
  !67.66      112.52      150.22      336.33!
ZeroEnergy[kcal/mol]      14.8
```

```
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    409.8372
    WellDepth[kcal/mol]         21.4
    WellDepth[kcal/mol]         3.1
    End
End
!-------------------------------------------------------
!-------------------------WELL 4 to Products ------------
!-------------------------------------------------------
Bimolecular         P5    # CCC=O  +  [CH2]OH
    Fragment  CCC=O
        RRHO
    Geometry[angstrom]        10
     C         -0.0000566396    0.0062360295    -0.0000851688
     C         0.0002269459    -0.0058860377    1.5176215585
     C         1.3811361699    -0.0034523604    2.1113838536
     H         1.4229848487    -0.0120720663    3.2179002795
     O         2.393691471    0.0069513451    1.4676073164
     H         0.5150796789    0.8884132091    -0.3758097392
     H         -1.0166443986    0.0040558499    -0.3884237127
     H         0.524187663    -0.8644258075    -0.3898116873
     H         -0.5289339007    0.8570574089    1.9342051971
     H         -0.5199028418    -0.8808265682    1.9203230958
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    6 7 8
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.12
    End
    Rotor        Hindered
        Group                    1 9 10
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  2.36  1.42  2.11  1.42  2.36
    End
    Frequencies[1/cm]    22
            266.82      673.44      677.86      873.63      908.86
   1008.52      1121.87      1156.86
            1283.93      1372.83      1414.21      1430.39      1457.55
        1497.45      1504.73      1866.92      2945.02      3050.32
```

```
            3077.74      3081.28      3153.86      3156.87
     !148.66      238.11!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH2]OH
        RRHO
    Geometry[angstrom]        5
     C        0.0017104629    0.0006805334    0.006036701
     O        0.0003059126    -0.011024407    1.3662696453
     H        0.9891006186    0.005542419    -0.425002778
     H        -0.8280003133    0.4619257545    -0.5108130333
     H        -0.8993908337    0.0682737923    1.6902499792
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    3 4
        Axis                     1 2
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  4.41  0.0  4.7
    End
    Frequencies[1/cm]    8
           605.38      1066.47      1240.91      1364.7      1496.89
      3154.31      3293.73      3901.11
     !413.46!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]    -1.1
End
!-------------------------------------------------------------
Barrier        B10  W4  P5    # TS_CCC=O_[CH2]OH
    Variational
        RRHO
    Geometry[angstrom]        15
     C        0.0055772018    -0.0245570763    0.0031798375
     C        -0.0061060076    0.0193262645    1.523519484
     C        1.3710238776    -0.0155499813    2.120354704
     H        1.4464168115    -0.1650017094    3.2051619105
     O        2.4169678187    0.1018376156    1.4406785191
     C        3.0228402306    -1.5750326439    0.6650856755
     O        2.132966505    -2.4830525743    1.1127056781
     H        0.6242318656    0.7756793818    -0.3994722334
     H        -1.0019293687    0.0791630355    -0.3962846412
```

```
     H         0.4136546961     -0.9727248948     -0.3455081377
     H         -0.5098258795     0.9274835882     1.876145547
     H         -0.5890664712     -0.8126688856     1.9297083642
     H         2.9093956255     -1.3565630707     -0.3842231321
     H         4.0146405217     -1.5758440753     1.0948908028
     H         2.2716825869     -2.6436949599     2.051446609
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    8 9 10
        Axis                     1 2
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  2.58  0.0  2.59  0.0  2.58
    End
    Rotor        Hindered
        Group                    1 11 12
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  0.95  0.39  1.29
    End
    Rotor        Hindered
        Group                    3
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  4.07  3.24  3.82
    End
    Rotor        Hindered
        Group                    15
        Axis                     7 6
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  2.9  0.43  5.3
    End
    Frequencies[1/cm]    34
           116.67      217.85      312.31      439.59      628.0
   678.56
           702.65      818.42      879.42      936.61      1009.78
    1077.19      1089.4      1113.56      1215.44      1270.04
           1341.18      1363.03      1384.78      1406.79      1466.13
        1495.16      1506.28      1519.92      1526.38      3013.76
           3026.18      3058.36      3075.48      3145.51      3151.0
       3155.67      3289.3      3854.19
     !55.62      96.39      254.08      277.94!
    ZeroEnergy[kcal/mol]      14.4
```

```
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    649.7726
    WellDepth[kcal/mol]         24.4
    WellDepth[kcal/mol]         15.5
    End
End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
Bimolecular         P6    # C=COCO  +  [CH3]
    Fragment  C=COCO
        RRHO
    Geometry[angstrom]        11
     C        0.0013601933    0.0057058929    -0.0003134127
     C        0.0016491502    -0.0036923609    1.3245431897
     H        0.9170463758    -0.0206423495    1.9008590388
     O        -1.0738188154    -0.0025648474    2.1582830484
     C        -2.3378811366    -0.1866279717    1.5724223705
     O        -2.7663939592    0.914462695    0.8351387573
     H        0.9496318576    -0.0285387338    -0.5135908198
     H        -0.9003197225    0.0760488618    -0.5886499238
     H        -2.3067080309    -1.0285364804    0.87890601
     H        -3.0036461967    -0.4011762725    2.4085064045
     H        -2.8311556979    1.6717785765    1.4237413182
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    1 3
        Axis                     2 4
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  4.72  0.92  4.75
    End
    Rotor        Hindered
        Group                    2
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  9.0  1.08  4.48  1.42  4.61
    End
    Rotor        Hindered
        Group                    4 9 10
        Axis                     5 6
        Symmetry                  1
```

```
        Potential[kcal/mol]        4
         0.0   2.16   0.6   3.84
    End
    Frequencies[1/cm]    24
           365.26       496.28       665.29       735.43       894.99
   925.35       1016.4
           1028.45       1095.18       1139.24       1246.95       1301.96
        1364.75       1396.66       1431.58       1471.29       1533.28
           1726.67       3073.86       3127.55       3198.16       3216.26
        3292.08       3872.9
     !168.43       199.6       307.74!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH3]
        RRHO
    Geometry[angstrom]        4
    C                  0.00000000    0.00000000    0.00000000
    H                  0.00000000    0.00000000    1.07652900
    H                  0.93230200    0.00000000   -0.53826500
    H                 -0.93230200   -0.00000000   -0.53826500
    Core RigidRotor
        SymmetryFactor    6
    End
    Frequencies[1/cm]    6
           436.03       1412.64       1412.73       3144.41       3323.11
       3323.14
     !   !
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]    12.6
End
!------------------------------------------------------
Barrier        B11   W4   P6    # TS_[CH3]_C=COCOH
    Variational
        RRHO
    Geometry[angstrom]        15
     C        0.0099326936    0.0134730456    -0.0060153825
     C        -0.004342837    -0.0060842891    2.2640991858
     C        1.2596630616    -0.0086612646    2.7412367849
     H        1.8087404664    0.9010300062    2.9371578014
     O        2.0583985969    -1.0962758198    2.9247660037
     C        1.516690575    -2.3549569593    2.6135399846
     O        0.5266394069    -2.7568610064    3.5077872822
     H        -1.049331931    -0.0894932564    -0.1967175195
```

```
     H         0.6276253731     -0.8367971282     -0.2576616415
     H         0.4418282762     0.984799225     -0.1972112281
     H         -0.5286146523     0.9367693364     2.2689929907
     H         -0.6053942044     -0.9023242524     2.26343908
     H         1.0494195921     -2.3339399677     1.6285607817
     H         2.3700758369     -3.0330923183     2.6169713626
     H         0.9124567393     -2.8133973554     4.3866075076
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    8 9 10
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  0.2
    End
    Rotor        Hindered
        Group                    6
        Axis                     5 3
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  3.33  0.28  4.0
    End
    Rotor        Hindered
        Group                    3
        Axis                     5 6
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  8.5  0.0  4.14  1.79  4.42
    End
    Rotor        Hindered
        Group                    5 13 14
        Axis                     6 7
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  2.3  0.99  3.86
    End
    Frequencies[1/cm]    34
           124.86       287.4       372.08       484.59       507.81
    526.08
           655.57       761.74       809.75       910.81       933.7
    961.41       1031.02       1092.75       1136.71       1234.63
           1297.11       1331.97       1394.47       1420.14       1426.16
         1429.53       1467.39       1537.14       1605.69       3080.42
           3108.86       3133.42       3193.87       3224.87       3264.79
         3270.98       3284.95       3871.22
      !52.79       84.62       169.35       324.88!
```

```
    ZeroEnergy[kcal/mol]       21.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    595.1808
    WellDepth[kcal/mol]         31.2
    WellDepth[kcal/mol]         8.6
    End
End
!------------------------------------------------------------
!-------------------------WELL 5 to Products ------------
!------------------------------------------------------------
Bimolecular         P7    # CC[CH2] + O=CO
    Fragment  CC[CH2]
        RRHO
    Geometry[angstrom]        10
     C                 -1.21576400   -0.24393400   -0.03513100
     C                  0.07906700    0.55925200    0.04786100
     C                  1.29106100   -0.29615900   -0.03188100
     H                 -1.27316400   -0.78426700   -0.98002700
     H                 -2.09049500    0.40029700    0.04349600
     H                 -1.26327100   -0.97710700    0.77093600
     H                  0.10443800    1.31177800   -0.74483100
     H                  0.08395300    1.13114900    0.98641300
     H                  2.25628600    0.12468300   -0.26877100
     H                  1.25606300   -1.32148700    0.30769100
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                     4 5 6
        Axis                      1 2
        Symmetry                  3
        Potential[kcal/mol]       6
         0. 3.0 0. 3.0 0. 3.0
    End
    Rotor        Hindered
        Group                     9 10
        Axis                      3 2
        Symmetry                  2
        Potential[kcal/mol]       2
         0. 0.26
    End
    Frequencies[1/cm]    22
    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
    ! 93.61 253.67 ! Torsions
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  O=CO
        RRHO
    Geometry[angstrom]        5
   O                 -1.12637500   -0.26441800    0.00000000
   C                 -0.13498100    0.39859000    0.00000000
   H                 -0.10944700    1.49339600    0.00000000
   O                  1.11063300   -0.08930300    0.00000000
   H                  1.04527400   -1.05517000    0.00000000
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                     5
        Axis                      4 2
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   12.62   4.68   12.62
    End
    Frequencies[1/cm]    8
   645.59 1077.81 1164.30 1323.84 1418.68 1881.20 3099.91 3799.58
     ! 680.89 !
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]    -18.5
End
!------------------------------------------------------------
Barrier        B12  W5  P7    # TS_CC[CH2]_O=CO
    Variational
        RRHO
    Geometry[angstrom]        15
   C                  2.12326100   -0.78051400   -0.19320400
   C                  1.32670200    0.12577600    0.73728900
   C                  0.62133900    1.21307100    0.00667400
   O                 -0.71729600    0.36770200   -0.93138400
   C                 -1.30714500   -0.56586900   -0.33753400
   H                 -0.97976700   -1.60104300   -0.33630300
   O                 -2.26108900   -0.31984700    0.59343300
   H                  1.47512300   -1.20300500   -0.96105600
   H                  2.59299000   -1.59826200    0.35116400
   H                  2.90728800   -0.21535800   -0.69843200
```

```
H                  0.58398800   -0.46237600    1.29097400
H                  1.98157200    0.55751200    1.50036800
H                  0.05459900    1.91947800    0.60064900
H                  1.13107000    1.65500300   -0.83912600
H                 -2.50472700    0.61042400    0.51601200
 Core RigidRotor
     SymmetryFactor    1
 End
 Rotor        Hindered
     Group                     4 13 14
     Axis                      3 2
     Symmetry                  1
     Potential[kcal/mol]       6
      0.0  2.75  1.2  2.14  1.18  6.58
 End
 Rotor        Hindered
     Group                     5
     Axis                      4 3
     Symmetry                  1
     Potential[kcal/mol]       4
      0.0  2.25  1.44  3.15
 End
 Rotor        Hindered
     Group                     8 9 10
     Axis                      1 2
     Symmetry                  3
     Potential[kcal/mol]       2
      0.0  2.76
 End
 Rotor        Hindered
     Group                     15
     Axis                      7 5
     Symmetry                  1
     Potential[kcal/mol]       4
      0.0  6.79  2.67  7.95
 End
 Frequencies[1/cm]    34
141.79 289.91 346.88 423.27 606.94 710.97 756.12 797.86 910.05
940.14 969.04 1072.03 1100.97 1124.80 1194.71 1282.06 1296.69
1336.40 1375.41 1414.26 1475.59 1481.20
1497.72 1509.19 1515.12 3019.91 3054.81 3064.95 3131.92 3143.57
3146.64 3169.47 3236.30 3838.45
  !62.20 107.56 201.78 506.83!
 ZeroEnergy[kcal/mol]      5.0
 ElectronicLevels[1/cm]    1
     0  2
 End
 Tunneling               Eckart
```

```
    ImaginaryFrequency[1/cm]    775.36
    WellDepth[kcal/mol]         14.0
    WellDepth[kcal/mol]         23.5
    End
End
End
```

E.8 CCOCO[CH2]

```
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
PressureList[atm]                 0.00001 0.001  0.01  0.1  1  10  100.
!PressureList[bar]                1.
EnergyStepOverTemperature         .2
ExcessEnergyOverTemperature       30
ModelEnergyLimit[kcal/mol]        400
CalculationMethod                 direct
!CalculationMethod                low-eigenvalue !direct
WellCutoff                        10
ChemicalEigenvalueMax             0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                200
      Power                       .85
      ExponentCutoff              15
    End
  CollisionFrequency
    LennardJones
      Epsilons[1/cm]     94.87    268.26  !Ar and CCOCO[CH2]
  Sigmas[angstrom]       3.33     5.83
  Masses[amu]            39.88    89.11
    End
!-------------------------------------------------------------
!-------------------------WELL 1 to Products ----------------
!-------------------------------------------------------------
Well        W1        # W_CCOCO[CH2]_m062x.log
    Species
```

```
        RRHO
    Geometry[angstrom]        15
     C         0.014783426    -0.0119935837    -0.0103422635
     O         -0.0024138094    -0.0072930793    1.3451304474
     C         1.2749942279    0.0030002078    1.9462362319
     O         2.0172040058    -1.1279838406    1.6497614135
     C         1.4631221731    -2.3265914553    2.1742206778
     C         2.4147811714    -3.4570840431    1.8630714045
     H         -0.9632988961    -0.0640728065    -0.4584452616
     H         0.8927735478    -0.4012129986    -0.5058708057
     H         1.8486369535    0.855942202    1.5802591448
     H         1.0815352411    0.0864282337    3.0184158142
     H         1.3243046626    -2.2143854687    3.2558566152
     H         0.4817444164    -2.5049247984    1.7275679455
     H         3.3886945035    -3.2685235324    2.3119151449
     H         2.025993717    -4.3974046839    2.251629836
     H         2.5446136254    -3.5535303802    0.7862036653
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                    7 8
        Axis                     1 2
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   11.55   0.67   5.05
    End
    Rotor        Hindered
        Group                    1
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   4.28   1.6   2.6   2.18   2.93
    End
    Rotor        Hindered
        Group                    5
        Axis                     4 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   6.91   1.95   4.46   3.8   4.79
    End
    Rotor        Hindered
        Group                    6 11 12
        Axis                     5 4
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0   1.63   1.05   1.12   1.07   4.61   0.77   1.23
    End
```

```
    Rotor        Hindered
        Group                      13 14 15
        Axis                       6 5
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  3.05
    End
    Frequencies[1/cm]    34
           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      1536.64
           3024.66      3057.19      3073.81      3076.5      3115.41
       3150.44      3152.21      3161.74      3302.14
     !57.06      80.74   241.97   172.0      273.48! Torsions
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Well        W2        # W_CCO[CH]OC_m062x.log
    Species
        RRHO
    Geometry[angstrom]        15
     C        0.0699272834    -0.2329127203    0.1220920593
     C        0.0572517118    0.0547689702    1.6103102573
     O        1.3705742127    0.05159696    2.1723508234
     C        2.0559467553    -1.1022857866    2.0595549147
     O        1.3401533619    -2.2095278274    2.4168176471
     C        2.0643469632    -3.4083486534    2.2438179794
     H        2.9744115926    -3.4034632774    2.8507258204
     H        1.4223319889    -4.2223348495    2.5672777004
     H        0.7322124267    0.4618336631    -0.3930385392
     H        -0.9354490276    -0.1246549191    -0.2841290767
     H        0.4131887368    -1.2483510453    -0.0717335853
     H        -0.3228015833    1.0539334302    1.8111880621
     H        -0.5649783367    -0.6662397399    2.141132132
     H        2.3375939447    -3.5467752781    1.1952853545
     H        3.0618994777    -1.0300334995    2.4702782091
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor        Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
```

```
         0.0   3.03   0.0   3.03   0.0   3.04
    End
    Rotor        Hindered
        Group                    1 12 13
        Axis                     2 3
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0   3.64   0.48   1.17   -0.03   1.28
    End
    Rotor        Hindered
        Group                    5 15
        Axis                     4 3
        Symmetry                  1
        Potential[kcal/mol]       8
         0.0   2.95   2.9   2.93   2.4   2.72   2.46   3.17
    End
    Rotor        Hindered
        Group                    6
        Axis                     5 4
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0   2.01   1.51   9.16
    End
    Rotor        Hindered
        Group                    7 8 14
        Axis                     6 5
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0   1.68
    End
    Frequencies[1/cm]    34
           261.43      359.21      465.24      608.02      814.33
           868.02      935.18      1035.69      1078.87      1117.23
      1181.07      1189.85      1203.18      1257.75      1294.09
           1334.16      1367.61      1402.81      1437.73      1484.97
        1489.09      1499.82      1500.37      1515.64      1526.76
           3033.69      3069.78      3087.02      3092.63      3110.12
        3131.62      3145.65      3155.53      3167.04
     !58.3      86.38      156.53      199.9       264.34! Torsions
    ZeroEnergy[kcal/mol]      0.9
    ElectronicLevels[1/cm]    1
        0  2
    End
End
Barrier        B1   W1   W2    # W_CCO[CH]OC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]        15
```

```
     C         -0.0031229326    -0.0002946779     0.0024794799
     O         0.0010685985     0.0005787559     1.4166009498
     C         1.3964138969     0.0001817209     1.5568609442
     O         1.9293318661     1.0718202924     2.1876269907
     C         1.5337121159     2.339622929     1.6687003979
     C         2.2122302579     3.4086224443     2.4903582059
     H         -0.4293786919     -0.8951424429     -0.4414621763
     H         -0.3088045542     0.9475030211     -0.4352966762
     H         1.9089376396     3.3310624749     3.5330777801
     H         1.9394878892     4.3962048525     2.1209410053
     H         3.2942743371     3.3015707085     2.4361730227
     H         0.4474446291     2.4278705118     1.7192874346
     H         1.8355968218     2.3940791411     0.6170400505
     H         1.4057443327     -0.023697597     0.1675068693
     H         1.7934807387     -0.9217531164     1.9781027147
   Core RigidRotor
       SymmetryFactor    0.5
   End
   Rotor        Hindered
       Group                     5
       Axis                      4 3
       Symmetry                   1
       Potential[kcal/mol]        6
        0.0   4.17   3.02   4.24   2.25   5.16
   End
   Rotor        Hindered
       Group                     6 12 13
       Axis                      5 4
       Symmetry                   1
       Potential[kcal/mol]        6
        0.0   1.82   0.58   5.03   0.88   1.43
   End
   Rotor        Hindered
       Group                     9 10 11
       Axis                      6 5
       Symmetry                   3
       Potential[kcal/mol]        2
        0.0   3.06
   End
   Frequencies[1/cm]    35
          72.17       110.51       285.9       379.03       418.52
  633.32       675.32       827.93
          876.15       950.42       1053.38       1078.82       1111.84
     1115.76       1156.82       1171.94       1189.82       1248.11
          1308.35       1313.71       1378.97       1402.65       1435.5
      1481.13       1488.77       1506.59       1534.82       1898.59
          3034.38       3075.73       3082.39       3099.53       3124.65
       3153.12       3155.12       3194.63
```

```
     !72.17     169.36      252.96! Torsions
    ZeroEnergy[kcal/mol]       39.0
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1970.1498
    WellDepth[kcal/mol]          39.0
    WellDepth[kcal/mol]          38.01
    End
End
Well         W3         # W_C[CH]OCOC_m062x.log
    Species
        RRHO
    Geometry[angstrom]         15
     C         -0.0002279902     0.0061809167     0.0003026867
     C         -0.0040373378     -0.000581162     1.4805027374
     O         1.2387260795     -0.0064992508     2.0463699564
     C         1.2415577268     0.0515942031     3.452565855
     O         0.7500033514     1.2536271627     3.9421447285
     C         1.554435286     2.3631284082     3.5962623325
     H         2.5794865858     2.2235594912     3.9542365888
     H         1.1211626686     3.235272807     4.0778759228
     H         -1.0124289015     -0.1123419807     -0.3815468419
     H         0.615661016     -0.8080059985     -0.3849228637
     H         0.4069314615     0.9406473     -0.40554913
     H         1.5755193419     2.5152821638     2.5155919351
     H         -0.7847400456     0.4836138141     2.0545226728
     H         0.6012324122     -0.7318230706     3.8610473116
     H         2.2845443533     -0.0978417948     3.7436230713
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                       9 10 11
        Axis                        1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.32   -0.0   1.32   0.0   1.32
    End
    Rotor         Hindered
        Group                       1 13
        Axis                        2 3
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   4.53   1.35   4.31
    End
    Rotor         Hindered
```

```
        Group                         5 14 15
        Axis                          4 3
        Symmetry                      1
        Potential[kcal/mol]           6
         0.0   8.67   1.63   2.71   2.34   2.96
    End
    Rotor         Hindered
        Group                         6
        Axis                          5 4
        Symmetry                      1
        Potential[kcal/mol]           6
         0.0   6.57   2.12   3.82   2.99   4.25
    End
    Rotor         Hindered
        Group                         7 8 12
        Axis                          6 5
        Symmetry                      3
        Potential[kcal/mol]           2
         0.0   1.68
    End
    Frequencies[1/cm]     34
           273.74       367.73       465.44       573.91       661.75
           900.08       986.06       1022.77       1092.72       1112.32
      1163.45       1190.54       1214.72       1223.09       1276.07
           1350.93       1383.16       1427.77       1456.74       1470.03
        1485.59       1497.12       1498.86       1516.09       1524.33
           3006.98       3033.17       3054.74       3089.06       3100.99
        3115.39       3146.67       3162.32       3184.8
     !65.87       86.32       137.71       180.69       228.59! Torsions
    ZeroEnergy[kcal/mol]       -1.2
    ElectronicLevels[1/cm]     1
        0  2
    End
End
Barrier         B2   W1   W3     # W_C[CH]OCOC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.004383189     -0.0071387273     0.0249854039
     C         0.0269540707     0.0220603329     1.5202150774
     O         1.3386914694     0.0852174634     1.9898389405
     C         1.4479984124     0.2448632454     3.3795120904
     O         0.4092586481     1.0141291867     3.9308795512
     C         -0.0737710045     1.9991652361     3.0807011571
     H         0.6852812779     2.6858150747     2.7016628415
     H         -0.9417923716     2.4717419417     3.5244502692
     H         0.5097743458     0.8709219823     -0.3771344514
     H         -1.0219782253     -0.0178215861     -0.3377524636
```

```
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
```

```
 H         1.1292951908    2.8670831183    4.4459717034
 H         2.7268079594    1.9773904448    4.1084002444
 H         0.4060710255    2.4023228471    2.1185342023
 H         1.9608507414    3.1691166887    1.7984384667
 H         1.8910309154   -0.8157182285    1.5346881621
 H         1.1750078469   -0.1237928542    3.0336974419
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    7 8 9
    Axis                     1 2
    Symmetry                  3
    Potential[kcal/mol]       2
     0.0  1.61
End
Rotor        Hindered
    Group                    1
    Axis                     2 3
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  4.15  2.69  3.24  3.01  7.32
End
Rotor        Hindered
    Group                    5
    Axis                     4 3
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  3.64  2.97  3.82  3.56  8.66
End
Rotor        Hindered
    Group                    6 12 13
    Axis                     5 4
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  1.8  0.35  1.38  0.54  3.18
End
Rotor        Hindered
    Group                    10 11
    Axis                     6 5
    Symmetry                  2
    Potential[kcal/mol]       2
     0.0  1.76
End
Frequencies[1/cm]    34
       284.64      426.35      465.79      527.84      620.67
       848.01      943.33      983.22     1055.39     1103.23
 1131.72     1168.46     1190.19     1209.24     1252.5
```

```
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
```

```
    WellDepth[kcal/mol]          22.8
    WellDepth[kcal/mol]          17.0
    End
End
Bimolecular         P1     # C=O  +  CCO[CH2]
    Fragment  C=O
        RRHO
    Geometry[angstrom]         4
     O         -0.000000016     -0.0000022088     0.0061054213
     C         -0.0000000144     0.0000068137     1.2014608526
     H         0.9375275336     -0.0000022726     1.7838372267
     H         -0.9375275608     0.0000246367     1.7838372291
    Core RigidRotor
        SymmetryFactor    2
    End
    Frequencies[1/cm]    6
           1216.69       1279.34       1545.84       1876.79       2940.94
        3011.91
     !! Torsions
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  1
    End
    Fragment  CCO[CH2]
        RRHO
    Geometry[angstrom]         11
     O         -0.0014817113     -0.0155848882     0.0002794589
     C         -0.0005868038     -0.0090032165     1.4196033317
     C         1.4321878366     0.002078756     1.894442275
     C         -1.2263142708     -0.008203098     -0.5632685818
     H         -1.2161425723     0.0491526598     -1.6394562426
     H         -2.0502495284     0.3960187506     0.0122880813
     H         -0.5404318214     0.8764641954     1.7712477052
     H         -0.53190841     -0.8946070834     1.779843481
     H         1.9477347437     0.8859620831     1.5224489139
     H         1.4686074424     0.0086994034     2.9829490596
     H         1.9564191269     -0.8810975598     1.5333225193
    Core RigidRotor
        SymmetryFactor    1
    End
    Rotor         Hindered
        Group                      4
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.51   0.6   4.08   0.15   1.5
    End
    Rotor         Hindered
```

```
        Group                       5 6
        Axis                        4 1
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   5.25   0.0   0.3   0.0   4.79
    End
    Rotor         Hindered
        Group                       9 10 11
        Axis                        3 2
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   3.0
    End
    Frequencies[1/cm]    24
           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
     !99.2       239.29       290.05!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          12.7
End
Barrier         B4   W1   P1     # TS_CCO[CH2]+C=O_m062x.log
    Variational
        RRHO
    Geometry[angstrom]          15
     C         -0.0126362017     -0.0167350269     -0.0036094738
     C         -0.0028985098      0.0073244075      1.5044261861
     O          1.3569275776      0.0075381778      1.9422594928
     C          1.5111559737      0.2309457065      3.2453005624
     O          1.2835517687      2.2118374673      3.3657040161
     C          1.4702801407      2.7829202085      2.2743342918
     H          0.6401989795      2.9808830755      1.5872667998
     H          2.4735844614      3.0699371577      1.9459207157
     H          0.486544643      0.8681404507     -0.3959216961
     H         -1.0371055731     -0.0341244932     -0.37246207
     H          0.5061090852     -0.8997410198     -0.3731759416
     H         -0.4955242657      0.8991649057      1.8989726018
     H         -0.4996793959     -0.8731416125      1.9228907883
     H          0.6978205298     -0.0233475994      3.912462351
     H          2.5303737997      0.1513601889      3.5869173613
    Core RigidRotor
        SymmetryFactor    1
```

```
    End
    Rotor        Hindered
        Group                     9 10 11
        Axis                      1 2
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0   3.01
    End
    Rotor        Hindered
        Group                     1 12 13
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.16   0.87   3.7   1.28   2.74
    End
    Rotor        Hindered
        Group                     5 14 15
        Axis                      4 3
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   13.46   2.08   7.72
    End
    Rotor        Hindered
        Group                     6
        Axis                      5 4
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   4.72   3.04   3.59
    End
    Frequencies[1/cm]    34
           152.21      250.77      275.62      313.52      408.85
   516.33      651.78
           823.52      879.13      895.35      936.22      1072.73
    1123.64      1185.68      1234.34      1249.56      1257.19
           1308.65      1397.01      1402.08      1437.49      1486.72
        1504.79      1518.67      1532.74      1581.9      3008.94
           3042.43      3074.86      3087.49      3094.72      3148.47
        3152.22      3154.29      3288.62
     !67.63   110.38   207.35!
    ZeroEnergy[kcal/mol]      25.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    606.8734
    WellDepth[kcal/mol]         25.21
    WellDepth[kcal/mol]         12.5
    End
```

```
End
!------------------------------------------------------------
!-------------------------WELL 2 to Products ----------------
!------------------------------------------------------------
Barrier         B5   W2   W4     # W_[CH2]COCOC_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0004665243     0.0012264764     0.00012082
     C         0.000205991     0.0001034846     1.5039700908
     O         1.3754025349     -0.0006875452     1.9588537021
     C         2.2379853956     0.4348991236     0.9772003995
     H         3.0779655847     -0.2366129579     0.8224864415
     O         2.7176629545     1.7077906116     1.1237395014
     C         1.7293653338     2.6825231041     1.3899984385
     H         1.3685569653     0.3605575271     -0.0249015063
     H         -0.5853642353     0.7575306655     -0.5074149172
     H         -0.0183544803     -0.96626422     -0.489062994
     H         -0.5007523005     0.883470427     1.9057091931
     H         -0.4628121328     -0.886027322     1.9348411675
     H         0.968301959     2.685171994     0.6029648204
     H         1.2521460322     2.5001796088     2.3536929883
     H         2.2313528794     3.645374994     1.4073388295
    Core RigidRotor
        SymmetryFactor             0.5
    End
    Rotor         Hindered
        Group                       7
        Axis                        6 4
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.64   1.34   2.74   0.82   3.99
    End
    Rotor         Hindered
        Group                       13 14 15
        Axis                        7 6
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.53   0.0   2.53   0.0   2.53
    End
    Frequencies[1/cm]     36
            152.47       178.85       333.19       474.32       576.96
   649.78       699.63       845.3
            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
```

```
            3034.25       3065.48       3109.0       3119.09       3139.3
      3146.9       3168.13       3224.66
     !113.16       237.76!
    ZeroEnergy[kcal/mol]       25.5
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                Eckart
    ImaginaryFrequency[1/cm]    1749.2129
    WellDepth[kcal/mol]          24.6
    WellDepth[kcal/mol]          19.7
    End
End
Bimolecular         P2    # Bi_O=COC_E2-75  +  [CH2]C
    Fragment  Bi_O=COC_E2-75
        RRHO
    Geometry[angstrom]        8
     O         0.0418924661    0.0001246289    0.0116965965
     C         0.0167993753    0.0000166154    1.2063812612
     O         1.0865652314    -0.0000631766    1.9997896845
     C         2.3431972004    -0.0000105584    1.318127389
     H         -0.8942447797    -0.0000317404    1.8147181938
     H         3.1023784274    -0.0000881096    2.0924532518
     H         2.4312544895    -0.8854855669    0.6918659719
     H         2.4312687749    0.885578481    0.6920292162
    Core RigidRotor
        SymmetryFactor            1.0
    End
    Rotor        Hindered
        Group                     1 5
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0  13.48  5.51  13.48
    End
    Rotor        Hindered
        Group                      2
        Axis                       3 4
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0  1.12
    End
    Frequencies[1/cm]    16
           319.89       792.46       984.42       1064.87       1192.28
     1207.29       1273.14       1410.45
           1481.65       1497.47       1509.45       1856.01       3083.57
        3088.44       3158.89       3195.05
     !155.75       343.39!
```

```
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  1
    End
    Fragment   [CH2]C
        RRHO
    Geometry[angstrom]         7
     C         0.0002983383     -0.0005389889     0.0004031088
     C         0.0047388604     -0.0084680438     1.4846485597
     H         1.0125028336     -0.0004449026     -0.404522378
     H         -0.4985399523     0.8907396606     -0.4014899118
     H         -0.5291032253     -0.8632636678     -0.4045194797
     H         0.770457535     0.5135203684     2.0371553306
     H         -0.8406008348     -0.3881967978     2.037158663
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor         Hindered
        Group                      3 4 5
        Axis                       1 2
        Symmetry                   1
        Potential[kcal/mol]        12
         0.0  0.07  0.0  0.08  0.0  0.07  0.0  0.08  0.0  0.07  0.0
   0.08
    End
    Frequencies[1/cm]     14
           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
     !125.25!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]     -10.1
End
Barrier         B6   W2   P2     # TS_C[CH2]_COC=O_E9-19_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0129958622     -0.0472878214     0.0051768466
     C         -0.0043234375     0.0120890428     1.4921754805
     O         1.7447963624     -0.0000412445     2.0205324676
     C         2.6224009901     -0.2457458213     1.1562992952
     H         3.0693174825     0.4999060305     0.5066969116
     O         2.9346035332     -1.5024581724     0.7666288127
     C         2.3997365092     -2.5410471892     1.5722559441
     H         0.5957874919     0.7790284508     -0.4064620928
```

```
 H         -0.9949407565    0.0230300161    -0.4093652809
 H         0.4557787819    -0.9794192134    -0.3497070049
 H         -0.3109117808    0.9472815886    1.940094423
 H         -0.3695585512    -0.8610028794    2.0169819706
 H         2.6436667486    -2.3809861672    2.6224196991
 H         1.3151333867    -2.5967731632    1.4676831822
 H         2.8484474121    -3.4635104441    1.2168283353
Core RigidRotor
    SymmetryFactor            1.0
End
Rotor        Hindered
    Group                     8 9 10
    Axis                      1 2
    Symmetry                  3
    Potential[kcal/mol]       2
     0.0  1.14
End
Rotor        Hindered
    Group                     1
    Axis                      2 3
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0  2.29  1.0  1.65
End
Rotor        Hindered
    Group                     7
    Axis                      6 4
    Symmetry                  1
    Potential[kcal/mol]       4
     0.0  7.72  1.93  6.85
End
Rotor        Hindered
    Group                     13 14 15
    Axis                      7 6
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  1.09  0.0  1.09  0.0  1.1
End
Frequencies[1/cm]    34
       154.43      289.57      324.48      439.06      701.73
722.97
       771.24      856.37      921.81      979.66      1068.28
 1105.26      1184.61      1195.76      1223.39      1226.69
       1349.53      1401.57      1448.0      1485.1      1488.97
   1493.32      1501.27      1510.25      1518.0      3048.0
       3059.06      3108.04      3121.84      3124.62      3153.38
      3170.37      3174.84      3240.03
 !56.0      99.37      178.85      203.48!
```

```
    ZeroEnergy[kcal/mol]       15.6
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     791.3312
    WellDepth[kcal/mol]          14.7
    WellDepth[kcal/mol]          25.7
    End
End
Bimolecular         P3     # CCOC=O  +  [CH3]
    Fragment  CCOC=O
        RRHO
    Geometry[angstrom]         11
     O         0.0001875982     0.0001810121     -0.0000045809
     C         0.0000360448     0.0001495603     1.1954700817
     H         0.9006620095     0.000133797     1.8198581397
     O         -1.0833263564     0.0001288025     1.9687150237
     C         -2.3413617547     0.0001474237     1.272369565
     C         -3.4340641981     0.0001156125     2.3120371537
     H         -2.3828528182     0.8801670343     0.6309353146
     H         -2.3828502516     -0.8798347151     0.6308837924
     H         -3.3624530972     0.8838386974     2.9438172999
     H         -4.407993839     0.0001325389     1.8247539829
     H         -3.3624553661     -0.8836477651     2.9437612352
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor         Hindered
        Group                      1 3
        Axis                       2 4
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0   12.99   5.27   12.99
    End
    Rotor         Hindered
        Group                      2
        Axis                       4 5
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.12   0.01   6.55   0.01   1.12
    End
    Rotor         Hindered
        Group                      4 7 8
        Axis                       5 6
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.12   0.0   3.12   0.0   3.12
```

```
    End
    Frequencies[1/cm]    24
           237.16       389.93       806.77       814.71       883.19
   1062.71       1063.87
           1145.7       1187.56       1261.98       1310.78       1399.55
       1413.17       1434.43       1490.84       1503.7       1528.65
           1852.53       3076.3       3081.04       3086.08       3124.94
       3153.11       3158.28
     !77.65       236.19       344.76!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH3]
        RRHO
    Geometry[angstrom]    4
     C         0.     0.     0.
     H         0.     0.     1.0765291468
     H         0.9323015891     0.     -0.5382645734
     H        -0.9323015891     0.     -0.5382645734
    Core RigidRotor
        SymmetryFactor    6.0
    End
    Frequencies[1/cm]    6
           436.03       1412.64       1412.73       3144.41       3323.11
       3323.14
     !!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]    -12.6
End
Barrier         B7  W2  P3    # TS_CCOC=O_[CH3]_E10-34_m062x.log
    Variational
        RRHO
    Geometry[angstrom]        15
     C         0.0023743634     0.0161461555     0.006978212
     C         -0.0017707082     -0.0123431369     1.5217506171
     O         1.3295426905     -0.0088055975     2.0462635879
     C         2.0098507254     1.1496383336     1.9424611857
     H         3.043169333     1.037193216     2.2592431337
     O         1.4459651558     2.2595726382     1.7936265056
     C         0.7470175462     3.027148304     3.2998826895
     H         0.4386393622     0.9460650747     -0.3538159623
     H         -1.0174011965     -0.0569525977     -0.3699679938
     H         0.5790265479     -0.8203033123     -0.3853633626
     H         -0.5563991334     0.8348404914     1.9244357714
```

```
 H         -0.4435010827    -0.9313650019     1.8997341219
 H         0.3207480141     2.1896056453     3.8365114546
 H         1.6176965773     3.4767902391     3.754981222
 H         0.0344678096     3.719180553     2.8762348137
Core RigidRotor
    SymmetryFactor              1.0
End
Rotor        Hindered
    Group                       8 9 10
    Axis                        1 2
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0  3.02  0.0  3.02  0.0  3.02
End
Rotor        Hindered
    Group                       1 11 12
    Axis                        2 3
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0  1.12  0.1  1.2  0.66  5.68
End
Rotor        Hindered
    Group                       2
    Axis                        3 4
    Symmetry                    1
    Potential[kcal/mol]         4
     0.0  7.64  2.44  9.18
End
Rotor        Hindered
    Group                       13 14 15
    Axis                        7 6
    Symmetry                    1
    Potential[kcal/mol]         6
     0.0  0.4  0.0  0.4  0.0  0.4
End
Frequencies[1/cm]    34
        112.74       325.73       347.05       460.3       692.9
   736.52
        757.47       813.74       829.66       875.63       1032.08
    1066.01       1121.89       1190.07       1207.3       1332.33
        1354.97       1391.46       1418.0       1442.78       1447.61
       1479.1       1492.3       1504.3       1527.63       3072.7
        3093.86       3110.91       3138.43       3147.8       3155.85
       3162.69       3258.74       3274.46
    !60.97       85.53       164.81       228.76!
ZeroEnergy[kcal/mol]       16.5
ElectronicLevels[1/cm]    1
    0  2
```

```
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    880.1354
    WellDepth[kcal/mol]         15.6
    WellDepth[kcal/mol]         29.1
    End
End
!------------------------------------------------------------
!-------------------------WELL 3 to Products -----------------
!------------------------------------------------------------
Bimolecular         P4    # CC=O  +  CO[CH2]_E3-61
    Fragment  CC=O
        RRHO
    Geometry[angstrom]        7
     C         0.0168373546    0.0074667344    0.0239483472
     C         0.0532684252    -0.0026225916    1.5228064476
     O         1.0089808942    0.305132101    2.1786132672
     H         -0.2265979192    -0.9922483978    -0.340091758
     H         0.9738375724    0.3312736039    -0.375444231
     H         -0.7794935524    0.6722088819    -0.315449875
     H         -0.8836735886    -0.3212103319    2.0198178019
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor         Hindered
        Group                      4 5 6
        Axis                       1 2
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.2   0.01   1.2   0.0   1.19
    End
    Frequencies[1/cm]    14
           513.29       776.08       900.41       1138.06       1146.18
     1379.69       1433.6       1464.85       1474.9
           1874.29       2942.78       3063.51       3127.31       3180.67
     !157.82!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  1
    End
    Fragment  CO[CH2]_E3-61
        RRHO
    Geometry[angstrom]        8
     C         0.0026902296    -0.0018733009    0.0160456217
     O         -0.0078291385    0.0076990299    1.3645690081
     C         1.273786629    0.0049260623    1.95715442
     H         -0.9758393198    0.0608442139    -0.431273488
     H         0.877362312    0.3899910944    -0.4891132431
```

```
     H         1.8220579152     -0.8982084317     1.6804741972
     H         1.8440457298     0.8825642786     1.6409888636
     H         1.1333897905     0.0323929123     3.0337908614
    Core RigidRotor
        SymmetryFactor              1.0
    End
    Rotor         Hindered
        Group                       4 5
        Axis                        1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   0.29   0.0   5.48   0.0   5.4
    End
    Rotor         Hindered
        Group                       1
        Axis                        2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.56   0.0   1.56   0.0   1.56
    End
    Frequencies[1/cm]     16
           445.06       597.39       1006.96       1150.37       1184.95
      1269.45       1323.39       1465.29
           1498.89       1507.76       1515.58       3037.89       3099.15
        3133.66       3168.24       3282.25
     !171.34       290.38!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   2
    End
    GroundEnergy[kcal/mol]     7.8
End
Barrier         B8   W3   P4     # TS_CC=O_CO[CH2]_E18-12_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0317419102     0.0308463666     0.016964234
     C         -0.0311620838     -0.0103136546     1.508658573
     H         0.9117575303     -0.0447957299     2.0669606279
     O         -1.113688194     0.1189456755     2.1244161273
     C         -1.6706203211     1.999108624     2.2185220311
     O         -0.5069501117     2.6576450908     2.1690019564
     C         0.2069939266     2.64030135     3.3952372329
     H         -0.8429111005     -0.4581019599     -0.4114357185
     H         0.938138769     -0.4382180667     -0.362543433
     H         0.0294586299     1.0747017254     -0.318346403
     H         -2.2518592346     2.0854090635     1.3140183026
     H         -2.1789745589     1.9356825238     3.1724390117
```

```
 H         -0.3338034931    3.2169985413    4.1499666012
 H         0.331039549    1.6138151989    3.7437547989
 H         1.1755467298    3.0946372684    3.2105710721
Core RigidRotor
    SymmetryFactor             1.0
End
Rotor        Hindered
    Group                      8 9 10
    Axis                       1 2
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  0.5
End
Rotor        Hindered
    Group                      2
    Axis                       4 5
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0  4.93  3.33  3.84
End
Rotor        Hindered
    Group                      7
    Axis                       6 5
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0  10.46  2.64  6.85
End
Rotor        Hindered
    Group                      13 14 15
    Axis                       7 6
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  1.92
End
Frequencies[1/cm]    34
       111.15      248.53      407.81      478.12      499.65
662.39
       704.65      908.78      939.76      1004.63      1026.06
  1123.02      1154.43      1185.55      1265.51      1283.96
       1354.07      1389.76      1463.83      1469.36      1476.2
   1495.16      1513.67      1516.68      1528.96      3023.74
       3037.01      3044.66      3103.72      3112.14      3143.18
    3151.58      3176.67      3279.52
  !67.34      95.87      149.45      178.93!
ZeroEnergy[kcal/mol]      22.4
ElectronicLevels[1/cm]    1
    0  2
End
```

```
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    655.7407
    WellDepth[kcal/mol]         23.6
    WellDepth[kcal/mol]         14.6
    End
End
!------------------------------------------------------------
!-------------------------WELL 4 to Products -----------------
!------------------------------------------------------------
Bimolecular         P5    # C=C  +  [O]COC
    Fragment  C=C
        RRHO
    Geometry[angstrom]        6
     C         0.0000005934    -0.0000013257    0.005740686
     C         -0.00000068    0.0000017949    1.3272371407
     H         0.9217469077    -0.0000000153    -0.5612441874
     H         -0.9217446282    -0.0000053139    -0.5612459638
     H         0.9217445416    0.000005783    1.8942237904
     H         -0.9217469943    0.0000004844    1.894222014
    Core RigidRotor
        SymmetryFactor    4.0
    End
    Frequencies[1/cm]    12
           829.14      990.39      1002.91      1070.95      1243.09
      1388.1      1473.76      1718.54      3159.72      3175.83
           3235.55      3261.94
     !!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [O]COC
        RRHO
    Geometry[angstrom]        9
     O         0.6190925539    1.2333026374    0.1745233226
     C         0.9876560396    1.6303870496    1.4046807256
     O         0.4947479953    0.8876174447    2.469301145
     C         -0.9151817518    0.9194994719    2.5570147608
     H         2.0837969907    1.6157267218    1.4807404905
     H         0.6693669199    2.6924348993    1.4784997506
     H         -1.2719639526    1.9471586296    2.6879247658
     H         -1.3752133308    0.4934711935    1.6640667461
     H         -1.1965461365    0.3309141128    3.4254024352
    Core RigidRotor
        SymmetryFactor            1.0
    End
    Rotor        Hindered
        Group                     2
```

```
        Axis                         3 4
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   1.7
    End
    Rotor         Hindered
        Group                        1 5 6
        Axis                         2 3
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   2.19   0.04   3.53   2.25   3.54
    End
    Frequencies[1/cm]    19
           363.19       613.76       810.76       976.59       1076.02
    1152.39       1189.69       1224.58
           1273.63       1355.26       1400.69       1485.0       1497.47
       1521.26       2881.46       3014.09       3026.92       3102.78
           3166.67
     !132.13       202.72!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   2
    End
    GroundEnergy[kcal/mol]     23.9
End
Barrier         B9   W4   P5     # TS_COC[O]_C=C_E14-03_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         15
     C         0.0099792477     0.0057414095     -0.0163221748
     H         0.0394840421     0.0246198733     1.0641611622
     H         0.9586407167     -0.0111077785     -0.5333432198
     C         -1.1607454082     0.0923300166     -0.6842231582
     O         -1.4110944857     2.1331579164     -0.7853241691
     C         -0.2984505195     2.7027686085     -1.3194182368
     O         0.7788879599     2.8663094478     -0.4390966055
     C         0.4432650295     3.6055448958     0.7144572404
     H         -1.195022608     -0.0126301152     -1.7593882654
     H         -2.1036408607     0.0242749283     -0.1635075777
     H         0.1039091516     2.1470428531     -2.1727916156
     H         -0.6416067418     3.6937893187     -1.6748528992
     H         0.0445177693     4.5896508011     0.4435789093
     H         -0.2994364616     3.0826867368     1.3188123991
     H         1.356841189     3.7372620636     1.2885442607
    Core RigidRotor
        SymmetryFactor             1.0
    End
    Rotor         Hindered
```

```
        Group                       1 9 10
        Axis                        4 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0  2.92  0.34  1.24
    End
    Rotor        Hindered
        Group                       7 11 12
        Axis                        6 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0  15.0  2.66  8.8
    End
    Rotor        Hindered
        Group                       8
        Axis                        7 6
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0  6.26  3.1  5.41  2.68  4.41
    End
    Rotor        Hindered
        Group                       13 14 15
        Axis                        8 7
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0  1.64
    End
    Frequencies[1/cm]    33
           187.56      230.32     379.93      422.91      623.62
   826.32
           937.6      960.23      987.25      1018.47      1045.37
    1129.88      1181.25      1190.55      1218.27      1242.37
           1289.66      1328.58      1402.43      1448.87      1476.15
        1481.56      1494.35      1520.67      1603.59      2917.56
           3024.4      3048.12      3099.37      3155.94      3173.92
       3181.75      3257.03      3281.68
     !70.01      76.43      124.06      258.12!
    ZeroEnergy[kcal/mol]      28.9
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    490.0031
    WellDepth[kcal/mol]         23.1
    WellDepth[kcal/mol]         5.0
    End
End
End
```

E.9 CCCOCO[CH2]

```
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
PressureList[atm]                 0.00001 0.001  0.01  0.1  1  10  100.
!PressureList[bar]                1.
EnergyStepOverTemperature         .2
ExcessEnergyOverTemperature       30
ModelEnergyLimit[kcal/mol]        400
CalculationMethod                 direct
!CalculationMethod                low-eigenvalue !direct
WellCutoff                        10
ChemicalEigenvalueMax             0.2
Model
  EnergyRelaxation
    Exponential
      Factor[1/cm]                200
      Power                       .85
      ExponentCutoff              15
    End
  CollisionFrequency
    LennardJones
      Epsilons[1/cm]     94.87    280.62 !Ar and CCCOCO[CH2]
  Sigmas[angstrom]       3.33     6.14
  Masses[amu]            49.88    103.14
    End
!-------------------------------------------------------------
!-------------------------WELL 1 to Products --------------
!-------------------------------------------------------------
Well        W1        # W_CCCOCO[CH2]_m062x.log
    Species
        RRHO
    Geometry[angstrom]        18
     C        0.0311661217    0.0273945471    -0.0073920717
     O        0.0008726024    -0.0003344328    1.3470971999
     C        1.2718969625    -0.0010868223    1.9625522936
     O        2.0371738652    -1.0984453087    1.6053349774
     C        1.5046898095    -2.3365310186    2.0569645026
```

```
 C         2.3492102059    -3.4541398315     1.4846601166
 C         2.3025725506    -3.4829732554    -0.0378694179
 H         -0.9417292694     -0.0219034321     -0.4666927815
 H         0.9209060385    -0.3283557532    -0.5065696589
 H         1.8325501568    0.8825769852    1.6535709655
 H         1.0659106826    0.0161076734    3.0355048638
 H         1.5127942182    -2.3523341223     3.1526831659
 H         0.4678291934    -2.4341429204     1.7204628624
 H         3.3773835247    -3.3296150904     1.8290629402
 H         1.9846590054    -4.3981463638     1.8940489802
 H         2.7040927723    -2.5582183692    -0.4491108344
 H         2.8824681573    -4.3140906107    -0.4365831457
 H         1.2744294983    -3.5876778898    -0.389485947
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                    8 9
    Axis                     1 2
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  4.95  0.1  0.21  0.02  4.6
End
Rotor        Hindered
    Group                    1
    Axis                     2 3
    Symmetry                  1
    Potential[kcal/mol]       10
     0.0  4.26  3.39  3.65  2.5  2.79  2.48  2.86  2.44  3.18
End
Rotor        Hindered
    Group                    2 10 11
    Axis                     3 4
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  7.1  2.28  2.38  2.11  4.66  3.93  4.87
End
Rotor        Hindered
    Group                    3
    Axis                     4 5
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  1.83  1.29  1.32  1.19  7.27  2.94  3.12
End
Rotor        Hindered
    Group                    4 12 13
    Axis                     5 6
    Symmetry                  1
```

```
        Potential[kcal/mol]        6
         0.0   4.98   0.13   3.74   0.48   3.62
    End
    Rotor        Hindered
        Group                     16 17 18
        Axis                      7 6
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.64   0.0   2.64   0.0   2.64
    End
    Frequencies[1/cm]    42
           302.98       320.4       403.52       484.76
           547.99       651.91       771.94       901.65       924.85
   964.05       992.83       1089.89       1113.29       1146.62
           1185.12       1193.4       1241.82       1269.08       1286.98
       1309.09       1347.55       1378.42       1412.76       1430.59
           1447.63       1484.95       1492.6       1497.44       1511.48
       1521.44       1528.95       3024.07       3057.9       3061.28
           3063.87       3075.38       3106.52       3116.5       3132.47
       3148.95       3164.17       3304.07
     !38.26       72.94       136.42       190.27       212.06       270.87!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
End
!-------------------------------------------------
!-------------------------WELLS 2---------------
!-------------------------------------------------
Well         W2         # W_CC[CH]OCOC_E-1-8_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         0.0028423816     -0.0249239537     0.0030295185
     C         0.0005044272     0.0174150195     1.5380352406
     C         1.3678050207     0.0016653397     2.113363171
     O         2.0509353064     -1.1601337519     1.8936556461
     C         3.3950807684     -1.142286269     2.3107121127
     O         4.1632646334     -0.223649471     1.6095705534
     C         4.238538618     -0.5041693767     0.2263584152
     H         4.5983363856     -1.5241071383     0.0568889623
     H         4.9422911205     0.202235123     -0.2050416611
     H         0.5214882623     0.8435640275     -0.4046240996
     H         -1.0123105919     -0.0344141692     -0.3933531335
     H         0.5154022368     -0.9213300521     -0.3446132147
     H         -0.5137009449     0.9135868098     1.8862503877
     H         -0.555261177     -0.8435335937     1.918272619
     H         3.2648274917     -0.3886903531     -0.2543700634
```

```
 H         1.969506135    0.9010265374    2.1800738419
 H         3.458610755    -0.8567632591    3.3619874133
 H         3.7556961192    -2.1623735123    2.154802268
Core RigidRotor
    SymmetryFactor    1
End
Rotor        Hindered
    Group                     10 11 12
    Axis                      1 2
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  3.18
End
Rotor        Hindered
    Group                     1 13 14
    Axis                      2 3
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  2.27  0.23  1.75  0.38  1.71
End
Rotor        Hindered
    Group                     2 16
    Axis                      3 4
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  5.11  1.84  4.56  3.32  5.68
End
Rotor        Hindered
    Group                     3
    Axis                      4 5
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  6.92  1.78  2.86  2.5  3.19
End
Rotor        Hindered
    Group                     4 17 18
    Axis                      5 6
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  6.64  2.0  4.29  3.22  4.48
End
Rotor        Hindered
    Group                     8 9 15
    Axis                       7 6
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  1.77
End
```

```
    Frequencies[1/cm]     42
           283.58       310.77       406.83       479.47
           619.62       658.05       782.12       911.25       969.67
   988.56       1059.02       1099.56       1120.62       1164.85
           1190.42       1215.04       1221.16       1266.95       1301.16
        1335.82       1351.98       1392.97       1419.34       1459.67
           1477.17       1488.23       1496.41       1498.39       1510.72
        1515.11       1525.21       3032.22       3054.8       3055.97
           3060.11       3098.14       3107.6       3115.62       3131.47
       3141.77       3161.95       3174.3
     !46.9       67.92       114.68       149.75       212.4       237.0!
    ZeroEnergy[kcal/mol]       -1.0
    ElectronicLevels[1/cm]     1
        0  2
    End
End
!------------------------------------------------------------
Barrier         B1   W1   W2     # W_CC[CH]OCOC_E-1-8_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0038526119     0.0305653071     0.0015185603
     C         0.0000084586     -0.0149788276     1.5264671357
     C         1.3870186623     0.0011838062     2.0994709805
     O         2.1070485088     -1.1370647318     1.7243508416
     C         3.4889774642     -0.923835811     1.7170206742
     O         3.8463143631     -0.0062018604     0.7232399138
     C         3.3768794474     1.2711695708     1.01156829
     H         3.2970841683     1.8638853232     0.1070179808
     H         3.9201685954     1.7585714645     1.8248871848
     H         0.4433240804     0.9631021092     -0.3544740395
     H         -1.0067978731     -0.0421749505     -0.3973039247
     H         0.5930508278     -0.7922162412     -0.4000778069
     H         -0.5511973325     0.8333458598     1.9350786679
     H         -0.5128158275     -0.9206974979     1.8680402839
     H         2.1395561773     0.9811703869     1.5405487547
     H         1.4550938371     0.1869699507     3.1760262117
     H         3.8186974441     -0.5577910451     2.7007314494
     H         3.9623433901     -1.8694898203     1.473558817
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                      10 11 12
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   2.46   0.0   2.46   0.0   2.46
```

```
    End
    Rotor         Hindered
        Group                       1 13 14
        Axis                        2 3
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   3.82   0.43   3.09   0.5   3.08
    End
    Frequencies[1/cm]     45
           67.38       235.18       297.53       376.14       409.7
   444.69       513.23       610.1
           669.19       777.23       902.98       954.37       980.84
   1001.69       1068.8       1108.29       1128.45       1131.01
           1161.79       1180.98       1221.61       1256.89       1301.83
        1328.8       1363.12       1366.84       1411.44       1435.31
           1441.01       1476.11       1479.37       1499.78       1510.64
        1523.94       1627.99       2990.43       3031.63       3046.56
           3051.59       3068.21       3098.18       3136.74       3150.98
        3170.49       3192.23
     !91.87       172.73!
    ZeroEnergy[kcal/mol]       18.8
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     1716.6001
    WellDepth[kcal/mol]     18.8
    WellDepth[kcal/mol]     19.8
    End
End
!-----------------------------------------------
!-------------------------WELLS 3-------------
!-----------------------------------------------
Well         W3         # W_C[CH]COCOC_E2-4_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         -0.0151155348     0.0251243656     0.0220460786
     C         0.0185385656     0.0018804974     1.5075658012
     C         1.3214764469     -0.0209672625     2.2283356905
     O         2.2242949304     0.9832774407     1.7678353321
     C         1.8358575763     2.2799829911     2.1158880674
     O         1.8771207436     2.5108678271     3.490267469
     C         3.1831441766     2.4366474857     4.021725255
     H         3.116842277     2.6924019807     5.0759273853
     H         3.8464738174     3.148292961     3.5189327148
     H         -0.9652205541     0.4007787668     -0.3557422099
     H         0.1219929081     -0.980639303     -0.3966552721
```

```
 H         0.7909392206    0.6434538384    -0.374497348
 H         3.6006773723    1.4337539746    3.9143550563
 H         -0.8796457033    -0.2353425061    2.059540505
 H         1.1698636531    0.0790236462    3.3054876763
 H         1.8520293688    -0.9631376226    2.0502085926
 H         2.529491376    2.9427536065    1.5898077629
 H         0.8048003922    2.4781113324    1.8122054517
Core RigidRotor
    SymmetryFactor    1.0
End
Rotor        Hindered
    Group                    10 11 12
    Axis                     1 2
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  0.25  0.0  0.25  -0.0  0.25
End
Rotor        Hindered
    Group                    1 14
    Axis                     2 3
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  2.48  0.47  0.68  0.67  6.64  1.96  1.99
End
Rotor        Hindered
    Group                    2 15 16
    Axis                     3 4
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  2.11  0.7  1.55  0.5  4.08
End
Rotor        Hindered
    Group                    3
    Axis                     4 5
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  3.49  2.64  3.9  3.19  8.12
End
Rotor        Hindered
    Group                    4 17 18
    Axis                     5 6
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  4.16  2.69  3.07  2.87  3.79  3.08  7.33
End
Rotor        Hindered
    Group                    8 9 13
    Axis                     7 6
```

```
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.61   -0.0   1.61   0.0   1.61
    End
    Frequencies[1/cm]    42
           253.42       342.57       383.19       444.25
           606.04       622.4       885.11       926.99       953.88
   983.94       996.37       1102.31       1109.71       1156.62
           1168.35       1189.95       1209.25       1251.41       1311.17
        1350.6       1378.7       1392.86       1417.0       1445.5
           1480.99       1481.04       1489.87       1494.3       1497.28
        1514.79       1522.93       3001.02       3021.45       3028.87
           3043.73       3083.86       3091.1       3096.05       3097.75
        3137.11       3158.07       3209.22
     !38.72       61.31       81.88       107.75       157.14       208.82!
    ZeroEnergy[kcal/mol]       2.7
    ElectronicLevels[1/cm]    1
        0  2
    End
End
!------------------------------------------------------
Barrier         B2   W1   W3    # W_C[CH]COCOC_E2-4_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.013332019    0.0462895608    0.0301809319
     C         -0.0157956863    -0.0228217745    1.5322451633
     C         1.3280523964    -0.0145554422    2.2200800187
     O         1.2092559542    0.467203913    3.5564481504
     C         1.4720632631    1.8296530341    3.6912270355
     O         0.8106218676    2.6213099197    2.7378621518
     C         -0.5408355356    2.3333452749    2.6179652592
     H         -1.0149312613    3.059695028    1.9663102548
     H         -1.0519850548    2.1841203651    3.5710003801
     H         -0.9916626882    0.0620222494    -0.3895223737
     H         0.5366590376    -0.8106184706    -0.4069398061
     H         0.5346140228    0.9469709471    -0.3014299359
     H         -0.5512757375    1.1420412806    2.0022234596
     H         -0.6922749534    -0.7693709522    1.944745563
     H         1.7454078684    -1.0221660587    2.2915769124
     H         2.036040409    0.6039745878    1.6584474927
     H         1.1516405072    2.0934373584    4.7027654135
     H         2.5337666755    2.0493242538    3.5506939724
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor         Hindered
        Group                     10 11 12
```

```
        Axis                        1 2
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   2.03   0.0   2.03   0.0   2.03
    End
    Frequencies[1/cm]    46
           65.99       146.93       272.93       310.47       350.82
   393.66       433.37       496.98       574.42
           670.67       849.45       912.37       930.36       975.22
   1001.36       1090.4       1103.57       1135.55       1160.98
           1174.14       1178.58       1219.7       1254.65       1302.91
       1334.09       1336.9       1399.22       1409.42       1427.85
           1447.41       1472.23       1490.36       1494.84       1502.05
        1524.76       1529.74       3028.71       3035.54       3044.33
           3064.81       3077.93       3087.26       3095.24       3118.83
        3134.49       3189.65
     !185.1!
    ZeroEnergy[kcal/mol]       20.8
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    1694.8723
    WellDepth[kcal/mol]    20.8
    WellDepth[kcal/mol]    18.1
    End
End
!----------------------------------------
!-------------------------WELLS 4----------
!----------------------------------------
Well         W4         # W_[CH2]CCOCOC_E5-7_m062x.log
    Species
        RRHO
    Geometry[angstrom]         18
     C         0.0087443749     -0.0009686721     -0.0019382697
     C         0.0012366037     -0.0051500282     1.484358929
     C         1.4054364741     -0.0037323494     2.0679125979
     O         2.0668425775     -1.1716224307     1.6153728279
     C         3.4093871382     -1.2294376141     1.9894588583
     O         4.1797277591     -0.2099840296     1.4327687306
     C         4.1783071283     -0.2289587236     0.0206562464
     H         4.4581089383     -1.218702392     -0.3553455502
     H         4.9111448224     0.5020309211     -0.3105755504
     H         3.1955429729     0.032609855     -0.3795584903
     H         -0.6893251476     0.5983117692     -0.5646432906
     H         0.6115965171     -0.7235404158     -0.5297056763
     H         -0.5398212772     0.8583975316     1.8728790725
     H         -0.5125201048     -0.8985727251     1.8624255165
```

```
 H         1.951289928    0.8853370012    1.7403019962
 H         1.3712316293    -0.0035042691    3.1638016122
 H         3.5197420091    -1.1254951656    3.0728144271
 H         3.7637737098    -2.2098462683    1.6568590309
Core RigidRotor
    SymmetryFactor    1.0
End
Rotor        Hindered
    Group                     11 12
    Axis                      1 2
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   0.03   0.03   0.63   -0.0   0.62
End
Rotor        Hindered
    Group                     1 13 14
    Axis                      2 3
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   5.21   0.24   3.75   0.61   3.65
End
Rotor        Hindered
    Group                     2 15 16
    Axis                      3 4
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   1.83   0.71   4.91   1.83   2.55
End
Rotor        Hindered
    Group                     3
    Axis                      4 5
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0   2511.67   190.34   1876.7
End
Rotor        Hindered
    Group                     4 17 18
    Axis                      5 6
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   7.15   2.91   4.99   3.06   4.39
End
Rotor        Hindered
    Group                     8 9 10
    Axis                      7 6
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0   1.79   0.0   1.79   0.0   1.79
```

```
    End
    Frequencies[1/cm]    42
           272.11       309.13       409.79       467.51
           518.4       659.86       756.65       921.37       956.17
   984.03       1064.2       1087.81       1113.22       1147.69
           1183.72       1192.07       1211.6       1244.78       1253.49
       1301.96       1343.27       1364.76       1416.29       1444.55
           1459.94       1472.62       1485.84       1498.49       1514.27
        1521.31       1532.54       3005.67       3020.69       3027.01
           3036.94       3076.82       3087.7       3090.65       3104.27
       3157.34       3180.16       3286.06
     !40.71       81.71       104.05       147.71       176.95       235.43!
    ZeroEnergy[kcal/mol]       4.6
    ElectronicLevels[1/cm]    1
        0  2
    End
End
!-------------------------------------------------------
Barrier         B3   W1   W4     # W_[CH2]CCOCOC_E5-7_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0217818783     -0.0053373722     0.0053519893
     C         -0.0009547028     0.0302106621     1.5104545302
     C         1.4035162348     0.0105308793     2.109165689
     O         2.3261231784     0.8631817117     1.4483128941
     C         2.1793802984     2.2206209103     1.6941476668
     O         1.0214091643     2.7770667567     1.1266030435
     C         0.8892327909     2.5142287019     -0.230369056
     H         1.8334754381     2.5556898181     -0.7779624182
     H         0.1129151372     3.1469791813     -0.6489734089
     H         0.4688496093     1.2640932298     -0.3283286917
     H         -0.950877751     -0.077793005     -0.4721713229
     H         0.7619521152     -0.6680564913     -0.4366731754
     H         -0.5400307011     0.9174362539     1.8481950632
     H         -0.5394101907     -0.8326716343     1.9188800198
     H         1.3706502264     0.2614522097     3.1753427714
     H         1.8294567895     -0.9876507914     2.0079186906
     H         2.106185363     2.4289085138     2.7652047245
     H         3.0667436674     2.6944380206     1.2650609322
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Frequencies[1/cm]    47
           93.88       230.37       265.83       279.91       328.04
   364.55       441.18       499.06       537.05       654.25
           696.83       805.96       890.18       929.32       957.78
   991.47       1060.99       1102.42       1113.22       1171.62
```

```
           1175.28       1196.76       1207.46       1258.07       1264.42
        1323.8       1354.41       1383.39       1412.07       1418.78
           1447.03       1456.82       1465.49       1481.21       1495.95
        1505.71       1521.37       3025.02       3035.62       3041.53
           3058.67       3082.74       3093.97       3105.99       3113.56
        3180.11       3188.87
     !  !
    ZeroEnergy[kcal/mol]      20.7
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1690.6325
    WellDepth[kcal/mol]    20.7
    WellDepth[kcal/mol]    16.1
    End
End
!---------------------------------------------------------
!------------------------------W1 - > P1------------------
!---------------------------------------------------------
Bimolecular         P1    # CCCO[CH2]_E7-7  +  CH2O_E6-5
    Fragment  CCCO[CH2]_E7-7
        RRHO
    Geometry[angstrom]        14
     C        0.0070851475    0.0232118319    0.0109696271
     C        0.0058550135    -0.0033377688    1.5332072907
     C        1.4126553548    -0.0158334403    2.1083640106
     O        2.1877841031    1.0872630349    1.6603269035
     C        1.8048504376    2.2857337517    2.1470205263
     H        0.5081713734    0.9191365584    -0.3532886702
     H        -1.007670756    0.0150590007    -0.3838679522
     H        0.5345133038    -0.8424832541    -0.3925986491
     H        -0.5302933857    0.8650499511    1.9213899356
     H        -0.5138666687    -0.8899359573    1.9025516626
     H        1.3868472355    -0.0128997673    3.2032344178
     H        1.9530152869    -0.9020974475    1.7767367299
     H        1.3125870489    2.3071560172    3.1128682676
     H        2.4215295358    3.1077684911    1.8213449113
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    6 7 8
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.78
    End
```

```
    Rotor        Hindered
        Group                     1 9 10
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.74   0.47   3.46   0.73   4.79
    End
    Rotor        Hindered
        Group                     2 11 12
        Axis                      3 4
        Symmetry                   1
        Potential[kcal/mol]        8
         0.0   1.6   0.11   1.17   1.1   1.41   1.01   5.99
    End
    Rotor        Hindered
        Group                     3
        Axis                      4 5
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   5.36   0.0   5.54   0.6   0.64
    End
    Frequencies[1/cm]    32
           282.38       440.57       525.81       631.8       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
     !70.3       168.24       232.83       307.28!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    Fragment  CH2O_E6-5
        RRHO
    Geometry[angstrom]         4
     O         -0.000000016     -0.0000022088     0.0061054213
     C         -0.0000000144     0.0000068137     1.2014608526
     H         0.9375275336     -0.0000022726     1.7838372267
     H         -0.9375275608     0.0000246367     1.7838372291
    Core RigidRotor
        SymmetryFactor     2.0
    End
    Frequencies[1/cm]    6
           1216.69       1279.34       1545.84       1876.79       2940.94
        3011.91
```

```
     !   !
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    GroundEnergy[kcal/mol]         13.2
End
!-------------------------------------------------------------------
Barrier         B4   W1   P1    # TS_CH2O_CCCO[CH2]_E18-0_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.004569429    -0.0382212236    0.0022661482
     C         0.0015684435    0.0222930036    1.5242762327
     C         1.3935548921    0.0008175665    2.1138990233
     O         1.9997166134    -1.2546481475    1.8012542879
     C         3.2569451126    -1.3778140286    2.2202898358
     O         4.2977981142    -0.3817630222    0.8288952344
     C         3.6800232701    -0.2510189576    -0.2438631868
     H         3.0963936722    0.6505990505    -0.4565186239
     H         3.6712823964    -1.0444740262    -0.9976133752
     H         0.5167137176    0.8288241017    -0.4174993791
     H         -1.0107328559    -0.0520138352    -0.3914222651
     H         0.5200586808    -0.9326356047    -0.3449769452
     H         -0.4935131432    0.9328620281    1.8666148052
     H         -0.5584975015    -0.819372932    1.9354966433
     H         2.0172005237    0.8017179817    1.705507451
     H         1.3644748401    0.1060256495    3.2026995147
     H         3.5793728774    -0.7803101764    3.0631013026
     H         3.6787069832    -2.3569564452    2.0624083305
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      10 11 12
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   3.05   0.0   3.06   -0.0   3.05
    End
    Rotor         Hindered
        Group                      1 13 14
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   4.63   0.41   3.88   0.7   3.72
    End
    Rotor         Hindered
```

```
        Group                       2 15 16
        Axis                        3 4
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   2.58   1.21   7.72   2.7   4.41
    End
    Rotor         Hindered
        Group                       3
        Axis                        4 5
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   15.89   2.72   9.56
    End
    Rotor         Hindered
        Group                       4 17 18
        Axis                        5 6
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   4.91   3.47   4.1
    End
    Frequencies[1/cm]    42
           232.41       286.06       309.81       364.13       424.14
           536.31       648.0       765.93       886.55       902.05
   923.71       940.33       966.73       1094.54       1125.48
           1174.54       1234.04       1241.4       1255.91       1281.77
       1316.45       1381.92       1400.31       1415.19       1432.26
           1480.74       1499.8       1510.42       1514.96       1526.0
      1582.62       3010.99       3037.48       3064.57       3067.73
           3082.95       3096.11       3107.71       3135.81       3147.75
       3149.53       3290.61
     !77.53       92.54       112.51       168.64       215.71!
    ZeroEnergy[kcal/mol]       25.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    599.9148
    WellDepth[kcal/mol]    25.2
    WellDepth[kcal/mol]    12.0
    End
End
!------------------------------------------------------------
!-------------------------WELL 2 to Products -------------
!------------------------------------------------------------
Bimolecular         P2    # CCC=O_E3-61  +  CO[CH2]_E3-61
    Fragment  CCC=O_E3-61
        RRHO
    Geometry[angstrom]         10
```

```
     C         -0.0000566396     0.0062360295     -0.0000851688
     C         0.0002269459     -0.0058860377     1.5176215585
     C         1.3811361699     -0.0034523604     2.1113838536
     H         1.4229848487     -0.0120720663     3.2179002795
     O         2.393691471     0.0069513451     1.4676073164
     H         0.5150796789     0.8884132091     -0.3758097392
     H         -1.0166443986     0.0040558499     -0.3884237127
     H         0.524187663     -0.8644258075     -0.3898116873
     H         -0.5289339007     0.8570574089     1.9342051971
     H         -0.5199028418     -0.8808265682     1.9203230958
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                     6 7 8
        Axis                      1 2
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0   2.12
    End
    Rotor        Hindered
        Group                     1 9 10
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.36   1.42   2.11   1.42   2.36
    End
    Frequencies[1/cm]    22
           266.82       673.44       677.86       873.63       908.86
   1008.52       1121.87       1156.86
           1283.93       1372.83       1414.21       1430.39       1457.55
        1497.45       1504.73       1866.92       2945.02       3050.32
           3077.74       3081.28       3153.86       3156.87
     !148.66       238.11!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0   1
    End
    Fragment  CO[CH2]_E3-61
        RRHO
    Geometry[angstrom]         8
     C         0.0026902296     -0.0018733009     0.0160456217
     O         -0.0078291385     0.0076990299     1.3645690081
     C         1.273786629     0.0049260623     1.95715442
     H         -0.9758393198     0.0608442139     -0.431273488
     H         0.877362312     0.3899910944     -0.4891132431
     H         1.8220579152     -0.8982084317     1.6804741972
     H         1.8440457298     0.8825642786     1.6409888636
```

```
     H         1.1333897905     0.0323929123     3.0337908614
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      4 5
        Axis                       1 2
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   0.29   0.0   5.48   0.0   5.4
    End
    Rotor         Hindered
        Group                      1
        Axis                       2 3
        Symmetry                    1
        Potential[kcal/mol]         6
         0.0   1.56   0.0   1.56   0.0   1.56
    End
    Frequencies[1/cm]     16
            445.06       597.39       1006.96       1150.37       1184.95
      1269.45       1323.39       1465.29
            1498.89       1507.76       1515.58       3037.89       3099.15
        3133.66       3168.24       3282.25
     !171.34       290.38!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]     7.6
End
!------------------------------------------------------------
Barrier         B5   W2   P2     # TS_CCC=O_CO[CH2]_E16-71_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.0011630263     0.0025368695     -0.0005050648
     C         0.000876069     -0.0016432682     1.5236164973
     C         1.381585976     -0.0007083721     2.1061770685
     H         1.5086115545     0.390582317     3.1225973234
     O         2.3479850031     -0.549905182     1.5269870771
     C         2.3522672705     -2.4864727641     1.8028039032
     O         1.7562365404     -2.6235585259     2.9930028445
     C         2.5964237139     -2.2980432386     4.0891760791
     H         0.4728163509     0.9060005189     -0.3832367711
     H         -1.0168390478     -0.0467128565     -0.3900790764
     H         0.559275012     -0.8470296056     -0.3862808893
     H         -0.5565383202     0.8479088034     1.922487319
     H         -0.5132036643     -0.9000532309     1.8926950377
```

```
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
```

```
           1154.65       1185.61       1258.54       1276.5       1285.47
       1350.54       1367.47       1406.84       1465.8       1469.32
           1493.88       1496.49       1502.13       1513.47       1515.96
        1526.54       3000.53       3032.58       3045.05       3072.42
           3089.59       3113.15       3139.71       3141.95       3150.85
        3175.11       3275.12
     !42.64       60.58       92.11      175.79       211.29!
    ZeroEnergy[kcal/mol]       22.6
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]    664.2086
    WellDepth[kcal/mol]    23.6
    WellDepth[kcal/mol]    15.0
    End
End
!--------------------------------
!--------------------------------
Bimolecular         P3    # C=COCOC_E21-90  +  [CH3]
    Fragment  C=COCOC_E21-90
        RRHO
    Geometry[angstrom]        14
     C         -0.0042800966    -0.0127363074    0.000882754
     C         -0.0091071243    0.0177581663    1.3258701105
     H         0.9044122917    0.0662452593    1.9036685686
     O         -1.0844170454    -0.0100492049    2.157704227
     C         -2.3398965536    -0.2645899287    1.574290547
     O         -2.8074788365    0.7763954673    0.7880448361
     C         -3.0135846937    1.9736060286    1.5100755402
     H         0.9471989404    -0.0124121091    -0.5077237278
     H         -0.9055287428    -0.013043779    -0.592143188
     H         -2.2769011173    -1.141302371    0.9274444408
     H         -3.0060010358    -0.4452064422    2.4220736225
     H         -3.6822813906    1.8026023057    2.359974189
     H         -2.0701641663    2.3808548695    1.8769606607
     H         -3.4736414239    2.6823350448    0.8273313887
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    1 3
        Axis                     2 4
        Symmetry                  1
        Potential[kcal/mol]       4
         0.0  4.73  1.0  4.9
    End
    Rotor        Hindered
```

```
        Group                       2
        Axis                        4 5
        Symmetry                     1
        Potential[kcal/mol]          4
         0.0   9.45   2.8   4.21
    End
    Rotor         Hindered
        Group                       4 10 11
        Axis                        5 6
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   6.7   3.43   5.29   3.2   4.11
    End
    Rotor         Hindered
        Group                       5
        Axis                        6 7
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   1.65
    End
    Frequencies[1/cm]    32
           295.64       417.77       528.27       679.3       737.35
   895.85
           923.42       988.32       1017.02       1046.75       1142.16
      1190.24       1215.13       1241.44       1260.45       1351.18
           1365.1       1429.97       1460.05       1489.2       1498.99
      1515.51       1524.42       1723.84       3032.33       3054.61
           3104.55       3116.0       3164.69       3198.31       3215.11
       3292.5
     !75.3       144.64       174.73       232.59!
    ZeroEnergy[kcal/mol]    0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  [CH3]
        RRHO
    Geometry[angstrom]        4
    C                  0.00000000    0.00000000    0.00000000
    H                  0.00000000    0.00000000    1.07652900
    H                  0.93230200    0.00000000   -0.53826500
    H                 -0.93230200   -0.00000000   -0.53826500
    Core RigidRotor
        SymmetryFactor    6
    End
    Frequencies[1/cm]    6
           436.03       1412.64       1412.73       3144.41       3323.11
       3323.14
     !   !
```

```
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          21.6
End
!------------------------------------------------------
Barrier         B6   W2   P3     # TS_[CH3]_C=COCOC_E29-03_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.0100032207     -0.0101254289     0.0043009665
     C         0.0061409792     0.0059435675     2.2737739811
     C         1.2778661742     0.0086729316     2.7313146353
     H         1.83015515     0.9215467843     2.9029406904
     O         2.0794216656     -1.0748012905     2.9198848531
     C         1.5256965418     -2.3416168511     2.6562846801
     O         0.5366781631     -2.7077079806     3.5563247829
     C         1.0019863378     -2.812242977     4.8868345785
     H         0.4404115132     0.9478451287     -0.2101158466
     H         -1.073824061     -0.093213389     -0.1700701975
     H         0.5853433359     -0.878462067     -0.2393180223
     H         -0.5160290675     0.9500654196     2.272336116
     H         -0.595769074     -0.8893222703     2.2922949564
     H         1.0661715477     -2.3553488533     1.6672997828
     H         2.3749105282     -3.0281505606     2.704393077
     H         1.8528367466     -3.4986263903     4.9463628765
     H         1.3028808328     -1.8389454666     5.2776059741
     H         0.1814049321     -3.2041802813     5.4811171226
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor         Hindered
        Group                      9 10 11
        Axis                       1 2
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   0.21
    End
    Rotor         Hindered
        Group                      2 4
        Axis                       3 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   3.35   0.21   4.11
    End
    Rotor         Hindered
        Group                      3
```

```
        Axis                        5 6
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   8.44   2.1   3.18   3.14   3.5
    End
    Rotor         Hindered
        Group                       5 14 15
        Axis                        6 7
        Symmetry                     1
        Potential[kcal/mol]          6
         0.0   6.56   3.23   5.4   3.18   4.14
    End
    Rotor         Hindered
        Group                       16 17 18
        Axis                        8 7
        Symmetry                     3
        Potential[kcal/mol]          2
         0.0   1.66
    End
    Frequencies[1/cm]     42
            225.26       264.68       333.14       419.71       495.45
            517.1       533.0       672.36       762.8       809.91
   910.07       933.35       960.8       990.13       1045.78
            1140.65       1190.08       1212.3       1236.95       1251.87
       1331.12       1349.48       1419.86       1425.5       1429.5
            1457.4       1488.41       1499.05       1515.96       1526.6
      1605.05       3033.41       3058.71       3104.61       3107.39
            3121.81       3164.18       3194.22       3221.39       3264.38
        3268.84       3285.64
     !59.33       67.41       70.32       119.01       149.08!
    ZeroEnergy[kcal/mol]       30.2
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     597.1092
    WellDepth[kcal/mol]     31.2
    WellDepth[kcal/mol]     8.6
    End
End
!------------------------------------------------------------
!-------------------------WELL 3 to Products --------------
!------------------------------------------------------------
!------------------------------------------------------------
!-------------------------WELL 3 -> Well 5 ----------------
!------------------------------------------------------------
Well         W5         # W_CCCO[CH]OC_E-2-17_m062x.log
    Species
```

```
        RRHO
    Geometry[angstrom]         18
     C         0.0056925347    0.0044067557    0.0015999622
     C         -0.0022423148    -0.0020167887    1.5240639341
     H         1.0202126636    -0.0069673417    1.9066935904
     C         -0.7456009953    1.1872020646    2.1085325526
     O         -0.2498938736    2.4382908827    1.6258247597
     C         1.0567165598    2.6755122063    1.8446701726
     O         1.459722845    2.4287799297    3.1254055531
     C         2.8445539972    2.6280186628    3.311818763
     H         0.5225298623    0.8872116323    -0.3731939831
     H         -1.0114020003    0.0190602357    -0.3932597238
     H         0.508708402    -0.877232491    -0.39325078
     H         -1.790417469    1.1738739896    1.8008031478
     H         -0.6996355274    1.1762590787    3.1979495002
     H         -0.4858755871    -0.905902841    1.9005490745
     H         1.388188563    3.6179790858    1.4113779235
     H         3.4205245525    1.9489848958    2.6789914016
     H         3.124033852    3.6586094571    3.0746000072
     H         3.0607628967    2.4294136094    4.3573431234
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    9 10 11
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.65
    End
    Rotor        Hindered
        Group                    1 3 14
        Axis                     2 4
        Symmetry                  1
        Potential[kcal/mol]       6
         0.0  5.38  1.07  3.42  0.67  3.96
    End
    Rotor        Hindered
        Group                    2 12 13
        Axis                     4 5
        Symmetry                  1
        Potential[kcal/mol]       9
         0.0  4.96  3.57  3.71  2.49  2.86  1.91  3.37  2.68
    End
    Rotor        Hindered
        Group                    4
        Axis                     5 6
        Symmetry                  1
```

```
        Potential[kcal/mol]        6
         0.0   3.36   2.17   2.72   2.66   3.5
    End
    Rotor        Hindered
        Group                     5 15
        Axis                      6 7
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.01   1.58   4.0   1.12   4.31
    End
    Rotor        Hindered
        Group                     6
        Axis                      7 8
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   1.68   0.0   1.68   0.0   1.68
    End
    Frequencies[1/cm]    42
           280.93       328.38       387.3       509.59
           616.8       769.08       878.88       916.68       924.7
   968.52       1060.43       1087.23       1120.2       1180.06
           1190.66       1195.24       1253.43       1285.2       1304.07
       1316.9       1368.72       1383.14       1414.16       1439.17
           1484.98       1488.95       1499.58       1501.07       1509.18
        1515.19       1519.42       3035.02       3062.93       3066.77
           3081.11       3093.63       3101.95       3112.16       3129.53
        3135.24       3144.09       3167.96
     !53.2       88.5       112.35       180.39       204.78       222.29!
    ZeroEnergy[kcal/mol]       0.9
    ElectronicLevels[1/cm]     1
        0  2
    End
End
!------------------------------------------------
Barrier        B7   W3   W5     # W_CCCO[CH]OC_E-2-17_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0010976419     0.0007769054     0.0011240581
     C         -0.0009818838     -0.0007991689     1.5064497278
     H         0.9777141295     -0.0015446348     1.9750424626
     C         -1.0562309474     -0.8437124054     2.1715126496
     O         -2.2557689941     -0.0415598397     2.2852748769
     C         -1.9643957309     1.3065179632     2.2812899654
     O         -2.0264548     1.9376736813     3.4938535658
     C         -1.3169156789     1.2921460053     4.5312655126
     H         0.3538379792     -0.9548720991     -0.3978521351
     H         0.6430477634     0.7839688497     -0.4006672011
```

```
     H         -1.0089760679    0.1600471213    -0.3817049931
     H         -1.3329804005    -1.720959764    1.5850120728
     H         -0.7485067804    -1.1711782052    3.1670902545
     H         -0.6855754965    1.1594165074    1.8613504691
     H         -2.5637270319    1.865045516    1.5676359021
     H         -1.7546948873    0.3185784458    4.7561648925
     H         -0.2650605201    1.1619285183    4.2561245709
     H         -1.3830332936    1.9320986561    5.4063003159
    Core RigidRotor
        SymmetryFactor    0.25
    End
    Rotor        Hindered
        Group                     9 10 11
        Axis                      1 2
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0  2.02
    End
    Rotor        Hindered
        Group                     8
        Axis                      7 6
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  3.57  0.61  2.51  1.01  3.42
    End
    Rotor        Hindered
        Group                     16 17 18
        Axis                      8 7
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  2.42  0.0  2.41  0.0  2.42
    End
    Frequencies[1/cm]    44
           81.6      137.75      165.46      336.49      373.4
   575.26      639.51
           695.84      793.67      902.09      930.18      961.35
   992.46      1054.08      1067.08      1121.49      1153.82
           1160.67      1184.11      1213.26      1252.62      1263.46
        1345.89      1379.42      1388.67      1411.77      1423.17
           1482.28      1491.21      1496.18      1498.88      1516.31
        1530.5      1703.43      3032.24      3037.1      3058.93
           3096.51      3103.21      3106.78      3130.07      3145.06
        3162.77      3167.48
     !187.62      197.45      253.39!
    ZeroEnergy[kcal/mol]      23.6
    ElectronicLevels[1/cm]    1
        0  2
    End
```

```
    Tunneling                Eckart
    ImaginaryFrequency[1/cm]    1725.1957
    WellDepth[kcal/mol]    20.9
    WellDepth[kcal/mol]    22.7
    End
End
!------------------------------------------------------------
!------------------------------------------------------------
!------------------------------------------------------------
Bimolecular         P4    # C=CC_E11-71  +  COC[O]_E11-71
    Fragment  C=CC_E11-71
        RRHO
    Geometry[angstrom]        9
     C         -0.0036173945     -0.0000157516     0.0051672399
     C         0.0040011912     -0.000049678     1.5008982519
     H         0.9797799476     -0.000127773     1.9768349341
     C         -1.079110104     0.0000087324     2.2615933185
     H         0.5151885421     0.876581567     -0.3868008481
     H         -1.0214504945     0.000056787     -0.3822056223
     H         0.5150788396     -0.8766602561     -0.3868403603
     H         -1.0141839757     -0.0000194025     3.3409791477
     H         -2.0713139546     0.0000868059     1.8258205252
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                    5 6 7
        Axis                     1 2
        Symmetry                  3
        Potential[kcal/mol]       2
         0.0  2.01
    End
    Frequencies[1/cm]    20
           430.51      596.0      938.41      947.42      967.29
   1036.32      1079.5      1195.46      1330.57
           1407.13      1454.25      1484.54      1497.22      1742.34
        3056.62      3111.88      3138.7      3159.03      3168.59
           3248.77
     !206.03!
    ZeroEnergy[kcal/mol]      0
    ElectronicLevels[1/cm]    1
        0  1
    End
    Fragment  COC[O]_E11-71
        RRHO
    Geometry[angstrom]        9
     O         0.0382289661     0.0593540051     0.0002215994
     C         0.0163591446     -0.0053691118     1.3426864214
```

```
     O         1.2470216178     0.0291171317     1.9848552562
     C         2.0739168416     -1.0665836523     1.6497473096
     H         -0.5784125533     0.8290686934     1.7395124689
     H         -0.5325957919     -0.941059928     1.5830535233
     H         1.5946834284     -2.0122857372     1.9263423625
     H         2.2976209058     -1.0792041752     0.5818999592
     H         2.9967462355     -0.9565845871     2.2118752179
    Core RigidRotor
        SymmetryFactor    1.0
    End
    Rotor        Hindered
        Group                     1 5 6
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.2   0.04   3.53   2.25   3.54
    End
    Rotor        Hindered
        Group                     2
        Axis                      3 4
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0   1.7
    End
    Frequencies[1/cm]    19
           361.51       613.33       797.04       976.27       1074.59
    1151.14       1189.22       1223.98
           1273.03       1355.26       1400.31       1484.97       1497.95
        1521.41       2879.7       3012.82       3026.97       3103.17
           3167.4
     !132.69       204.03!
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]    1
        0  2
    End
    GroundEnergy[kcal/mol]          21.4
End
!-------------------------------------------------------------
Barrier         B8   W3   P4    # TS_COC[O]_C=CC_E14-83_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0725627534     -0.2581512192     0.0902507739
     C         -0.004478305     -0.1046136918     1.5675602085
     H         0.9369868047     -0.08397223     2.1045997473
     C         -1.1597095345     -0.0848849787     2.2681203162
     O         -1.5122260274     -2.1320054686     2.4598551948
     C         -0.395714855     -2.7453021389     2.931075682
```

```
     O         0.6055726696     -2.9845156664     1.9745371002
     C         0.1575895909     -3.786013023     0.9043121795
     H         0.5974458395     0.5853620619     -0.3637312515
     H         -0.9193449637     -0.3336968983     -0.3523967407
     H         0.6392456317     -1.1576303042     -0.1589793878
     H         -1.1612002724     0.0860607652     3.3348071685
     H         -2.1110693186     -0.0150305425     1.7606018363
     H         0.0975806778     -2.1870603892     3.7332468081
     H         -0.7517981394     -3.7097289463     3.3405844154
     H         -0.1873267399     -4.76105631     1.2663812613
     H         -0.6595113597     -3.3056336616     0.3627094859
     H         1.0025332315     -3.9349736194     0.2358972602
  Core RigidRotor
      SymmetryFactor    1.0
  End
  Rotor        Hindered
      Group                     9 10 11
      Axis                      1 2
      Symmetry                   3
      Potential[kcal/mol]        2
       0.0  1.6
  End
  Rotor        Hindered
      Group                     2 12 13
      Axis                      4 5
      Symmetry                   1
      Potential[kcal/mol]        4
       0.0  3.24  0.03  1.4
  End
  Rotor        Hindered
      Group                     4
      Axis                      5 6
      Symmetry                   1
      Potential[kcal/mol]        6
       0.0  1.37  0.29  12.2  2.37  11.59
  End
  Rotor        Hindered
      Group                     5 14 15
      Axis                      6 7
      Symmetry                   1
      Potential[kcal/mol]        6
       0.0  6.83  4.14  5.26  2.17  4.03
  End
  Rotor        Hindered
      Group                     6
      Axis                      7 8
      Symmetry                   3
      Potential[kcal/mol]        2
```

```
         0.0  1.82
    End
    Frequencies[1/cm]    41
           195.38       247.19       297.27       407.14       432.05
           620.12       685.71       935.49       944.71       949.02
   978.28       997.42       1042.04       1050.82       1128.54
           1179.63       1187.05       1201.42       1218.09       1293.17
        1311.07       1391.99       1403.1       1445.27       1454.19
           1473.88       1482.5       1493.58       1494.6       1522.73
      1624.19       2923.75       3023.66       3049.11       3052.2
           3094.78       3106.78       3143.08       3150.74       3177.37
        3182.68       3269.64
     !59.11       85.07       116.46       134.26       177.17!
    ZeroEnergy[kcal/mol]       24.1
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    412.3313
    WellDepth[kcal/mol]    21.4
    WellDepth[kcal/mol]    2.7
    End
End
!-----------------------------------------------------
!-------------------------WELL 4 to Products ----------
!-----------------------------------------------------
Barrier         B9   W4   W5    # W_CCCO[CH]OC_E-2-17_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         -0.0254824206    0.0123942831    0.0093596899
     H         -0.0868588063    0.0771749799    1.0924065767
     H         0.9924278485    -0.0582674723    -0.358580221
     C         -1.0463476798    -0.8867014661    -0.6400477549
     C         -2.4292274841    -0.2386447978    -0.6114283095
     O         -2.4061370088    1.0055278987    -1.3056990103
     C         -1.5955434085    1.9438855892    -0.6970142396
     O         -2.0489284834    2.3804371351    0.5307910026
     C         -3.2356711965    3.1530424952    0.4486475843
     H         -0.7790398162    -1.0774465184    -1.6802990193
     H         -1.1148283618    -1.8570988297    -0.1376013223
     H         -3.1657975786    -0.8532605442    -1.1235548945
     H         -2.7557197503    -0.0789581346    0.420258726
     H         -0.5131515908    1.2348974904    -0.3803830498
     H         -1.4012045532    2.7528503003    -1.4042290067
     H         -3.0730899717    4.0427773736    -0.1668426414
     H         -4.0525945194    2.5694726611    0.020502296
     H         -3.4924204081    3.4562720943    1.4602777565
```

```
    Core RigidRotor
        SymmetryFactor    0.5
    End
    Rotor        Hindered
        Group                     9
        Axis                      8 7
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  4.8  2.16  3.95  0.23  2.21
    End
    Rotor        Hindered
        Group                     16 17 18
        Axis                      9 8
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0  1.67  0.0  1.67  0.0  1.67
    End
    Frequencies[1/cm]    45
           112.89      189.38      299.27      322.25      429.32
   492.97      570.51      636.56
           655.79      826.53      898.98      933.21      949.81
   996.68      1048.87      1085.04      1109.22      1164.68
           1173.49      1183.15      1189.05      1237.55      1248.26
        1302.12      1356.64      1372.09      1410.55      1441.51
           1456.04      1478.5      1481.61      1495.47      1512.14
       1516.7      1577.26      3035.76      3036.49      3057.35
           3083.07      3100.94      3103.68      3116.31      3142.43
        3159.37      3201.04
     !72.4 142.59!
    ZeroEnergy[kcal/mol]      20.1
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    1732.7857
    WellDepth[kcal/mol]    15.5
    WellDepth[kcal/mol]    19.2
    End
End
!------------------------------------------------
!------------------------------------------------
!------------------------------------------------
Bimolecular         P5    # COCO[CH2]_E15-75  +  C=C
    Fragment  COCO[CH2]_E15-75
        RRHO
    Geometry[angstrom]        12
     C        0.0197985211    -0.087165151    0.0620000365
     O        0.01946667    0.0123433083    1.4144452787
```

```
     C         1.3033513113     0.0311999237     1.9991668647
     O         2.0080247069     -1.1421201916     1.7832282701
     C         1.4109833384     -2.2694954831     2.3939239059
     H         -0.9648560036     -0.14532655     -0.3706391162
     H         0.8812797475     -0.5336234028     -0.4138682818
     H         1.8984994652     0.8345471969     1.562446873
     H         1.1266582     0.2015697102     3.0640889162
     H         1.2881378939     -2.1058815072     3.4691277788
     H         0.4358203934     -2.4865939515     1.954487254
     H         2.0783884372     -3.1111023038     2.231721833
   Core RigidRotor
       SymmetryFactor    1.0
   End
   Rotor        Hindered
       Group                    6 7
       Axis                     1 2
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0   4.94   0.3   0.36   0.01   4.58
   End
   Rotor        Hindered
       Group                    1
       Axis                     2 3
       Symmetry                  1
       Potential[kcal/mol]       8
        0.0   4.59   3.83   4.02   3.36   6.06   5.8   6.47
   End
   Rotor        Hindered
       Group                    2 8 9
       Axis                     3 4
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0   6.82   2.13   4.68   3.81   4.95
   End
   Rotor        Hindered
       Group                    3
       Axis                     4 5
       Symmetry                  1
       Potential[kcal/mol]       6
        0.0   1.67   0.0   1.67   0.0   1.67
   End
   Frequencies[1/cm]    26
          339.67      453.44      580.33      624.75      980.8
  998.64
          1110.72      1182.67      1195.46      1222.42      1257.14
       1279.35      1349.19      1441.0      1475.73      1496.72
          1500.6      1515.37      1524.93      3033.95      3057.42
      3102.22      3117.1      3163.57      3164.38      3303.62
```

```
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
        3175.83 3235.53 3261.92
1413    !!torsions
1414   ZeroEnergy[kcal/mol]      0
1415   ElectronicLevels[1/cm]      1
1416     0 1
1417    End
1418      GroundEnergy[kcal/mol]            24.7
1419 End
1420 Barrier         B10   W4   P5     # TS_C=C_COCO[CH2]_E23-71_m062x.log
1421     Variational
1422         RRHO
1423     Geometry[angstrom]         18
1424      C         -0.0084563854    0.0113946248    0.0102818023
1425      H         -0.0028056647    0.0318809306    1.0913826245
1426      H         0.9526089303    -0.0006686567    -0.4853111238
1427      C         -1.1640689608    0.071901169    -0.6889430574
1428      C         -1.7314054695    2.1976802129    -1.1008864362
1429      O         -2.7983603998    2.2570628036    -1.9499085498
1430      C         -4.0588434007    2.1982948195    -1.3295445703
1431      O         -4.3393648937    0.9557460081    -0.7810004328
1432      C         -4.5109616643    -0.0557125816    -1.7552873847
1433      H         -1.1621009229    -0.0867267465    -1.760595625
1434      H         -2.1183065145    -0.0506823553    -0.1935184875
1435      H         -1.9148757423    2.5321775922    -0.083874255
1436      H         -0.814185569    2.5124546371    -1.5770488189
1437      H         -4.1020446823    2.91490141    -0.5066844902
1438      H         -4.7768709737    2.4554489574    -2.1126865255
1439      H         -5.3327313879    0.1987353406    -2.4317163555
```

```
 H         -3.6003188028    -0.2007752829    -2.3387756751
 H         -4.7510955195    -0.9732488777    -1.2253256447
Core RigidRotor
    SymmetryFactor    1.0
End
Rotor        Hindered
    Group                    6 12 13
    Axis                     5 4
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  1.36  1.01  2.07  0.31  1.62
End
Rotor        Hindered
    Group                    7
    Axis                     6 5
    Symmetry                  1
    Potential[kcal/mol]       8
     0.0  1.3  0.87  2.27  2.17  2.76  2.47  3.8
End
Rotor        Hindered
    Group                    8 14 15
    Axis                     7 6
    Symmetry                  1
    Potential[kcal/mol]       7
     0.0  8.76  2.7  2.9  2.7  5.81  3.55
End
Rotor        Hindered
    Group                    9
    Axis                     8 7
    Symmetry                  1
    Potential[kcal/mol]       6
     0.0  10.44  3.0  4.16  3.14  4.23
End
Rotor        Hindered
    Group                    16 17 18
    Axis                     9 8
    Symmetry                  3
    Potential[kcal/mol]       2
     0.0  1.45
End
Frequencies[1/cm]    42
       214.81       290.15       340.53       393.53       474.57
       566.07       641.15       824.77       847.1       889.25
    978.43       997.95       1004.84       1039.94       1107.06
       1185.76       1192.58       1209.64       1239.75       1260.17
       1272.43       1309.75       1353.67       1442.22       1468.34
       1475.59       1493.92       1498.45       1516.06       1523.94
       1591.9       3037.01       3051.25       3106.83       3107.63
```

```
            3109.99       3149.56       3165.46       3166.69       3231.58
         3250.33       3259.37
      !65.17       84.75       97.02       132.81       141.21!
    ZeroEnergy[kcal/mol]       32.2
    ElectronicLevels[1/cm]    1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]    493.5002
    WellDepth[kcal/mol]    27.6
    WellDepth[kcal/mol]    7.5
    End
End
!------------------------------------------------
!-------------------------WELL 5 to Products ------
!------------------------------------------------
Bimolecular         P6    # Bi_O=COC_E2-75  +  CC[CH2]
    Fragment  Bi_O=COC_E2-75
        RRHO
    Geometry[angstrom]        8
     O         0.0418924661    0.0001246289    0.0116965965
     C         0.0167993753    0.0000166154    1.2063812612
     O         1.0865652314    -0.0000631766    1.9997896845
     C         2.3431972004    -0.0000105584    1.318127389
     H         -0.8942447797    -0.0000317404    1.8147181938
     H         3.1023784274    -0.0000881096    2.0924532518
     H         2.4312544895    -0.8854855669    0.6918659719
     H         2.4312687749    0.885578481    0.6920292162
    Core RigidRotor
        SymmetryFactor            1.0
    End
    Rotor         Hindered
        Group                      1 5
        Axis                       2 3
        Symmetry                   1
        Potential[kcal/mol]        4
         0.0  13.48  5.51  13.48
    End
    Rotor         Hindered
        Group                      6 7 8
        Axis                       4 3
        Symmetry                   3
        Potential[kcal/mol]        2
         0.0  1.12
    End
    Frequencies[1/cm]    16
       319.89       792.46       984.42       1064.87       1192.28
   1207.29       1273.14       1410.45
```

```
          1481.65      1497.47      1509.45      1856.01      3083.57
       3088.44      3158.89      3195.05
    !155.75 343.39!
   ZeroEnergy[kcal/mol]      0
   ElectronicLevels[1/cm]    1
       0  1
   End
   Fragment  CC[CH2]
       RRHO
   Geometry[angstrom]        10
    C        0.0039898156    -0.000284903    0.0092188719
    C        -0.008868217    0.0003344799    1.5351340559
    C        1.3565231458    0.0092275888    2.1204915126
    H        0.5041293962    0.8902436397    -0.3714390075
    H        -1.0058550385    -0.0252075459    -0.3981664794
    H        0.5415835145    -0.8709328996    -0.3682851152
    H        -0.5754642035    0.8592966151    1.9045280897
    H        -0.5627597195    -0.8813306258    1.8870425312
    H        1.5205327058    0.2907319782    3.1494417973
    H        2.1839314077    -0.4238248045    1.576714433
   Core RigidRotor
       SymmetryFactor            1.0
   End
   Rotor        Hindered
       Group                     4 5 6
       Axis                      1 2
       Symmetry                   3
       Potential[kcal/mol]        2
        0.0  3.01
   End
   Rotor        Hindered
       Group                     1 7 8
       Axis                      2 3
       Symmetry                   1
       Potential[kcal/mol]        12
        0.0  0.05  0.01  0.28  0.26  0.28  0.0  0.05  0.01  0.28  0.26
    0.28
   End
   Frequencies[1/cm]    22
          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
    !93.61      253.67!
   ZeroEnergy[kcal/mol]      0
   ElectronicLevels[1/cm]    1
       0  2
```

```
    End
    GroundEnergy[kcal/mol]          -9.3
End
Barrier         B11   W5   P6    # TS_CC[CH2]_O=COC_E10-62_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0284366395     -0.0170060218     -0.0169333001
     C         -0.0219067159     0.0303409796     1.505303022
     C         1.3343043082     0.0117089011     2.1180473682
     O         1.9650016396     -1.686966595     1.8522142967
     C         1.1294480776     -2.6245123574     1.8753301407
     H         0.5226080268     -2.9216718448     1.0251745569
     O         0.7027606488     -3.1987965225     3.020877944
     C         1.5069796255     -2.9532032456     4.1654627765
     H         0.5241095357     0.8712515011     -0.4102611894
     H         -0.9696336878     -0.0672939418     -0.44949597
     H         0.5952533376     -0.8853391171     -0.3533023182
     H         -0.5687307603     0.9169713444     1.8399050458
     H         -0.5911746634     -0.825652915     1.8896373876
     H         2.1188139482     0.5425963857     1.5947417134
     H         1.3893963616     0.0966805284     3.1962521149
     H         2.5480689189     -3.2060795019     3.9636416677
     H         1.451491679     -1.9085276175     4.4692641653
     H         1.112290057     -3.5857189669     4.9546386048
    Core RigidRotor
        SymmetryFactor            1.0
    End
    Rotor         Hindered
        Group                     9 10 11
        Axis                      1 2
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   2.74   0.0   2.74   0.0   2.74
    End
    Rotor         Hindered
        Group                     1 12 13
        Axis                      2 3
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   5.51   1.57   3.37   1.87   3.29
    End
    Rotor         Hindered
        Group                     2 14 15
        Axis                      3 4
        Symmetry                   1
        Potential[kcal/mol]        6
         0.0   3.14   2.19   3.81   1.87   2.5
```

```
    End
    Rotor         Hindered
        Group                      8
        Axis                       7 5
        Symmetry                    1
        Potential[kcal/mol]         4
         0.0   7.5   1.69   6.68
    End
    Rotor         Hindered
        Group                      16 17 18
        Axis                       8 7
        Symmetry                    3
        Potential[kcal/mol]         2
         0.0   0.94
    End
    Frequencies[1/cm]     42
           140.36       294.02       331.58       382.31       461.13
           703.89       708.9       760.43       810.97       910.03
   943.89       971.51       987.54       1090.0       1115.96
           1183.81       1194.46       1197.63       1223.9       1283.32
       1349.36       1375.37       1416.7       1448.81       1475.87
           1481.69       1496.73       1500.62       1508.53       1512.82
        1519.23       3017.68       3056.14       3063.97       3066.28
           3130.82       3133.59       3142.46       3145.57       3165.03
        3175.56       3234.18
     !38.57       96.58       127.86       181.41       214.12!
    ZeroEnergy[kcal/mol]       13.2
    ElectronicLevels[1/cm]     1
        0   2
    End
    Tunneling                  Eckart
    ImaginaryFrequency[1/cm]     776.8227
    WellDepth[kcal/mol]          12.3
    WellDepth[kcal/mol]          22.5
    End
End
!---------------------------------------------------------------
!---------------------------------------------------------------
!---------------------------------------------------------------
Bimolecular         P7     # Bi_CCCOC=O_E4-4  +  [CH3]
    Fragment  Bi_CCCOC=O_E4-4
        RRHO
    Geometry[angstrom]         14
     C         0.0240964182     0.0095221715     0.0177319524
     C         -0.0030425293     -0.0039903355     1.5406932512
     C         1.3810526487     0.0075489273     2.1477852797
     O         2.0145018277     1.2430203364     1.7720768004
     C         3.2624172943     1.4051392265     2.20525629
```

```
     O         3.8765204621    0.6198108646    2.8648746235
     H         0.5240548293    0.9039028938    -0.3506417673
     H         -0.9838521124    -0.009648659    -0.3935102324
     H         0.5610273437    -0.858905151    -0.3666945599
     H         -0.5595170156    0.8555979426    1.9180905613
     H         -0.514632694    -0.8978448249    1.9021761279
     H         1.3548784005    -0.0512964009    3.2356710446
     H         1.9904306763    -0.8198792418    1.7803288283
     H         3.6490536234    2.3730992117    1.8666815551
   Core RigidRotor
       SymmetryFactor            1.0
   End
   Rotor        Hindered
       Group                     7 8 9
       Axis                      1 2
       Symmetry                   3
       Potential[kcal/mol]        2
        0.0  2.75
   End
   Rotor        Hindered
       Group                     1 10 11
       Axis                      2 3
       Symmetry                   1
       Potential[kcal/mol]        6
        0.0  3.6  0.28  3.6  0.03  4.82
   End
   Rotor        Hindered
       Group                     2 12 13
       Axis                      3 4
       Symmetry                   1
       Potential[kcal/mol]        8
        0.0  0.92  0.45  3.63  3.5  7.41  0.15  1.16
   End
   Rotor        Hindered
       Group                     3
       Axis                      4 5
       Symmetry                   1
       Potential[kcal/mol]        4
        0.0  12.84  4.65  12.83
   End
   Frequencies[1/cm]    32
          261.94      351.0      467.28      768.7      797.8
  912.78
          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
```

```
            3076.24       3084.0       3107.9       3126.48       3138.05
      3150.08
     !55.58       128.77       199.8      299.37 !
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  1
    End
    Fragment  [CH3]
        RRHO
    Geometry[angstrom]         4
     C         0.     0.     0.
     H         0.     0.     1.0765291468
     H         0.9323015891     0.     -0.5382645734
     H        -0.9323015891     0.     -0.5382645734
    Core RigidRotor
        SymmetryFactor           6.0
    End
    Frequencies[1/cm]     6
           436.03       1412.64       1412.73       3144.41       3323.11
       3323.14
     !   !
    ZeroEnergy[kcal/mol]       0
    ElectronicLevels[1/cm]     1
        0  2
    End
    GroundEnergy[kcal/mol]          -12.5
End
Barrier         B12  W5  P7     # TS_CCCOC=O_[CH3]_E11-74_m062x.log
    Variational
        RRHO
    Geometry[angstrom]         18
     C         0.0179906848     -0.0173519364     -0.0044379667
     C         -0.0076605888     0.0184238393     1.5182617704
     C         1.3803600465     0.0083999702     2.1190305173
     O         2.0454184047     1.2033066436     1.7008809262
     C         3.2906740238     1.3854777637     2.1794091652
     H         3.6942802614     2.3531674115     1.8937185402
     O         3.9866774718     0.4462998928     2.6316656258
     C         4.8265576836     -0.6087582945     1.3980626923
     H         0.5455409505     0.8494348829     -0.3991445919
     H         -0.9899181554     -0.0197959385     -0.4166469006
     H         0.5288099463     -0.9136288791     -0.3606662728
     H         -0.5340461001     0.9083705272     1.8671437259
     H         -0.5471792927     -0.8466003159     1.9084887306
     H         1.3521673638     -0.0133753658     3.2104808819
     H         1.9451036601     -0.8627271422     1.780334797
     H         5.7211910636     -0.0432680373     1.180758965
     H         4.9766989419     -1.5185186733     1.9601231634
```

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 H        4.1098656247    -0.6745173682    0.5894812211
Core RigidRotor
    SymmetryFactor            1.0
End
Rotor        Hindered
    Group                     9 10 11
    Axis                      1 2
    Symmetry                   3
    Potential[kcal/mol]        2
     0.0  2.76
End
Rotor        Hindered
    Group                     1 12 13
    Axis                      2 3
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  3.66  0.35  3.68  0.06  4.92
End
Rotor        Hindered
    Group                     2 14 15
    Axis                      3 4
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  4.13  0.9  5.81  0.18  1.22
End
Rotor        Hindered
    Group                     3
    Axis                      4 5
    Symmetry                   1
    Potential[kcal/mol]        4
     0.0  6.93  2.16  7.75
End
Rotor        Hindered
    Group                     16 17 18
    Axis                      8 7
    Symmetry                   1
    Potential[kcal/mol]        6
     0.0  0.39  0.0  0.39  -0.0  0.39
End
Frequencies[1/cm]    42
        188.33       259.51       313.59       363.53       467.44
        710.79       734.52       765.37       769.89       822.99
906.39       921.7       958.47       1067.3       1089.94
        1133.56       1178.3       1203.46       1282.85       1309.71
    1353.97       1377.35       1412.38       1423.05       1443.38
        1447.1       1484.06       1487.81       1500.39       1512.34
    1523.74       3058.14       3063.8       3069.78       3099.28
```

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            3109.87       3110.85       3134.64       3149.96       3153.33
         3257.13       3274.57
      !29.42       59.39       101.34       138.09       197.6!
    ZeroEnergy[kcal/mol]       14.5
    ElectronicLevels[1/cm]     1
        0  2
    End
    Tunneling                 Eckart
    ImaginaryFrequency[1/cm]     880.2786
    WellDepth[kcal/mol]          13.6
    WellDepth[kcal/mol]          27.0
    End
End
End
```