ABSTRACT

THERMOCHEMISTRY OF FLUORINATED ALDEHYDES AND CORRESPONDING RADICALS;THERMOCHEMISTRY AND KINETICS OF DIETHYL ETHER AND ETHYL OXIRANE RELATIVE TO REACTIONS UNDER ATMOSPHERIC AND COMBUSTION CONDITIONS

by
Douglas Lee Purnell, Jr.

Fundamental thermochemical properties including enthalpies ($\Delta H^{\circ}_{f\,298}$), entropies ($S^{\circ}(T)$), heat capacities ($C_p(T)$), and bond dissociation energies (BDEs) for several common and complex hydrocarbon fuel species are determined using computational chemical methods. $\Delta H^{\circ}f\ 298$ values are calculated using isodesmic reactions with the CBS-APNO, CBS-4M, CBS-QB3, G2, G3, G4, Weizmann-1 (W1U) and M06-2X, ωB97X, B3-LYP with basis set 6-31G+ (d,p) and 6-31G++(d,p) calculation methods. Structures, moments of inertia, vibrational frequencies, and internal rotor potentials are calculated for contributions to entropies and heat capacities. Kinetic rate parameters are calculated for hydrogen abstraction and chemical activation reactions.

The recommended ideal gas phase ΔH°f298 (kcal mole^{-1}) values calculated for several normal hydrocarbons and fluorinated species including corresponding radicals from loss of hydrogen atoms show strong comparison to available literature values.

Ethers C—H BDEs in the primary position in comparison to the secondary position increase by 3-8 kcal mole^{-1} for aliphatic chains. Cyclic ethers posses

Entropies (S*298 in cal/mole K) are estimated using B3-LYP methodology with basis sets 6-31+G(d,p) and 6-31++G(d,p) computed frequencies and geometries. Rotational barriers are determined and hindered internal rotational contributions for

S*298K and Cp(T) are calculated using the rigid rotor harmonic oscillator approximation, with direct integration over energy levels of intramolecular rotation potential energy curve.

Thermochemical properties for the fluorinated carbon groups CO/C/F, C/CO/F3, C/CO/F/H2, C/C/CO/F/H, C/C/CO/F2, and C/C/CO/F/H are investigated. Previously published enthalpies for fluoroacetaldehyde, fluoroacetaldehyde fluoride, difluoroacetaldehyde, difluoroacetaldehyde fluoride, trifluoroacetaldehyde and trifluoroacetaldehyde fluoride that were previously determined via isodesmic reactions schemes are revised using updated reference species values.

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by
Douglas Lee Purnell, Jr.

A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Chemistry

Department of Chemistry and Environmental Science
December 2017

APPROVAL PAGE

THERMOCHEMISTRY AND KINETICS OF DIETHYL ETHER AND ETHYL OXIRANE RELATIVE TO REACTIONS UNDER ATMOSPHERIC AND COMBUSTION CONDITION; THERMOCHEMISTRY OF FLUORINATED ALDEHYDES AND CORRESPONDING RADICALS

Douglas Lee Purnell, Jr.

Dr. Joseph W. Bozzelli, Dissertation Advisor
Professor of Chemical Engineering, Chemistry and Environmental Science
NJIT

Dr. Tamara Gund, Committee Member
Professor of Chemistry and Environmental Science
NJIT

Dr. Alexei Khalizov, Committee Member
Assistant Professor of Chemistry and Environmental Science
NJIT

Dr. Mengyan Li, Committee Member
Assistant Professor of Chemistry and Environmental Science
NJIT

Dr. Gennady Gor, Committee Member
Assistant Professor of Chemical, Biological and Pharmaceutical Engineering
NJIT

BIOGRAPHICAL SKETCH

Author: Douglas Lee Purnell, Jr.

Degree: Doctor of Philosophy in Chemistry

Date: August 2017

Undergraduate Education:

- Doctor of Philosophy in Chemistry
  New Jersey Institute of Technology, Newark, NJ, 2017

- Bachelor of Science in Chemistry
  Delaware State University, Dover, DE, 2010

Major: Chemistry

Presentations and Publications:

Purnell, Jr., Douglas Lee and Bozzelli, Bozzelli W. "Thermochemistry and Kinetic Parameters for Diethyl Ether (CCOCC) and Diethyl Ether-1yl Radicals (C•COCC and CC•OCC) Reactions with Oxygen $^3O_2$: Atmospheric and Lower Temperature Oxidation Reactions." *32nd Regional Meeting on Kinetics and Dynamics.* Hartford, CT, 25 January 2014

Purnell, Jr., Douglas Lee and Bozzelli, Bozzelli W. "Thermochemistry and Kinetic Parameters for Diethyl Ether (CCOCC) and Diethyl Ether-1yl Radicals (C•COCC and CC•OCC) Reactions with Oxygen $^3O_2$: Atmospheric and Lower Temperature Oxidation Reactions." *Philly AMP Research Symposium.* Philadelphia, PA, 16 November 2013

This thesis is dedicated to my loving parents
Jessilene and David Corbett

Words cannot explain how I feel about you two,
I am truly blessed and appreciative to have such encouraging figures in my life.
For your continuous love and support of my dreams, I will always love you

ACKNOWLEDGMENT

I wish to express his sincere gratitude to my advisor, Professor Joseph W. Bozzelli, for his guidance, friendship, financial and moral support throughout this research.

Special thanks to Professors Tamara Gund, Alexei Khalizov, Mengyan Li and Gennady Gor for serving as members of the committee.

I am also is grateful to the Louis Stokes AMP program for the initial funding of this research, through the National Science Foundation, and Dr. Kevin Belfield, Dr. Laurence Howell and Mrs. Genti Price for their support during the duration of this research.

The timely help and suggestions from the Bozzelli Group members, including: Suarwee Snitsiriwat, Suriykit Yomme, Heng Wang and Francisco Guzman are highly appreciated.

Finally, a special a thank you to my family and friends for their continuous support and motivation during this process.

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NOMENCLATURE

Abbreviations are utilized in this thesis as illustrated below:

- C(=O) represents an carbonyl group,
- CO represents an aldehyde group in group additivity
- (C) represents a methyl substituent on the preceding carbon atom,
- TVR denotes translation, vibration and external rotation,
- IR denotes internal rotation,
- Hydrogen atoms are used to complete the valence and serve as an abbreviation for the chemical formula,
- J represents a radical on the molecule,
- Hydrogen atoms are used to complete the valence and serve as an abbreviation for the chemical formula,
- BDE represents bond dissociation energy,
- Ts represents transition state,
- Y represents a cyclic group,
- = (equal sign) represents a double bond between to atoms,
- Q represents OOH peroxy group.
- # represents a triple bond.

CHAPTER 1

INTRODUCTION

The increased atmospheric concentrations of halogenated organic compounds are partially responsible for the change in global climate[1, 2]. With concentrations of haloalkanes being nearly a millionth of carbon dioxide in the atmosphere, these compounds have a 13% share in the radiative forcing. Radiative forcing is a large contributing factor and can be explained by considering their higher global warming potentials; they are typically a couple of thousand times of the reference CO_2[3].

In the evaluation of climate change, a focus has been placed on fluorinated hydrocarbons. Fluorinated hydrocarbons are present in the atmosphere, hydrosphere, and lithosphere as a result of the past use of solvents and propellants; in addition to the current wide spread use of refrigerants, heat exchange fluids and polymers. Other uses include lubricants, blowing and sterilizing agents, coatings, anaesthetics, and agents in the preparation of semiconductors. Fluorinated hydrocarbons have been regarded as the replacement of greenhouse gases like chlorofluorocarbons, because of the nonexistent or less adverse effects on global warming from the greenhouse gas effect in the troposphere layer [4].

Quantum chemical calculations on small molecules can result in thermochemical values with a low degree in uncertainties, often outperforming experimental results [1, 5-8]. The precise knowledge of the thermodynamic and kinetic properties of the atmospheric reactions as well as the physical parameters of the corresponding species is required for chemistry-climate models. Databases such as NIST-JANAF[9], CODATA[10], ATcT[11], JPL[12] and Burcat's Third Millennium Thermodynamic Database[13], contain the relevant physicochemical parameters, where many discrepancies exist and contain considerably large error bars. Such data uncertainty is mostly due to the fact that the chemistry of the troposphere and stratosphere is dominated by free radical reactions and experimental determination of physical and chemical parameters of radicals and radical reaction is still challenging[3].

One of the studies presented displays calculated standard enthalpy of formation for a series of fluoro and multifluoro acetaldehydes ($C_2H_xOF_{4-x}$) and propanals ($C_3H_xOF_{6-x}$) using computational chemistry and isodesmic work reactions. This study will determine the ideal gas thermodynamic properties, with the purpose for these values being to understand reactions, warming potentials, lifetime, etc. The final portion of the fluorinated aldehyde study is to determine group additivity values for groups for CO/C/F, C/CO/F3, C/CO/F/H2, C/C/CO/F/H, C/C/CO/F2, C/C/CO/F/H and interaction group terms, in addition to verifying values from previous works based on calculated values.

Fuel and energy sources are a major component of the global community, which will certainly continue into the future, so their continual monitoring and analysis is essential. As stated in the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, "The observed widespread warming of the atmosphere and ocean, together with ice-mass loss, support the conclusion that it is extremely unlikely that global climate change of the past 50 years can be explained without external forcing and very likely that it is not due to known natural causes alone[14]." There are several research evaluations that have shown, with the continued growth of the world population, that within a few decades the current petroleum industry and supply chain will not be able to meet the projected demands[15,16]. Another issue arises from the storage of ethers under improper conditions and exposure to oxygen in air for an extended period of time is known to result in formation of peroxide bearing intermediates. This is considered to be a primary factor in laboratory accidents resulting from the stored ethers[17-19].

Reactions of hydrocarbon radicals substituted as saturated with oxygen have received more investigational study in recent years, due to the advancement of engine designs and large effort over the past years to focus our attention on cleaner air and atmospheric pollution. As engines are developed with more advanced designs, it is required that there be more detailed knowledge of auto ignition chemistry for predictive modeling as a result of vast concentrations of oxygenated compounds such as ethers present in the atmosphere, where they are culminated from solvents, fuel additives or biodiesel fuels[20, 21].

With the development of bio-fuels, modeling of ignition chemistry of a wide range of substituted hydrocarbons[22]. Bio-fuels are not limited to the prediction of alcohols and fatty acid esters, there has been an increased aim at designing biochemical pathways for efficient combustible organic molecules[14,23], many with nearly unexplored ignition or combustion chemistry.

Auzmendi Muria *et al.*[24] have noted that the carbon radical adjacent to the ether, in cyclic ethers, has a stronger bond to molecular oxygen ($^3O_2$) forming peroxy radicals, then more distant carbons in the ethers and also stronger than corresponding alkyl carbon radical $^3O_2$ bonds. This stronger bonding is a result of interaction of the two oxygen bonded to the carbon.

The structural features such as, alpha activated hydrogen atom on the primary and secondary carbon causes ethers to readily react in the process of autoxidation[6], and the radical and self-propagating process have the ability to generate a large array of peroxide bearing species. The carbon – hydrogen bonds and the carbon – carbon bonds on carbons adjacent to the ether carbon are several kcal/mol-1 weaker than corresponding carbon – hydrogen or carbon – carbon bonds on alkanes resulting from the radical resonance with the ether oxygen.

The oxidation chemistry of branched ethers has been compared and suggested to have similarities in comparison to the more well-known alkanes[25-28]. There are detailed mechanistic studies in both dimethyl ether[29] as well as diethyl ether[30]. These studies show that the ether radicals can undergo beta scission reactions, intramolecular isomerization (hydrogen atom transfers) or undergo reaction with can travel in a path of β-scission or isomerization or association with $^3O_2$ to form a peroxy radical[29, 30]. The peroxy radical is formed with the added energy of the R-OO bond and this initially energized peroxy radical can undergo reactions before stabilization, where these reactions play a central role in further oxidation reactions of hydrocarbons as well as ethers.

With a number of experimental and theoretical studies performed on the formation of cyclic ethers under ambient conditions, in addition to early stages of combustion[31-34], the data remains minimal. Of studies performed, Baldwin *et al.*[35] has been noted to one of the earliest of such reactions, where the formation of molecular oxirane from an ethyl radicals with oxygen was observed. Daqaut *et al.*[32,33] and Yakyaoui *et al.*[34] have also reported results showing the formation of cyclic ethers in significant concentrations from the oxidation of hydrocarbons over a low to moderate temperature for combustion chemistry. There have been computational studies performed on the formation of three to five membered cyclic ethers from hydroxyl radicals by Wijaya *et al*.[36] and Zadar *et al.*[22].

In the process utilized by Wijaya and Zador, hydrocarbon radicals react with oxygen forming a peroxyl radical. This allows the hydrocarbon to undergo hydrogen transfer, forming an alkyl radical. The radical site then attacks the oxygen atom located on the peroxy group, due to the weak bond energy associated with the RO-OH bound resulting in the formation of a cyclic ether and a hydroxyl radical.

Another focus will be aimed at ethyl oxirane, radicals and many other species that can be formed under oxidation and decomposition reactions to determine the fate of the species. Thermochemical properties of each species in the study will be determined, with bond dissociation energies, activation energies and dissociation and oxidation kinetics. Data from works similar to the ethyl oxirane system will also be evaluated.

DEE may play a role in the formation of photochemical aerosols or smog[37, 38]. DEE has the ability to form explosive peroxides[39-43], and is known to form unstable peroxides during distillation, evaporation and concentration processes. DEE molecule will be the focal point of another study with a target on secondary carbon radical reactions with molecular oxygen. Diethyl-ether there is more limited data on mechanistic studies on the oxidation kinetics, than there is for the more widely used dimethyl ether diesel additive. The diethyl ether has been widely studied from an experimental as well as the theoretical perspectives[29, 44-49] with specific studies on combustion[29], pyrolysis[50], or atmospheric chemistry[51, 52].

This study illustrates favorable thermodynamics applied in ethers proposed by a study performed by Crounse *et al.*[53]. Following Crounse *et al.* study on the atmospheric oxidation of 3-pentanone, a set of consecutive reactions starting with radical site formation via OH abstraction, where the H atom is removed from a resonantly stabilized C—H bond adjacent to the carbonyl group. The C—H bond dissociation energy is lower than a conventional secondary bond by 5 kcal mol^{-1} due to the resonance of the carbon radical site with the carbonyl group. This work suggests the oxidation of diethyl ether in the atmospheric conditions will undergo the reaction set below:

$$\begin{array}{llcl}
 & \mathrm{CH_3CH{\bullet}OCH_2CH_3 + O_2} & \rightarrow & \mathrm{CH_3CH_2OCH(OO{\bullet})CH_3} \\
 & \mathrm{CH_3CH{\bullet}OCH(OOH)CH_3} & \rightarrow & \mathrm{CH_3CH{\bullet}OCH(OOH)CH_3 + O_2} \\
 & \mathrm{CH_3CH{\bullet}OCH(OOH)CH_3 + O_2} & \rightarrow & \mathrm{CH_3CH(OO{\bullet})OCH(OOH)CH_3} \\
 & \mathrm{CH_3CH(OO{\bullet})OCH(OOH)CH_3} & \rightarrow & \mathrm{[CH_3CH(OOH)OC{\bullet}(OOH)CH_3]^*} \\
 & \mathrm{[CH_3CH(OOH)OC{\bullet}\ (OOH)CH_3]^*} & \rightarrow & \mathrm{CH_3CH(OOH)OC(=O)CH_3 + OH} \\
\hline
\textbf{Overall :} & \mathbf{CH_3CH_2OCH_2H_3 + OH + 2O_2} & \rightarrow & \mathbf{CH_3CH(OOH)OC(=O)CH_3 + OH}
\end{array}$$

(OH regeneration)

It is accepted that ethers undergo the oxidation that is initiated by a hydroxyl radical under atmospheric conditions[50, 54 -56]. DEE in experimental literature of low temperature oxidation is the decomposition of the alkyl radical as shown in a kinetic study done by Waddington *et al.*[56]. This study thoroughly investigates DEE oxidation, where lists of all possible reaction paths were reached through the use of thermochemical data and previous literature[30]. This study is similar to works carried out by S. Di Tommaso *et al.* Data in this study will be directed towards molecules in the gas phase, where Tommaso *et al.* work focuses on molecules in solution. Di Tommaso used Density Function Theory (DFT) to study the process of low temperature oxidation of several ether species such as dimethyl ether, methyl ethyl ether and diethyl ether. From past works performed, DEE was utilized as the focus where a mechanism was created to show different reaction pathways in competition for the fate of DEE in the atmospheric conditions. Where there may be a lack of experimental data available, the purpose of this study is to take a in-depth look of two steps of oxidation in DEE. The focus of this study is mainly the secondary ether radical site, the oxygen adding to this and the intermolecular H transfers of the secondary peroxy radical to new radicals and products to further reaction of the new carbon radical formed.

In recent years, computational chemistry evolved to a stage where the calculation of thermodynamic functions of small molecules can achieve experimental or even higher accuracy. Density function theory and Composite *ab initio* methods in the Gaussian suite program was used to develop thermochemical properties and a group additivity scheme for estimation of larger hydrocarbons values. Computational chemistry methods used for accuracy include CBS-APNO, CBS-4M, CBS-QB3, M062X, ωB97X, B3LYP, G2, G3, G4 and Weizmann-1 (W1U) methodology with the basis set 6-31G+ (d,p) and6-31G++ (d,p).

By using computational methods based on Density Functional Theory and Compostie *ab initio* methodology, accurate thermochemical data are provided in addition to presenting a theoretical investigation that will help identify possible reaction paths at low temperature oxidation.

Results of mechanistic studies of possible reactions involved in ethyl oxirane and diethyl ether processes will be displayed and used to create a kinetic model using Chemkin. A Chemkin reaction mechanism is generated for initial unimolecular reactions and the oxidation of this initial secondary ether radical and the formation of its initial products as well as new hydroperoxide carbon radicals on the ether. The mechanism includes reactions of molecular oxygen to the secondary carbon radical of ethyl oxirane and diethyl ether.

The Chemkin program determines species concentrations at a set temperature, and pressure and initial reaction concentrations versus time. Species profiles are calculated using both forward and reverse reactions, where reverse reactions rate constants are calculated thermodynamics.

CHAPTER 2
COMPUTATIONAL METHODS

2.1 BACKGROUND

Electronic structure theory, based on the laws of motion for microscopic particles from quantum mechanics, is used to determine the energy of a species using different approximations to solve the Schrödinger equation. This energy, with several other calculated properties from statistical mechanics, allows for the determination of key fundamental thermochemical properties, which are imperative due to their influence on reaction mechanisms and in constructing detailed chemical kinetic models.

The Schrödinger equation can be represented as

$$H\Psi = E\Psi \tag{2.1}$$

where H, is the Hamiltonian operator composed of kinetic and potential energy terms; Ψ is the wave function, a set of solutions of the Hamiltonian, describing the positions of the electrons and nuclei; and E is the energy of the system, an eigenvalue of the Eigen function Ψ. The wave function describes the state of the system, which is a function of the particles' coordinates (*x*) and time (*t*), giving the relationship $\Psi = \Psi(x,t)$ for a one-particle, one-dimension system. This is used to define an equation which describes the system and how the wave function changes with time,

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \tag{2.2}$$

where ħ is Planck's constant divided by 2π, *i* is √-1 , *m* is the mass of the particle, and *V(x,t)* is the potential energy of the system. Specific positions of the coordinates cannot be determined with certainty, but the probability density,

$$|\Psi(x,t)|^2$$

can be used to find the probability,

$$|\Psi(x,t)|^2\partial x$$

of locating the particle within a specific region between *x* and *x* + *dx* at a certain time.

A simplifying approximation can be made using a stationary state where a time-independent potential energy exists. Solutions of equation 2.2 can be found which satisfy

$$\Psi(x,t) = f(t)_{\psi}(x) \tag{2.3}$$

where *f(t)* is a function of time and ψ is a function of just position. The system can then exist in a number of fixed energy stationary states where the wave function satisfies

$$\Psi(x,t) = e^{\frac{-iEt}{\hbar}}\psi(x) \tag{2.4}$$

for the one-particle, one-dimensional case, the time-independent Schrödinger equation can then be written as

$$-\frac{\hbar}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \tag{2.5}$$

where the left-hand side of the equation can be rearranged into an operator expression, denoted by brackets, which transforms a function into another function as,

$$\left[\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \tag{2.6}$$

This equation implies that an allowed energy value can be determined from an energy operator operating on the wave function. The Hamiltonian operator $\hat{H}$ is the energy operator representing the total energy from the potential,$\hat{V}$, and kinetic,$\hat{T}$, energy operators as shown below.

$$\hat{H} = T + V = -\frac{\hbar}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x) \tag{2.7}$$

The Hamiltonian can also be written to include *n* particles where each particle, *i*, has mass, *mi*, and coordinates (*xi*,*yi*,*zi*),

$$\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, \dots, z_n) \tag{2.8}$$

where (V)^2 is the Laplacian operator defined as

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i{}^2} + \frac{\partial^2}{\partial y_i{}^2} + \frac{\partial^2}{\partial z_i{}^2} \tag{2.9}$$

The time-independent Schrödinger equation in equation 2.6 can then be written as,

$$\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, \dots, z_n)\right] \psi = E\psi \tag{2.10}$$

where the time-independent wave function incorporates each of the coordinates from the *n* particles as

$$\psi = \psi(x_1 y_1 z_1, \dots, x_n y_n z_n) \tag{2.11}$$

The Born-Oppenheimer approximation can also be applied allowing for the separation of the nuclear and electronic motions. The mass of an electron is negligible compared to the nuclei that electrons appear to be moving through a system of the fix positioned nuclei. Electrons will assume an optimal distribution representing the lowest energy, the ground state, based on the arrangement of the nuclei. This approximation creates two independent problems and reduces the complexity of the solution to the Schrödinger equation. The Hamiltonian operator in equation 2.8 involving interactions of numerous electrons and nuclei can then be represented as

$$\hat{H} = T_N + T_E + V_{NE} + V_{EE} + V_{NN}$$

which includes the kinetic energy operators of the nuclei (T_N) and electrons (T_E) and the potential energy operators of the repulsions between the nuclei (V_{NN}), attractions between the electrons and nuclei (V_{NE}), and the repulsions from the electrons (V_{EE}).

Solving the Schrödinger equation at this point is still a daunting task. For *n* electrons, there are 3*n* degrees of freedom and *n* spin coordinates, resulting in calculating many electronic wave functions while the repulsions from the other electrons are simultaneously considered. Different methods, or levels of theory, utilize approximations affecting both accuracy and computational cost, in addition to time and computer resources. These approximations depend on the calculation method and can be broadly categorized as semi-empirical, *ab initio*, and density functional theory.

The first two calculation types, semi-empirical and *ab initio*, are based on molecular orbital theory, where the lower-energy orbitals are occupied with electrons before the higher-energy orbitals. Semi-empirical methods are the most basic quantum mechanical methods and require minimal computational resources. Approximate solutions to the Schrödinger equation are calculated using a simpler Hamiltonian with parameters fit to experimental data. Higher-level calculations are currently available, but semi-empirical methods are still practical for the analysis of very large species.

The second type of calculation method, *ab initio*, is more resource-demanding and uses mathematical representations of orbitals from linear combinations of basis functions, called a basis set, which constrains electrons into specific orbitals. These approximated orbitals are centered on the nucleus of an atom and range in size. Larger basis sets allow for a more accurate representation of the orbitals by decreasing the restrictions on the electrons, but as a result bring forth computational cost. These calculations do not incorporate empirical parameters and vary in the degrees of treating instantaneous electron-electron interaction, recognized as electron correlation energy. Hartree-Fock (HF) is the simplest *ab initio* method, which calculates a wave function based on an average repulsion between the electrons in place of the instantaneous interaction. This limitation in HF decreases its accuracy but serves as a starting point for other methods. Higher-level methods such as configuration interaction, perturbation theory, and coupled cluster theory, referred to as post-HF, improve on the HF wave function but have higher computational costs to accompany the increase in accuracy.

The final calculation method, density functional theory (DFT), does not calculate molecular wave functions. Basis sets are used to determine the electron probability density, then a functional calculates the electronic energy as well as electron correlation. Hohenberg and Kohn put forth two mathematical theorems which serve as the basis for DFT. The first theorem demonstrates that the ground state electronic energy, $E0$, from the Schrödinger equation is a unique functional of the ground state electron probability density, $\rho0(x, y, z)$, which relies only on three variables. The Hohenberg-Kohn variational theorem then shows that the minimal energy functional corresponds to the true ground state electron density.

The Kohn-Sham (KS) method serves as a blueprint to solve the Hohenberg-Kohn theorem by finding $\rho0$ and then $E0$ from a set of the KS equations, which in theory can determine the exact solution. Approximations are still required through the functional describing the exchange and correlation treatment if the electron interaction and repulsion energies are unknown.

2.2 Density Functional Theory Methods

The steady developments of more efficient and accurate functionals have allowed DFT calculations for chemical properties in a variety of fields. Analyses of larger molecules are possible with DFT, considering its lower calculation time and computational costs, while providing equivalent accuracy compared to other calculation methods. DFT is the primary tool for the analysis of species in this dissertation, while use of *ab initio* calculations is primarily restricted to their use in composite methods.

One of the most widely used DFT methods is B3-LYP which combines the three-parameter Becke exchange functional, B3[57], with the Lee-Yang-Parr correlation functional, LYP[58]. B3-LYP is one of the most frequently used and reliable DFT methods available.[59] Curtiss *et al.*[60] reported that it has the smallest average absolute deviation, 3.11 kcal mol-1, of the seven DFT methods studied using the G2 test set of molecules. For the analysis of certain species, other DFT methods including ωB97x, G2, G3, G4 and M06-2X[61, 62].

M06 and M06-2x are hybrid meta exchange-correlation functionals that are a high nonlocality functionals with double the amount of nonlocal exchanges[61]. ωB97X is a long-range corrected functional, created by Head-Gordon and coworkers, which includes empirical dispersion[63].

Molecular orbitals are represented using linear combinations of basis functions, which are commonly the resource efficient Gaussian Type Orbtials (GTO). Pople basis sets, including the split-valence double-zeta basis set 6-31G(d,p), are selected for analysis of the species. This basis set is of moderate size and provides a good combination between accuracy are computational resources. Six primitives for each core atomic orbital basis functions and used with two basis functions for the valence shells, where one is composed of three primitives and the other only one primitive. Five d-type and three p-type polarization functions are added to the non-hydrogen and hydrogen species, respectively, adding additional orbital space for the electron. A larger split-valence triple-zeta 6-

311G(2d,2p) basis set is also utilized and serves as a comparison to 6-31G(d,p). This basis set includes an additional basis function for the valence shells and an additional two sets of d-type and p-type polarization functions to the non-hydrogen and hydrogen species, respectively.

2.3 Composite Methods

The tradeoff between accuracy and computational resources invariably exists. To obtain the most accurate calculations, high level methods using large basis sets are necessary, but often the size of the molecular system makes applications of such methods difficult, if not impossible.

The development of composite and/or compound methods has allowed for high-level calculations to be performed on large chemical systems, producing values within standard chemical accuracy of 1 kcal mol^{-1}. Composite methods use predetermined procedures of combined results from multiple levels of theory to mimic much higher, and more expensive, calculations while running in significantly less time. These methods are continually modified for improved accuracy and efficiency to help offset the high computational cost and resource demands of these methods. Higher-level corrections, which compensate for remaining deficiencies, are incorporated in the energy calculation.

Another commonly employed composite method is the complete basis set method CBS-QB3[64, 65], from Peterson and coworkers, where energies from several calculations are extrapolated to the complete basis set limit. A mean absolute deviation of 1.10 kcal mol^{-1} from the G2/97 test set for CBS-QB3 was calculated[61]. Geometries and frequencies are determined from the B3LYP/6-311G(2d,d,p) level with ZPVE, scaled by 0.99 and single-point energy calculations at the CCSD(T)/6-31+G(d'), MP4SDQ/CBSB4, and MP2/CBSB3 levels. The complete basis set is extrapolated with corrections for spin contamination to calculate final energies.

CBS-APNO is a more expensive procedure than other CBS methods. The acronym APNO stands for atomic pair natural orbital, which allows for accurate extrapolations to the complete basis set limit. This is accomplished with (U)HF/6/311G(d,P) geometry optimization and frequency calculations to obtain enthalpic and free-energy corrections. This step is followed by a second geometry optimization at the QCISD(T), MP2(full), HF and MP2 levels, each with different basis sets. The CBS-4M method is a complete basis set method that is parameterized to the original CBS-4 method, where M is referring to the use of minimal population localization. In addition, this method includes empirical corrections[28].

The final method that will be used in this study is W1U theory, which is a modification of W1[66]. The mechanism of calculation in this method is very similar to that of CBS methods, where the basis function is extrapolated to infinity with the use of very large basis sets up to cc-pVQZ + 2d1g and cc-pV5Z + 2d1f and calculations at the CCSD and CCSD(T) level. W1U theory is an unrestricted coupled cluster spin contamination corrected method.

2.4 Gaussian-n Methods

Gaussian-n is a series of quantum chemical methods based on a sequence of single-point energy calculations. These methods are able to provide high-accuracy complex-energy computations in Gaussian, which uses defined calculations in tandem to compute energies with a low error tolerance. All of the methods are constructed from row 1 and 2 atoms on the periodic table. Each method was developed over the one before, where G-2 is an improvement of G-1, G-3 on G-2 and G-4 on G-3. High accuracy in these methods is obtained by determining a higher-level correction based on calculations for the hydrogen atom and hydrogen molecule.

G-2 improves on G-1 by correcting for the non-additivity of diffuse sp polarization by including 2df basis set extension. The use of a basis set that contains a third d-function on non-hydrogen atoms and a second p-function on hydrogen and the modification of the high-level calculations which included MP4 FU/6-31G* in G-1, where G-2 uses 6-311G*.

G-3 takes a step further by using 6-31G* instead of using 6-311G*, this decreases computational cost. G-3 also corrects for spin-orbit coupling in atoms and core electron correlation. By making these changes, accuracy is improved. The calculations are split into two parts: atoms and molecules. This allows for significant impacts on calculated values for electron affinity and ionization potential.

G-4 is different that the other Gaussian-n methods; it depends on the cancellation of error for its accuracy. The mechanism of G-4 is identical to that of G-3. The gain in accuracy comes from determining the heat of formation limit for total inclusion of energy. Increasing d-polarization to 3d on first row atoms, and 4d on second-row atoms. G4 replaces QCISD(T) with CCSD(T) in high-level calculations and calculates geometry and SPE at B3-LYP/6-31G (2df,p) level.

2.5 Calculated Thermochemical Properties

Calculation of thermochemical properties for each species is outlined in the following sections.

2.5.1 Initial Species Parameters

Species are initially optimized using the B3-LYP/6-31G(d,p) method[57, 58] implemented in the Gaussian 09[67] program suites. Vibrational frequencies were examined to verify stable, all-positive frequencies, and transition state, one-negative-frequency, species. Potential energy curves for single-bond internal rotations are calculated at 10 degree intervals as the rest of the species is allowed to relax. Potential energy curves verify that the converged optimized species is in the lowest energy conformation. If a lower energy conformation is found, this geometry is optimized and potential energy curves are calculated again. The potential energy barriers from these curves are also utilized to determine entropy and heat capacity contributions from internal rotations.

2.5.2 Enthalpy

DFT methods are popular in this type of analysis because of their lower computation costs, but their accuracy is not as high compared to the results of composite methods[68-71]. Errors encountered may seem miniscule in small-molecule systems but compound as the molecule size increases. To improve the accuracy in the enthalpy calculations, it is common to implement diverse work reactions, which conserve mass balance, hybridization, and bond type for reactants and products. Work reactions grant significant systematic method error cancellation due to similar chemical environments on both sides of the reaction. This allows lower-level and less computationally demanding methods, such as DFT, to be used without sacrificing accuracy[70].

Work reactions are used to calculate Δ*H°f 298* for all species which incorporate molecules with similar atomic and bonding arrangement on both sides of the reaction. Total enthalpies, including zero-point vibrational and thermal corrections, for the optimized products and reactants are calculated at different levels of theory. The enthalpy change for each reaction, Δ*H°rxn 298*, is then calculated using Hess's Law in equation 2.13. Combining Δ*H°rxn 298* with literature enthalpies of formation values, Lit Δ*H°f 298*, of the known products and reactants results in a Δ*H°f 298* for the target species in equation 2.14. An example calculation is provided in Appendix A.

$$\Delta H°rxn\ 298 = \sum(Total\ Enthalpy\ of\ Products) - \sum(Total\ Enthalpy\ of\ Reactants) \tag{2.13}$$

$$\Delta H°rxn\ 298 = \sum(\text{Lit } \Delta H°f\ 298 \text{ Products}) - \sum(\text{Lit } \Delta H°f\ 298 \text{ Reactants} + \Delta H°f\ 298 \text{ Target Species}) \tag{2.14}$$

Comparison of the DFT values to experimental data or higher-level composite methods provides more accurate thermochemical properties[69, 72], which allows for comparing and gauging the accuracy of work-reaction methodology using DFT calculations.

2.5.3 Bond Dissociation Energy

Bond dissociation energies (BDE) are important to determine initial reaction pathways and kinetics. The stability of the radicals determines the relative energy needed to cleave a carbon-hydrogen bond or a carbon-carbon bond via beta scission reactions in hydrocarbons, for instance. Lower-bond energies are more vulnerable to hydrogen abstraction by radical species.

BDEs for the species in this study include carbon-hydrogen (C–H), oxygen-hydrogen (O–H), carbon-carbon (C–C), and oxygen-oxygen (O–O) bonds. For the homo- and heteroatomic bonds, C–H, O–H, and O–O, a bond cleavage reaction with the calculated Δ*H°f 298* value is utilized. For example, the bond cleavage reaction used to calculate C–H or O–H BDEs is the difference in the calculated Δ*H°f 298* for the parent compound (R–H) and the corresponding radical (R•) plus hydrogen atom (H•),

$$\mathrm{R{-}H} \rightarrow \mathrm{R}\bullet + \mathrm{H}\bullet$$

A sample calculation is provided in Appendix A. In the case of the O–O BDE calculation, the bond is in a hydroperoxide group, so a hydroxyl radical is formed and a similar bond cleavage reaction is used:

$$\mathrm{RO{-}OH} \rightarrow \mathrm{RO}\bullet + \mathrm{OH}\bullet$$

Established literature values of 52.103 kcal mol-1 for a hydrogen atom[9] and 8.93 kcal mol-1 for a hydroxyl radical[73] (update reference) were used in these calculations.

The calculated C-C and C-O BDEs are in all hydrocarbon species and cyclic ethers that correspond to ring opening, and do not generate two separate species. For these calculations, the difference between the Δ*H°f 298* values for the parent and radical is used to determine the C–C and C-O BDEs.

2.5.4 Entropy and Heat Capacity

Entropy (*S(T)*) and heat capacity (*Cp(T)*) calculations utilize the simple rigid-rotor harmonic-oscillator (HO) to describe the 3*n*-6 vibrations for non-linear species. In a Simple rigid-rotor harmonic-oscillator, it is well-known that there are accuracy issues while determining the lower frequency torsions corresponding to internal rotations using this approximation. Replacing these frequencies with methods to treat the internal rotations as hindered rotors increases the accuracy for *S(T)* and *Cp(T)*.

The initial research of Pitzer and Gwinn[74-76] addressed contributions from symmetrical and asymmetrical rotating groups on a rigid frame. Later, work by Kilpatrick and Pitzer[76] was expanded to include balanced and unbalanced linked rotating groups. These studies still serve as a basis for current research and development for new methods for treating internal rotations.

Determining which low-range frequency corresponds to a given bond rotation can oftentimes be challenging and is characteristic of large molecules containing multiple rotating species. Coupling can also occur between various rotations or other types of motion, which increases the difficulty in properly accounting for rotational contributions. A number of studies utilizing different techniques for handling coupled and uncoupled internal rotors contributions have been reported[77-85]. Despite the fact that more advanced methods addressing coupled internal rotator are available, basic treatment of internal rotations as uncoupled rotations provides improved accuracy over the HO approximation alone[80, 82, 86].

The HO approximation from translations, vibrations, and external rotation contributions to entropy and heat capacity are determined using the Statistical Mechanics for Heat Capacity and Entropy (SMCPS) program[87]. SMCPS uses the geometry, frequencies, and moments of inertia from the optimized methods calculation for the structure along with the mass, electronic degeneracy, symmetry, and number of optical isomers for the species. Vibrations corresponding to torsion frequencies are removed and treated using a hindered rotor model. Internal rotation contributions are then added to the SMCPS values.

The equations for entropy and heat capacity used in SMCPS come from standard statistical mechanics, allowing for macroscopic thermochemical properties to be calculated based on molecular energies from electronic structure calculations. These equations are summed from the individual contributions where entropy is calculated as

$$\mathrm{S(T)} = \mathrm{S_{Trans}} + \mathrm{S_{Rot}} + \mathrm{S_{Vib}} + \mathrm{S_{Elec}} + \mathrm{S_{OI}} + \mathrm{S_{Sym}}$$

(2.15)

$$S_{Trans} = 37.0 + \frac{3}{2}R\, ln\left(\frac{m}{40}\right) + \frac{3}{2}R\ln\left(\frac{T}{298}\right)$$

$$S_{Rot} = 11.5 + \frac{R}{2}\ln\left(\frac{I_m^3}{\sigma_e}\right) + \frac{3}{2}R\ln\left(\frac{T}{298}\right)\ (non - linear\ molecules)$$

$$S_{Rot} = 6.9 + R\ln\left(\frac{I}{\sigma_e}\right) + R\ln\left(\frac{T}{298}\right)\ (linear\ molecules)$$

$$S_{Rot} = 4.6 + R\ln\left(\frac{I_r^{1/2}}{\sigma_l}\right) + \frac{R}{2}\ln\left(\frac{T}{298}\right)\ (one - dimensional, free\ rotor)$$

$$S_{Vib} = R\sum_{K=1}^{3N-6}\left(\frac{hv_k}{e^{\frac{hv_t}{k_bT}} - 1} - \ln\left(1 - e^{-\frac{h_v}{k_bT}}\right)\right)$$

$$S_{Elec} = Rln(sm)$$

$$S_{OI} = Rln(n)$$

$$S_{Sym} = -Rln(\sigma_e)$$

and heat capacity is calculated as

$$C_p(T) = C_{Trans}C_{Rot}C_{Vib}C_{Elec} + R \tag{2.16}$$

$$C_{Trans} = \frac{3}{2}R$$

$$C_{Rot} = \frac{3}{2}R\ (non - linear\ molecules)$$

$$C_{Rot} = R\ (linear\ molecules)$$

$$C_{Rot} = \frac{1}{2}R\ (one - dimensional, free\ rotor)$$

$$C_{vib} = R\sum_{K=1}^{3N-6}\left(\frac{(hv_k/k_BT^2)\ e^{-\frac{hv_k}{k_bT}}}{e^{\frac{hv_k}{k_bT}}-1^2}\right)$$

$$C_{Elec} = R\ ln(sm)$$

Notation in equations 2.15 and 2.16 includes the following: molecular weight in amu (*m*), temperature in Kelvin (*T*), ideal gas constant (*R*), number of optical isomers (*n*), Planck's constant (*h*), vibrational frequency for the kth normal mode (*vk*), Boltzmann's constant (*kB*), external symmetry number of the molecule (*σe*), symmetry of the internal rotation (*σi*), moment of inertia for a linear molecule about its center of mass (*I*), product of the three principle moments of inertia about its center of gravity (*Im3*), reduced moment of inertia for the internal rotation (*Ir*), and spin multiplicity (*sm*).

Internal rotation contributions are calculated using the Pitzer and Gwinn[74, 75, 88] approximation method as calculated in the VIBIR[89] code. This method is best suited for rotations where the potential energy as a function of the angle, $V(\Phi)$, can be expressed as

$$V(\phi) = \sum_m \frac{1}{2}V_m 1 - \cos\sigma_m\phi_m \tag{2.17}$$

where V_m is the height of the potential barriers and m is the foldness of the potential energy graphs for each bond rotation. Reduced moments of inertia are calculated based on the optimized geometries using the mass and radius of rotation for the rotational groups. There are no adjustments for coupling of internal rotor motion with vibration, and VIBIR assumes that the rotational groups are symmetrical, which is accurate for primary and terminal methyl group rotation, for example. Other types of rotational barriers are also estimated using averages of the calculated barrier heights. A second method for calculation of internal rotation contribution is the ROTATOR code[90]. ROTATOR uses the potential energy curves with expansion of the hindrance potential at discrete torsion angles in the truncated Fourier series,

$$V(\phi) = a_0 + \sum a_i \cos(i\phi) + \sum b_i \sin(i\phi)\,, where\ i = l - 7 \quad (2.18)$$

where ao, ai, and bi provide the minima and maxima of the torsion potentials with allowance for a shift of the theoretical extreme angular positions. ROTATOR calculates the Hamiltonian matrix in the basis of wave functions of free internal rotor with subsequent calculation of energy levels by direct diagonalization. Direct summation over the energy levels allows for calculation of the partition function, where the entropy and heat capacity contributions are found using standard statistical thermodynamics. By fitting the actual potential energy graph of a rotational bond, ROTATOR can accurately describe both symmetrical and asymmetrical group rotations.

2.5.5 Group Additivity

The group additivity (GA) method, as developed by Benson[91], is a practical method for rapid estimation of thermochemical properties, especially for larger compounds. The success of this empirical method is based on the accurate knowledge of the contributions of representative groups, obtained from smaller molecules, and their established linear consistency in thermochemical property contribution. Corrections for rotors, symmetry, electron degeneracy, optical isomers, and other interactions are also taken into account. The hydrogen-bond increment (HBI) method for group additivity[89] allows calculation of the thermochemical properties of radicals with only one additional group to that of the parent species. Thermodynamic properties, including $\Delta H°f\ 298$, $S°298$, and $Cp(T)$, can be approximated as the sum of the individual groups and used as a comparison for calculated values[91-93]. The GA and HBI methods are implemented using the Thermodynamic Property Estimation for Radicals and Molecules (THERM) code[94, 95]. Adaptability of the GA and HBI methods allows method application to a wide range of compounds, where thermochemical properties are estimated for the development and engineering of chemical kinetic modeling. Groups are constantly being developed for unique classes of compounds which are gaining attention. Possible biofuel compounds, for example, can be easily approximated and applied in models as the search for alternative fuel sources advance.

2.5.6 Kinetic Analysis

Canonical transition state theory (CTST), where a transition state maximum energy barrier connecting the reactants and products exists, is used to calculate high-pressure rate constants, k(T), in the 298-2000 K temperature range. Using the previously calculated enthalpies, entropies, and heat capacities for the reactants and the transition state species, high-pressure rate constants are calculated:

$$k(T) = \frac{k_b T}{h} exp^{\left(\frac{\Delta S^{\ddagger}}{R}\right)} exp^{\left(-\frac{\Delta H^{\ddagger}}{RT}\right)} \left(\frac{RT}{P^0}\right)^{\Delta n^{\ddagger}} \tag{2.19}$$

where k_b is Boltzmann's constant, h is Planck's constant, T is temperature, p_o is standard pressure, R is the ideal gas constant, and $\Delta S\ddagger$, $\Delta H\ddagger$, and $\Delta n\ddagger$ are the changes in entropy, enthalpy, and the number of molecules between the reactant and transition state, respectively.

These high-pressure rate constants were fit using a nonlinear least-squares method to the modified form of the Arrhenius equation,

$$k(T) = AT^n \exp\left(\frac{-E_a}{RT}\right) \tag{2.20}$$

to determine the elementary rate parameters, A, n, and Ea. The program Thermkin was used in calculating both the high-pressure rate constants and the elementary rate parameters.

Variational transition state theory (VTST) was used in barrier-less, no transition states, situations common for radical and O_2 association. A scan of the bond length for the radical + O_2 adduct was completed by incrementing the length until a limit in the maximum energy was reached. High-pressure rate constants for each bond length position were then calculated, equation 2.19, for the 298-2000 K temperature range. The minimum rate constants at each temperature were fit to the modified Arrhenius equation, equation 2.20, to determine the elementary rate parameters.

Chemical activation of bimolecular reactions involves the formation of energized adducts containing a large excess of energy from bond formation. The adduct can undergo unimolecular reactions, including isomerization and dissociation, in addition to returning to the original reactants, and deactivation through collisional stabilization. These reactions compete with both temperature- and pressure-dependencies, but the energy dependence of the rate constant, *k*(E), must also be considered to correctly account for product distributions. Full descriptions of the models utilized for chemical activation and unimolecular dissociation are given by Sheng *et al.*[96].

Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used for *k*(E) calculation based on statistical assumptions for the number of ways in which energy can be distributed among the vibrational degrees of freedom in a molecule. The proportion of energy located in a critical oscillator leading to a reaction allows for the calculation of rate constants. While more accurate models exist, such as Rice-Ramsperger-Kassel-Marcus (RRKM), higher demands for specific details about the transition state species are necessary. With uncertainty and questionable accuracy of geometrical structure and modes of vibration in some of these transition state structures, QRRK provides acceptable analysis with fewer input parameters.

Bimolecular chemical activation reactions use QRRK in the analysis of rate constants and can be schematically represented in Figure 2.1, where A_e^* is the entrance of isomer activated complex formed from the initial reactants R and R', and A_e is the entrance isomer collisionally stabilized adduct. A_e^* can go products, return to reactants, or subsequent isomerizations, A_{i*}, which can further dissociate to products, by collisionally stabilized to A_i, or reisomerize.

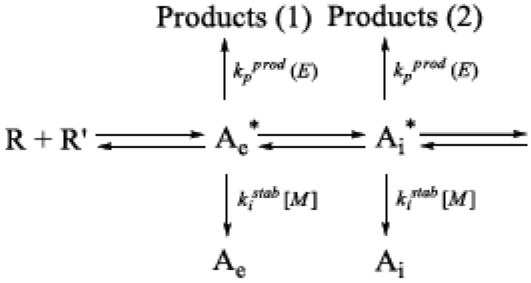

Figure 2.1 Schematic representation of chemical activation reactions.

Rate constants for chemical activations can be defined as a function of temperature, pressure, and collision parameters as

$$\frac{d[A_i]}{dt} = [R][R']k_i^{stab}(T,P) \tag{2.21}$$

$$\frac{d[Products]}{dt} = [R][R']k_p^{prod}(T,P) \tag{2.22}$$

the overall rate constants to a given product channel can be determined from parameters in the master equation model by summing the dissociation differential rate constant, d_{pi}^{q}, from isomer *i* to product *p* at energy *q* times the population vectors, n_i^q, which are functions of temperature, pressure, and collider molecule properties as shown below.

$$k_p^{prod}(T,P) = \sum_q d_{p,i}^q n_i^q \tag{2.23}$$

Rate constants for the formation of a stabilized adduct were calculated from the product of the population, n_i^r, and frequency of collisions between the adduct and the bath gas, ω, using the standard Lennard-Jones model, and the probability matrix representing the fraction of deactivating collisions resulting in a change from energy level *r* to *q* (where $q_{\min}^i$ is the lowest activated energy level) of isomer *i*, P_i^{qr},

$$k_i^{stab}(T,P) = \omega \sum_r \left(1 - \sum_{q>q_{min}^i} P_i^{qr}\right) n_i^r \tag{2.24}$$

Substantial information was generated from the rate constants from chemical activation analysis; additional dissociation analysis is necessary to completely build chemical kinetic models. Dissociation reactions are schematically represented as

$$
\begin{aligned}
A_c &\xrightarrow{k_p^{prod}} \text{Products (1)} \\
&\xrightarrow{k_p^{prod}} \text{Products (2)}
\end{aligned}
$$

where isomers are treated as irreversible product channels, which immediately stabilized with no distinction made towards the activated and stabilized adducts. With the simplification of product channels including isomers, the rate constant calculation is defined as Equation 2.25.

$$\frac{d[Products]}{dt} = [A_i]k_p^{prod}(T,P) \tag{2.25}$$

Rate constants can be determined from parameters in the master equation model by summing, over all energy levels q, the product of the differential rate constant, $d^q{}_{p,}$ and the normalized population distribution function, g_i^q, illustrated in equation 2.26.

$$k_p^{prod} = \sum_q d_{p,i}^q g_i^q \,/\, \sum_q g_i^q \tag{2.26}$$

These calculations for the temperature-and-pressure dependent rate constants were implemented in the CHEMASTER code[96], which uses a multi-frequency QRRK analysis for *k*(E) with master equation for falloff and stabilization. The steady-state assumption was applied to the energized adduct, where both forward and reverse reaction paths are calculated while formation of adjacent products is not reversible. Chemical activation analysis includes all products, while dissociation analysis only considers immediate reactions from the species in the well. Further reactions need to be considered separately.

The CHEMASTER input file includes temperature and pressure ranges of interest, mass of chemical species, the previously calculated elementary rate parameters from the high pressure rate constants, Lennard-Jones transport parameters of collisional diameter and well-depth for the collider molecule, the third-body bath gas, and reactants, as well as a reduced set of three representative vibrations and their degeneracies. The vibrations used are from the full set of $3n$-6 frequency vibrations and reproduce heat capacity values, including one external rotation which can be used for estimation of the molecular density of states.[108] The average energy removed on a per-collision basis from the adduct, and the energy grid integration interval with corresponding maximum energy level for the adduct, are also included in the input file.

CHAPTER 3

THERMOCHEMISTRY OF FLUORINATED ALDEHYDES

3.1 Overview

Fluorinated hydrocarbons are present in the atmosphere, hydrosphere, and lithosphere as a result of the past use of solvents and propellants; in addition to the current wide spread use of refrigerants and heat exchange fluids and polymers. Other uses include lubricants, blowing and sterilizing agents, coatings, anaesthetics, and agents in the preparation of semiconductors. They have been regarded as the replacement of greenhouse gasses like chlorofluorocarbons, because of their nonexistent or less adverse effects on global warming from the greenhouse gas effect in the troposphere layer[4].

As stated in the Fourth Assessment Report of the Inter-governmental Panel on Climate Change, "The observed widespread warming of the atmosphere and ocean, together with ice-mass loss, support the conclusion that it is extremely unlikely that global climate change of the past 50 years can be explained without external forcing and very likely that it is not due to known natural causes alone[97]." The emission of greenhouse gasses and ozone depletion agents as a byproduct of human activities remains the most important factor for the drive in climate change.

The increased atmospheric concentrations of halogenated organic compounds are partially responsible for the change in global climate[98, 99]. Due to the concentration of haloalkanes being nearly a millionth of that of carbon dioxide in the atmosphere, these compounds have a 13% share in the radiative forcing. Being that this is a large contributing factor, it can be explained by considering their higher global warming potentials; they are typically a couple of thousand times of the reference CO_2[3].

Fluorocarbons and hydrofluorocarbons have been identified as promising candidates as fire surpressants[100], and considerable effort is being devoted to their study, what has resulted in the generation of extensive thermochemical and kinetic databases[101, 102].

Quantum chemical calculations on small molecules can result in thermochemical values with low degrees of uncertainty, sometimes outperforming experimental results [2 5-8]. The precise knowledge of the thermodynamic and kinetic properties of the atmospheric reactions as well as the physical parameters of the corresponding species is required for chemistry-climate models. Databases such as NIST-JANAF[9], CODATA[10], ATcT[11], JPL[12] and Burcat's Third Millennium Thermodynamic Database[13], contain the relevant physicochemical parameters, where many discrepancies exist and contain considerably large error bars. Such data uncertainty is mostly due to the fact that the chemistry of the troposphere and stratosphere is dominated by free radical reactions and experimental determination of physical and chemical parameters of radicals and radical reaction is still challenging[3].

In recent years, computational chemistry evolved to a stage where the calculation of thermodynamic functions of small molecules and can achieve experimental or even higher accuracy. DFT, and Composite *ab initio* methods in the Gaussian suite of programs, were used to develop thermochemical properties and a group additivity scheme for estimation of larger flourinated hydrocarbons values.

The standard enthalpy of formation for this series of fluoro and multifluoro acetaldehydes ($C_2H_xOF_{4-x}$) and propanals ($C_3H_xOF_{6-x}$) have been calculated using computational chemistry and isodesmic work reactions. Eleven computational chemistry methods have been used for accuracy; these include CBS-APNO, CBS-4M, CBS-QB3, M062X, ωB97X, B3-LYP, G-2, G-3, G-4 and Weizmann-1 (W1U) methodology. Group additivity values for CO/C/F, C/CO/F3, C/CO/F/H2, C/C/CO/F/H, C/C/CO/F2, and C/C/CO/F/H have also been determined for use in estimation of the thermochemistry larger fluorinated aldehydes. Comparisons are made to previously published values for a number of the fluorinated aldehydes.

3.2 Nomenclature

Table 3.1: Nomenclature, IUPAC nomenclature and Molecular Formula of Fluorinated Aldehydes

IUPAC Nomenclature	Nomenclature	Species	Formula
fluoroacetaldehyde	CFC(=O)	$CH_2FCH(=O)$	C_2H_3OF
Fluoroacetyl fluoride	CFCF(=O)	$CH_2FCF(=O)$	$C_2H_2OF_2$
difluoroacetaldehyde	CF2C(=O)	$CHF_2CH(=O)$	$C_2H_2OF_2$
Difluoroacetyl fluoride	CF2CF(=O)	$CHF_2CF(=O)$	C_2HOF_3
Trifluoroacetyl fluoride	CF3CF(=O)	$CF_3CF(=O)$	C_2OF4
trifluoroacetaldehyde	CF3C(=O)	$CF_3CH(=O)$	C_2H_3OF
Acetyl fluoride	CCF(=O)	$CH_3CF(=O)$	C_2H_3OF
3-fluoropropanal	CFCC(=O)	$CH_2FCH_2CH(=O)$	C_3H_5OF
2,3-difluoropropanal	CFCFC(=O)	$CH_2FCHFCH(=O)$	$C_3H_4OF_2$
2,3-propanoyl fluoride	CFCFCF(=O)	$CH_2FCHFCF(=O)$	$C_3H_3OF_3$
3,3-difluoropropanal	CF2CC(=O)	$CHF_2CH_2CH(=O)$	$C_3H_4OF_2$
2,3,3-trifluoropropanal	CF2CFC(=O)	$CHF_2CHFCH(=O)$	$C_3H_3OF_3$
2,3-dipropanoyl fluoride	CF2CFCF(=O)	$CHF_2CHFCF(=O)$	$C_3H_2OF_4$
3,3,3-trifluoropropanal	CF3CC(=O)	$CF_3CH_2CH(=O)$	$C_3H_3OF_3$
2,3,3,3-tetrafluoropropanal	CF3CFC(=O)	$CF_3CHFCH(=O)$	$C_3H_2OF_4$
2,3,3,3-tetrapropanoyl fluoride	CF3CFCF(=O)	$CF_3CHFCF(=O)$	C_3HOF_5
2-fluoropropanal	CCFC(=O)	$CH_3CHFCH(=O)$	C_3H_5OF
2-propanoyl fluoride	CCFCF(=O)	$CH_3CHFCF(=O)$	$C_3H_4OF_2$
2,2-difluoropropanal	CCF2C(=O)	$CH_3CF_2CH(=O)$	$C_3H_4OF_2$

Table 3.1: Nomenclature, IUPAC nomenclature and Molecular Formula of Fluorinated Aldehydes (Continued)

IUPAC Nomenclature	Nomenclature	Species	Formula
2,2,3-trifluoropropanal	CFCF2C(=O)	$CH_2FCF_2CH(=O)$	$C_3H_3OF_3$
2,2,3-tripropanoyl fluoride	CFCF2CF(=O)	$CH_2FCF_2CF(=O)$	$C_3H_2OF_4$
2,2,3,3-tetrafluoropropanal	CF2CF2C(=O)	$CHF_2CF_2CH(=O)$	$C_3H_2OF_4$
2,2,3,3-tetrapropanoyl fluoride	CF2CF2CF(=O)	$CHF_2CF_2CF(=O)$	C_3HOF_5
2,2,3,3,3-pentafluoropropanal	CF3CF2C(=O)	$CF_3CHFCH(=O)$	C_3HOF_5
2,2,3,3-tetrapropanoyl fluoride	CF3CF2CF(=O)	$CF_3CF_2CF(=O)$	C_3OF_6
2,2-dipropanoyl fluoride	CCF2CF(=O)	$CH_3CF_2CF(=O)$	$C_3H_3OF_3$
propanoyl fluoride	CCCF(=O)	$CH_3CH_2CF(=O)$	C_3H_5OF
3-propanoyl fluoride	CFCCF(=O)	$CH_2FCH_2CF(O)$	$C_3H_4OF_2$
3,3-dipropanoyl fluoride	CF2CCF(=O)	$CHF_2CH_2CF(=O)$	$C_3H_3OF_3$
3,3,3-tripropanoyl fluoride	CF3CCF(=O)	$CF_3CH_2CF(=O)$	$C_3H_2OF_4$
Fluoroacet-2-yl aldehyde	CJFC(=O)	CHFCH(=O)	C_2H_2OF
Acet-2-yl fluoride	CJCF(=O)	$CH_2CF(=O)$	C_2H_2OF
Fluoroacet-1-yl aldehyde	CFCJ(=O)	$CH_2FC(=O)$	C_2H_2OF
Fluoroacet-2-yl fluoride	CJFCF(=O)	CHFCF(=O)	C_2HOF_2
Difluoroacet-2-yl aldehyde	CJF2C(=O)	$CF_2CH(=O)$	C_2HOF_2
Difluoroacet-1-yl aldehyde	CF2CJ(=O)	$CHF_2C(=O)$	C_2HOF_2
Difluoroacet-2-yl fluoride	CJF2CF(=O)	$CF_2CF(=O)$	C_2OF_3
Trifluoroacet-2-yl aldehyde	CF3CJ(=O)	$CF_3C(=O)$	C_2OF_3

3.3 Computational Mehods

Optimized geometries for the parent and radicals are initially calculated at the B3-LYP/6-31G++(d,p) level of theory[123]. Potential energy curves for the single bond internal rotation barriers are used to verify the lowest energy conformation and for calculation of entropies and heat capacities. These potential energy graphs are available in Appendix B.

Molecular heat of formation values are calculated using a set of isodesmic reactions, in which the number of each bond type is conserved in products and reactants. This is to try and affect a cancellation of systematic errors in the molecular calculations[35]. Table 3.2 lists the reference specie ΔH°f(298) values used in the isodesmic reactions.

Table 3.2 Reference Species $\Delta H^{\circ}_{f(298)}$ Values used in the Isodesmic Reactions

Species	$\Delta_f H^{\circ}_{298}$ (kcal mol^{-1})	Error Values	Reference
CH_4	-17.78	± 0.10	103
CH_3CH_3	-20.03	± 0.10	103
CH_3F	-56.30	± 0.30	104
CH_2FCH_3	-65.42	± 1.11	104
$CHF(=O)$	-92.00	± 2.00	56
$CH_2(=O)$	-25.96	± 0.12	103
$CH_3CH(=O)$	-39.70	± 0.12	103
$CH_3CH_2CH_3$	-28.9	± 0.10	103
$CH_2FCH_2CH_3$	-70.24	± 1.30	104
CHF_2CH_3	-120.87	± 1.62	104
CH_2F_2	-108.07	± 1.46	104
CH_3CHFCH_3	-75.26	± 1.30	104
$CH_3CH_2CH_2CH_3$	-30.00	± 0.10	105
$CH_3CF_2CH_3$	-133.25	± 1.65	104
$C(CH_3)_2(=O)$	-51.89	± 0.16	9
CHF_3	-166.71	± 1.97	104
$CH_3CH_2CH(=O)$	-44.36	± 0.19	103
$CH_3CH_2CH_2CH(=O)$	-50.61	± 0.22	106
$CH_3CH(CH_3)\ CH(=O)$	-51.57	± 0.37	106
CHF_2CF_2	-160.3	± 1.40	107
CF_2CH_2F	-110.0	± 2.50	107
CF_3CJF_2	-264.1	± 1.10	107
CH_2CH_3	28.9	± 0.40	105
$CH(=O)OH$	-90.5	± 0.10	105
$CJ(=O)OH$	-43.7	± 0.50	105
$CH_3C(=O)$	-2.3	± 0.90	105
$CH_3CH=CH_2$	4.6	± 0.30	105
$CH_3C=CH_2$	60.5	± 0.90	105
$CH_3CH_2Cj(=O)$	-6.9	± 0.90	105
$CH_2CH(=O)$	4.4	± 0.90	105
CH3J	35.2	± 0.2	105
CHF_2CJHF	-110.6	± 1.6	107
$CH_3CH_2CH_3$	-28.9	± 0.10	103
$CJH_2CH_2CH_3$	24.3	± 0.9	105
$CH_3CH_2CH_2CH_3$	-30.1	± 0.1	105
$CJH_2CH_2CH_2CH_3$	19.3	± 0.9	105
$(CH_3)_3CH$	-32	± 0.4	105
$CJH_2C(CH_3)_2$	17.8	± 0.9	105

Table 3.2 Reference Species ΔH°$_{f(298)}$ Values used in the Isodesmic Reactions (Continued)

Species	$\Delta_fH°_{298}$ (kcal mol^{-1})	Error Values	Reference
CH_2FCH_2F	-107.65	± 1.17	107
CF_3CH_3	-180.51	± 2.05	104
CJHFCH$_2$F	-58.1	± 1.10	107
CHF_2CH_2F	-161.1	± 2.20	107
CF_3CH_2F	-214.15	± 1.9	107

Isodesmic work reactions are implemented for the calculation of enthalpies of formation (Δ*H*°$_{f\,298}$) using computational methodology from CBS-APNO, CBS-4M, CBS-QB3, M062X/6-31G+(d,p), ωB97X/6-31G+(d,p), B3-LYP/6-31G+(d,p), G-2, G-3, G-4 and Weizmann-1 (W1U). All calculations performed were accomplished using Gaussian 09 program suite[18]. Taking the following three isodesmic reactions Table 3.3 are selected to determine the ΔH$_{f298}$ of the target molecule, fluoro-acetaldehyde, as an example.

Table 3.3 Isodesmic Reactions and Enthalpies of Formation for Fluoroacetaldehyde using ϖB97x/6-31++G(d,p) Methodology

							$\Delta_fH°_{298}$ (kcal/mol)	Eqn
CH$_2$FCH(=O)	+	CH_4	=	CH$_3$CH(=O)	+	CH_3F		
-252.956646*		-40.457381*		-153.738297*		-139.673045*	X	
x		-17.78 ^{103**}		-39.70 ^{103**}		-56.30 ^{104**}	-79.90	1
CH$_2$FCH(=O)	+	CH_3CH_3	=	CH$_3$CH(=O)	+	CH$_2$FCH3		
-252.956646*		-79.731404*		-153.738297*		-178.957686*	X	
x		-20.03 ^{103**}		-39.70 ^{39**}		-65.42 ^{104**}	-80.11	2
CH$_2$FCH(=O)	+	CH$_2$(=O)	=	CH$_3$CH(=O)	+	CHF(=O)		
-252.956646*		-114.445571*		-153.738297*		-213.703787*	X	
x		-25.96 ^{103**}		-39.70 ^{103**}		-91.60 ^{104**}	-80.33	3

*Hartrees, **kcal mol-1

The good agreement between the 3-5 isodesmic reactions used in our calculations and the computational methods as well comparison to available literature supports the accuracy of our calculations. The overall average of fluoroacetaldehyde was observed using the 11 methods discussed over the set of isodesmic reactions and was observed to be -80.41 kcal mol^{-1}. The methods averages for fluoroacetaldehyde are M06 (-80.12), M06-2X (-80.27), Wb97x (-80.11), B3-LYP (-80.18), CBS-APNO (-80.86), CBS-4M (-81.00), CBS-QB3 (-80.04), G-2 (-81.05), G-3 (-81.04), G-4 (-79.97) and W1U (-79.90) kcal mol^{-1}.

Entropies and heat capacities were determined using B3-LYP/6-31++G(d,p) optimized geometries and frequencies. Entropy and heat capacity values were calculated as a function of temperature from the optimized structures, moments of inertia, vibration frequencies, internal rotor potentials, symmetry, electron degeneracy, the number of optical isomers and the mass of each molecule. This calculation uses a standard formula from statistical mechanics for the contributions of translation, vibrations, and external rotation (TVR) using the SMCPS (Statistical Mechanics−Heat Capacity, and Entropy) program[87]. SMCPS utilizes the rigid- rotor-harmonic oscillator approximation from the frequencies, as well as moments of inertia from the optimized B3-LYP/6-31G++(d,p) level calculations. Contributions from internal rotors are calculated using the program Rotator are substituted for contributions from the corresponding internal rotor torsion frequencies. The Rotator program calculates thermodynamic functions from hindered rotations with arbitrary potentials based on the method developed by Krasnoperov, Lay, and Shokhirev[90]. The technique employs expansion of the hindrance potential in the fourier series, calculation of the Hamiltonian matrix in the subsequent calculate ion of energy levels by direct diagonalization barrier versus dihedral angle are fit by a cosine curve. In This study, the rotational potential calculated at discrete torsional angles is represented by a truncated ten-parameter Fourier series (equation 1) of the following for:

$$\mathbf{V}(\emptyset) = \boldsymbol{a_0} + \sum_{i=1}^{10}(\boldsymbol{a_0}\,\mathbf{cos}(\mathbf{i}\emptyset)) + \sum_{j=1}^{10}(\boldsymbol{b}_\mathbf{j}\,\mathbf{cos}(\mathbf{j}\emptyset)) \qquad (3.1)$$

The values of the coefficients a_i and b_j are calculated to provide minimum and maximum values of torsional potentials with the allowance for a shift of theoretical extreme angular positions. Vibrational frequencies for B3-LYP/6-31+G(d,p) are scaled by a factor of 0.964 in the calculation of standard entropy and heat capacity based on computational chemistry comparison and benchmark databases[108].

Groups were developed for use in the Group Additivity (GA) method developed by Benson[91], and comparisons are made between the values determined using the developed group values and the computational chemistry calculated $\Delta_f H°_{298}$, S°(T), and C (T) values. The GA method is based on knowledge of the contributions of representative groups in similar molecules and their properties showing linear consistency in thermochemical properties. Thermodynamic properties of larger species, such as those in this study, were accurately approximated based on the sum of smaller representative groups where there are corrections for rotors, symmetry, electron degeneracy, optical isomers, and gauche and other interactions are included.

The following groups were determined by averaging values of entropy and heat capacities of molecules that have the same group present:

CO/C/F, C/CO/F3, C/CO/F/H2, C/C/CO/F/H, C/C/CO/F2, C/C/F2/H and C/C/CO/F/H.

Calculated enthalpies formations and hydrocarbon molecule groups that have been published are used to solve for the unknown fluorocarbon groups where the molecules have hydrocarbon components. We show in this chapter that when a fluorine atom is present on adjacent carbon atoms - Fluorine / Fluorine interaction terms needed to be developed, and included in the group additivity, to adjust the enthalpy values for the F/F repulsions.

3.4 Results and Discussion

Isodesmic work reactions are used to calculate the standard enthalpy of formation ($\Delta H°_f$ 298) for each target species at the CBS-APNO, CBS-4M CBS-QB3, M062X/6-13+(G(d,p), ωB97X/6-13+(G(d,p), B3-LYP/6-13+(G(d,p), G-2, G-3, G-4 and Weizmann-1 (W1U) levels of theory. All of the species in the work reactions, except for the target compound, have standard well-established standard enthalpy of formation ($\Delta H°_{f\ 298}$); [83,120,121,168] these are listed in Table 3.3. In some cases, the work reactions incorporate an aldehyde compound that is analyzed in this study. The reference standard enthalpy of formation ($\Delta H°_{f\ 298}$) values in these cases are from literature values[169-172] shown in Table 3.4. The work reactions are presented in Table 3.5. Reactions that are not shown in table 3.5 are located in Appendix B.

Table 3.4 Standard Enthalpies of Formation for Reference Species for Fluoroaldehydes

Species	$\Delta H°_{f\ 298}$ (kcal mol^{-1})	Reference
CH_4	-17.78 ± 0.10	103
CH_3CH_3	-20.03 ± 0.10	103
CH_3F	-56.30 ± 0.24	104
CH_2FCH_3	-65.42 ± 1.11	104
CHF(=O)	-91.60 ± 1.70	56
CH_2(=O)	-25.96 ± 0.12	103
CH_3CH(=O)	-39.70 ± 0.12	103
$CH_3CH_2CH_3$	-28.9 ± 0.10	103
CH_2FCH2CH3	-70.24 ± 1.30	104
CHF_2CH_3	-120.87 ± 1.62	104
CH_2F_2	-108.07 ± 1.46	104
CH_3CHFCH_3	-75.26 ± 1.30	104

Table 3.4 Standard Enthalpies of Formation for Reference Species for Fluoroaldehydes

Species	$\Delta H^{\circ}_{f\ 298}$ (kcal mol^{-1})	Reference
$CH_3CH_2CH_2CH_3$	-80.25 ± 1.28	104
$CH_3CF_2CH_3$	-133.25 ± 1.65	104
CF_3CH_3	-65.42 ± 2.05	104
$C(CH_3)_2(=O)$	-51.89 ± 0.16	9
CHF_3	-166.71 ± 1.97	104
$CH_3CH_2CH(=O)$	-44.36 ± 0.19	103
$CH_3CH_2CH_2CH(=O)$	-50.61 ± 0.22	105
$CH_3CH(CH_3)$ $CH(=O)$	-51.57 ± 0.37	105

Table 3.5 Isodesmic Work Reactions and Calculated $\Delta H°_{f\,298}$ for Fluoroaldehydes

			CFC(=O)				**mo62x**	**m06**	**wb97x**	**b3plyp**	**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**G-2**	**G-3**	**G-4**	**W1U**
CFC(=O)	+	CH4	=	CC(=O)	+	CH3F	-79.7	-79.91	-79.9	-79.5	-80.04	-81.08	-80.64	-80.74	-80.71	-80.66	-80.02
CFC(=O)	+	CC	=	CC(=O)	+	CFC	-80.2	-80.08	-80.11	-79.94	-80.68	-81.18	-80.45	-81.34	-81.33	-80.89	-80.28
CFC(=O)	+	C(=O)	=	CC(=O)	+	CF(=O)	-79.31	-78.78	-78.73	-79.49	-80.26	-79.14	-77.43	-79.48	-79.47	-76.77	-77.79
			CFCF(=O)														
CFCF(=O)	+	C(=O)	=	CFC(=O)	+	CF(=O)	-141.37	-141.55	-140.68	-140.76	-141.51	-141.5	-141.4	-141.64	-141.64	-142.36	-141.33
CFCF(=O)	+	CH4	=	CCF(=O)	+	CH3F	-141.25	-141.61	-141.08	-141.04	-141.29	-141.03	-142.84	-141.99	-141.97	-143.65	-142.25
CFCF(=O)	+	CC	=	CCF(=O)	+	CFC	-141.74	-141.78	-141.3	-141.48	-141.92	-141.12	-142.65	-142.59	-142.58	-143.88	-142.5
			CF2C(=O)														
CF2C(=O)	+	CFCC	=	CFC(=O)	+	CCCF2	-129.25	-128.81	-129.32	-129.58	-129.36	-127.14	-129.96	-129.57	-129.58	-130.23	-129.86
CF2C(=O)	+	CFC	=	CFC(=O)	+	CCF2	-129.06	-128.76	-129.13	-129.39	-129.18	-127.57	-129.74	-129.45	-129.46	-130.11	-129.66
CF2C(=O)	+	CH3F	=	CFC(=O)	+	CH2F2	-129.41	-129.23	-129.29	-129.31	-129.06	-129.09	-129.76	-129.72	-129.73	-130.4	-129.47
			CF2CF(=O)														
CF2CF(=O)	+	CC(=O)	=	CF2C(=O)	+	CCF(=O)	-188.28	-188.54	-187.96	-188.15	-187.86	-185.88	-188.68	-188.58	-188.58	-190.47	-188.92
CF2CF(=O)	+	CFC(=O)	=	CFCF(=O)	+	CF2C(=O)	-187.06	-187.16	-187.11	-186.94	-186.95	-186.26	-186.81	-187.66	-187.65	-187.82	-187.02
CF2CF(=O)	+	CC(=O)	=	CCF(=O)	+	CF2C(=O)	-188.28	-188.54	-187.96	-188.15	-187.86	-185.88	-188.68	-188.58	-188.58	-190.47	-188.92
			CF3CF(=O)														
CF3CF(=O)	+	CFC(=O)	=	CF3C(=O)	+	CFCF(=O)	-243.14	-243.38	-243.23	-243.03	-242.93	-241.99	-243.17	-243.81	-243.81	-244.24	-243.25
CF3CF(=O)	+	CF2C(=O)	=	CF3C(=O)	+	CF2CF(=O)	-242.44	-242.58	-242.48	-242.46	-242.34	-242.09	-242.72	-242.51	-242.52	-242.78	-242.59
CF3CF(=O)	+	CF2C(=O)	=	CF2CF(=O)	+	CF3C(=O)	-245.91	-246.05	-245.95	-245.92	-245.81	-245.56	-246.19	-245.98	-245.98	-246.25	-246.06
			CF3C(=O)														
CF3C(=O)	+	CH2F2	=	CF2C(=O)	+	CHF3	-185.16	-185.2	-184.76	-184.64	-184.34	-185.06	-184.8	-184.48	-184.47	-185.69	-184.82
CF3C(=O)	+	CCF2	=	CF2C(=O)	+	CF3C	-184.97	-185.03	-184.84	-185	-184.48	-183.4	-185.34	-184.6	-184.59	-185.88	-185.39
			CCF(=O)														
CCF(=O)	+	C(=O)	=	CC(=O)	+	CF(=O)	-104.19	-104.2	-103.86	-103.59	-104.63	-105.91	-103.56	-104.76	-104.75	-103.74	-103.47
CCF(=O)	+	CFC(=O)	=	CC(=O)	+	CFCF(=O)	-104.61	-104.45	-104.97	-104.62	-104.91	-106.21	-103.96	-104.91	-104.91	-103.17	-103.93

Table 3.5 Isodesmic Work Reactions and Calculated Δ$H°_{f\,298}$ for Fluoroaldehydes (continued)

							mo62x	**m06**	**wb97x**	**b3plyp**	**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**G-2**	**G-3**	**G-4**	**W1U**
			CFCC(=O)														
CFCC(=O)	+	CH4	=	CCC(=O)	+	CH3F	-87.48	-87.72	-87.64	-87.4	-87.85	-89.41	-88.44	-88.19	-88.16	-88.1	-87.78
CFCC(=O)	+	CC	=	CCC(=O)	+	CFC	-87.98	-87.89	-87.85	-87.83	-88.49	-89.51	-88.26	-88.78	-88.78	-88.33	-88.04
CFCC(=O)	+	CC(=O)	=	CCC(=O)	+	CFC(=O)	-86.00	-86.03	-85.96	-86.11	-86.03	-86.55	-86.02	-85.66	-85.66	-85.66	-85.98
			CFCFC(=O)														
CFCFC(=O)	+	C(=O)	=	CFCC(=O)	+	CF(=O)	-129.36	-128.77	-128.54	-129.4	-129.6	-128.72	-127.83	-129.14	-129.13	-127.86	-128.11
CFCFC(=O)	+	CFC(=O)	=	CFCC(=O)	+	CFCF(=O)	-129.78	-129.02	-129.65	-130.43	-129.88	-129.02	-128.22	-129.29	-129.29	-127.3	-128.58
CFCFC(=O)	+	C(=O)	=	CCCF(=O)	+	CF(=O)	-130.24	-129	-129.1	-131.06	-130.97	-127.82	-127.47	-129.2	-129.2	-126.31	-128.18
			CFCFCF(=O)														
CFCFCF(=O)	+	CFC(=O)	=	CFCFC(=O)	+	CFCF(=O)	-189.33	-189.26	-189.28	-189.4	-189.13	-189.47	-189.44	-189.35	-189.35	-189.78	-189.44
CFCFCF(=O)	+	CCC(=O)	=	CFCFC(=O)	+	CCCF(=O)	-190.14	-190.09	-189.7	-190.08	-189.58	-188.25	-190.89	-189.77	-189.78	-192.03	-190.94
CFCFCF(=O)	+	C(=O)	=	CFCFC(=O)	+	CF(=O)	-188.91	-189.01	-188.17	-188.36	-188.85	-189.17	-189.04	-189.2	-189.2	-190.34	-188.98
CFCFCF(=O)	+	CC(=O)	=	CFCFC(=O)	+	CCF(=O)	-188.96	-189.05	-188.55	-189.02	-188.46	-187.5	-189.72	-188.68	-188.69	-190.85	-189.75
			CF2CC(=O)														
CF2CC(=O)	+	CFCC	=	CFCC(=O)	+	CCCF2	-140.98	-140.92	-140.97	-140.97	-141.03	-140.73	-141.26	-141.12	-141.12	-141.48	-141.19
CF2CC(=O)	+	CFC	=	CFCC(=O)	+	CF2C	-140.79	-140.88	-140.78	-140.78	-140.84	-141.16	-141.05	-141.01	-141	-141.36	-140.99
CF2CC(=O)	+	CH3F	=	CFCC(=O)	+	CH2F2	-141.14	-141.34	-140.93	-140.71	-140.73	-142.68	-141.07	-141.28	-141.27	-141.64	-140.8
CF2CC(=O)	+	CFC(=O)	=	CFCC(=O)	+	CF2C(=O)	-141.23	-141.61	-141.15	-140.89	-141.16	-143.09	-140.8	-141.05	-141.04	-140.74	-140.83
CF2CC(=O)	+	CFCF(=O)	=	CFCC(=O)	+	CF2CF(=O)	-140.52	-140.81	-140.4	-140.31	-140.57	-143.19	-140.35	-139.75	-139.75	-139.29	-140.16
			CF2CFC(=O)														
CF2CFC(=O)	+	CFC(=O)	=	CFCFC(=O)	+	CF2C(=O)	-180.11	-180.63	-179.84	-179.48	-180.18	-181.02	-179.46	-180.64	-180.63	-180.35	-179.65
CF2CFC(=O)	+	CF2C(=O)	=	CFCFC(=O)	+	CF2CF(=O)	-178.7	-177.72	-178.08	-178.12	-179.56	-180.16	-177.33	-179.79	-179.8	-176.96	-177.21
CF2CFC(=O)	+	CFCC	=	CFCFC(=O)	+	CCCF2	-179.86	-179.94	-179.66	-179.56	-180.05	-178.66	-179.92	-180.71	-180.71	-181.08	-180.01
			CF2CFCF(=O)														
CF2CFCF(=O)	+	CFC(=O)	=	CF2CFC(=O)	+	CFCF(=O)	-239.17	-238.82	-239.16	-239.34	-239.12	-239.65	-239.74	-239.68	-239.68	-240.2	-239.5
CF2CFCF(=O)	+	CF2C(=O)	=	CF2CFC(=O)	+	CF2CF(=O)	-238.47	-238.02	-238.41	-238.76	-238.53	-239.75	-239.29	-238.38	-238.39	-238.74	-238.74
CF2CFCF(=O)	+	CFCFC(=O)	=	CF2CFC(=O)	+	CFCFCF(=O)	-238.86	-238.58	-238.9	-238.96	-239.01	-239.21	-239.33	-239.35	-239.35	-239.44	-239.08

Table 3.5 Isodesmic Work Reactions and Calculated Δ*H*°$_{f\,298}$ for Fluoroaldehydes (continued)

CF3CC(=O)							mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
CF3CC(=O)	+	CH2F2	=	CF2CC(=O)	+	CHF3	-198.97	-199.63	-198.75	-198.6	-198.19	-199.81	-198.32	-198.41	-198.41	-198.93	-198.4
CF3CC(=O)	+	CF2C(=O)	=	CF2CC(=O)	+	CF3C(=O)	-198.68	-199.3	-198.85	-198.82	-198.71	-199.61	-198.38	-198.79	-198.8	-198.1	-198.44
CF3CFC(=O)																	
CF3CFC(=O)	+	CF2CC(=O)	=	CF3CC(=O)	+	CF2CFC(=O)	-216.17	-215.24	-215.85	-215.97	-216.19	-216.06	-216.47	-216.49	-216.48	-216.85	-216.26
CF3CFC(=O)	+	CFCC(=O)	=	CF3CC(=O)	+	CFCFC(=O)	-216.48	-215.7	-215.98	-215.99	-216.64	-215.42	-216.56	-217.5	-217.51	-217.89	-216.51
CF3CFC(=O)	+	CCC(=O)	=	CF3CC(=O)	+	CCFC(=O)	-217.49	-215.91	-216.76	-216.87	-217.38	-215.83	-217.9	-218.4	-218.4	-219.98	-217.91
CCFC(=O)																	
CCFC(=O)	+	CH4	=	CCC(=O)	+	CH3F	-89.17	-90.1	-89.35	-88.95	-89.05	-90.68	-90.12	-89.93	-89.9	-90.09	-89.36
CCFC(=O)	+	CC	=	CCC(=O)	+	CFC	-89.67	-90.27	-89.57	-89.38	-89.68	-90.78	-89.94	-90.53	-90.52	-90.32	-89.62
CCFC(=O)	+	CFCC(=O)	=	CCC(=O)	+	CFCFC(=O)	-88.37	-89.16	-88.59	-88.49	-88.63	-88.97	-88.04	-88.48	-88.48	-87.28	-87.98
CCFCF(=O)																	
CCFCF(=O)	+	CCC(=O)	=	CCFC(=O)	+	CCCF(=O)	-151.67	-150.87	-151.3	-151.62	-151.4	-150.46	-152.32	-151.54	-151.55	-153.18	-152.27
CCFCF(=O)	+	CF2C(=O)	=	CCFC(=O)	+	CF2CF(=O)	-150.16	-149.25	-150.13	-150.36	-150.36	-151.78	-150.4	-149.82	-149.82	-149.48	-150.11
CCFCF(=O)	+	CC(=O)	=	CCFC(=O)	+	CCF(=O)	-150.49	-149.84	-150.14	-150.56	-150.28	-149.71	-151.14	-150.45	-150.46	-152.01	-151.08
CCFCF(=O)	+	CFCFC(=O)	=	CCFC(=O)	+	CFCFCF(=O)	-150.55	-149.81	-150.62	-150.56	-150.84	-151.24	-150.44	-150.79	-150.79	-150.18	-150.35
CCF2C(=O)																	
CCF2C(=O)	+	CH3F	=	CCFC(=O)	+	CH2F2	-143.01	-142.73	-142.74	-142.43	-142.19	-143.92	-142.92	-142.88	-142.88	-143.58	-142.42
CCF2C(=O)	+	ccfc	=	CCFC(=O)	+	ccf2c	-142.68	-141.86	-142.73	-142.96	-142.65	-141.43	-143.4	-142.77	-142.77	-143.56	-143.18
CFCF2C(=O)																	
CFCF2C(=O)	+	CH3F	=	CFCFC(=O)	+	CH2F2	-179.71	-180	-179.24	-178.8	-179.18	-180.9	-179.58	-180.58	-180.58	-180.91	-178.96
CFCF2C(=O)	+	ccfc	=	CFCFC(=O)	+	ccf2c	-179.38	-179.13	-179.23	-179.33	-179.65	-178.41	-180.06	-180.47	-180.47	-180.89	-179.72
CFCF2C(=O)	+	CCC(=O)	=	CCF2C(=O)	+	CFCC(=O)	-180.5	-180.3	-180.09	-180.06	-180.55	-180.2	-180.81	-181.4	-181.4	-182.23	-180.74
CFCF2CF(=O)																	
CFCF2CF(=O)	+	CFC(=O)	=	CFCFCF(=O)	+	CFCF(=O)	-237.8	-236.88	-237.1	-236.73	-238.29	-239.63	-236.35	-239.99	-239.99	-237.28	-235.82
CFCF2CF(=O)	+	CF2C(=O)	=	CFCFCF(=O)	+	CF2CF(=O)	-236.55	-235.53	-235.8	-235.6	-237.16	-239.18	-235.35	-238.15	-238.15	-235.28	-234.61
CFCF2CF(=O)	+	CC(=O)	=	CFCFCF(=O)	+	CCF(=O)	-237.43	-236.67	-236.37	-236.35	-237.62	-237.66	-236.63	-239.33	-239.33	-238.35	-236.13
CFCF2CF(=O)	+	CCC(=O)	=	CFCFCF(=O)	+	CFCC(=O)	-237.73	-237.48	-236.96	-235.75	-237.38	-239.31	-238.16	-240.36	-240.36	-241.08	-237.24

Each of the fluorinated compounds are analyzed using two to five isodesmic work reactions where the reference species reacts and yields a molecule with the number of each bond types conserved in products and reactants. This leads to the cancellation of systematic errors in the molecular orbital calculations[109].

Optimized structure parameters, symmetry values, moments of inertia, vibrational frequencies, internal rotor potentials, entropies, and heat capacities for each species from the B3-LYP/6-31G(d,p) level of theory are presented in Appendix B.

3.4.1 Heat of Formation $\Delta H°_{f\,298}$

A summary of the standard enthalpy of formation $(\Delta H°_{f\ 298})_{averages}$ from DFT and composite methods for species from work reactions illustrated in Table 3.3 are summarized in Table 3.4. Evaluation of the error for these standard enthalpies of formation are provided in several ways. Table 3.4 list the average reference species uncertainty when available, along with the standard deviation from the calculated standard enthalpy of formation ($\Delta H°_{f\ 298}$) values from the computational methodology utilized in work reactions. The resulting standard deviations from the reactions show an average standard deviation of 0.96 kcal mole^{-1}. These standard deviations coincide with the average standard deviations, on a per work reaction basis determined in Table 3.3. Values in Table 3.3 are recommended for evaluation of accuracy and note that the uncertainty in the reference species also needs to be considered.

On the basis of the correlations in these different techniques, error values are provided in Table 3.6 using the standard deviation from the individual calculated standard enthalpy of formation ($\Delta H°f_{298}$) values.

Table 3.6 Summary of Average $\Delta H^\circ f_{298}$ and Literature Values[a] for Fluoroaldehydes

Species	Calculated Enthalpy of Formation (kcal mole^{-1})	Literature Values (kcal mole^{-1})
$CH_2FCH(=O)$	-80.4 ± 0.7	-60.17 [109], -80.2 [56]
$CH_2FCF(=O)$	-143.6 ± 0.7	-143.6 [56]
$CHF_2CH(=O)$	-130.0 ± 0.6	-83.80 [109], -130.0 [56]
$CHF_2CF(=O)$	-190.1 ± 1.0	-190.2 [56]
$CF_3CH(=O)$	-185.4 ± 0.5	-107.43 [109], 186.5 [56]
$CF_3CF(=O)$	-245.8 ± 1.4	−239.30 [111], -246.3 [56]
$CH_3CF(=O)$	-105.8 ± 0.7	-106.7 ± 0.2 [112], -106.4 [113], -105.8 [56]
$CH_2FCH_2CH(=O)$	-87.4 ± 1.2	This work
$CH_2FCHFCH(=O)$	-130.6 ± 1.1	This work
$CH_2FCHFCF(=O)$	-192.3 ± 0.7	This work
$CHF_2CH_2CH(=O)$	-141.1 ± 0.6	This work
$CHF_2CHFCH(=O)$	-181.8 ± 0.8	This work
$CHF_2CHFCF(=O)$	-242.8 ± 0.4	This work
$CF_3CH_2CH(=O)$	-181.8 ± 0.8	This work
$CF_3CHFCH(=O)$	-220.4 ± 0.8	This work
$CF_3CHFCF(=O)$	-282.7 ± 2.2	This work
$CH_3CHFCH(=O)$	-89.9 ± 0.5	This work
$CH_3CHFCF(=O)$	-152.6 ± 0.6	This work
$CH_3CF_2CH(=O)$	-143.4 ± 0.6	This work
$CH_2FCF_2CH(=O)$	-181.4 ± 0.7	This work
$CH_2FCF_2CF(=O)$	-242.0 ± 1.4	This work
$CHF_2CF_2CH(=O)$	-230.7 ± 0.6	This work
$CHF_2CF_2CF(=O)$	-289.9 ± 1.5	This work
$CF_3CF_2CH(=O)$	-330.5 ± 2.6	This work
$CF_3CF_2CF(=O)$	-344.7 ± 2.0	This work
$CH_3CF_2CF(=O)$	-203.9 ± 0.5	This work
$CH_3CH_2CF(=O)$	-110.7 ± 1.2	This work
$CH_2FCH_2CF(=O)$	-153.1 ± 0.8	This work
$CHF_2CH_2CF(=O)$	-206.7 ± 1.2	This work
$CF_3CH_2CF(=O)$	-262.5 ± 0.6	This work
$CHFCH(=O)$	-45.3 ± 1.6	This work
$CH_2CF(=O)$	-60.1 ± 0.7	This work
$CH_2FC(=O)$	-40.9 ± 2.2	-41.9[56]
$CHFCF(=O)$	-104.1 ± 1.7	This work
$CF_2CH(=O)$	-92.6 ± 2.5	This work

[a] Units kcal mole^{-1}. Error is standard deviation from work reaction table; see also table 3.2 for reference species uncertainties.

Table 3.6 Summary of Average ΔH°*f* $_{298}$ and Literature Values[a] for Fluoroaldehydes (Continued)

Species	**Calculated Enthalpy of Formation (kcal mole^{-1})**	**Literature Values (kcal mole^{-1})**
$CHF_2C(=O)$	-89.3 ± 2.2	-90.3[56]
$CF_2CF(=O)$	-148.5 ± 2.9	This work
$CF_3C(=O)$	-140.6 ± 0.9	-145.6[56]

[a] Units kcal mole^{-1}. Error is standard deviation from work reaction table; see also table 3.2 for reference species uncertainties.

These data demonstrate good agreement for the Δ*H°f 298* values between the DFT and the higher level methods, which results from the use of work reactions. The average difference in species comparable to literature values is reported as 0.31 kcal mole^{-1}, with the maximum difference being 1.11 kcal mole^{-1}. Good agreement from the computational methods and work reactions utilized in this segment provide acceptable values.

Trends in the enthalpy change when a fluorine atom is substituted for a hydrogen atom.

The replacement of a hydrogen atom on the methyl group of acetaldehyde, $CH_3CH=O$, with a fluorine atom, results in a decrease in standard enthalpy of 40 kcal mol^{-1}. A second and a third fluorine atom substitution on this methyl group decrease the enthalpy by 50 and 55 kcal mol^{-1}, respectively.

Alkane fluorocarbons Δ Δ_fH H atom F atom:	ch3ch3 =>	ch2fch3 =>	chf2ch3 =>	cf3ch3
		-45	-55	-59
Aldehyde => acetyl fluoride Δ Δ_fH	ch3cho =>	ch3fcho =>	chf2cho =>	cf3cho
		-40	-50	-55

The above trend shows that the addition of an fluorine atom to the carbonyl oxygen group results in a near consistent ~ 5 kcal mol^{-1} smaller lowering of enthalpy per fluorine for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon. In substitution of a fluorine atom for a hydrogen on the carbonyl (C(=O)) carbon: the enthalpy of formation decrease is 66.1 kcal mol^{-1} from the acetyl aldehyde to acetyl fluoride. From fluoroaldehyde to fluoroacetyl fluoride the enthalpy of formation decrease is 63.2 kcal mol^{-1}; the enthalpy of formation decreases 60.1 kcal mol^{-1} from difluoroaldehyde to difluoroacetyl fluoride; (vi) from trifluoroaldehyde to trifluoroacetyl fluoride, the enthalpy of formation decreases 60.4 kcal mol^{-1}.

ch3cho => ch3cfo => ch2fcfo => chf2cfo => cf3cfo
-66.1 - 63.2 - 60.1 -60.4 Changes in enthalpy
Changes in enthalpy for substitution of fluorines on the methyl group of propanol
ch3ch2cho => ch2fch2cho => chf2ch2cho => cf3ch2cho
-53.6 -53.6 -57.8 Changes in enthalpy

Table 3.7 shows the trends in enthalpy change when a fluorine atom is substituted for a hydrogen atom in the noted reactions. The remaining calculations of changes in enthalpy for substitution of fluorines on aldehyde species is located in Appendix B.

Table 3.7 Trends in Enthalpy Change when a Fluorine Atom in Substituted for a Hydrogen Atom in the Noted Reactions

	ch3cho	=>	ch2fcho	=>	chf2cho	=>	cf3cho		
$\Delta_f H^o_{298}$		-40		-50		-55			
	ch3ch3	=>	ch2fch3	=>	chf2ch3	=>	cf3ch3		
$\Delta_f H^o_{298}$		-45		-55		-59			
	Ch3cho	=>	ch3cfo	=>	ch2fcfo	=>	chf2cfo	=>	cf3cfo
$\Delta_f H^o_{298}$		-66.1		-63.2		-60.1		-60.4	
	ch3ch2ch3	=>	ch2fch2ch3	=>	chf2ch2ch3	=>	cf3ch2ch3		
$\Delta_f H^o_{298}$		-46		-55.6		-59.7			
	ch3ch2cho	=>	ch2fch2cho	=>	chf2ch2cho	=>	cf3ch2cho		
$\Delta_f H^o_{298}$		-43		-53.7		-40.7			
	Ch3ch2cho	=>	Ch3ch2cfo	=>	ch2fch2cfo	=>	chf2ch2cfo	=>	cf3ch2cfo
$\Delta_f H^o_{298}$		-66.3		-42.4		-53.6		-55.8	
	ch3ch2ch3	=>	ch3chfch3	=>	ch3cf2ch3				
$\Delta_f H^o_{298}$		-46.4		-58					
	ch3ch2cho	=>	ch3chfcho	=>	ch3cf2cho				
$\Delta_f H^o_{298}$		-45.5		-53.5					
	Ch3ch2cho	=>	Ch3ch2cfo	=>	ch3chfcfo	=>	ch3cf2cfo		
$\Delta_f H^o_{298}$		-66.3		-41.9		-51.3			
	ch3chfch3	=>	ch2fchfch3	=>	chf2chfch3	=>	cf3chfch3		
$\Delta_f H^o_{298}$		-34.5		-54.9		-56.4			

Table 3.7 Trends in Enthalpy Change when a Fluorine Atom is Substituted for a Hydrogen Atom in the Noted Reactions (Continued)

	ch3chfcho	**=>**	**ch2fchfcho**	**=>**	**chf2chfcho**	**=>**	**cf3chfcho**		
$\mathbf{\Delta_f H^o_{298}}$		-40.7		-51.2		-38.6			
	ch3chfch3	=>	ch2fchfch3	=>	chf2chfch3	=>	cf3chfch3		
$\mathbf{\Delta_f H^o_{298}}$		-34.5		-54.9		-56.4			
	ch3chfco	=>	ch3chfcfo	=>	ch2fchfcfo	=>	chf2chfcfo	=>	cf3chfcfo
$\mathbf{\Delta_f H^o_{298}}$		-62.7		-39.7		-50.5		-39.9	
	ch3cf2ch3	=>	ch2fcf2ch3	=>	chf2cf2ch3	=>	cf3cf2ch3		
$\mathbf{\Delta_f H^o_{298}}$		-41.8		-53.0		-51.2			
	ch3cf2cho	=>	ch2fcf2cho	=>	chf2chfcho	=>	cf3chfcho		
$\mathbf{\Delta_f H^o_{298}}$		-38.4		-49.3		-99.8			
	ch3cf2cho	=>	ch3cf2cfo	=>	ch2fcf2cfo	=>	chf2chfcfo	=>	cf3chfcfo
$\mathbf{\Delta_f H^o_{298}}$		-60.9		-38.1		-47.7		-54.8	

3.4.2 Internal Rotors

Potential energy curves for internal rotations within the parent and radical species are calculated using the B3-LYP/6-31G(d,p) level of theory. Relaxed scans at 10 degree intervals are used to determine the lowest energy geometries. If a lower energy conformation is found, previous scans are re-run to insure the lowest energy conformation is located. These potential energy curves are also used to determine entropy and heat capacity internal rotational contributions.

All of the parent ketone terminal methyl (not adjacent to the carbonyl) groups, exhibit three-fold symmetry with energy barriers between 2-3 kcal mol$_{-1}$. The three-fold barriers are 0.5 kcal mol$_{-1}$ for methyl rotations adjacent to the carbonyl group. Upon radical formation at the methyl site, there is a decrease to two-fold symmetry and a decrease in the barrier energy ranging from below 0.1 to 3.0 kcal mol$_{-1}$ except for the groups adjacent to the carbonyl. Radical sites adjacent to the carbonyl group, regardless of primary, secondary, or tertiary location, have energy barriers over 10 kcal mol$_{-1}$ upon radical formation resulting from the resonance with the carbonyl group.

3.4.3 Entropies (S(T)) and Heat Capacities (C_p(T))

Contributions from each species translations, vibrational frequencies, and external rotations, represented as TVR, are calculated using the rigid-rotor harmonic-oscillator approximation SMCPS[87] code with the zero-point vibration energies (ZPVE) scaled by 0.9806 for B3-LYP/6-31G(d,p) as recommended by Scott and Radom[114].

The contributions from internal rotations, represented by IR, are determined using the calculated potential energy rotational barriers, moments of inertia for each group in the rotor, and barrier foldness. Internal rotor torsion frequencies, including terminal methyl groups, are identified using visual inspection in GaussView and removed from vibration contribution. In cases where identification of a frequency is uncertain due to coupling to other motions, the lower frequency is selected. These are replaced with entropy and heat capacity contributions from the Pitzer and Gwinn method for hindered rotor analysis. Use of the Pitzer and Gwinn methods is described in detail[90]. Complete entropy and heat capacity values from the B3-LYP/6-31++G(d,p) geometries and frequencies are listed in Supporting Information, section S6. TVR represents the sum of the translation, vibration and rotational contributions; IR indicates the contribution from hindered internal rotations, which replace the contribution calculated from reported torsion frequency for the internal rotor(s) in the TVR heat capacity and entropy data.

Table 3.8 illustrates results from several different models for inclusion of internal rotor versus torsion frequency contributions; it also provides comparison with experimental data for the species where it is available. Values from the group additivity (GA) method are also included which coincide well with data observed in this study and literature data providing some support for considering the GA data as reference in the comparisons.

Table 3.8 Entropy and Heat Capacities for Fluoroaldehyde Species for Fluoroaldehydes

Species	S°_{298}	C_P300	C_P 400	C_P 500	C_P 600	C_P 800	C_P 1000	C_P 1500	Rotors
CFC(=O)	65.61	14.27	16.88	19.44	21.71	25.36	28.05	32.14	
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	65.61	**14.27**	**16.88**	**19.44**	**21.71**	**25.36**	**28.05**	**32.14**	
CFCF(=O)	68.42	15.97	18.90	21.55	23.79	27.24	29.65	33.17	
	7.56	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	75.98	**16.96**	**19.89**	**22.54**	**24.78**	**28.23**	**30.64**	**34.16**	
CF2C(=O)	69.36	16.25	19.07	21.66	23.89	27.33	29.74	33.23	
	8.66	0.99	0.99	0.99	0.99	0.99	0.99	0.96	
	78.02	**17.24**	**20.06**	**22.65**	**24.88**	**28.32**	**30.73**	**34.19**	
CF2CF(=O)	73.55	18.00	21.10	23.78	26.00	29.23	31.37	34.28	
	7.88	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	81.43	**18.99**	**22.09**	**24.77**	**26.99**	**30.22**	**32.36**	**35.27**	
CF3CF(=O)	76.10	20.48	23.90	26.61	28.72	31.63	33.41	35.59	
	8.01	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	84.11	**21.47**	**24.89**	**27.60**	**29.71**	**32.62**	**34.40**	**36.58**	
CF3C(=O)	72.27	18.55	21.73	24.39	26.54	29.67	31.73	34.51	
	7.29	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	79.56	**19.54**	**22.72**	**25.38**	**27.53**	**30.66**	**32.72**	**35.50**	
CCF(=O)	64.41	14.43	17.20	19.75	21.97	25.50	28.10	32.13	
	5.71	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	70.12	**15.42**	**18.19**	**20.74**	**22.96**	**26.49**	**29.09**	**33.12**	
CFCC(=O)	71.75	18.61	22.72	26.74	30.31	36.02	40.24	46.70	
	7.90	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.21	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	86.86	**20.60**	**24.71**	**28.73**	**32.30**	**38.01**	**42.23**	**48.69**	
CFCFC(=O)	76.38	21.00	25.23	29.23	32.71	38.14	42.03	47.83	
	7.90	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.32	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	91.60	**22.99**	**27.22**	**31.22**	**34.70**	**40.13**	**44.02**	**49.82**	

[a] Units cal mol-1 K-1. [b] No rotors. Use of torsion frequencies for rotor contributions without reduction (correction) in entropy for equivalent hydrogen atoms in CH3 groups. [c] Only methyl rotors. [d] All internal rotors.

Table 3.8 Entropy and Heat Capacities for Fluoroaldehyde Species (continued)

Species	**$S°_{298}$**	**C_P300**	**C_P 400**	**C_P 500**	**C_P 600**	**C_P 800**	**C_P 1000**	**C_P 1500**	**Rotors**
CFCFCF(=O)	79.96	22.87	27.36	31.42	34.85	40.06	43.67	48.88	
	8.02	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.05	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	96.03	**24.86**	**29.35**	**33.41**	**36.84**	**42.05**	**45.66**	**50.87**	
CF2CC(=O)	75.57	20.67	25.07	29.16	32.68	38.15	42.05	47.85	
	8.34	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.34	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	91.26	**22.66**	**27.06**	**31.15**	**34.67**	**40.14**	**44.04**	**49.83**	
CF2CFC(=O)	80.08	23.04	27.51	31.57	35.01	40.22	43.82	48.98	
	8.41	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.39	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	95.88	**25.03**	**29.50**	**33.56**	**37.00**	**42.21**	**45.81**	**50.96**	
CF2CFCF(=O)	84.18	25.02	29.70	33.79	37.18	42.15	45.46	50.04	
	8.53	0.99	0.99	0.99	0.99	0.99	0.99	0.98	
	8.77	0.99	0.99	0.99	0.99	0.99	0.99	0.93	
	101.48	**27.01**	**31.69**	**35.78**	**39.17**	**44.14**	**47.44**	**51.95**	
CF3CC(=O)	79.72	23.20	27.91	32.02	35.44	40.56	44.08	49.14	
	7.38	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.32	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	95.42	**25.19**	**29.90**	**34.01**	**37.43**	**42.55**	**46.07**	**51.12**	
CF3CFC(=O)	83.52	25.59	30.35	34.42	37.75	42.62	45.84	50.27	
	7.41	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.62	0.99	0.99	0.99	0.99	0.99	0.99	0.97	
	99.55	**27.58**	**32.34**	**36.41**	**39.74**	**44.61**	**47.83**	**52.23**	
CF3CFCF(=O)	86.35	27.40	32.44	36.58	39.88	44.53	47.49	51.33	
	8.77	0.99	0.99	0.99	0.99	0.99	0.99	0.94	
	8.27	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	103.39	**29.39**	**34.43**	**38.57**	**41.87**	**46.52**	**49.47**	**53.26**	

[a] Units cal mol-1 K-1. [b] No rotors. Use of torsion frequencies for rotor contributions without reduction (correction) in entropy for equivalent hydrogen atoms in CH3 groups. [c] Only methyl rotors. [d] All internal rotors.

Table 3.8 Entropy and Heat Capacities for Fluoroaldehyde Species (continued)

Species	**S°_{298}**	**C_P300**	**C_P 400**	**C_P 500**	**C_P 600**	**C_P 800**	**C_P 1000**	**C_P 1500**	**Rotors**
CCFC(=O)	72.41	19.44	23.53	27.42	30.86	36.39	40.48	46.81	
	5.76	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.25	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	85.42	**21.43**	**25.52**	**29.41**	**32.85**	**38.38**	**42.47**	**48.80**	
CCFCF(=O)	75.02	21.23	25.60	29.58	32.99	38.29	42.11	47.84	
	5.76	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.91	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	88.70	**23.22**	**27.59**	**31.57**	**34.98**	**40.28**	**44.10**	**49.83**	
CCF2C(=O)	75.09	21.99	26.33	30.21	33.53	38.69	42.41	48.01	
	5.76	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.30	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	88.15	**23.98**	**28.32**	**32.20**	**35.52**	**40.68**	**44.40**	**50.00**	
CFCF2C(=O)	78.81	23.64	28.07	32.02	35.37	40.44	43.96	49.04	
	8.07	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.85	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	94.73	**25.63**	**30.06**	**34.01**	**37.36**	**42.43**	**45.95**	**51.03**	
CFCF2CF(=O)	83.24	25.51	30.22	34.24	37.55	42.39	45.63	50.11	
	8.21	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.00	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	99.45	**27.50**	**32.21**	**36.23**	**39.54**	**44.38**	**47.62**	**52.10**	

[a] Units cal mol-1 K-1. [b] No rotors. Use of torsion frequencies for rotor contributions without reduction (correction) in entropy for equivalent hydrogen atoms in CH3 groups. [c] Only methyl rotors. [d] All internal rotors.

3.4.4 Group Additivity (GA)

In this section we attempt to develop Benson Group Additivity values for the C2 and C3 fluorinated aldehydes for estimation of the standard enthalpy, entropy and heat capacity values versus temperature. Benson Group Additivity is based on the knowledge of the contributions of representative groups in similar molecules and the experimentally observed linear consistency in thermochemical properties such as heat capacity, entropy and enthalpy values with addition of different hydrocarbon groups.

Group values are initially determined when fluorines are added to only one of the carbons atoms in the acetaldehyde and in propanal in order to circumvent energy effects from fluorine / fluorine interactions on adjacent carbons. For example: the c/c/co/h/f and c/c/co/f2 groups are determined from ch3chfcho and ch3cf2cho respectively; the c/c/h2/f and c/c/h/f2 and c/c/f3 are determined from ch2fch2ch=o, chf2ch2ch=o and cf3ch2ch=o respectively.

The CO/C/F (-CF=O) group is developed from CH3CF=O and CH3CH2CF=O

Thermochemical data were developed for the following groups CO/C/F, C/CO/F/H2, C/CO/F2/H, C/CO/F3, C/C/CO/F2 and C/C/CO/F/H.

These groups can then be used to estimate properties of larger mono-fluoro-hydrocarbon aldehydes.

Fluoroacetaldehyde CH2FCH(=O)

Groups for group additivity contributions to mono fluoroacetaldehyde are:

$$CH_2FCH\ (=O) = C/CO/F/H2 + CO/C/H \qquad (3.4)$$

Fluoroacetaldehyde (CH_2FCH (=O)) consists of two groups: C/CO/F/H2 and CO/C/H.

The contribution of carbonyl group CO/C/H is taken from known hydrocarbon aldehydes and has a value of -29.10 kcal mole^{-1} [91].

The group C/CO/F/H2 is not reported in the literature and is determined in this study using our calculated value of the standard enthalpy of formation for $CH_2FCH(=O)$ above in Equation 4.

-80.41 = C/CO/F/H2 + -29.10 units: kcal mol^{-1}- (3.5)
C/CO/F/H2 = -80.41 – (-29.10) (3.6)
C/CO/F/H2 = -51.31 (3.7)

Difluoroacetaldehyde ($CHF_2C(=O)$), enthalpy of formation of the C/CO/F2/H group.

$CHF_2CH(=O)$ = C/CO/F2/H + CO/C/H (3.8)
-130.03 = C/CO/F2/H + (-10.08) (3.9)
C/CO/F2/H = -100.93 (3.10)

Trifluoroacetaldehyde ($CF_3C(=O)$), enthalpy of formation of the C/CO/F3 group.

$CF_3CH(=O)$ = C/CO/F3 + CO/C/H (3.11)
-185.39 = C/CO/F3 + (-10.08) (3.12)
C/CO/F3 = -156.29 (3.13)

Fluorine on the carbonyl group - acetylfluoride ($CH_3CF(=O)$)

The example below utilizes our calculated enthalpy of formation of acetylfluoride ($CH_3CF(=O)$), (-105.84) and the enthalpy of formation for the C/CO/H3 group from the oxygenated hydrocarbon aldehyde and ketone literature, to determine the values for the enthalpy of formation of the CO/C/F group.

$CH_3CF(=O)$ = C/CO/H3 + CO/C/F (3.14)
-105.84 = (-10.08) + CO/C/F (3.15)
CO/C/F = -95.76 (3.16)

A similar process is used for entropy and heat capacity values. It is important to note at this point that the groups derived above are only useful for fluoro acetaldehydes and fluoropropanals where fluorine(s) are only on one of the carbon atoms in the two or three carbon species. Group additivity will be shown (below) to require additional terms (non next neighbor interaction terms) when fluorine atoms are on more than 1 of the carbon atoms in the C2 and C3 aldehydes.

Standard molar enthalpy, entropy values and heat capacity values for the fluoro-aldehydes in this study are listed in Table 3.8. These values are used to determine the Group Additivity values for the groups listed below. Each target group was determined in a manner similar to the CO/C/F and C/CO/F/H2 examples, where there are fluorine atoms only on one of the carbons in the molecule. There are no fluorine atoms on adjacent or on other carbons. Table 3.9 lists the Benson type groups in each of the 30 species in this study.

Table 3.9 Groups for Fluorinated Aldehydes

Molecule	CFC(=O)	CFCF(=O)	CF2C(=O)	CF2CF(=O)	CF3CF(=O)
Group 1	C/CO/F/H2	C/CO/F/H2	C/CO/F2/H	C/CO/F2/H	C/CO/F3
Group 2	CO/C/H	CO/C/F	CO/C/H	CO/C/F	CO/C/F
Group 3	-	-	-	-	-
Molecule	CF3C(=O)	CCF(=O)	CFCC(=O)	CFCFC(=O)	CFCFCF(=O)
Group 1	C/CO/F3	C/CO/H3	C/C/F/H2	C/C/F/H2	C/C/F/H2
Group 2	CO/C/H	CO/C/F	C/C/CO/H2	C/C/CO/F/H	C/C/CO/F/H
Group 3	-	-	CO/C/H	CO/C/H	CO/C/F
Molecule	CF2CC(=O)	CF2CFC(=O)	CF2CFCF(=O)	CF3CC(=O)	CF3CFC(=O)
Group 1	C/C/F/H2	C/C/F2/H	C/C/F2/H	C/C/F3	C/C/F3
Group 2	C/C/CO/F/H	C/C/CO/F/H	C/C/CO/F/H	C/C/CO/H2	C/C/CO/F/H
Molecule	CF3CFCF(=O)	CCFC(=O)	CCFCF(=O)	CCF2C(=O)	CFCF2C(=O)
Group 1	C/C/F3	C/C/H3	C/C/H3	C/C/H3	C/C/F/H2
Group 2	C/C/CO/F/H	C/C/CO/F/H	C/C/CO/F/H	C/C/CO/F2	C/C/CO/F2
Group 3	CO/C/H	CO/C/H	CO/C/F	CO/C/H	CO/C/H
Molecule	CFCF2CF(=O)	CF2CF2CF(=O)	CF3CF2CF(=O)	CF3CF2C(=O)	CCF2CF(=O)
Group 1	C/C/F/H2	C/C/F2/H	C/C/F3	C/C/F3	C/C/H3
Group 2	C/C/CO/F2	C/C/CO/F2	C/C/CO/F2	C/C/CO/F2	C/C/CO/F2
Group 3	CO/C/F	CO/C/F	CO/C/F	CO/C/H	CO/C/F
Molecule	CCCF(=O)	CFCCF(=O)	CF2CCF(=O)	CF3CCF(=O)	CF2CF2C(=O)
Group 1	C/C/H3	C/C/F/H2	C/C/F2/H	C/C/F3	C/C/F2/H
Group 2	C/C/CO/H2	C/C/CO/H2	C/C/CO/H2	C/C/CO/H2	C/C/CO/F2
Group 3	CO/C/F	CO/C/F	CO/C/F	CO/C/F	CO/C/H
Group 3	CO/C/H	CO/C/H	CO/C/F	CO/C/H	CO/C/F

Table 3.10 lists the calculated enthalpy of formation value for the groups calculated as above, where there were no fluorine atoms on adjacent carbons.

Table 3.10 Standard Molar Enthalpy, Entropy and Heat Capacities (300-1500K) for Groups used in Benson[38] Group Additivity for the C_2 and C_3 Fluoroaldehydes

Group	HF	S_{298}	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
c/co/h3[38]	-10.08	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
c/co/f/h2*[1]	-51.31	60.98	18.00	21.63	24.74	27.32	31.01	33.61	50.96
c/co/f2/h *[2]	-100.93	53.25	16.95	20.45	23.38	25.84	29.48	32.20	50.00
c/co/f3 *[3]	-156.29	44.66	12.51	14.85	16.56	17.85	19.46	20.52	
co/c/h[38]	-29.1	34.9	7.03	7.87	8.82	9.68	11.2	12.2	
co/c/f *[4]	-95.76	39.71	9.23	10.35	11.34	12.17	13.47	14.32	15.54
c/c/f/h2[104]	-55.28	34.86	7.45	9.03	10.54	11.85	13.92	15.42	17.84
c/c/co/h2[38]	-5.2	9.6	6.2	7.7	8.7	9.5	11.1	12.2	14.07
c/c/co/f/h[5]	-46.23	6.22	2.48	2.99	3.18	3.25	3.11	3.02	16.32
c/c/f3[104]	-168.2	42.55	12.75	15.05	16.71	17.86	19.27	19.98	20.68
c/c/co/f2*[6]	-104.60	22.84	10.76	12.61	13.98	15.05	16.46	17.43	32.42
c/co/f2/h *[7]	-96.95	59.74	18.26	21.85	24.88	27.36	30.90	33.29	36.55
c/c2/co/h[38]	-1.7	-11.70	4.16	5.91	7.34	8.19	9.46	10.19	
c/c2/h2[38]	-5.00	9.40	5.50	6.95	8.25	9.35	11.07	12.34	14.20
c/c3/co[38]	1.40	-34.72	3.99	6.04	7.43	8.26	8.92	8.96	8.23

*This study, note the c/co notation assumes a hydrogen atom on the aldehyde carbon; a group derived from acetaldehyde, 1 group derived from fluoroaldehyde, 2 group derived from di fluoroaldehyde, 3 group derived from tri fluoroaldehyde, 4 group derived from acetyl fluoride, 5 group derived from cfcfc(=o), 6 group derived from ccf2c(=o), 7 group derived from cf2cf2c(=o), H atoms are assumed to fill valence.

Thermochemical data of species in this study calculated by group additivity can be found in Supporting Information, S7.

3.4.5 Interaction Group Terms (GA)

In conventional hydrocarbon and oxy-hydrocarbon group additivity the C/C/H/CO and C/CO/H3 group enthalpy values accurately predict enthalpy and heat capacities for acetaldehyde $CH_3CH=O$ and for larger aldehydes, where no additional non next nearest neighbor groups are needed. For the hydrocarbons and oxy-hydrocarbons one group for each central atom (atom with two or more bonds, provide accurate estimates of thermochemical values.

Example groups for ch3ch=o (a) groups are c/co/h3, co/c/h
ch3ch2ch=o (b) groups are c/c/h3, c/c/co/h2 and co/c/h
ch3ch2ch2ch=o (c) groups are c/c/h3, c/c2/h2, c/c/co/h2 and co/c/h
cc(c)c=o (d) groups c/c/h3, c/c2/co/h and co/c/h

The co/c/h group used in these pure hydrocarbon aldehydes provide correct data for ch3ch=o, ch3ch2ch=o, ch3ch2ch2ch=o and cc(c)c=o and the sum of group values shows good agreement with literature values -39.7, -44.36, -50.61, -51.57 kcal mole^{-1}, respectively. Similarly results for ch3ch=o, ch3ch2ch=o, ch3ch2ch2ch=o and cc(c)c=o from group additivity values are -39.18, -44.30, -49.3 and -50.80 kcal mole^{-1}, respectively. The literature and group additivity values show good agreement; there is no need for non next nearest neighbor specie contributions.

This lack of non next neighbor interactions in group additivity is not the case for fluorocarbons (ref h1, h2). As an example it is reported for CH_2FCH_2F would have two C/C/F/H2 groups; but sum value of the two C/C/F/H2 groups determined from the CH3CH2F molecule results in is an under estimate by some 3xx. kcal/mol due to the repulsions and electronic interactions of the two fluorine atoms, one on each of the adjacent carbons[104, 113, 115]. Here the fluorine atoms present interactions by non next nearest neighbors (NNN interaction).

The groups determined from the fluoro aldehydes above had fluorine atoms on only one of the carbon atoms. H. Wang *et al.*[104] and T. Yamada *et al*.[114, 115] have shown that molecules with fluorine on two adjacent carbon atoms do not follow conventional Benson Group Additivity where a group is identified by only the atoms bonded to it. Additional groups or interaction terms have to be implemented when fluorine and other halogen atoms are on two adjacent carbon atoms; this is a result of interactions between the halogens on adjacent carbons. The interaction terms incorporate adjustments for the electronic and steric interactions of the halogens on next nearest neighbor atoms. The examples below illustrate that interaction terms are needed when a fluorine atom is on each of any two adjacent carbons for the aldehydes in this study.

Molecules with fluorine atoms on the adjacent carbons.

Group additivity for multi-fluoro, fluorocarbon aldehydes. We show below that groups developed above: C/CO/F/H2, C/CO/F2/H and C/CO/F3, do not result in accurate enthalpy values for the three respective fluoroaldehydes when the CO/C/F fluoroacetyl group is present.

Table 3.11 illustrates the calculated fluorine/fluorine / CFO interaction group term enthalpies of formation in comparison for the fluoro acetaldehydes in the current study. The CFO nomenclature in the interaction term signifies a -CF(=O)- group.

The standard enthalpy of formation values for multifluorinated acetaldehydes and propanaldehydes in this study as listed in Table 3.11 are used as the target enthalpy for the group calculations. The following interaction groups have been developed to account for the structural difference new groups were created to better fit fluoroaldehydes. These groups include: F/CFO, F2/CFO, F3/CFO, F2/F/CO, F2/F2/CO, F3/F/CO, F3/F2/CO, RF/CFO, RF2/CFO and RF3/CFO.

Table 3.11 Fluorine-Fluorine Interaction Terms Needed for Group Additivity for Formation Enthalpy on C2 - C3 Aldehydes

Interaction Terms	$\Delta H°_{f\ 298\ (kcal\ mole^{-1})}$
F/F	2.6 [104]
2F/F	5.2 [104]
2F/2F	9.3 [104]
3F/F	7.4 [104]
3F/2F	13.4 [104]
F/CFO	3.50
F2/CFO	6.59
F3/CFO	13.45
F2/F/CO	-4.23
F3/F/CO	25.43
F3/F2/CO	-26.3
RF/CFO	3.14
RF2/CFO	4.96
RF3/CFO	8.98

Calculation of C2 Fluorine Interaction Terms

The following interaction groups have been developed to account for the different fluorine – fluorine interactions for the fluorinated aldehydes: F/CFO, F2/CFO and F3/CFO.

$CH_2FCF(=O)$ is reported to have a enthalpy of formation of -143.6 kcal-mol^{-1}. Utilizing only the group additivity terms C/CO/F/H2 and CO/C/F, the group term values requires a new group term as shown below. As a result of this inconsistency, $CH_2FCF(=O)$ was utilized to develop the interaction group F/CFO. Using additivity groups C/CO/F/H2 derived from $CH_2FCH(=O)$ and C/CO/F group derived from $CH_3CF(=O)$, we now follow the same steps in equations used to calculate new group additivity terms, only differing in the addition of Δ. Δ represents the interaction group being calculated. Calculation of Δ in Equation 3.17-3.19 is for interaction group F/CFO

$$CH_2FCF(=O) = C/CO/F/H2 + CO/C/F + \Delta \qquad (3.17)$$

$$-143.6 = (-51.31) + (-95.76) + \Delta\ (F/CFO) \qquad (3.18)$$

$$\Delta\ (F/CFO) = +3.50 \text{ kcal-mol}^{-1} \tag{3.19}$$

$CHF_2CF(=O)$ was utilized to develop the interaction group F2/CFO because of the same reason observed in the group terms utilized for $CH_2FCF(=O)$. Using additivity group terms C/CO/F2/H derived from $CHF_2CH(=O)$ and C/CO/F. The group additivity method resulted in an observed enthalpy of formation of -196.69 kcal-mol^{-1}. The poor agreement requires the same steps used during the calculation of F/CFO for F2/CFO. Calculation of Δ in Equations 3.20-3.22 are for interaction group F2/CFO.

$$CHF_2CF(O) = C/CO/F2/H + CO/C/F + \Delta \tag{3.20}$$

$$-190.1 = (-100.93) + (-95.76) + \Delta\ (F2/CFO) \tag{3.21}$$

$$\Delta\ (F2/CFO) = +6.59 \text{ kcal-mol}^{-1} \tag{3.22}$$

$CF_3CF(=O)$ was utilized to develop the interaction group F3/CFO as a result of poor agreement only using the additivity group terms C/CO/F3 derived from $CF_3CH(=O)$ and C/CO/F. Following the same steps used for F/CFO and F2/CFO. F3/CFO, represented as Δ will be the interaction group being calculated. Calculation of the interaction group F3/CFO is shown in Equations 3.23-3.25.

$$CF_3CF(O) = C/CO/F3 + CO/C/F + \Delta \tag{3.23}$$

$$-238.6 = (-156.29) + (-95.76) + \Delta\ (F3/CFO) \tag{3.24}$$

$$\Delta\ (F3/CFO) = +13.45 \text{ kcal-mol}^{-1} \tag{3.25}$$

The remainder of the interaction term calculations are located in Appendix B.

3.4.6 Bond Dissociation Energies of Fluorinated Aldehydes

Fluorocarbons have been shown to have strong carbon – fluorine bonds, they are highly stable, persist for long periods in the environment and are often a component in fire retardants. The presence of hydrogen on a fluorocarbon make the molecule subject to reactions with OH or other active radicals forming a fluorocarbon radical[56].

It is of value to determine the bond strength of fluorine and hydrogen to carbon bonds in fluorocarbons to understand and evaluate their reactions in various environments. The bond dissociation energies are determined for the fluoro acetaldehydes, fluoropropanals and corresponding fluoroacetyls using calculated enthalpies of formation for the radicals. This was accomplished by using bond dissociation reaction equations.

$$\Delta H_{reaction}=\Sigma\Delta H_{product}-\Sigma\Delta H_{reactants}$$

Where $\Delta H_{reaction}$ corresponds to the bond dissociation energy, $\Sigma\Delta H_{product}$ is the radical species enthalpy of formation with the enthalpy of a hydrogen atom, which has a $\Delta H_{f}^{\circ}{}_{298}$ of 52.103 kcal $mole^{-1}$ or a fluorine atom which has a $\Delta H_{f}^{\circ}{}_{298}$ of 18.97 kcal $mole^{-1}$.

When observing fluorinated C2 aldehyde species ($C_2H_{4-x}OF_x$), where x in this case corresponds to the number of fluorine atoms present in the structure. All BDE values calculated are located in Table 3.12 and compared with literature values to bolster results when available.

$CH_2FCH(=O)$

BDE in $CH_2FCH(=O)$ can be evaluated at both the primary carbon and the carbonyl carbon. On the primary carbon the carbon-hydrogen bond has an observed BDE of 87.2 kcal $mole^{-1}$, and a carbon-flourine BDE of 103.8 kcal $mole^{-1}$. The carbonyl carbon shows an observed BDE of 91.6 kcal $mole^{-1}$, consistent with literature where the same bond has a reported BDE of 90.6[56] kcal $mole^{-1}$.

$CH_3CF(=O)$

There are two sites where a radical can be formed on the $CH_3CF(=O)$species. These include the fluorine-carbon bond on the carbonyl group and the carbon-hydrogen bond located on the primary carbon. The fluorine-carbon bond at the carbonyl site is observed to have the highest bonding energy at 122.5 kcal mole^{-1}, consistent with the literature value of 122.7[56] kcal mole^{-1}. The carbon-hydrogen bond on the primary site has a bonding energy of 97.9 kcal mole^{-1}.

$CH_2FCF(=O)$

In the chemical species $CH_2FCF(=O)$ there are three BDE observed. The primary carbon bonds include the carbon-hydrogen and carbon-fluorine bonds that have a BDE of 91.6 and 102.5 kcal mole^{-1}, respectively. The carbonyl carbon-fluorine bond has a BDE of 121.6 kcal mole^{-1}, consistent with the literature value of 120.9 kcal mole^{-1} [56].

$CHF_2CH(=O)$

Similar to that of $CH_2FCH(=O)$, $CHF_2CH(=O)$ has three bonding sites which are analyzed at both the primary carbon and the carbonyl carbon. On the primary carbon the carbon-hydrogen bond has an observed BDE of 89.5 kcal mole-1, and a carbon-fluorine BDE of 103.7 kcal mole^{-1}. The carbon-fluorine bond is this species is consistent with the BDE of $CH_2FCH(=O)$. The carbonyl carbon shows an observed BDE of 92.8 kcal mole^{-1}, consistent with literature where the same bond has a BDE of 92.7[56] kcal mole^{-1}.

$CHF_2CF(=O)$

The CHF2CF(=O) species has a BDE at the primary carbon site has a BDE of 105.0 and 93.7 kcal mole^{-1} for the carbon-fluorine and carbon-hydrogen bond, respectively. The carbonyl group has a BDE of 119.8 kcal mole^{-1}, consistent with the literature value reported at 120.3[56] kcal mole^{-1}.

$CF_3CH(=O)$

The BDE for the species $CF_3CH(=O)$ are evaluated at the primary carbon site and the carbonyl group. The primary carbon site is a carbon-fluorine bond has a reported BDE of 111.8 kcal mole^{-1}. The carbonyl site has a BDE for the carbon-hydrogen bond of 96.9 kcal mole^{-1}, which is consistent with the literature value of 93.8[56] kcal mole^{-1}.

$CF_3CF(=O)$

The BDE of the carbon-fluorine bond in the species $CF_3CF(=O)$ at the primary carbon and carbonyl carbon location are 116.3 and 124.1 kcal mole^{-1}, respectively. The carbonyl carbon-fluorine bond is ~3 kcal mole^{-1} strong than that compared with literature where the same bond is reported to be 120.8[56] kcal mole^{-1}.

Table 3.12 Bond Dissociation Energies (BDE) of C2 Fluoroaldehydes Species in this Study

		Reaction			Bond Dissociation Energy (kcal mole^{-1})	
CCF(=O)						
CCF(=O)	=	H	+	CjCF(=O)		
-105.8		52.1		-60.1	97.9	This Study
CCF(=O)	=	F	+	CCj(=O)		
-105.8		18.97		-2.3	122.5	122.7 [69]
CFC(=O)						
CFC(=O)	=	F	+	CjC(=O)		
-80.4		18.97		4.4	103.8	This Study
CFC(=O)	=	H	+	CFCj(=O)		
-80.4		52.1		-40.9	91.6	90.6 [56]
CFC(=O)	=	H	+	CjFC(=O)		
-80.4		52.1		-45.3	87.2	This Study
CFCF(=O)						
CFCF(=O)	=	F	+	CFCj(=O)		
-143.6		18.97		-40.9	121.6	120.9[569]
CFCF(=O)	=	F	+	CjCF(=O)		
-143.6		18.97		-60.1	102.5	This Study
CFCF(=O)	=	H	+	CjFCF(=O)		
-143.6		52.1		-104.1	91.6	This Study
CF2C(=O)						
CF2C(=O)	=	F	+	CjFC(=O)		
-130.0		18.97		-45.3	103.7	This Study
CF2C(=O)						
CF2C(=O)	=	H	+	CjF2C(=O)		
-130.0		52.1		-92.6	89.5	This Study
CF2C(=O)						
CF2C(=O)	=	H	+	CF2Cj(=O)		
-130.0		52.1		-89.3	92.8	92.7 [56]

Table 3.12 Bond Dissociation Energies (BDE) of C2 Fluoroaldehydes Species in this Study (Continued)

CF2CF(=O)						
CF2CF(=O)	=	F	+	CjFCF(=O)		
-190.1		18.97		-104.1	105.0	This Study
CF2CF(=O)	=	F	+	CF2Cj(=O)		
-190.1		18.97		-89.3	119.8	120.3 [56]
CF2CF(=O)	=	H	+	CjF2CF(=O)		
-190.1		52.1		-148.5	93.7	This Study
CF3C(=O)						
CF3C(=O)	=	H	+	CF3Cj(=O)		
-185.3948581		52.103		-140.629	96.9	93.8 [56]
CF3C(=O)	=	F	+	CjF2C(=O)		
-185.3948581		18.97		-92.6	111.8	This Study
CF3CF(=O)						
CF3CF(=O)	=	F	+	CF3Cj(=O)		
-245.8		18.97		-140.629	124.1	120.8 [56]
CF3CF(=O)	=	F	+	CjF2CF(=O)		
-245.8		18.97		-148.5	116.3	This Study

3.5 Conclusions

Thermodynamic properties standard enthalpy, entropy and heat capacity of fluorinated two and three carbon aldehydes were calculated using density functional, *ab initio* and composite methods with the use of isodesmic reaction schemes for cancellation of calculation errors in enthalpy. Standard enthalpies of formation were determined using the average value observed in each species at the CBS-APNO, CBS-4M, CBS-QB3 M062X, ωB97X, B3-LYP, G-2, G-3, G-4 and Weizmann-1 (W1U) calculation levels and multiple work reactions. Entropies and heat capacities were determined using the B3-LYP/6-31++G(d,p) optimized geometries and frequencies. Hindered internal rotational contributions to entropy and heat capacities were calculated by intramolecular torsion potential curves at the B3-LYP/6-31+G(d,p) level, with an entropy correction of mixing of rotational conformers. This study also established a trend of for values when a fluorine is added to an aldehyde molecule, whether it is located on the primary, secondary or aldehyde double bond site. In addition, thermochemical data were established for groups CO/C/F, C/CO/F3, C/CO/F/H2, C/C/CO/F/H, C/C/CO/F2 and C/C/CO/F/H.

CHAPTER 4

THERMOCHEMICAL PROPERTIES ENTHALPY, ENTROPY, AND HEAT CAPACITY OF FLUORINATED KETONES AND CORRESPONDING RADICALS; COMPARISON OF FLUOROCARBON GROUP ADDIVITY

4.1 Overview

During the last several decades significant research efforts have been undertaken to find efficient and environmentally friendly substances with zero contribution to ozone depletion[116]. This is due to recent international restrictions on the production and deployment of chloro-fluorocarbons and bromo-fluorocarbons. Fluorinated hydrocarbons are present in the atmosphere, hydrosphere, and lithosphere as a result of the past use of solvents and propellants, in addition to the current wide spread use of refrigerants, fire retardants, and heat exchange fluids and polymers. Other uses include lubricants, blowing and sterilizing agents, coatings, anaesthetics, and agents in the preparation of semiconductors.

Fluorocarbons have no ozone depleting potential; they do however exhibit one important disadvantage: The long atmospheric lifetimes and strong absorption in the infrared spectral region give rise to high global warming potentials. Fluorocarbons and hydrofluorocarbons have been identified as promising candidates as fire surpressants[2], and considerable effort is being devoted to their study, which has resulted in the generation of extensive thermochemical and kinetic databases[101, 117].

Multiple studies have demonstrated the occurrence, bioaccumulation, and toxicity of perfluorinated chemicals (PFCs) in wildlife and humans around the world[118]. Perfluorinated chemicals are a class of anthropogenic chemicals that make up a large group of persistent anthropogenic chemicals used in industrial processes and commercial products over the past 60 years[119, 120]. Due to their widespread use and subsequent emissions, PFCs, have been detected not only in environmental matrices from populated urban areas[100], but also in samples from remote Arctic regions and mountaintops[121].

The 2011−2012 U.S. National Health and Nutrition Examination Survey reported detectable serum PFCS concentrations in virtually all individuals (97%)[100, 110]. Sources of human exposure to PFCs include drinking water, food, food packaging, treated carpets, upholstery, clothing, house dust, protective sprays and waxes, and indoor and outdoor air[116, 110]. Human PFCS exposure has been linked to cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption[3, 5, 117]. Because of the high percentage of human exposure, PFCs are present in human breast milk and umbilical cord blood, and serum levels in infants and children are generally higher than in adults.[116, 110] These prenatal and early life exposures are relevant to potential developmental effects[119, 120].

Bioaccumulation studies in fish and rodents have shown that linear PFCs, such as PFOS and PFOA, are more bioaccumulative compared to the corresponding branched isomers. It has also been reported that major branched isomers of PFOA and PFOS were more efficiently excreted from humans through urine compared to their corresponding linear isomers[38].

PFCs, more specifically PFAAs, were proposed to undergo long-range transport to the Arctic regions through a combination of ocean currents and atmosphere. Atmospheric particulate matter acts as a sink to accumulate atmospheric contaminants and brings the associated contaminants to the earth’s surface via dry deposition. The settled outdoor dust, especially the fine particles (1−50 μm), can also migrate globally via resuspension. As a result, the remigration of outdoor dust can contribute to the LRAT potential of contaminants via atmospheric resuspension and re-entrainment[118].

Quantum chemical calculations on small molecules can result in thermochemical values with a low degree in uncertainties, often outperforming experimental results[3, 5-7, 9]. The precise knowledge of the thermodynamic and kinetic properties of the atmospheric reactions, as well as the physical parameters of the corresponding species, is required for chemistry-climate models. Databases such as NIST-JANAF[9], CODATA[10], ATcT[11], JPL[12] and Burcat's Third Millennium Thermodynamic Database[13], contain the relevant physicochemical parameters; unfortunately, there are limited data for oxygenated fluorocarbon species and these data are needed to understand and evaluate the reactions of the many fluorocarbon species routinely detected in the environment[118- 121]. The limited available data and its uncertainty may well be due to the fact that the chemistry of the troposphere and stratosphere is dominated by free radical reactions and experimental determination of physical and chemical parameters of radicals and radical reaction is still challenginG-3. With respect to atmospheric concerns, C-F bonds are chemically inert and the fluorine atoms in the molecules also tend to deactivate the remaining C-H bonds[122].

In recent years computational chemistry has evolved to a stage where the calculation of thermodynamic functions of small molecules and can achieve experimental or even higher accuracy. DFT, and Composite *ab initio* methods in the Gaussian suite of programs, were used to develop thermochemical properties and a group additivity scheme for estimation of larger flourinated hydrocarbons values. We calculate the standard enthalpy of formation for this series of acetone and fluoro ketones ($C_3H_xOF_{6-x}$) using computational chemistry and isodesmic work reactions. Eleven computational chemistry methods have been used for accuracy; these include CBS-APNO, CBS-4M, CBS-QB3, M062X, ωB97X, B3-LYP, G-2, G-3, G-4 and Weizmann-1 (W1U) methodology.

In this work, we also present details of an addition to the group additivity method approach to estimate thermodynamic properties for a series of fluorinated ketone species. An advantage of this approach is the use of single hydrogen-bond increment (HBI) groups to predict accurate properties of corresponding radical species. This method utilizes ~~the~~ thermodynamic properties of stable parent molecules incorporated with HBI groups for each corresponding radical species reflecting the thermodynamic changes due to the loss of a hydrogen atom.

HBI groups are derived on the basis of the fundamental principles of statistical mechanics and thermochemistry. Considering the following homolytic reaction in Equation 4.1:

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet},\ \Delta H^{\circ}_{rxn,298} = \mathrm{BDE}_{(R\text{---}H)} \tag{4.1}$$

The radical, $R^{\bullet}$, enthalpy of formation can be written as

$$\Delta H^{\circ}_{rxn,298}\ (\mathrm{R}^{\bullet}) = \mathrm{BDE}_{(R\text{---}H)} + \Delta H^{\circ}_{rxn}\ (\mathrm{RH}) - 52.1\ \mathrm{kcal\ mole}^{-1} \tag{4.2}$$

To calculate $\Delta H^{\circ}_{rxn,298}$ ($R^{\bullet}$), we must know the ΔH°_{rxn} (RH) and the bond strength of the R---H bond broken to form the radical and H atom. Bond dissociation energies, $\mathrm{BDE}_{(R\text{---}H)}$, in the HBI database, correspond to radicals that are adopted from the evaluation of the literature if they exist.

The molecular structure of a radical is similar to that of the corresponding stable molecule. The unpaired electron located on the radical-centered atom is replaced by a bond to a hydrogen atom in the stable molecule, while most of the atom sequence and chemical bonds remain the same in the two species. The differences in molecular structure and thermochemical properties for the radical and parent species are properly taken into account to calculate entropy and heat capacity values for radical species from properties that correspond to parent species, in addition to increment group values for $\Delta Cp(T)$ and $\Delta S°_{298}$ that account for these changes:

$$S_{inter}°298\ (R^{\bullet}) = S_{inter}°_{298}(RH) + \Delta S°_{298} \tag{4.3}$$

$$Cp(T)(R^{\bullet}) = Cp(T)(RH) + \Delta Cp(T) \tag{4.4}$$

Where $S_{int}°$ represents intrinsic entropy, excluding symmetry.

These $\Delta S°_{298}$ and $\Delta Cp(T)$ ($300 \leq T/K \leq 1500$) increments are group values for estimating the radical from the parent and are termed HBIs ($\Delta S°_{298}$(HBI) and $\Delta Cp(T)$(HBI)). They are used to calculate $S°_{298}$ and Cp(T) for a free radical species formed during the elimination of a hydrogen atom from its parent molecule. The values we report for $\Delta S°_{298}$ and $\Delta Cp(T)$ are obtained by applying principles of the rigid-rotor harmonic oscillator model to account for the differences in molecular structures between $R^{\bullet}$ (radical species) and the corresponding RH (parent species). Increment changes in the potential barriers of internal rotations about C--C(=O) bonds next to the radical center are also incorporated. Some increment values are obtained by calculating the difference using known thermochemical properties of the parent molecule and the corresponding radical.

The classification of HBI terms is based on generic types of R---H bonds. This work considers 11 types of fluorocarbon radicals. The development of HBI groups incorporates the following: (1) evaluated literature data corresponding to the bond energies, BDE(R---H) of the specific R---H bond for species containing one to five fluorine atoms attached;

(2) entropy and heat capacity corrections accounting for the differences in rotational barriers of internal rotors in parent and radical.

Entropy corrections accounting for changes in symmetry between the parent molecule and radical are not included in the HBI group values. These corrections need to be separately considered for each radical and parent molecule.

The objective of this study is to determine thermochemical properties of oxygenated fluorocarbons and their derivatives for understanding the stability and reaction processes in environmental systems.

4.2 Nomenclature

Table 4.1 Nomenclature of Species in Fluoroketone Study

Nomenclature	Species	Formula
CFC(=O)C	$CH_2FC(=O)CH_3$	C_3H_5OF
CFC(=O)CF	$CH_2FC(=O)CH_2F$	$C_3H_4OF_2$
CF2C(=O)C	$CHF_2C(=O)CH_3$	$C_3H_4OF_2$
CF2C(=O)CF	$CHF_2C(=O)CH_2F$	$C_3H_3OF_3$
CF2C(=O)CF2	$CHF_2C(=O)CHF_2$	$C_3H_2OF_4$
CF3C(=O)C	$CF_3C(=O)CH_3$	$C_3H_3OF_3$
CF3C(=O)CF	$CF_3C(=O)CH_2F$	$C_3H_2OF_4$
CF3C(=O)CF2	$CF_3C(=O)CHF_2$	C_3HOF_5
CF3C(=O)CF3	$CF_3C(=O)CF_3$	C_3OF_6
CjFC(=O)C	$CHFC(=O)CH_3$	C_3H_4OF
CFC(=O)Cj	$CH_2FC(=O)CH_2$	C_3H_4OF
CjFC(=O)CF	$CHFC(=O)CH_2F$	$C_3H_3OF_2$
CjF2C(=O)C	$CF_2C(=O)CH_3$	$C_3H_3OF_2$
CF2C(=O)Cj	$CHF_2C(=O)CH_2$	$C_3H_3OF_2$
CF2C(=O)CjF	$CHF_2C(=O)CHF$	$C_3H_2OF_3$
CjF2C(=O)CF	$CF_2C(=O)CH_2F$	$C_3H_2OF_3$
CjF2C(=O)CF2	$CF_2C(=O)CHF_2$	C_3HOF_4
CjF2C(=O)CF3	$CF_2C(=O)CHF_3$	C_3OF_5
CF3C(=O)Cj	$CF_3C(=O)CH_2$	$C_3H_2OF_3$
CF3C(=O)CjF	$CF_3C(=O)CHF$	C_3HOF_4

4.3 Computational Methods

All calculations were performed using the Gaussian 09 program suite[67]. Molecule structures were initially optimized using the B3-LYP DFT method with the 6-31G++(d,p) basis set. The B3-LYP method combines the three parameter Becke exchange functional, B3, with the Lee-Yang-Parr correlation functional, LYP[123]. It is used to scan each dihedral angle corresponding to an internal rotor between zero and 360 degrees in steps of 10 degrees, in order to find the minimum energy conformer. A new set of scans was initiated each time a lower energy conformer was identified. The total energy corresponding to the most stable conformation was obtained and used as reference in plots of the potential barriers.

The composite methods CBS-APNO[124], CBS-4M[125], CBS-QB3[64], Gaussian-n methods G-2[126], G-3[127], G-4[128] and Weizmann-1 (W1U)[129] plus the DFT methods M062X[130], ωB97X[131], B3-LYP[123] with the 6-13+(G(d,p) basis set were utilized in the study.

Entropy and heat capacity values were calculated as a function of temperature from the optimized structures, moments of inertia, vibration frequencies, internal rotor potentials, symmetry, electron degeneracy, the number of optical isomers and the mass of each molecule. This calculation uses a standard formula from statistical mechanics for the contributions of translation, vibrations, and external rotation (TVR) using the SMCPS (Statistical Mechanics−Heat Capacity, and Entropy) program[87]. SMCPS utilizes the rigid-rotor harmonic oscillator approximation from the frequencies, as well as moments of inertia from the optimized B3-LYP/6-31G++(d,p) level calculations. Contributions from internal rotors calculated using the program Rotator are substituted for contributions from the corresponding internal rotor torsion frequencies. Rotator calculates thermodynamic functions from hindered rotations with arbitrary potentials based on the method developed by Krasnoperov, Lay, and Shokhirev[90]. This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the subsequent calculation of energy levels by direct diagonalization barrier versus dihedral angle are fit by a cosine curve. In this work, the rotational potential calculated at discrete torsional angles is represented by a truncated ten-parameter Fourier series (Equation 4.5) of the following for:

$$\mathrm{V}(\emptyset) = a_0 + \textstyle\sum_{i=1}^{10}(a_0 \cos(\mathrm{i}\emptyset)) + \displaystyle\sum_{j=1}^{10}\left(b_{\mathrm{j}} \cos(\mathrm{j}\emptyset)\right) \tag{4.5}$$

The values of the coefficients a_i and b_j are calculated to provide minimum and maximum values of torsional potentials with the allowance for a shift of theoretical extreme angular positions. Vibrational frequencies for B3-LYP/6-31+G(d,p) are scaled by a factor of 0.964 in the calculation of standard entropy and heat capacity based on computational chemistry comparison and benchmark databases[87].

Groups comparisons for use in the group additivity method, developed by Benson[91] were established and compared to our calculated values for parent $H°_{f\ 298}$, $S°(T)$; C (T) values are illustrated. This method is based on the knowledge of the contributions of representative groups in similar molecules and their properties in linear consistency in thermochemical properties. Thermodynamic properties of larger species, such as those in this study, were accurately approximated based on the sum of smaller representative groups where there are corrections for rotors, symmetry, electron degeneracy, optical isomers, gauche and other interactions. The group additivity and calculated Density Functional Theory values are compared.

The calculation of $\Delta H^\circ_{298}(R^\bullet)$ for a specific radical species uses literature values or group additivity (GA) for enthalpy of the parent molecule ($\Delta H^\circ 298(RH)$) and a bond energy, BDE(R---H), for the specific hydrogen atom removed from the parent molecule to form the desired radical; see Equation 4.2. S°_{298} and heat capacities Cp(T) of free radicals are calculated by applying HBI values (ΔS°_{298} and $\Delta Cp(T)$) in Equation 4.3 and 4.4.

4.4 Results and Discussion

Molecular structures were initially optimized using B3-LYP Density Functional Theory[123] methodology with the 6-31G++(d,p) basis set. The B3-LYP method combines the three-parameter Becke exchange functional, B3, with the Lee-Yang-Parr (LYP) correlation. The calculations scanned each dihedral angle corresponding to an internal rotor, between zero and 360 degrees in steps of 10 degrees. The molecular structure was optimized at each fixed scan step (point). The minimum energy point was taken from each scan; if a lower energy point was found in subsequent scan, then that structure was taken as a start point and all other scans were repeated to verify the lowest energy. The minimum energy was used as a reference in plots of the potential barriers. Figure 4.1 illustrates the potential energy for the internal rotor scan of fluoroacetone ($CH_2FC(O)CH_3$).

Data for the optimized structures are located in Appendix B. Vibrational frequencies and moments of inertia can be found in Appendix B, respectively.

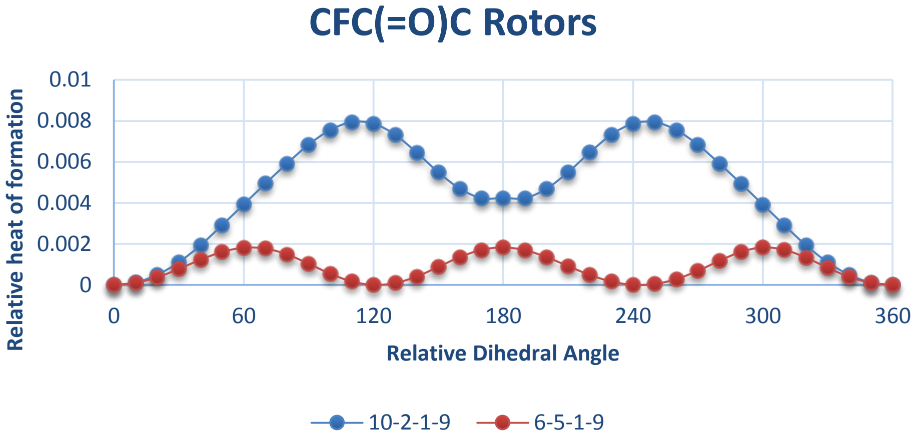

Figure 4.1 Potential Energy Profiles of $CH_2FC(O)CH_3$.

The Rotator code[36] was utilized to calculate the contributions to entropy and heat capacity for each internal rotor. These contributions were substituted for the corresponding, calculated torsion frequencies. Rotator code uses a calculated sine-cosine hindrance potential (Fourier series), when calculating the Hamiltonian matrix, using free rotor wave functions, calculates energy levels by direct diagonalization of the Hamiltonian matrix. The Hindered internal rotational contributions to entropy and heat capacities were calculated from intramolecular torsion potential curves calculated at the B3-LYP/6-31+G(d,p) level.

The isodesmic work reactions were used in the process in the analysis of reference species $\Delta H°_{f\ (298)}$ values. Fluorocarbon enthalpies of formation were calculated using composite methods CBS-APNO, CBS-4M, and CBS-QB3. DFT methods M06-2X, ωB97X, B3-LYP with 6-13+(G(d,p) basis set were also utilized in the study. Gaussian-n methods G-2, G-3, G-4 and Weizmann-1 (W1U). Nomenclature for species identification and molecular formulas are listed in Table 4.1. Each isodesmic work reaction can be found in Appendix B.

4.4.1 Heat of Formation $\Delta H°_{f\ 298}$

Table 4.2 lists the reference species ΔH°f (298) values used in isodesmic reactions, and Table 4.3 illustrates several isodesmic reactions, where 1,1,3 trifluoroacetone (CHF2C(=O)CH2F) is used as an example. The three isodesmic reactions (Table 4.3) are selected to determine the ΔHf298 using the B3-LYP/6-13+(G(d,p) computational chemistry calculation method to determine the standard enthalpy of formation, ΔfH^{o}(298) of fluoroacetone.

Table 4.2 $\Delta H°_{f\ 298}$ for Reference Species in the Isodesmic Reactions for Fluorinated Ketones

Species	$\Delta H°_{f\ 298}$ (kcal mol^{-1})	Error Values	Reference
CH_4	-17.78	± 0.10	103
CH_3F	-56.3	± 0.24	104
CH_2F_2	-108.07	± 1.46	104
CHF_3	-166.71	± 1.97	104
CH_3CH_3	-20.03	± 0.10	103
CH_2FCH_3	-65.42	± 1.11	104
CHF_2CH_3	-120.87	± 1.62	104
CF_3CH_3	-180.51	± 2.05	104
$CH_3CH_2CH_3$	-28.9	± 0.10	103
$CH_2FCH_2CH_3$	-70.24	± 1.30	104
$CH_3CH_2CH(=O)$	-44.36	± 0.19	103
$CH_2FCH_2CH(=O)$	-87.44	± 1.16	132
$CH_3C(=O)CH_3$	-51.89	± 0.16	30
$CH_3CH_2CH_2CH_3$	-30.10	± 0.10	9
CH_3	35.20	± 0.20	9
CH_2CH_3	28.90	± 0.40	9
$CH_2CH_3CH_3$	24.30	± 0.90	9
$CHF_2CH_2CH_3$	-125.82	± 1.65	104
$CF_3CH_2CH_3$	-185.48	± 2.15	104
$CH_3CH(=O)$	-39.7	± 0.12	103
$CH_2FCH(=O)$	-80.41	± 0.73	132
$CH_2FCF(=O)$	-143.57	± 0.71	132
$CHF_2CH(=O)$	-130.03	± 0.64	132
$C(CH_3)_3$	-32.00	± 0.40	9
$CH_2C(CH_3)_2$	17.80	± 0.90	9
CH_2FCH_2F	-161.10	± 2.20	56

Table 4.2 $\Delta H^\circ_{f\,298}$ for Reference Species in the Isodesmic Reactions for Fluorinated Ketones (Continued)

Species	$\Delta H^\circ_{f\,298}$ (kcal mol^{-1})	Error Values	Reference
$CHFCH_2F$	-110.60	± 1.60	56
CHF_2CHF	-58.10	± 1.10	56
CF_3CHF	-168.30	± 5.60	56
CF_2CH_3	-72.30	± 0.40	56
$CH_3CH_2CH_2CH_3$	-30.10	± 0.10	9
$CH_2CH_2CH_2CH_3$	19.30	± 0.90	9
CH_2F	-7.70	± 0.10	56
$CHFCH_3$	-18.20	± 1.40	56
CF_2CH_2F	-110.00	± 2.50	56
CF_2CHF_2	-160.30	± 1.40	56
$CH_2C(=O)CH_3$	-6.9	± 1.10	9
$CHF_2CF(=O)$	-190.14	± 1.02	132

Table 4.3 Isodesmic Reactions and Enthalpies of Formation for fluoroacetone using B3-LYP/6-31++G(d,p) Methodology

							ΔHf_{298} (kcal/mol)	ΔHf_{rxn} (kcal/mol)
CF2C(=O)CF	+	$CHF_2CH_2CH_3$	=	CFC(=O)CF	+	$CHF_2CH_2CH_3$		
-490.914671		*-218.338626*		*-391.641572*		*-317.621512*	x	
x		**-70.24**[9]		**-133.28**[a]		**-125.82**[104]	-182.6	-6.16
CF2C(=O)CF	+	CFC	=	CFC(=O)CF	+	CF2C		
-490.914671		*-179.043334*		*-391.641572*		*-278.326356*	X	
x		**-65.42**[104]		**-133.28**[a]		**-120.87**[104]	-182.4	-6.23
CF2C(=O)CF	+	CH3F	=	CFC(=O)CF	+	CH2F2		
-490.914671		*-139.739967*		*-391.641572*		*-239.017088*	x	
x		**-56.3**[104]		**-133.28**[a]		**-108.07**[104]	-182.4	-2.55

Hartrees, **kcal mole^{-1}** , [a] this study

The agreement between the 3-5 isodesmic reactions and the computational methods, as well as a comparison to available literature, supports the accuracy of our calculations. Entropies and heat capacities were determined using B3-LYP/6-31++G(d,p) optimized geometries and frequencies.

In this case, the overall average of 1,1,3- trifluoro acetone was observed using the 11 methods discussed over the set of isodesmic reactions and was observed to be -182.1 kcal mol^{-1}. The methods averages for fluoro acetaldehyde are M06 (-182.5), M06-2X (-181.5), ωb97x (-182.2), B3-LYP (-182.3), CBS-APNO (-182.0), CBS-4M (-181.9), CBS-QB3 (-182.4), G-2 (-182.2), G-3 (-182.2), G-4 (-182.7) and W1U (-182.4) kcal mol^{-1}.

A summary of the standard enthalpy of formation ($\Delta H°_{f\ 298}$)$_{averages}$ from DFT and composite methods for species from work reactions illustrated in Table 4.4. Table 4.4 shows the average of each molecule, in addition to the average of the molecule with each method with the standard deviation. With many of these molecules never being studied or due to the wide range of inconsistencies observed from past works, this portion will also compare literature data to what is observed in this study.

Table 4.4 Average, Method Average from each Calculation Method and the Overall Average Enthalpy of Formation for Fluorinated Ketones and Corresponding Radicals, and Differences between the Calculation vs. Experimental/Literature Reference Values

	ΔH°f 298 (kcal/mol)										
	M062x	M06	ωb97x	B3-LYP	CBS-APNO	CBS-4M*	CBS-QB3	G-2	G-3	G-4	W1U
	$CH_2FC(=O)CH_3$ -94.3 ± 1.4 Average										
Method Average	-93.4	-93.4	-93.4	-93.2	-93.6	-95.3	-93.8	-93.9	-93.9	-94.4	-93.7
Standard Deviation	1.0	1.0	1.0	0.9	1.3	1.7	1.4	1.7	1.7	1.5	1.1
Literature	-96.68 [133]										
	$CH_2FC(=O)CH_2F$ -133.2 ± 1.5 Average										
Method Average	-132.9	-132.2	-131.9	-132.0	-132.3	-133.0	-133.1	-132.7	-132.7	-134.1	-132.9
Standard Deviation	1.0	1.0	1.0	0.9	1.3	1.7	1.4	1.7	1.7	1.5	1.1
Literature	NA										
	$CHF_2C(=O)CH_3$ -144.5 ± 0.4 Average										
Method Average	-145.1	-144.9	-144.4	-144.5	-144.3	-144.6	-144.6	-144.5	-144.5	-144.9	-144.6
Standard Deviation	0.17	0.30	0.14	0.11	0.17	1.25	0.20	0.43	0.43	0.79	0.23
Literature	NA										
	$CHF_2C(=O)CH_2F$ -182.0 ± 0.5 Average										
Method Average	-181.5	-182.2	-182.2	-182.3	-182.0	-181.9	-182.4	-182.2	-182.2	-182.7	-182.4
Standard Deviation	0.2	0.3	0.1	0.1	0.2	1.3	0.2	0.4	0.4	0.8	0.2
Literature	NA										
	$CHF_2C(=O)CHF_2$ -230.0 ± 0.8 Average										
Method Average	-229.5	-230.4	-229.41	-229.3	-230.0	-230.3	-230.0	-231.2	-231.2	-231.1	-229.7
Standard Deviation	0.2	0.3	0.1	0.1	0.2	1.3	0.2	0.4	0.4	0.8	0.2
Literature	NA										
	$CF_3C(=O)CH_2F$ -237.2 ± 1.6 Average										
Method Average	-236.7	-236.3	-235.9	-236.0	-236.0	-235.8	-237.2	-236.9	-236.3	-238.3	-237.1
Standard Deviation	1.0	1.0	1.0	0.9	1.3	1.7	1.4	1.7	1.7	1.5	1.1
Literature	NA										

Table 4.4 Average, Method Average from each Calculation Method and the Overall Average Enthalpy of Formation for Fluorinated Ketones and Corresponding Radicals, and Differences between the Calculation vs. Experimental/Literature Reference Values (Continued)

	ΔH°f 298 (kcal/mol)										
	M062x	M06	ωb97x	B3-LYP	CBS-APNO	CBS-4M*	CBS-QB3	G-2	G-3	G-4	W1U
	CF$_3$C(=O)CF$_3$ -340.0 ± 0.4 Average										
Method Average	-340.7	-340.7	-340.5	-340.4	-339.9	-340.2	-340.5	-340.1	-	-	-
Standard Deviation	0.2	0.2	0.1	0.2	0.4	0.1	0.0	0.3	-	-	1
Literature	NA										
	CHF$_2$C(=O)CH$_2$ -100.5 ± 2.8 Average										
Method Average	-99.5	-99.4	-100.3	-101.1	-101.7	-108.8	-100.8	-102.6	-102.6	-101.9	-100.8
Standard Deviation	2.2	2.2	2.2	2.4	1.9	1.8	2.4	1.9	1.9	2.4	2.4
	CF$_3$C(=O)CHF$_2$ -285.5 ± 1.0 Average										
Method Average	-285.4	-284.8	-284.9	-284.1	-285.3	-288.5	-285.7	-286.8	-286.8	-287.6	-
Standard Deviation	0.17	0.30	0.14	0.11	0.17	1.25	0.20	0.43	0.43	0.79	-
Literature	NA										
	CF$_3$C(=O)CH$_3$ -200.0 ± 0.4 Average										
Method Average	-199.8	-199.9	-200.1	-200.1	-199.8	-200.8	-200.1	-199.9	-199.9	-200.6	-200.1
Standard Deviation	0.2	0.2	0.1	0.2	0.3	0.9	0.3	0.2	0.2	0.5	0.3
Literature	NA										
Literature	NA										
	CHF$_2$C(=O)CHF -147.1 ± 1.6 Average										
Method Average	-145.3	-145.8	-145.8	-146.7	-145.8	-152.6	-145.8	-149.0	-146.6	-146.8	-146.5
Standard Deviation	1.1	1.3	1.2	1.5	0.2	0.2	1.1	0.4	0.4	1.0	1.2
Literature	NA										
	CHF$_2$C(=O)CHF -142.8 ± 2.2 Average										
Method Average	-142.8	-144.1	-142.2	-143.0	-141.1	-150.7	-144.2	-141.6	-141.6	-146.6	-144.0
Standard Deviation	2.4	2.4	2.4	2.4	2.4	3.1	2.4	2.4	2.4	2.2	2.4
Literature	NA										
	CF$_2$C(=O)CHF$_3$ -249.3 ± 2.2 Average										
Method Average	-249.7	-251.7	-249.1	-250.2	-248.0	-258.7	-251.1	-247.8	-247.8	-251.8	-
Standard Deviation	2.4	2.4	2.4	2.4	2.4	3.1	2.4	2.4	2.4	2.2	2.4
Literature	NA										
	CF$_3$C(=O)CH$_2$ -156.5 ± 2.9 Average										
Method Average	-156.3	-155.4	-155.9	-156.6	-157.6	-165.2	-156.4	-159.3	-159.2	-157.5	-156.3
Standard Deviation	2.2	2.2	2.2	2.4	1.9	1.8	2.4	1.9	1.9	2.4	2.4
Literature	NA										

Table 4.4 Average, Method Average from each Calculation Method and the Overall Average Enthalpy of Formation for Fluorinated Ketones and Corresponding Radicals, and Differences between the Calculation vs. Experimental/Literature Reference Values (Continued)

	ΔH°f 298 (kcal/mol)										
	M062x	M06	ωb97x	B3-LYP	CBS-APNO	CBS-4M*	CBS-QB3	G-2	G-3	G-4	W1U
	$CF_3C(=O)CF_2$ -249.3 ± 2.2 Average										
Method Average	-249.4	-251.4	-248.8	-249.8	-247.7	-258.4	-250.8	-247.5	-247.5	-251.5	-
Standard Deviation	2.2	2.2	2.2	2.2	2.3	3.0	2.2	2.2	2.2	2.0	-
	$CF_3C(=O)CHF$ -202.4 ± 1.6 Average										
Method Average	-201.0	-202.7	-202.0	-202.3	-202.4	-210.9	-202.2	-202.7	-203.3	-202.9	-202.2
Standard Deviation	1.8	1.9	1.7	1.7	1.8	2.3	1.6	1.6	1.6	1.5	1.6
Literature	NA										
	$CF_2C(=O)CHF_2$ -193.0 ± 1.8 Average										
Method Average	-193.2	-194.0	-192.7	-192.7	-190.9	-201.0	-194.3	-190.7	-190.7	-195.2	-194.5
Standard Deviation	1.0	1.0	1.0	1.1	0.6	1.3	0.9	0.4	0.4	0.4	1.0
Literature	NA										
Literature	NA										

4.4.2 Internal Rotors

Potential energy curves for internal rotations within the parent and radical species are calculated using the B3-LYP/6-31G(d,p) level of theory. Relaxed scans at 10 degree intervals are used to determine the lowest energy geometries. If a lower energy conformation is found, previous scans are re-run to insure the lowest energy conformation is located. These potential energy curves are also used to determine entropy and heat capacity internal rotational contributions.

All of the parent ketone terminal methyl (not adjacent to the carbonyl) groups, exhibit three-fold symmetry with energy barriers between 2-3 kcal mol-1. The three-fold barriers are 0.5 kcal mol-1 for methyl rotations adjacent to the carbonyl group. Upon radical formation at the methyl site, there is a decrease to two-fold symmetry and a decrease in the barrier energy ranging from below 0.1 to 3.0 kcal mol-1 except for the groups adjacent to the carbonyl. Radical sites adjacent to the carbonyl group, regardless of primary, secondary, or tertiary location, have energy barriers over 10 kcal mol^{-1} upon radical formation resulting from the resonance with the carbonyl group.

4.4.3 Entropies (S(T)) and Heat Capacities (C_p(T))

Contributions from each species translations, vibrational frequencies, and external rotations, represented as TVR, are calculated using the rigid-rotor harmonic-oscillator approximation SMCPS[87] code with the zero-point vibration energies (ZPVE) scaled by 0.9806 for B3-LYP/6-31G(d,p) as recommended.

The contributions from internal rotations, represented by IR, are determined using the calculated potential energy rotational barriers, moments of inertia for each group in the rotor, and barrier foldness. Internal rotor torsion frequencies, including terminal methyl groups, are identified using visual inspection in GaussView and removed from vibration contribution. In cases where identification of a frequency is uncertain due to coupling to other motions, the lower frequency is selected. These are replaced with entropy and heat capacity contributions from the Pitzer and Gwinn method for hindered rotor analysis. Values from the group additivity (GA) method are also included which coincide well with data observed in this study and literature data providing some support for considering the GA data as reference in the comparisons.

For this limited set of ketones, contributions to entropy and heat capacity from all of the internal rotors in each of the parent ketones need to be included in order to match the literature data if available, entropy is significantly underestimated when only the low barrier methyl rotors are considered, in one case by more than 5 cal mol-1 K-1, relative to values observed prior to this analysis.

Ketone sp3 carbon bonds have lower barriers than those in alkane hydrocarbons, and these internal rotors should have important contributions, but there are also internal rotors in the larger ketones that have barriers higher than 6 kcal mol-1. There are a number of studies on methods and the importance for calculating contributions from internal rotations to obtain more accurate entropies and heat capacity estimates.[89-96] It is known that torsion frequency estimates of the contributions to heat capacity contribute a full R (ideal gas constant) to Cp(T) at high temperatures, whereas a free rotor contributes only R/2. The computer code THERM,[93, 94] which is often used to extrapolate Cp(T) data to higher temperatures and generate NASA polynomials, allows researchers to incorporate the number of internal rotors in the target Cp(T)(infinity) value. This allows some adjustment for anharmonic effects by under-representing the number of rotors, one can add R/2 to Cp(T)(infinity), where each rotor omitted would be counted by THERM as frequency contribution. Our recommendation is to underestimate the number of rotors contribution to Cp(T)(infinity) by one-half.

Entropies and heat capacities in the 298-1500 K temperature range for the fluorinated aldehydes from B3-LYP/6-31G(d,p) calculations are presented in Appendix C. For the fluorinated aldehyde species, all of the single bond rotations are included. The energy barriers for these primary and secondary locations are all in excess of 10 kcal mol-1 where contributions are treated as torsion frequencies. These barriers result from resonance between the radical site and the adjacent, electronegative carbonyl group. The resonance also accounts for the low bond dissociation energies. Potential barriers for rotors, where S(T) and Cp(T) values are determined from torsion frequencies, are denoted in the potential energy diagrams in Appendix C.

TVR represents the sum of the Translation External Rotation and Vibration contributions. IR indicates the contribution from hindered internal rotation, which replaces the calculated contribution for these internal rotors in the TVR heat capacity and entropy data. Table 4.5 lists the standard entropy and heat capacities as a function of temperature. Entropy and heat capacity results are from B3-LYP/6-31++G(d,p) calculated geometries and frequencies, which are listed in Appendix C. Each molecule is labeled as seen in Table 4.1.

Table 4.5 TVR Ideal Gas Phase Entropy and Heat Capacity Obtained by B3-LYP/6-31+G(d,p) for Fluorinated Ketones

Species	S	CP 300	400	500	600	800	1000	1500
$CH_2FC(=O)CH_3$	86.42	22.62	27.08	31.11	34.54	39.86	43.72	49.60
$CH_2FC(=O)CH_2F$	93.63	24.32	28.96	33.09	36.53	41.71	45.34	50.66
$CHF_2C(=O)CH_3$	91.41	24.90	29.49	33.51	36.85	41.89	45.43	50.67
$CHF_2C(=O)CH_2F$	95.17	26.60	31.37	35.48	38.84	43.74	47.05	51.73
$CHF_2C(=O)CHF_2$	102.63	28.94	33.83	37.93	41.18	45.80	48.79	52.82
$CF_3C(=O)CH_3$	96.81	27.62	32.42	36.39	39.58	44.23	47.38	51.88
$CF_3C(=O)CH_2F$	104.47	29.32	34.29	38.35	41.55	46.07	49.00	52.94
$CF_3C(=O)CHF_2$	107.80	31.63	36.75	40.80	43.91	48.14	50.73	53.95
$CF_3C(=O)CF_3$	108.25	34.34	39.67	43.68	46.64	50.47	52.67	55.09
$CHFC(=O)CH_3$	86.74	22.47	26.45	29.87	32.64	36.57	39.05	42.23
$CH_2FC(=O)CH_2$	84.07	22.00	26.30	29.93	32.89	37.32	40.45	45.16
$CHFC(=O)CH_2F$	91.97	23.97	28.18	31.77	34.70	38.99	41.92	46.15
$CF_2C(=O)CH_3$	94.18	24.96	28.81	32.15	34.92	39.09	41.99	46.19
$CHF_2C(=O)CH_2$	94.53	24.31	28.75	32.38	35.25	39.39	42.18	46.17
$CHF_2C(=O)CHF$	92.34	24.27	28.63	32.22	35.06	39.07	41.69	45.27
$CF_2C(=O)CH_2F$	97.47	26.44	30.54	34.01	36.82	40.88	43.55	47.22
$CF_2C(=O)CHF_2$	98.83	26.44	30.54	34.01	36.82	40.88	43.55	47.20
$CF_2C(=O)CHF_3$	106.95	31.42	35.92	39.35	41.93	45.30	47.24	49.36
$CF_3C(=O)CH_2$	94.16	27.02	31.68	35.26	37.98	41.73	44.15	47.47
$CF_3C(=O)CHF$	103.07	28.91	33.51	37.07	39.78	43.41	45.63	48.46

4.4.4 Group Additivity

Group additivity is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons; it is however useful for application to larger molecules and in codes or databases for the estimation of thermochemical properties in reaction mechanism generation. Groups used in the group additivity as designed by Benson[34] are based on knowledge of the contributions of representative groups in similar molecules and experimentally observed in the determination of thermochemical properties such as heat capacity and enthalpy values. In this study, groups for fluoro-ketones species such as CJFC(=O)C, CJF2(=O)C, CF3C(=O)CJ, CJF2C(=O)CF2 and CF3C(=O)CJF2 were derived to calculate enthalpy, entropy and heat capacity values versus temperature ($H_{f298,}$ S°(T), and C (T)).

Example fluoroacetone $CH_2FC(O)CH_3$

The example below utilizes calculated enthalpy of formation of groups present in fluoroacetone ($CH_2FC(O)CH_3$). Data for thermodynamic properties for the group C/CO/F/H2 were calculated in previous work [29] and groups CO/C2 and C/CO/H3 were calculated by Benson *et al.*[34].

$$(CH_2FC(O)CH_3) = C/CO/F/H2 + CO/C2 + C/CO/H3 \tag{4.8}$$

$$(CH_2FC(O)CH_3) = (-51.31) + (-32.10) + (-10.08) \tag{4.9}$$

$$(CH_2FC(O)CH_3) = -93.49 \tag{4.10}$$

Table 4.6 labels standard molar enthalpy and entropy values and heat capacities for Benson Group Additivity. Table 4.7 lists the groups that are found in each of the species identified in this study.

Table 4.6 Standard Molar Enthalpy and Entropy Values and Heat Capacities (300-1500K) for use in Benson[34] Group Additivity for Fluorinated Ketones

Group	HF	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
C/C/H3	-10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C/CO/H2[91]	-5.2	9.6	6.2	7.7	8.7	9.5	11.1	12.2	14.07
C/C2/H2[91]	-5.00	9.40	5.50	6.95	8.25	9.35	11.07	12.34	14.20
CO/C2 [91]	-32.10	34.90	7.03	7.87	8.82	9.68	11.20	12.20	
C/CO/H3 [91]	-10.08	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
C/ CO/F/H2* [9]	-51.31	60.98	18.00	21.63	24.74	27.32	31.01	33.61	50.96
C/ CO/F2/H *[9]	-100.93	53.25	16.95	20.45	23.38	25.84	29.48	32.20	50.00
C/ CO/F3 *[9]	-156.29	44.66	12.51	14.85	16.56	17.85	19.46	20.52	
CJC(=O)C	96.05	-1.16	0.32	0.19	-0.15	-0.57	-1.43	-2.22	-3.67
CJFC(=O)C	89.00	-0.32	0.15	0.63	1.24	1.90	3.29	4.67	7.37
CJF2C(=O)C	92.40	-2.77	-0.06	0.68	1.36	1.93	2.8	3.44	4.48
CF2C(=O)CJ	96.10	-3.12	0.59	0.74	1.13	1.60	2.50	3.25	4.50
CF3C(=O)CJ	95.60	2.65	0.60	0.74	1.13	1.60	2.50	3.23	4.41
CJF2C(=O)CF2	89.10	3.80	2.50	3.29	3.92	4.36	4.92	5.24	5.62
CJF2C(=O)CF3	88.30	0.85	0.21	0.83	1.45	1.98	2.84	3.49	4.59

Table 4.7: Groups for the Fluorinated Ketones in this Study not including fluorine-fluorine repulsive interactions between fluorine atoms on adjacent or nearby carbon atoms

Species	Group 1	Group 2	Group 3	Group 4
CFC(=O)C	C/CO/H3	CO/C2	-	-
CFC(=O)CF	C/CO/F/H2	CO/C2	-	-
$CF_2C(=O)C$	C/CO/F2/H	CO/C2	C/CO/H3	-
$CF_2C(=O)CF$	C/CO/F2/H	CO/C2	C/ CO/F/H2	-
$CF_2C(=O)CF_2$	C/CO/F2/H	CO/C2	-	-
$CF_3C(=O)C$	C/CO/F3	CO/C2	C/CO/H3	-
$CF_3C(=O)CF$	C/CO/F3	CO/C2	C/ CO/F/H2	-
$CF_3C(=O)CF_2$	C/CO/F3	CO/C2	C/ CO/F2/H	-
$CF_3C(=O)CF_3$	C/CO/F3	CO/C2	-	-
$CHFC(=O)CH_3$	C/CO/F/H2	C/CO/H3	CO/C2	CJFC(=O)C
$CH_2FC(=O)CH_2$	C/CO/F/H2	C/CO/H3	CO/C2	CJC(=O)C
$CHFC(=O)CH_2F$	C/CO/F/H2	C/CO/F/H2	CO/C2	CJFC(=O)C
$CF_2C(=O)CH_3$	C/CO/F2/H	C/CO/H3	CO/C2	CJF2(=O)C
$CHF_2C(=O)CH_2$	C/CO/F2/H	C/CO/H3	CO/C2	CF3C(=O)CJ
$CHF_2C(=O)CHF$	C/CO/F2/H	C/CO/F/H2	CO/C2	CJFC(=O)C

Table 4.7: Groups for the Fluorinated Ketones in this Study not including fluorine-fluorine repulsive interactions between fluorine atoms on adjacent or nearby carbon atoms (continued)

Species	Group 1	Group 2	Group 3	Group 4
$CF_2C(=O)CH_2F$	C/CO/F2/H	C/CO/F/H2	CO/C2	CJFC(=O)C
$CF_2C(=O)CHF_2$	C/CO/F2/H	C/CO/F/H2	CO/C2	CJF2(=O)C
$CF_2C(=O)CHF_3$	C/CO/F2/H	C/CO/F2/H	CO/C2	CJF2C(=O)CF2
$CF_3C(=O)CH_2$	C/CO/F3	C/CO/H3	CO/C2	CF3C(=O)CJ
$CF_3C(=O)CHF$	C/CO/F3	C/CO/F/H2	CO/C2	CJFC(=O)C
$CF_3C(=O)CF_2$	C/CO/F3	C/CO/F/H2	CO/C2	

4.4.5 Interaction Terms for Fluorinated Acetone Species

In conventional hydrocarbon and oxy-hydrocarbon group additivity, the C/C/H3, C/C2/H2, CO/C2, C/C/CO/H2 and C/CO/H3 group enthalpy values accurately predict enthalpy and other thermochemical properties for acetone, $CH_3C(=O)CH_3$, and for larger ketone molecules with no additional groups needed. For the hydrocarbons and oxy-hydrocarbons, one group for each central atom (atom with two or more bonds), provide accurate thermochemical values.

Example groups for $CH_3C(=O)CH_3$ (a) groups are CO/C2[34] and C/CO/H3[34]

$CH_3CH_2C(=O)CH_3$ (b) groups are C/C/H3, CO/C2[34], C/C/CO/H2 and C/CO/H3[34]
$CH_3CH_2CH_2C(=O)CH_3$ (c) groups are C/C/H3, C/C2/H2, CO/C2, C/C/CO/H2 and C/CO/H3
$CH_3CH_2C(=O)CH_2CH_3$ (d) groups are C/C/H3, C/C2/H2, CO/C2[34] and C/C/CO/H2
$CH_3CH_2C(=O)CH_2CH_2CH_3$ (e) groups are C/C/H3, C/C2/H2, CO/C2 [34]and C/C/CO/H2

The groups used in these ketone species provide correct data for $CH_3C(=O)CH_3$, $CH_3CH_2C(=O)CH_3$, $CH_3CH_2CH_2C(=O)CH_3$, $CH_3CH_2C(=O)CH_2CH_3$ and $CH_3CH_2C(=O)CH_2CH_2CH_3$ agrees with literature values -51.89[134] (a), -57.02[121] (b), -61.91[135] (c), -60.6[136] (d) and -66.50[135] (e) kcal $mole^{-1}$, respectively. Similarly, results for

$CH_3C(=O)CH_3$, $CH_3CH_2C(=O)CH_3$, $CH_3CH_2CH_2C(=O)CH_3$, $CH_3CH_2C(=O)CH_2CH_3$ and $CH_3CH_2C(=O)CH_2CH_2CH$ from group additivity values are -51.56, -56.68, -61.91, -61.80 and -66.80 kcal mole^{-1}, respectively. The literature and group additivity values show good agreement, and there is no need for additional (interaction) groups.

In a previous study[132], we have shown that fluorinated aldehydes required interactions terms from very strong F/F interactions. For example, $CH_2FCF(=O)$ was utilized to develop the interaction group F/CFO. Using additivtiy groups C/CO/F/H2 and C/CO/F, the enthalpy of formation using group additivity calculation for the species $CH_2FCF(=O)$ was calculated. The values from the two groups mentioned gives this species an enthalpy of formation of -147.07. Computational calculations in this study and in the literature show $CH_2FCF(=O)$ to have an enthalpy of formation of -143.57 [132] and -143.6 45 kcal mole^{-1}, respectively. Here, calculated values for this $CH_2FCF(=O)$ molecule are not in agreement. As shown in Equation 3.8-3.9

$$CH_2FCF(=O) = C/CO/F/H2 + CO/C/F \tag{3.8}$$
$$CH_2FCF(=O) = (-51.31) + (-95.76) \tag{3.9}$$
$$CH_2FCF(=O) = -147.07 \tag{3.10}$$

Due to this groups not being in good agreement, a third group is needed. Here needs to be a fluorine/fluorine interaction group added to the group addivity calculation to account for the interactions of the two fluorine atoms in order for the group additivity to accurately estimate the thermochemistry of fluoroaldehydes where there is a fluorine atom on adjacent carbons of the aldehyde. $CH_2FCF(=O)$ was utilized to develop the interaction group F/FCO. Δ represents the value needed by the interaction group being calculated. The calculation of Δ below is for the interaction group F/CFO.

$$CH_2FCF(=O) = C/CO/F/H2 + CO/C/F + \Delta \tag{3.11}$$
$$-143.57 = (-51.31) + (-95.76) + F/CFO \tag{3.12}$$
$$F/FCO = 3.50 \tag{3.13}$$

Following the same procedure as above, we will analyze 1,3 difluoro acetone. In this specific molecule, there are three groups that contribute to the enthalpy of formation. These groups include two C/CO/F/H2 groups and one CO/C2 group.

$$CH_2FC(=O)CH_2F = 2\ C/CO/F/H2 + CO/C2 \tag{3.14}$$
$$CH_2FC(=O)CH_2F = 2\ (-51.31) + (-32.1) \tag{3.15}$$
$$CH_2FC(=O)CH_2F = -134.72 \tag{3.16}$$

We illustrate that the thermochemistry for fluorinated ketones such as $CH_2FC(=O)CH_2F$ is not accurately predicted by three groups, in this case one CO/C2 and two C/CO/F/H2 groups. For this same species, computational calculations show an observed enthalpy of formation of -133.2 kcal mole^{-1}, in comparison to the group additivity methodology which gives a value of -134.72 kcal mole^{-1}. Here an additional term will be added to account for the interaction of the fluorine interactions on each of the methyl groups to accurately estimate the thermochemistry of fluorinated ketones where there are fluorine atoms located on each side of the C=O of the molecule. $CH_2FC(=O)CH_2F$ was utilized to develop the interaction group CF/CO/CF. Below, Δ represents the value needed by the interaction group being calculated. The calculation of Δ below is for the interaction group CF/CO/CF.

$$CH_2FC(=O)CH_2F = 2\ (C/CO/F/H2) + CO/C2 + \Delta \tag{17}$$
$$-133.2 = 2\ (-51.31) + (-32.1) + CF/CO/CF \tag{18}$$
$$CF/CO/CF = 1.52 \tag{19}$$

Fluorinated ketone molecule types require new set of interaction terms from those that are pre-existing, as shown in previous study[29] and work performed by Heng *et al.*[28]. The nomenclature of these new interaction terms are CFx/CO/CFy. As shown in Figure

4.2, the CFx represents the Fx portion of the interaction term, where x coincides with the number of fluorines attached to the primary carbon site. Similarly, CFy follows the same scheme as CFx. The CO portion of the term represents the C(=O) group located between the methyl groups.

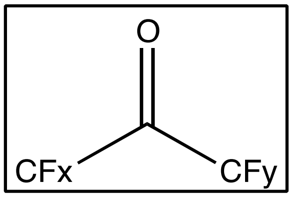

Figure 4.2 Structural formula for Fx/CO/Fy interaction group terms.

Species $CH_2FC(=O)CH_2F$, $CHF_2C(=O)CH_2F$, $CHF_2C(=O)CHF_2$, $CF_3C(=O)CH_2F$, $CF_3C(=O)CHF_2$ and $CF_3C(=O)CF_3$ were utilized to calculate interaction group terms for new interaction terms CF/CO/CF, CF2/CO/CF, CF2/CO/F2, CF3/CO/CF, CF3/CO/CF2 and CF3/CO/CF3. These groups were developed to be utilized in the group additivity method determined within this study. Table 4.8 displays interaction term data observed.

Table 4.8 Enthalpy of Formation Values of Formation of Fluorine-Fluorine Interaction Terms

Interactions	$\Delta H^\circ_{f\ 298\ (kcal\ mole^{-1})}$ In This Study (avg)
CF/CO/CF	1.52
CF2/CO/CF	1.54
CF2/CO/F2	3.26
CF3/CO/CF	1.80
CF3/CO/CF2	3.12
CF3/CO/CF3	3.98

When comparing these interaction terms with the previous study[132], we observed that the interactions of those species that have multiple fluorines on adjacent carbon atoms have a much larger interaction energy than those with a carbonyl group between them.

This is due to the repulsive nature of the fluorine atom. For example, when comparing interaction terms from ketones and aldehydes, the interaction terms in the aldehydes are larger. For instance, the CF/CO/CF interaction group in ketones and the F/CFO interaction group both contain two fluorines. However, the CF/CO/CF interaction term has an enthalpy of formation of 1.44 kcal mole^{-1}, where the F/CFO[132] interaction group term has an observed enthalpy of formation of 3.50 kcal mole^{-1}. The lower energy observed in the ketone interaction groups is a result of the carbonyl group in between the methyl groups reducing the amount of interactions possible in the structure.

During this study a comparison between calculated enthalpies of formation with computational methodology and group additivity was made. In the absence of missing literature values, we relied on the accuracies our reference species in work reactions to determine precise enthalpies of formations of each species. Table 4.9 illustrates results of the calculated enthalpy of formation in comparison with group additivity values and literature values when observed. Literature values in the comparison have been observed to be a ~2 kcal mole^{-1} lower than our calculated values; this could be a result of the amount or level of fluorocarbon data present during the time of the study.

Table 4.9 Enthalpy of Formation of Species in Study Compared to Group Additivity Calculations for Fluorinated Ketones

Species	Calculated Enthalpy of Formation (kcal mole^{-1})	% Error	Group Additivity (kcal mole^{-1})	Lit. Values (kcal mole^{-1})
$CH_2FC(=O)CH_3$	-94.3	± 1.4	-92.79	-96.68[133]
$CH_2FC(=O)CH_2F$	-133.2	± 1.5	-132.50	This work
$CHF_2C(=O)CH_3$	-144.5	± 0.4	-142.4	This work
$CHF_2C(=O)CH_2F$	-182.1	± 0.6	-182.10	This work
$CHF_2C(=O)CHF_2$	-230.0	± 0.8	-230.00	This work
$CF_3C(=O)CH_3$	-200.0	± 0.4	-198.47	This work
$CF_3C(=O)CH_2F$	-237.2	± 1.6	-237.20	This work
$CF_3C(=O)CHF_2$	-285.5	± 1.0	-285.50	This work

Table 4.9 Enthalpy of Formation of Species in Study Compared to Group Additivity Calculations for Fluorinated Ketones (Continued)

Species	**Calculated Enthalpy of Formation (kcal mole^{-1})**	**% Error**	**Group Additivity (kcal mole^{-1})**	**Lit. Values (kcal mole^{-1})**
$CF_3C(=O)CF_3$	-340.0	± 0.4	-340.00	This work
$CHFC(=O)CH_3$	-57.4	± 1.6	-57.40	This work
$CHFC(=O)CH_2F$	-97.2	± 1.6	-97.11	This work
$CF_2C(=O)CH_3$	-104.2	± 2.6	-104.20	This work
$CHF_2C(=O)CH_2$	-100.5	± 2.8	-100.50	This work
$CHF_2C(=O)CHF$	-147.1	± 1.6	-146.71	This work
$CF_2C(=O)CH_2F$	-142.8	± 2.2	-1423.89	This work
$CF_2C(=O)CHF_2$	-193.0	± 1.8	-193.00	This work
$CF_2C(=O)CHF_3$	-249.3	± 2.2	--249.3	This work
$CF_3C(=O)CH_2$	-156.5	± 2.9	-156.50	This work
$CF_3C(=O)CHF$	-202.4	± 1.6	-201.81	This work
$CF_3C(=O)CF_2$	-249.3	± 2.2	-249.3	This work
$CH_2FC(=O)CH_2$	-50.3	± 1.9	-47.06	This work

4.4.6 Bond Dissociation Energies for Fluorinated Acetone Species

Fluorocarbons have been shown to have strong bonds even in the presences of fire making them very stable and very effective fire retardants. Unlike other halogens such as bromine and chlorine, fluorine bonds are much stronger due to their electronegative nature. In the presence of flame it has been shown by Haworth *et al.*[56] that the hydrogen bond will be terminated, forming a radical. To determine the bond strength, fluorine-carbon bonds and hydrogen-carbon bonds must be calculated. This was accomplished by using the following equation,

$$\Delta H_{reaction}=\Sigma\Delta H_{product}-\ \Sigma\Delta H_{reactants}$$

Where $\Delta H_{reaction}$ corresponds to the bond dissociation energy, $\Sigma\Delta H_{product}$ is the radical species enthalpy of formation with the enthalpy of a hydrogen atom, which has a

$\Delta H_f{}^{\circ}{}_{298}$ of 52.103 kcal mole^{-1} or a fluorine atom which has a $\Delta H_f{}^{\circ}{}_{298}$ of 18.97 kcal mole^{-1}, depending on the site being analyzed.

A bond dissociation enthalpy reflects the thermodynamic stability of two species: the parent molecule and the corresponding radical fragment. A low bond dissociation energy can be a result of the stabilization of the radical, a destabilization of the parent, or a combination of the two. By understanding this principle, it is of interest to further investigate at the molecular level what factors may contribute to the thermodynamic stabilization of radical species.

When observing fluorinated acetone species ($C_3H_{6-x}O$), where x in this case corresponds to the number of fluorine atoms present in the structure. All BDE values calculated are located in Table 9 and compared with literature values to bolster results when available.

Acetone

BDE in acetone shows bond dissociation energy of 97.1 kcal mole^{-1}, consistent with that in literature. The same primary bond has an observed BDE of 97.2[105]. Comparing the primary bond from acetone with the bond energies associated with hydrocarbons, the bonding energy is ~4 kcal mole^{-1} weaker.

Fluoroacetone

There are three sites where a radical can be formed on the fluoro acetone species. These include the fluorine-carbon bond, the hydrogen-carbon bond adjacent to the fluorine atom and the hydrogen-carbon bond opposite of the fluorine atom. The fluorine-carbon bond is observed to have the highest bonding energy at 106.5 kcal mole^{-1}. The hydrogen-carbon bond adjacent to the fluorine atom and the hydrogen-carbon bond opposite of the fluorine atom have a bonding energy of 89.0 and 96.1 kcal mole^{-1}, respectively.

1,3-Difluoroacetone

The bonding energies in 1,3-difluoroacetone are evaluated at the fluorine-carbon bond and the hydrogen-carbon with energy values of 101.9 and 88.1 kcal mole^{-1}, respectively.

Difluoroacentone

Similar to that of fluoroacetone, difluoroacetone has three bonding sites which are analyzed, including the fluorine-carbon bond, the hydrogen-carbon bond adjacent to the fluorine atom and the hydrogen-carbon bond opposite of the fluorine atom. The fluorine-carbon bond is observed to have the highest bonding energy at 106.1 kcal mole^{-1}. The hydrogen-carbon bond adjacent to the fluorine atom and the hydrogen-carbon bond opposite of the fluorine atom have a bonding energy of 92.4 and 96.1 kcal mole^{-1}, respectively.

1,1,3-Trifluoroacetone

There are four sites where a radical can be formed. These locations include a fluorine-carbon bond connected to the 1- carbon and 3- carbon sites, and the hydrogen-carbon bond on the 1-carbon and the 3- carbon site. The fluorine-carbon bonds located on the 1 and 3 carbon site have recorded bond energies of 103.9 and 100.6 kcal mole^{-1}, respectively. The fluorine-carbon bond adjacent to another fluorine-carbon bond has a stronger bond in comparison to the fluorine-carbon bond with two existing hydrogen-carbon bonds by 3.3 kcal mole^{-1}. The hydrogen-carbon bonds show energies on the 1-

carbon and 3-carbon sites to have bond dissociation energies of 91.4 and 87.1 kcal mole^{-1}, respectively.

1,1,3,3-Tetrafluoroacetone

Bonding sites in 1,1,3,3-tetrafluoroacetone are similar to that of 1,3-difluoro acetone, only different by another fluorine-carbon bond being present on both the 1-and-3 carbon site. In this species, the fluorine-carbon bond has a recorded value of 101.9 kcal mole^{-1} and the hydrogen-carbon bond has an observed value of 89.1 kcal mole^{-1}.

Trifluoroacetone

Trifluoroacetone has two bonding sites. The first site is the fluorine-carbon bound where the species shows bond dissociation energy of 114.8 kcal mole^{-1}. The other site that has been analyzed is the hydrogen-carbon bond with bond dissociation energy of 95.6 kcal mole^{-1}.

1,1,1,3-Tetrafluoroacetone

The 1,1,1,3-tetrafluoroacetone molecule has three sites where bond dissociation energies were analyzed. These sites include the fluorine-carbon site on the 1-carbon, where three fluorine atoms are attached to the same carbon, the fluorine-carbon site on the 3-carbon and a hydrogen-carbon bond. These sites have bond dissociation energies of 113.4, 99.6 and 86.9 kcal mole^{-1}, respectively.

1,1,1,3,3-Pentafluoroacetone

1,1,1,3,3-pentafluoroacetone has similar bonding sites to that of 1,1,1,3-tetrafluoroacetone. The fluorine-carbon site on the 1-carbon has bond dissociation energy of 111.5 kcal mole^{-1}. The fluorine-carbon site on the 3-carbon has an observed bond dissociation energy of 102.1 kcal mole^{-1}. The final site is the hydrogen-carbon bond, which has a bond dissociation energy of 88.3 kcal mole^{-1}.

1,1,1,3,3,3-Hexafluoroacetone

1,1,1,3,3,3-hexafluoroacetone was analyzed to determine the bond dissociation energy of an acetone molecule that is completely saturated with fluorine atoms as substituents. This analysis reveals the fluorine-carbon bond to have a bond dissociation energy of 109.7.

Table 4.10 Bond Dissociation Energy (BDE) of Fluorinated Ketone Species in this Study

CC(=O)C						
CC(=O)C	=	H	+	CJC(=O)C		
-51.89		52.103		-6.9	97.1	97.2[105]
CFC(=O)C						
CFC(=O)C	=	H	+	CJFC(=O)C		
-94.3		52.103		-57.4	89.0	This Work
CFC(=O)C	=	H	+	CFC(=O)Cj		
-94.39		52.103		-50.3	96.1	This Work
CFC(=O)C	=	F	+	CJC(=O)C		
-94.39		18.97		-6.9	106.5	This Work
CFC(=O)CF						
CFC(=O)CF	=	H	+	CJFC(=O)CF		
-133.2		52.103		-97.2	88.1	This Work
CFC(=O)CF	=	F	+	CFC(=O)Cj		
-133.2		18.97		-50.3	101.9	This Work
CF2C(=O)C						
CF2C(=O)C	=	F	+	CJFC(=O)C		
-144.5		18.97		-57.47	106.1	This Work
CF2C(=O)C	=	H	+	CF2C(=O)Cj		
-144.5		52.103		-100.55	96.1	This Work
CF2C(=O)C	=	H	+	CJF2C(=O)C		
-144.5		52.103		-104.21	92.4	This Work

Table 4.10 Bond Dissociation Energy (BDE) of Fluorinated Ketone Species in this Study (Continued)

CF2C(=O)CF						
CF2C(=O)CF	=	F	+	CJFC(=O)CF		
-182.1		18.97		-97.2	103.9	This Work
CF2C(=O)CF	=	F	+	CF2C(=O)Cj		
-182.1		18.97		-100.5	100.6	This Work
CF2C(=O)CF	=	H	+	CF2C(=O)CjF		
-182.1		52.103		-147.1	87.1	This Work
CF2C(=O)CF	=	H	+	CjF2C(=O)CF		
-182.1		52.103		-142.8	91.4	This Work
CF2C(=O)CF2						
CF2C(=O)CF2	=	H	+	CjF2C(=O)CF2		
-230.0		52.103		-193.0	89.1	This Work
CF2C(=O)CF2	=	F	+	CF2C(=O)CjF		
-230.0		18.97		-147.1	101.9	This Work
CF3C(=O)C						
CF3C(=O)C	=	F	+	CjF2C(=O)C		
-200.0		18.97		-104.2	114.8	This Work
CF3C(=O)C	=	H	+	CF3C(=O)Cj		
-200.0		52.103		-156.5	95.6	This Work
CF3C(=O)CF						
CF3C(=O)CF	=	F	+	CjF2C(=O)CF		
-237.2		18.97		-142.8	113.4	This Work
CF3C(=O)CF	=	F	+	CF3C(=O)Cj		
-237.2		18.97		-156.5	99.6	This Work
CF3C(=O)CF	=	H	+	CF3C(=O)CjF		
-237.2		52.103		-202.4	86.9	This Work
CF3C(=O)CF2						
CF3C(=O)CF2	=	F	+	CjF2C(=O)CF2		
-285.5		18.97		-193.0	111.5	This Work
CF3C(=O)CF2	=	F	+	CF3C(=O)CjF		
-285.5		18.97		-202.4	102.1	This Work
CF3C(=O)CF2	=	H	+	CF3C(=O)CjF2		
-285.5		52.103		-249.3	88.3	This Work
CF3C(=O)CF3						
CF3C(=O)CF3	=	F	+	CF3C(=O)CjF2	109.7	This Work
-340.0		18.97		-249.3		

From the analysis of the BDE’s, it was observed that the strongest bond in this specific system comes from fluorine-carbon bond in the trifluoro acetone species. Fluorine-carbon bonds attached to a single carbon site have stronger bonds in comparison to those species that have fluorine atoms on both the carbon sites where an atom could bind. In this same study, it has been observed that hydrogen-carbon bonds are weaker when they are attached to a carbon site where there is a fluorine-carbon bond located in comparison to a carbon site where there are no fluorine-carbon bonds present.

The HBI groups have the simplifying advantage that only one HBI term set is needed for a given generic class radical. In the normal GA scheme, a radical group is needed for each radical site, in addition to the groups for each central atom adjacent to the radical center.

The first requirement for obtaining thermodynamic property data on radical species using the HBI group approach is to acquire the corresponding properties of the parents. This implies that the absolute accuracy of thermodynamic data for radicals using the HBI group approach also relies on the accuracy of the data for the corresponding stable molecules. The discussion of the accuracy of current thermodynamic data for the fluorocarbons (FC) compounds is beyond the scope and context of this paper. In most cases, the ideal gas thermodynamic data for FC stable molecules determined by experiment or high-level *ab initio* MO calculations are more reliable than the calculated values for the corresponding free radicals. Benson's GA approach has also proven to be an accurate method for thermodynamic properties of stable FC molecules. Errors in the determination of the thermodynamic properties of the corresponding free radicals using the HBI procedure resulting from the errors of parent's thermodynamic data should be minor.

When the thermodynamic data of the parent molecules are not correct, equilibrium calculations for free radicals relative to the parent will not be affected, but both will be in error relative to other radicals and molecules.

The objective of developing the HBI database is to develop an accessible and fundamental approach to estimate thermodynamic properties for a wide range of radicals on where data are not currently available.

In this paper, we present an initial database of HBI terms for fluorinated ketone radicals relevant to fluorocarbon chemistry for combustion, atmospheric, and other chemical modeling communities.

4.5 Summary and Conclusion

Thermodynamic properties of fluorinated ketones and corresponding radicals were calculated at each site where hydrogen would be attached using density functional theory, *ab initio* and composite methods with the use of isodesmic reaction schemes for cancellation of calculation errors. Standard enthalpies of formation were determined using the average value observed in each species with CBS-APNO, CBS-4M, CBS-QB3 M062X, ωB97X, B3-LYP, G-2, G-3, G-4 and Weizmann-1 (W1U) calculation levels and multiple work reactions. Entropies and heat capacities were determined using the B3-LYP/6-31++G(d,p) optimized geometries and frequencies. Hindered internal rotational contributions to entropy and heat capacities were calculated by intramolecular torsion potential curves at the B3-LYP/6-31+G(d,p) level, with an entropy correction mixing of rotational conformers. In addition, thermochemical data were utilized from recent studies verify the accuracy of contributions for groups C/ CO/F/H2, C/ CO/F2/H, C/ CO/F3, cjfc(c=o)c, cjf2c(=o)c, cf3c(=o)cj, and cjf2c(=o)cf2. Interaction terms were developed to account for fluorine-fluorine interactions. Finally, bond dissociations energies were calculated to determine the bond strengths for each species.

We have calculated HBI groups, which when applied to the respective thermodynamic properties of a parent hydrocarbon molecule, yield the thermodynamic properties, (S°298 and Cp- (T, $300 \leq T/K \leq 1500$) of a radical corresponding to loss of a hydrogen atom. The enthalpy term ($\Delta Hf°_{298}$) in the HBI database is related to the bond energy (BDE) of the corresponding C-H bond for each radical group. We evaluate and present a listing of the respective C-H bond energies for the 11 fluorocarbon species. The entropy term ($\Delta S°_{298}$) and heat capacity terms $\Delta Cp(T)$ in the HBI database are added to the corresponding properties of the parent molecule, to obtain the thermodynamic properties of the radical. Values of the respective $\Delta S°_{298}$ and $\Delta Cp(T)$ terms in the HBI groups include contributions resulting from changes in barriers of internal rotations and vibrational frequencies (including frequencies of radical center inversion). The entropy values include correction for the electron spin degeneracy, but do not include symmetry corrections from the parent to the radical. The calculations for hydrogen atom bond increments ΔS°298 and $\Delta Cp(T)$ are based on the listed vibration and internal rotation changes and are determined using principles of statistical mechanics. Comparisons to previously published literature values, where available, show good agreement.

CHAPTER 5

THERMOCHEMISTRY AND KINETICS FOR UNIMOLECULAR DISSOCIATION OF THE SECONDARY ALKY RADICAL ON ETHYL OXIRANE

5.1 Overview

Substituted ethers such as piennes are present in the atmosphere in large quantities via emission of pine trees. This study is directed towards the unimolecular reactions of the secondary ethyl radical unimolecular and isomerization reactions of ethyl oxirane, as this species can be readily formed by reactions of molecular oxygen with secondary alkyl radicals. Specifically an alkyl radical can react with OH radical in the atmosphere or in combustion systems to form H_2O plus an alkyl radical. Here the radical site favors secondary carbon sites because the secondary C—H bond is weaker than that of a primary C-H bond. We are interested in the fate of the reactions of alkyl oxiranes, specifically ethyl oxirane and its oxidation byproducts under atmospheric and combustion conditions. The ethyl oxirane moiety is used as a generic oxirane produced under atmospheric and combustion oxidation of a normal alkane. Previous research has focused more on reactions of hydrocarbon radicals and the peroxy radicals and there are few studies on product alkyl-oxiranes and other substituted cyclic ethers. It is of value to study the reactions relevant to auto ignition and atmospheric reactions for predictive modeling of the chemistry. Data for predictive modeling will help us understand the lifetime potentials of chemical species in this investigation over a range of temperatures for corresponding hydrocarbons[10]. The further study of the ethyl oxirane oxidation should also be relevant to thermal reactions and combustion of bio-fuels which also include cyclic ethers such as furans. There has been an increase in research to understand biochemical oxidation pathways for their efficient combustible.[14,105]

There are a number of experimental and theoretical studies on the early stages of combustion[31-34], but data of cyclic ethers under ambient and combustion conditions is limited. Baldwin *et al.* [35] has shown, in one of the earliest and also a landmark study on alkyl oxidation reactions; the formation of molecular oxirane as a product of ethyl radicals with oxygen. Dagaut *et al.* [32, 33] and Yakyaoui *et al.*[34] have also reported results showing the formation of cyclic ethers in significant concentrations from the oxidation of hydrocarbons from low to moderate temperatures for combustion chemistry. There have also been computational studies performed on the formation of three-to five-membered cyclic ethers from hydroxyl radicals by Wijaya *et al.*[36] and Zadar et al[22].

The focus in this study, is aimed at the initial unimolecular reaction of the ethyl oxirane secondary radical because this the radical most easily formed by reaction with hydroxyl and other radicals in both combustion and atmospheric chemistry. Thermochemical properties of target parent molecule, and other radicals corresponding to loss of a hydrogen atom are determined. Thermochemical properties are also determined for unimolecular reaction products of this secondary ethyl oxirane intermediate. In addition to the thermochemistry of oxirane and its radical data on bond dissociation energies, unimolecular reaction activation energies along with kinetic parameters for each reaction and modeling of the overall unimolecular dissociation kinetics versus time are presented.

5.2 Nomenclature

Table 5.1 Nomenclature of the reactants, intermediates and products for Oxirane System

Nomenclature	Species	Formula
CC-Y(COC)	CH3CH2-Y[CHOCH2]	C_4H_8O
CJC-Y(COC)	CH2CH2-Y[CHOCH2]	C_4H_7O
CCJ-Y(COC)	CH3CH-Y[CHOCH2]	C_4H_7O
CC-Y(CJOC)	CH3CH2-Y[COCH2]	C_4H_7O
CC-Y(COCJ)	CH3CH2-Y[CHOCH]	C_4H_7O
C=C-Y(COC)	CH2CH-Y[CHOCH2]	C_4H_6O
CC=COCJ	CH3CH=CHOCH2	C_4H_7O
CC=CCOJ	CH3CH=CHCH2O	C_4H_7O
TY2-(CCH)-Y(COC)	CH3-CH[Y4(CHOCH)H]	C_4H_7O
TCY2-[C-Y(COC)-H]	CH3-Y3[CH(COCH2)]	C_4H_7O
TCY2-[C-Y(CCO)-H]	Y3(CH2CH-H)-Y(CHOCH2)	C_4H_7O
TS1	CH2CH2---Y(CHOCH2)	C_4H_7O
TS2	CH2---(H)CH-Y(CHOCH2)	C_4H_7O
TS3	CH3CH(OOH)-Y(CH(O)---CH2)	C_4H_7O
TS4	CH3CHCH---OCH2	C_4H_7O
TS5	CH3CH-Y(CH---OCH2)	C_4H_7O
TS6	CH3CHCH---CH2O	C_4H_7O

5.3 Computational Methods

All calculations performed were accomplished using the Gaussian 09 program suite[67]. Molecules were optimized using B3-LYP methodology with the 6-31G++(d,p) basis set. The B3-LYP method combines the three-parameter Becke exchange functional (B3), with the Lee-Yang-Parr correlation functional (LYP)[12]. The minimum energy conformation of each species is identified by performing a relaxed internal rotor scan for each of the two carbon – carbon single bonds in ethyl oxirane. The dihedral angle is scanned from zero to 360 degrees in 10-degrees increments with optimization of the remaining molecular structure at each step (relaxed scan). After scanning each of the dihedral angles corresponding to an internal rotor, the total energy corresponding to the most stable conformation was identified and used as a reference in plots of the potential barriers.

Isodesmic work reactions were employed for molecules in the study, to obtain accurate standard enthalpy of formation - energy calculations ($\Delta H°_{f298}$), using the composite methods CBS-APNO[124], CBS-4M[125] and CBS-QB3[137], and the DFT methods M06-2X[130], ωB97X[131], B2P-LYP[123] with a 6-31+(G(d,p) basis set.

The CBS models are based on a series of calculations made on a defined optimized lowest, molecular geometry, combined with a complete basis set extrapolation using model chemistry corrections for basis set truncation errors. These methods show a degree of accuracy in structure and energies that require convergence in basis set size. CBS-APNO is a more computationally expensive procedure than the CBS-QB3 method. (The acronym APNO stands for atomic pair natural orbital.) The CBS steps of this method allows for accurate extrapolations of the structure to the complete basis set limit. This is accomplished with (U)HF/6-311G(d,p) geometry optimization and frequency calculations to obtain enthalpic and free energy corrections. This then followed by a second geometry optimization at the QCISD(T), MP2(full), HF and MP2 levels, each with different basis sets.

CBS-QB3 is a five-step methodology that employs geometry optimization utilizing B3-LYP level calculations, frequency calculations to obtain thermal corrections, zero-point vibrational energy, and entropic information. The next steps of the computations are single point calculations at the CCSD(T), MP4SQ and MP2 levels. When all the steps are completed, CBS extrapolation then computes the final energies[138].

CBS-4M method is a complete basis-set method that is parameterized to the original CBS-4 method, where M is referring to the use of minimal population localization. In addition, this method includes empirical corrections[124].

M062x is a hybrid meta exchange-correlation functional that is a high nonlocality functional with double the amount of nonlocal exchange[61].

ωB97X is a long range corrected functional created by Head-Gordon and coworkers, which includes empirical dispersion[63].

B2P-LYP[123] is a double hybrid density functional that expands the DFT exchange correlation energies by a combination of mixing Gradient-Corrected (GCA) functional and exact exchange. The sum of these terms derived from GCA functions and correlation energies is calculated with second order perturbation theory.

Data from the methods mentioned above allowed for the determination of entropy and heat capacity values as a function of the following parameters: optimized structure, moments of inertia, vibration frequencies, internal rotor potentials, molecular symmetry, electron degeneracy, number of optical isomers and the mass of each molecule with respect to temperature. This calculation uses standard formulas from statistical mechanics to determine the contributions of translational, vibrational, and external rotation (TVR) and mass, using the SMCPS (Statistical Mechanics−Heat Capacity, and Entropy) program[87]. SMCPS utilizes the rigid-rotor harmonic oscillator approximation on the vibrational frequencies of the individual chemical species with moments of inertia from the optimized structure at the B3-LYP/6- 31G(d,p) level.

Transition-state properties (structures) for reactions that do not have potential barriers do not follow the same calculation procedures as transition states with saddle point

– potential barriers and other also species in this study. For reaction transition states where there is no barrier (saddle point); variational transition state theory (VTST) analysis is peroformed. Variational TST analysis is accomplished by running an energy scan along the selected bond of interest. Then from each optimized structure in the transition state region at the fixed bond distance, the vibrational frequencies were calculated. Rate constants are determined from the reactant to each of the points (TST_i): AB → TST_i (k_i) –> A + B. The distances that possess the minimum rate constant at each corresponding bond length are then reported with respect to the temperature at which they were evaluated. The variational rate constant is then determined from the fit of these rate constants to the modified Arrhenius equation:

$$k = A\ T^n\ \mathrm{Exp}(-Ea/RT)$$

The kinetic parameters for bimolecular chemical activation reactions, stabilization of chemically energized adducts, and unimolecular thermal dissociation reactions of the stabilized isomers were calculated by using a mutli frequency quantum Rice-Ramsperger-Kassel (qRRK) analysis for k(E). This was accomplished with steady state approximation on the energized adduct. Reaction kinetic parameters for the association forming chemically activated peroxy radical are reported to all stabilized adduct product channels as a function of pressure and temperature. Reaction kinetic parameters of stabilized intermediates are calculated only to adducts and products that are adjacent to the adduct/intermediate. The current version of the qRRRK computer code utilizes a reduced set of three vibrational frequencies that accurately reproduce the heat capacity of each species.

The group additivity method also known as second order approximation, developed by Benson[91], was used as a comparison for the determined parent $\Delta H°_{f\ 298}$, S°(T), and C (T) values. This method utilizes additivity behavior for each carbon and oxygen component in the molecules, - Group Additivity. This is based on the knowledge of the contributions of representative groups in similar molecules, and the thermochemical properties of the group, in linear consistency for oxygenated hydrocarbon molecules. Thermodynamic properties of species, such as those in this study, were accurately approximated based on the sum of smaller representative groups, where there are corrections for rotors, symmetry, electron degeneracy, optical isomers, and gauche and other interactions. The group additivity and calculated Density Functional Theory values are then compared. The good agreement between the two methods supports the accuracy of the study.

5.4 Results and Discussion

The isodesmic work reactions were used in the analysis of reference species $\Delta H°_{f\ (298)}$ values listed Table 5.2. The CBS-APNO, CBS-4M, CBS-QB3, M062X, ωB97X, B2PLYP composite and the DFT methods were used to calculate ethyl oxirane enthalpies of formation, along with radicals and products formed through oxidation reaction steps. Nomenclature for species identification and molecular formulas are listed in Table 5.1. Evaluation of the thermochemical enthalpies of the reactants, intermediates, and transition states using three different calculation methods provides a reinforcement of the accuracy and shows consistency of the data. The isodesmic reactions that were utilized have been averaged for each calculation method and are reported as method averages of the six methods. The standard deviation is listed for the calculation sets on each species. The smallest standard deviation of a set of molecules is 0.1 and the largest value is 3.6 kcal mol^{-1}.

Table 5.2 Standard Enthalpies of Formation used as Reference Species in Isodesmic Reactions for Ethyl Oxirane System

Species	**$\Delta H°_{f\ 298}$ (kcal mol^{-1})**	**Reference**
H	52.103 ± 0.001	139
CC=C	4.6 ± 0.3	105
CC=CJ	64.1 ± 0.9	105
Y(COC)	-12.4 ± 0.6	105
Y(COCJ)	40.0 ± 0.6	105
C=C	12.5 ± 0.1	105
CC	-20.0 ± 0.1	105
C=COH	-29.9 ± 0.6	105
C(OH)C=O	-76.0 ± 0.9	105
C=CCOH	-30.1 ± 0.9	105
C=COC	-51.72 [a]	103
C=CQ	-9.2 ± 0.9	105
C2CC	-32.0 ± 0.4	105
CC(OH)C	-65.4 ± 0.3	105
CC=CC (trans)	-2.7 ± 0.2	105
CC=CC (cis)	-1.5 ± 0.2	105
CCC	-25.2 ± 0.3	105
Y(CCC)	13.0 ± 0.4	105
Y(CJCC)	69.9 ± 0.9	105
CC=COH	-35.8 ± 0.9	105
C(OJ)C=O	-18.3 ± 0.9	105
CC=CQ	-15.3 ± 0.9	105
CCC(OH)C	-70.1 ± 0.35	140
C2-Y(COC)	-33.74 [a]	24
CC-Y(CCC)	0.3 [a]	141
CCJ (OH)C	-22.9 ± 0.9	105
CCCQ	-44.0 [a]	142
CCCC	-30.0 ± 0.1	105

[a] Species do not have uncertainty values available during the time of this study

Table 5.2 Standard Enthalpies of Formation used as Reference Species in Isodesmic Reactions for Ethyl Oxirane System (continued)

Species	**$\Delta H^\circ_{f\,298}$ (kcal mol^{-1})**	**Reference**
CCCCOH	-65.65 ± 0.07	106
CCJCQ	4.6 ± 0.9	105
CCCOH	-56.4 ± 0.4	105
CCJCOH	-13.0 ± 0.4	105
C-Y(CCC)	5.9 [a]	141
CCJCCOH	-18.73	143
COC=O	-85.6 ± 0.2	105
CY(COC)	-22.3 ± 0.9	105
CJOC	0.8 ± 0.9	105
COC	-43.9 ± 0.2	105
C-Y(COC)-C	-32.76	24
CJOCOH	-42.7 ± 0.9	105
COCOH	-86.74	144
CJOC=O	-37.3 ± 0.9	105
CCJC(OH)C	-22.58 ± 0.9	105
CJ-Y(COC)-C	13.59	24
C2-Y(COC)	13.35	24
C2-Y(COCJ)	18.39	24
C-Y(CJOC)-C	17.76	24
C=C(OJ)C	-6.9 ± 0.9	105
C=CCOH	-30.1 ± 0.9	105
C=CCOJ	23.7 ± 0.9	105
C=COC	-51.72	103
CCCC	-30 ± 0.1	105
C=C(OH)C	-40.6 ± 0.9	105
CC-Y(CCC)	0.3	141
CCCOJ	-8.1 ± 0.9	105
CCOCJ	-7.3 ± 0.9	105
CCCCOH	-65.65 ± 0.07	106
CCJCC	16.6 ± 0.9	105
C-Y(CCC)	5.9	141
COC=O	-85.6 ± 0.2	105
CJCCC	19.3 ± 0.9	105
CJCCOH	-11.5 ± 0.9	105
CCOC	-51.9 ± 0.9	105

[a] Species do not have uncertainty values available during the time of this study

The work reactions are illustrated in table 5.3 along with the corresponding composite and hybrid DFT methods with the 6-31G++ (d,p) basis set. Each species is evaluated using three to five isodesmic work reactions and different calculation methods. The reference species in the reactions conserve bond types in products and reactants (Isodesmic Reactions). The use of isodesmic reactions leads to the cancellation of systemic errors in the molecular orbital calculations[145].

Optimized structure parameters, symmetry values, moments of inertia, vibrational frequencies and internal rotor potentials for each species from B3-LYP/6-31G+(d,p) level of theory are present in Appendix D.

Table 5.3 Isodesmic Reactions of Species in Study for Oxirane System

Isodesmic Reactions							Heat of Formation (kcal/mol)					
							CBS-APNO	CBS-4M	CBS-QB3	MO62X	wb97x	B2-LYP
			CC-Y(COC)									
CC-Y(COC)	+	Y(CCC)	=	CC-Y(CCC)	+	Y(COC)	-28.7	-28.7	-28.8	-28.1	-28.2	-28.4
CC-Y(COC)	+	CCCOH	=	C-Y(COC)	+	CCC(OH)C	-27.6	-27.2	-27.2	-26.6	-26.7	-26.9
CC-Y(COC)	+	CCCOH	=	C-Y(COC)	+	CCCCOH	-27.1	-27.4	-27.2	-26.9	-26.7	-27.0
CC-Y(COC)	+	Y(CCC)	=	C-Y(CCC)	+	C-Y(COC)	-27.9	-28.1	-27.6	-27.6	-27.4	-27.4
CC-Y(COC)	+	C-Y(CCC)	=	CC-Y(CCC)	+	C-Y(COC)	-28.0	-28.3	-28.0	-27.7	-27.7	-27.8
						average	-27.9	-28.0	-27.8	-27.4	-27.3	-27.5
						st. dev.	0.6	0.6	0.7	0.6	0.6	0.6
			CJC-Y(COC)									
CJC-Y(COC)	+	CCCOH	=	CC-Y(COC)	+	CJCCOH	22.7	22.7	23.2	23.5	23.2	23.1
CJC-Y(COC)	+	CCCC	=	CC-Y(COC)	+	CJCCC	22.0	22.0	22.1	21.8	22.0	22.1
CJC-Y(COC)	+	CY-(COC)-C	=	CC-Y(COC)	+	CJY-(COC)-C	19.7	20.9	21.4	20.9	20.6	21.1
CJC-Y(COC)	+	C2-Y(COC)	=	CC-Y(COC)	+	CJ2-Y(COC)	20.1	20.8	21.5	20.7	20.6	21.0
						average	21.6	21.8	22.2	22.0	22.0	22.1
						st. dev.	1.4	0.9	0.8	1.3	1.2	1.0
			CJC-Y(COC)									
CC-Y(CJOC)	+	Y(COC)	=	CC-Y(COC)	+	Y(COCJ)	23.0	23.1	22.9	23.2	23.2	23.0
CC-Y(CJOC)	+	Y(CCC)	=	CC-Y(COC)	+	Y(CJCC)	25.3	25.6	22.4	23.8	23.0	22.6
CC-Y(CJOC)	+	CC(OH)C	=	CC-Y(COC)	+	CCJ(OH)C	23.9	25.5	24.0	23.9	23.9	23.4
CC-Y(CJOC)	+	C-Y(COC)-C	=	CC-Y(COC)	+	C-Y(CJOC)-C	23.2	23.2	23.4	23.4	23.34	23.4
						average	23.8	24.4	23.2	23.6	23.4	23.1
						st. dev.	1.0	1.4	0.7	0.3	0.4	0.4

Table 5.3 Isodesmic Reactions of Species in Study for Oxirane System (Continued)

							Heat of Formation (kcal/mol)					
							CBS-APNO	CBS-4M	CBS-QB3	MO62X	wb97x	B2-LYP
		CC-Y(COCJ)										
CC-Y(COCJ)	+	Y(COC)	=	CC-Y(COC)	+	Y(COCJ) 24.7		24.6	24.5	24.6	24.5	24.5
CC-Y(COCJ)	+	Y(CCC)	=	CC-Y(COC)	+	Y(CJCC)	26.9	27.1	24.1	25.2	24.4	24.1
CC-Y(COCJ)	+	CC(OH)C	=	CC-Y(COC)	+	CCJ(OH)C	25.6	27.0	25.7	25.3	25.2	24.8
CC-Y(COCJ)	+	CC(OH)C	=	CC-Y(COC)	+	CCJ(OH)C	24.7	24.7	24.9	24.9	24.8	24.9
						average	25.5	25.9	24.8	25.0	24.7	24.6
						st. dev.	1.0	1.4	0.7	0.3	0.4	0.4
		CC=COC										
CC=COC	+	CC=COH	=	C=COC	+	CC=CCOH	-59.2	-61.4	-61.5	-60.4	-60.4	-59.7
CC=COC	+	C=CQ	=	C=COC	+	CC=CQ	-57.6	-58.0	-57.7	-58.4	-58.3	-57.3
CC=COC	+	CC=C	=	CC=CC (cis)	+	C=COC	-58.0	-58.5	-57.6	-57.4	-57.5	-57.7
CC=COC	+	CC=C	=	CC=CC (trans)	+	C=COC	-57.5	-58.0	-57.4	-57.4	-57.5	-57.4
						average	-58.1	-58.9	-58.6	-58.4	-58.4	-58.0
						st. dev.	0.8	1.6	2.0	1.4	1.4	1.1
		CC=COC										
CC=COCJ	+	COC	=	CC=COC	+	CJOC	-12.6	-24.5*	-12.2	-11.4	-13.6	-12.5
CC=COCJ	+	COC=O	=	CC=COC	+	CJOC=O	-11.8	-10.3	-11.8	-10.4	-11.1	-11.4
CC=COCJ	+	CCOC	=	CC=COC	+	CCOCJ	-12.7	-11.7	-12.4	-11.5	-11.8	-12.0
CC=COCJ	+	COCOH	=	CC=COC	+	CJOCOH	-13.7	-12.9	-14.0	-12.9	-13.3	-13.7
						average	-12.7	-11.6	-12.6	-11.5	-12.4	-12.4
						st. dev.	0.8	1.3	1.0	1.0	1.2	1.0

Table 5.3 Isodesmic Reactions of Species in Study for Oxirane System (Continued)

							Heat of Formation (kcal/mol)					
							CBS-APNO	CBS-4M	CBS-QB3	MO62X	wb97x	B2-LYP
		CC=CCOH										
CC=CCOH	+	CC=C	=	CC=CC (trans)	+	C=CCOH	-37.8	-36.8	-37.6	-37.8	-38.1	-38.6
CC=CCOH	+	CC=C	=	CC=CC (cis)	+	C=CCOH	-38.3	-37.2	-37.7	-37.8	-38.7	-38.8
CC=CCOH	+	C=C	=	CC=C	+	C=CCOH	-37.8	-37.0	-37.6	-37.9	-38.1	-38.7
CC=CCOH	+	C=CQ	=	C=CCOH	+	CC=CQ	-38.0	-36.7	-37.8	-38.8	-38.9	-38.4
						average	-38.0	-36.9	-37.7	-38.1	-38.3	-38.6
						st. dev.	0.2	0.2	0.1	0.5	0.4	0.2
		CC=CCOJ										
CC=CCOJ	+	C(OH)C=O	=	CC=CCOH	+	C(OJ)C=O	17.4	18.0	17.6	16.8	16.8	17.2
CC=CCOJ	+	C=CCOH	=	CC=CCOH	+	C=CCOJ	15.8	14.9	15.6	15.8	16.0	16.5
CC=CCOJ	+	C=C(OH)C	=	CC=CCOH	+	C=C(OJ)C	12.7	6.8*	14.7	15.3	17.0	16.8
CC=CCOJ	+	CCCOH	=	CC=CCOH	+	CCCOJ	16.3	16.4	16.7	17.5	16.5	16.8
CC=CCOJ	+	C=COH	=	CC=CCOH	+	C=COJ	13.6	7.8*	14.7	15.3	16.3	16.6
						average	15.2	16.4	15.8	16.2	16.5	16.8
						st. dev.	2.0	1.5	1.3	1.0	0.5	0.3
		CC=CCOJ										
C=C-Y(COC)	+	CC	=	C=CCC	+	Y(COC)	2.6	2.0	1.7	2.7	2.6	2.1
C=C-Y(COC)	+	C2CC	=	C=CCC	+	C2-Y(COC)	2.1	1.3	1.6	1.5	2.0	1.8
C=C-Y(COC)	+	CCCC	=	C=CCC	+	C-Y(COC)-C	2.5	1.9	2.3	1.9	2.6	2.4
						average	2.4	1.7	1.9	2.0	2.4	2.1
						st. dev.	0.3	0.4	0.4	0.6	0.4	0.3

5.4.1 Heat of Formation $\Delta H^{\circ}_{f\,298}$

A summary of the average standard enthalpy of formation ($\Delta H^{\circ}_{f\ 298}$) values from computational methods for species illustrated from work reactions in Table 5.3 are summarized in Table 5.4. Table 5.4 lists the average enthalpy of formation for species calculated enthalpy of formation ($\Delta H^{\circ}_{f\,298}$) values from the computational methodology utilized in work reactions. On the basis of the correlations in these different techniques, error values are provided in Table 5.4 using the standard deviation from the individual calculated standard enthalpy of formation ($\Delta H^{\circ}f_{\ 298}$) values. The resulting standard deviations from the reactions show an average standard deviation of 1.06 kcal mole^{-1}. These standard deviations coincide with the average standard deviations, on a per work reaction basis determined in Table 5.3. Values in Table 5.4 are recommended for the evaluation of accuracy. It is noted that the uncertainty in the reference species also need to be considered.

Table 5.4 Summary of Average Heat of Formation $\Delta H^{\circ}_{f\,298}$ and Literature Values for Oxirane System

	Heat of Formation (kcal/mol)	
Species	**Calculated Enthalpy of Formation (kcal mole^{-1})**	**Literature**
CC-Y(COC)	-27.6 ± 0.63	This Study
CJC-Y(COC)	21.7 ± 1.04	This Study
CCJ-Y(COC)	18.3 ± 0.77	This Study
CC-Y(CJOC)	23.6 ± 0.83	This Study
CC-Y(COCJ)	25.1 ± 0.85	This Study
CC=COC	-54.8 ± 1.30	52.1[160]
CC=COCJ	-12.5 ± 2.90	This Study
CC=CCOH	-37.9 ± 0.60	This Study
CC=CCOJ	16.3 ± 1.22	This Study
C=C-Y(COC)	2.1 ± 0.43	This Study

5.4.2 Carbon-Hydrogen Bond Dissociation Energies

As noted earlier in this study the formation of the ethyl oxirane secondary radical is initiated via reaction with a (OH) hydroxyl radical. The OH radical abstracts a hydrogen atom, forming a water molecule and ethyl oxirane radical. To determine which carbon site the hydroxyl molecule would extract a hydrogen from, carbon-hydrogen bond dissociation energies for each site was calculated. This was achieved by using the following equation,

$$\Delta H_{reaction} = \Sigma\Delta H_{product} - \Sigma\Delta H_{reactants}$$

The $\Delta H_{reaction}$ here corresponds to the carbon-hydrogen bond dissociation energy (BDE); $\Sigma\Delta H_{product}$ represents the radical species enthalpy of formation plus the enthalpy of a hydrogen atom. The hydrogen atom has an enthalpy of formation ($H_{f\,298}^{\circ}$) of 52.103 kcal mole^{-1}.

The Ethyl Oxirane specie, shown below, has for four sites where a hydrogen atom could be extracted from Figure 5.1. The BDE values calculated are listed in Table 4 and are compared with literature values.

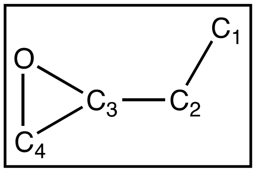

Figure 5.1 Possible radical site positions for ethyl oxirane.

In the ethyl oxirane molecule, C_1 is the primary carbon site. The primary carbon-hydrogen bond has an observed BDE 101.4 kcal/mol. Comparing this calculated value with literature by Auzmendi-Murua *et al.*[24] , the average BDE of primary oxirane radicals was observed to be 101.3 kcal/mol. The secondary carbon-hydrogen site labeled C_2, was observed to have a carbon-hydrogen bond dissociation energy of 98.1 kcal/mol. For the secondary carbon-hydrogen site, data have not yet been reported during the time of this study. Comparing data for primary and secondary carbon-hydrogen BDE with literature data, the results obtained are consistent with BDE values reported for alkanes having primary and secondary BDE of 101.3 and 98.5 kcal/mol[146], respectively.

The carbon-hydrogen bond attached to the secondary carbon and the ring portion of the ethyl oxirane species, labeled C_3, has a BDE of 103.1 kcal/mol. Studies by Auzmendi-Murua *et al.*[24] report BDE of similar oxirane radical species to be on average 102.4 kcal/mol. C_4 , the carbon-hydrogen bond, has been recorded to have a BDE of 104.8 kcal/mol. In comparison to the other carbon-hydrogen bonds observed, this is the strongest bond in the ethyl oxirane molecule. This finding is in good agreement with literature values observed by Auzmendi-Murua *et al.*[24], reporting 104.4 kcal/mol[24] for the similar carbon-hydrogen bond. C_2 has the lowest BDE in comparison to the other carbon-hydrogen bonding energies. In this study, because of this carbon-hydrogen site having the weakest bond strength, this is the location where we believe the hydroxyl radical extraction of a hydrogen atom will be favored.

Table 5.5 Bond Dissociation Energy (BDE) of Ethyl Oxirane and 2-(sec-Butyl)Oxirane

Reaction					Bond Dissociation Energies (kcal mol^{-1})	
CC-Y(COC)	=	CCJ-Y(COC)	+	H		
-27.6		18.4		52.103	98.1 ± 0.7	98.5 [146]
CC-Y(COC)	=	CJC-Y(COC)	+	H		
-27.6		21.7		52.103	101.4 ± 1.0	101.3 [146]
CC-Y(COC)	=	CC-Y(CjOC)	+	H		
-27.6		23.6		52.103	103.3 ± 0.8	103.1 [24]
CC-Y(COC)	=	CC-Y(COCj)	+	H		
-27.6		25.1		52.103	104.8 ± 0.9	104.4 [24]

5.4.3 Internal Rotors

Potential energy curves for internal rotations in the parent, radical and intermediate species resulting from unimolecular dissociation and oxidation reactions are calculated using the B3-LYP/6-31G(d,p) level of theory. Relaxed scans at 10 degree intervals are used to determine the lowest energy geometries. If a lower energy conformation is found, previous scans are re-run and reevaluated to insure the lowest energy conformation is located. These potential energy curves are also used to determine entropy, heat capacity and internal rotational contributions. These potential energy curves are presented in Appendix D and are used to calculate entropy and heat capacity contributions from internal rotations.

5.4.4 Entropies (S(T)) and Heat Capacities (C_p(T))

The method used to calculate entropies and heat capacities was SMCPS. SMCPS **(**Statistical Mechanics−Heat Capacity, and Entropy) applies only the rigid-rotor harmonic oscillator (HO) approximation without correction (subtraction) of R ln(σ) for the three fold symmetry of primary methyl groups using the torsion frequencies. Table 5.6 presents the calculated entropies and heat capacities for parent, radical and intermediate species.

Table 5.6 Entropies and Heat Capacities for Parent, Radical and Intermediate Species for Ethyl Oxirane System

Species	**Hf (kcal mol^{-1})**	**S**	**Cp300**	**Cp400**	**Cp500**	**Cp600**	**Cp800**	**Cp1000**	**Cp1500**
CC-Y(COC)	-27.6	71.06	20.22	26.09	31.82	36.88	44.94	50.92	60.24
CJC-Y(COC)	21.7	70.10	19.20	24.69	29.81	34.23	41.12	16.19	54.12
CCJ-Y(COC)	18.3	71.00	19.09	24.43	29.52	33.94	40.90	46.04	54.06
CC-Y(CJOC)	23.6	59.48	18.20	23.51	28.64	33.16	40.34	45.64	53.88
CC-Y(COCJ)	25.1	68.99	18.09	23.55	28.77	33.32	40.49	45.77	53.95
CC=COC	-54.8	69.86	20.58	25.44	29.60	33.12	38.67	42.80	49.27
CC=COCJ	-12.5	72.33	20.79	25.76	30.47	34.60	41.22	46.19	54.07

Table 5.6 Entropies and Heat Capacities for Parent, Radical and Intermediate Species for Ethyl Oxirane System (Continued)

Species	**Hf (kcal mol^{-1})**	**S**	**Cp300**	**Cp400**	**Cp500**	**Cp600**	**Cp800**	**Cp1000**	**Cp1500**
CC=CCOH	-37.9	83.04	23.93	29.26	34.16	38.51	45.56	50.76	58.66
CC=CCOJ	16.3	71.16	19.18	24.30	29.26	33.64	40.64	45.86	54.00
C=C-Y(COC)	2.1	69.52	18.39	23.61	28.50	32.69	39.18	43.89	51.17
TY2-(CCH)-Y(COC)	80.54	70.43	19.46	25.19	30.56	35.15	42.22	47.28	54.94
TCY2-[C-Y(COC)-H]	83.09	73.8	20.44	25.68	30.68	35.05	41.95	46.99	54.74
TCY2-[C-Y(CCO)-H]	71.45	72.2	20.26	25.86	31.01	35.4	42.19	47.12	54.73
TS1	59.0	77.86	21.53	26.89	31.78	35.91	42.28	46.97	54.43
TS2	57.7	73.45	21.79	27.5	32.63	36.93	43.44	48.11	55.28
TS3	30.5	73.23	21.17	26.4	31.21	35.34	41.85	46.69	54.36
TS4	22.8	82.39	23.75	28.49	32.88	36.68	42.74	47.32	54.68
TS5	23.1	73.52	20.18	25.21	30.08	34.35	41.15	46.2	54.14
TS6	48.5	80.56	22.98	27.72	32.18	36.07	42.3	47.01	54.54

The data in Table 5.6 for the parent molecules by the HO approximation method, as implemented in the SMCPS code, are shown to consistently under predict entropies by 4 to 9 cal mol$_{-1}$ K$_{-1}$ in this 298-1500 K temperature range. It is seen that as the branching of these isomers increases, the HO approximation provides a slight increase in accuracy.

5.4.5 Group Additivity

The group additivity (GA) method, as developed by Benson[91] is a rapid estimation method for ΔH° f 298, S° 298, and Cp(T) of stable species. This method is based on the knowledge of the contributions of representative groups in similar molecules, in addition to experimental linear consistency observed in thermochemical properties such as heat capacity and enthalpy values.

This study utilizes group additivity terms values to compare calculated enthalpies of formation for ethyl oxirane and ethyl oxirane radicals. The group terms employed for this section of research can be utilized to estimate enthalpy values to compare calculated enthalpy of formation values. Table 5.7 list the groups that are employed in group additivity methodology.

Table 5.7 Group Contribution Terms Used in the Calculation of Species

Group	Hf	S_{298}	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
C/C/H3[91]	-10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C2/H2[91]	-5.00	9.40	5.50	6.95	8.25	9.36	11.07	12.34	14.20
C/C2/H/O[91]	-7.20	-11.00	4.80	6.64	8.10	8.73	9.81	10.40	11.51
O/C2[91]	-23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.60	-
C/C/H2/O[91]	-8.10	9.80	4.99	6.85	8.30	9.43	11.11	12.33	-
RJCOC[91]	102.32	1.23	0.48	-0.11	-0.76	-1.36	-2.36	-3.11	-4.21
T[91]	96.50	5.24	-0.78	-2.48	-3.55	-4.15	-4.75	-5.02	-5.39
S[91]	98.45	4.44	-1.50	-2.33	-3.10	-3.39	-3.75	-4.45	-5.20
C/CD/H3[91]	-10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
CD/C/H[91]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
C/CD/H2/O[91]	-6.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.40
O/C/J[91]	-37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
O/C/D[91]	-23.73	9.70	3.91	4.31	4.60	4.84	5.32	5.80	-
CD/H2[91]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
P[91]	101.10	2.61	-0.77	-1.36	-1.91	-2.40	-3.16	-3.74	-4.66

Comparisons are completed using the sum of the group present in each species with the calculated enthalpy of formation are presented in Table 5.8.

Table 5.8 Comparison of Heat of Formation with Methods and Group Additivity

	Heat of Formation (kcal/mol)								
Species	CBS-APNO	CBS-4M	CBS-QB3	M062X	Wb97X	B2-LYP	Average	Lit.	G.A.
CC-Y(COC)	-27.9	-28.0	-27.8	-27.4	-27.3	-27.5	-27.6	This Study	-26.8
CjC-Y(COC)	21.6	21.8	22.2	22.0	22.0	22.1	21.7	This Study	22.2
CCj-Y(COC)	19.4	18.2	17.7	18.6	18.3	18.0	18.3	This Study	19.6
CCYCjOC	23.8	24.4	23.2	23.6	23.4	23.1	23.6	This Study	17.6
CCYCOCj	25.5	25.9	24.8	25.0	24.7	24.6	25.1	This Study	19.6
CCDCOC	-58.1	-58.9	-58.6	-58.4	-58.4	-58.0	-54.8	52.44	-41.3
CCDCOCj	-12.7	-11.6	-12.6	-11.5	-12.4	-12.4	-12.5	This Study	16.3
CCDCCOH	-38.0	-36.9	-37.7	-38.1	-38.3	-38.6	-37.9	This Study	-37.7
CCDCCOj	15.2	16.4	15.8	16.2	16.5	16.8	16.3	This Study	14.3
CDC-Y(COC)	2.4	1.7	1.9	2.0	2.4	2.1	2.1	This Study	0.8

5.4.6 Reactions

In this study, the majority of reactions can be divided into four different classes:

- Intramolecular hydrogen transfer
- β scission ring opening
- β scission hydrogen elimination
- Molecular β scission

These four classes will further the fate of the s-ethyloxirane radical species. Potential energy diagram can be see below in Figure 5.2.

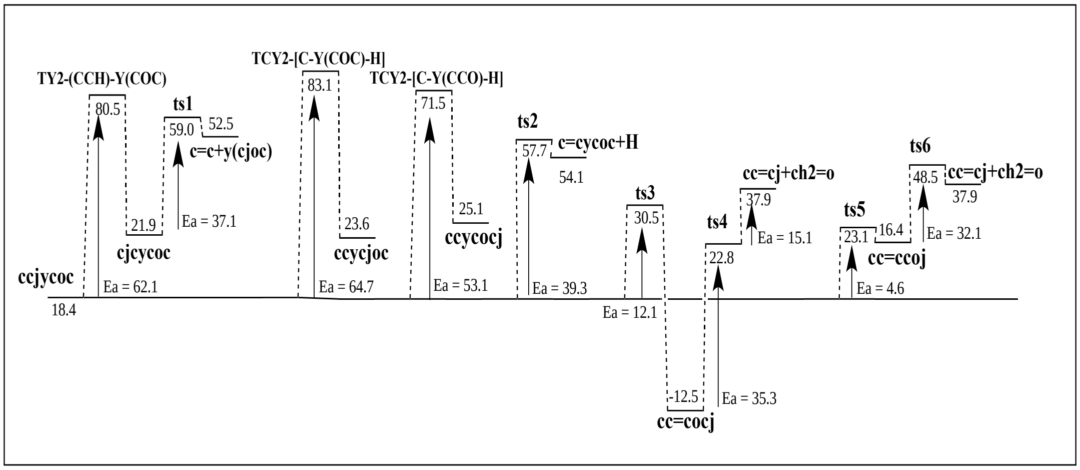

Figure 5.2 Potential Energy Diagram for Secondary-Ethyl Oxirane Radical Unimolecular Reactions vertical distance represents energy of species.

5.4.6.1 Hydrogen Transfer of CCJ-Y(COC). The first set of reactions observed are hydrogen transfer reactions. The CCj-Y(COC) species has four possible sites which a radical can exist. There are three separate intramolecular hydrogen transfers that could occur. The transfer of a H atom from carbons C_1, C_3 and C_4 to the indicated radical site C_2 are shown in Figure 5.2.

The CCj-Y(COC) radical abstract a H atom from the primary carbon, C_1, by forming a three-membered ring Transition State (TST), structure TY2-(CCH)-Y(COC) to form CjC-Y(COC). This reaction has a relatively high activation energy of 61.8 kcal/mol to the transition state resulting from the strain of the three member ring, and a reverse barrier of 58.5 kcal/mol.

Abstraction of a hydrogen atom from carbon C_3 follows the same trend, reacting through a three-membered ring TST to form TCY2-[C-Y(COC)-H] to further the reaction path to form the CC-Y(CjOC) species. This reaction has a forward barrier of 64.3 kcal/mol and a reverse barrier of 59.0 kcal/mol.

The remaining hydrogen transfer occurs from the C_4 carbon, forming a four-member ring TST, TCY2-[C-Y(CCO)-H], to form CC-Y(COCj). This reaction has an activation barrier of 52.8 kcal/mol and a reverse activation energy of 46.0 kcal/mol. Each of the hydrogen transfer reactions from sites C_1, C_3 and C_4 to the C_2 carbon are slightly endothermic reactions and have a positive enthalpy of reaction of 3.4, 5.3 and 6.8 kcal/mol, respectively.

5.4.6.2 β Scission - Hydrogen Elimination CCJ-Y(COC). β scission reactions involve the combination of two steps: (i.) the formation of a new π bond, either olefin (C=C) or carbonyl (C=O) and loss of a sigma (σ-bond) with both occurring simultaneously.

CH2•-CH3 => CH2=CH2 + H beta scission of H atom from ethyl radical

Energy is gained by the formation of the π bond and lost in the cleaving of the C—H bond.

β scission hydrogen elimination occurs when the C_2 labeled carbon starts to form a double bond to the C_1 carbon and simultaneously a hydrogen atom leaves the C_1. The overall reaction cleaves a C—H single sigma bond and forms a C—C π bond. The activation energy is observed to be 38.5 kcal/mol to the saddle point transition state, resulting in the formation of products C=C-Y(COC) + H. The products vinyl-oxirane + H are 3.9 kcal mol^{-1} below the TST (saddle point), and the endothermicity of the reaction is 35.8 kcal/mol.

5.4.6.3 β Scission Ring Opening CCJ-Y(COC). Two paths were observed for the the β scission ring opening reactions CCj-Y(COC). One path cleaves a C—C bond in the oxirane ring and one path cleaves a C--O bond in the oxirane ring; while both paths form a new C=C π bond between the secondary ethyl carbon atom and the ring carbon. The ring C-C cleaving β scission (ring opening) reaction forms CC=COCj by cleaving the bond between the carbons labeled C_3 and C_4, reacting through a saddle point transition state structure, ts3. This reaction has an activation energy of 12.1 kcal mole^{-1} and a reverse activation energy of 42.9 kcal/mol. This results in an exothermicity for the reaction of 30.8 kcal/mol. The low forward barrier, is a result of release of ring strain in the 3-member ring, while the reverse reaction barrier includes the formation of the 3 member ring with its strain.

The second ring-opening β scission reaction occurs when the secondary carbon radical site in the ethyl group forms a π bond to C3 as above, but now the C_3 carbon – oxygen bond cleaves CC=CCOJ is formed. The reaction also occurs through a saddle point transition state structure.

The reason for the significant difference in the thermochemistry for these two beta scission reactions lies in this last reaction forming CC=CCOJ, which is an alkoxy radical bonded to a –CH2- group. Here this -CH2- group has all sp3 bonds and this electronic configuration prevents resonance through this –CH2 group; the resonance would want to be between the electron rich O atom and the π bond. There is no resonance between these two unsaturated groups – the π bond and the Oj radical.

In contrast the CC=COCj as shown has a carbon radical site bonded through an oxygen atom to a π bonded carbon system. This oxygen atom linkage allows significant resonance between the π bond through the oxygen atom to the terminal, unsaturated carbon radical, which has a sp2 electronic configuration.

The resonance forms of C-C•CO•C are:

CC=COC• = C-C•C•OC• = C-C•C•O•C = C-C•CO•C•

The carbon radical here is sp2 bonded which allows the resonance. The resonance accounts for the much lower energy of the CC=COCj radical (-12.5 kcal mol^{-1} versus the CC=CCOj radical at 16,4 kcal mol^{-1} as shown in figure 5-2. It will be interesting to study the thermochemistry and reactions of the CC=COCj and similar radical systems.

In a previous oxirane radical unimolecular decomposition study by Wang *et al.* [147], they observed the saddle point transition state structure was formed at a bond angle of ~75 degrees when the carbon-oxygen bond was cleaved with an activation energy observed at 6.7 kcal/mol and a reverse barrier of 4.2 kcal mole^{-1}. In this study, a bond angle for the transition state is reported at 76 degrees for the carbon-oxygen bond cleavage showing agreement with literature data. The barrier observed in this reaction is 4.8 kcal mole^{-1}, with a reverse barrier of 6.9 kcal mole^{-1}. This exothermic reaction has a total heat of reaction of 2.2 kcal mole^{-1} released. The difference in the thermochemistry for these two different ring opening reactions is described above.

5.4.6.4 Uni-molecular Beta (β) Scission Reaction. In a beta scission reaction the radical a radical starts to form a π bond, sp2 bonding, to an adjacent atom and the bond beta (2 atoms away) from the radical site cleaves. Most often one new π bond (sp2 structure) forms and a single sigma (σ) bonds is cleaved. The result of a new bond being formed for a bond being cleaved often results in the overall reaction barrier being relatively low.

The following chemical species CjC-Y(COC), CC=COCj and CC=CCOj in this ethyl oxirane system, each undergo unimolecular β scission reactions. CjC-Y(COC moiety will a ch2=ch2 double bond (ethylene) with the C_2-C_3 carbon-carbon bond being cleaved to form an oxirane radical with a saddle point barrier of 37 kcal/mol. The reaction has a reverse barrier 6.2 kcal/mol

The CC=CCOj radical will beta scission to from a carbon to oxygen double (carbonyl) bond and cleave the C3 – C4 bond forming products CH2=O (formaldehyde) and 2-methyl-vinyl radical. The transition state is formed as the carbon-carbon bond is stretched between the double bond carbon and the carbon adjacent to the hydroxyl radical site. This reaction has an activation energy of 35.3 kcal mole^{-1} and a reverse barrier of 13 kcal mole^{-1}.

The CC=COCj radical will undergo beta scission to form the same products as just above, 2methylvinyl radical plus formaldehyde. The reaction has a forward and reverse barrier of 32.1 and 12.4 kcal mole^{-1}, respectively. Each of these reactions are mildly endothermic as noted.

5.5 Kinetics

In the systems described in the introduction, many of the reactions have high reaction barriers and effectively do not occur. Table 5.9 lists high pressure limits for elementary rate parameters used as input data for the QRRK calculations at one atmosphere, where rate constants are reported at 800K in this section. There are two reaction paths for the CCj-Y(COC) which results in the formation of CC=COCj and CC=CCOj. The formation of these two isomers have forward rate constants of $2.67\text{x}10^1$ and $1.92\text{x}10^2$ sec^{-1}, respectively at 800 ^{o}K. . The reverse reactions for these species, reversing and forming the isomer CCj-Y(COC), are unlikely for the CC=COCj species due to the high barrier 12.1 kcal mole^{-1} needed to achieve this reverse reaction. CC=CCOj is can react back to CCj-Y(COC) because of the barrier being only 7 kcal mole^{-1}. As the chemical species, CC=COCj and CC=CCOj are formed, it is observed under high temperature and pressure conditions, the beta scission rate constants become important allowing the two isomer paths to dissociate, forming Cj=CC and CH_2O. These reactions have rate constants of $3.74\text{x}10^3$ and $1.05\text{x}10^6$ sec^{-1}, respectively at 800^{o}K.

Table 5.9 High Pressure-Limit Elementary Rate Parameters for Dominate Species Formation

	k=A T^{n} exp$^{(-Ea/RT)}$			
Reactions	**A(cm^{3}molecules^{-1} s^{-1})**	**n**	**Ea (kcal mol^{-1})**	**k (sec^{-1}) at 800K**
CCJYCOC → C=CYCOC+H	5.33E+60	-14.67	75.07	4.28x10^{3}
CCJYCOC → CJCYCOC	7.45E+32	-6.68	75.08	9.30 x10^{-8}
CCJYCOC → CCYCJOC	1.43E+11	-0.27	75.09	7.23 x10^{-11}
CCJYCOC → CCYCOCJ	2.49E+10	-0.16	75.09	2.61 x10^{-11}
CCJYCOC → CC=COCJ	3.37E+67	-15.70	75.12	2.67 x10^{1}
CCJYCOC → CC=CCOJ	3.09E+69	-16.08	75.13	1.92 x10^{+2}
CJCYCOC → C=C + YCOCJ	1.11E+74	-16.75	99.12	2.19 x10^{-2}
CJCYCOC → CCJYCOC	1.13E+43	-8.04	99.13	4.29 x10^{-8}
CCYCJOC → CC=COCJ	6.28E+99	-24.88	85.84	1.31 x10^{4}
CCYCJOC → CCJYCOC	5.39E+38	-7.68	85.81	9.88 x10^{-8}
CCYCOCJ → CC=COCJ	9.75E+70	-16.25	83.74	8.69
CCYCOCJ → CCJYCOC	1.92E+10	1.00	83.73	2.06 x10^{-10}
CC=COCJ → CJ=CC+CH2O	7.23E+70	-16.66	69.26	3.74 x10^{3}
CC=COCJ → CCJYCOC	2.48E+68	-17.12	69.23	6.04 x10^{-1}
CC=CCOJ → CJ=CC+CH2O	4.17E+48	-10.74	41.80	1.05 x10^{6}
CC=CCOJ → CCJYCOC	5.79E+51	-16.00	71.20	7.30 x10^{-15}

Figure 5.3 shows the rate constant plot as a function of temperature, ranging from 298 K to 1200K, where temperatures are converted to 1000/T at one atmosphere for dominate channels during unimolecular dissociation.

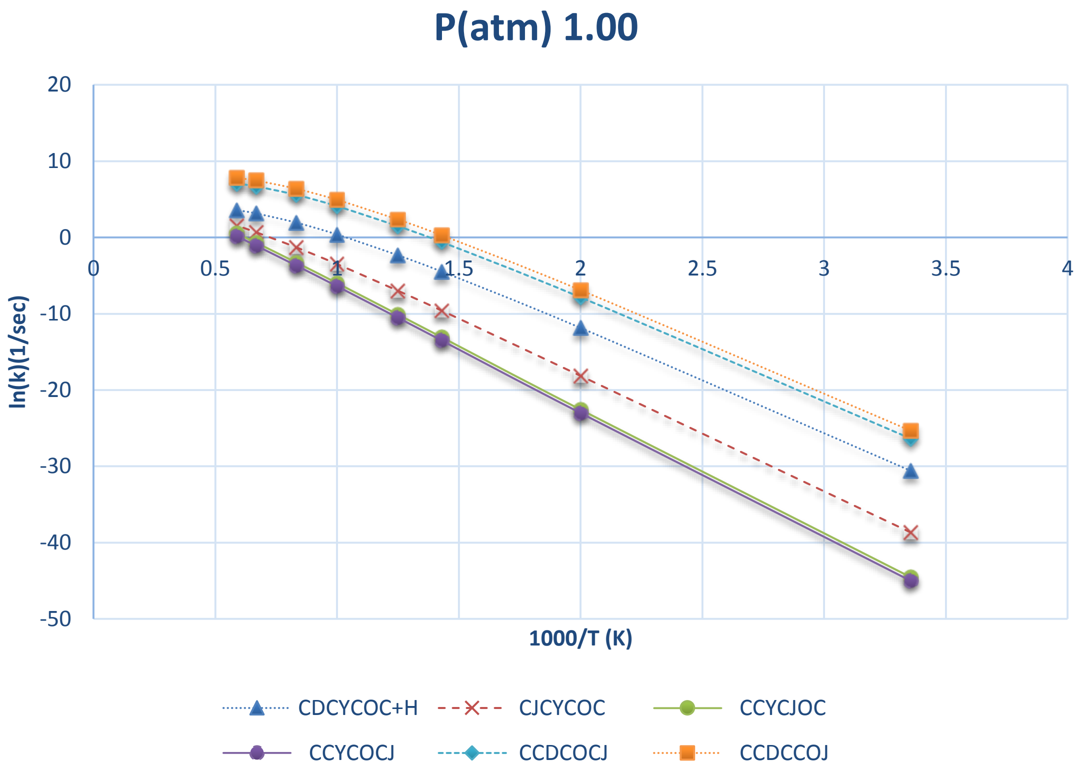

Figure 5.3 Rate constant plot as a function of temperature, ranging from 298 K to 1200K at one atmosphere.

Chemkin

To determine the mole fractions of products formed from the CCj-Y(COC) molecule, an initial concentration of 1 mM was used. Steps were analyzed at for reaction up to twelve milliseconds at 800 K. Figure 5.4 shows the Chemkin modeling of CCj-Y(COC) undergoing unimolecular dissociation at 1 atmosphere pressure and 800 K.

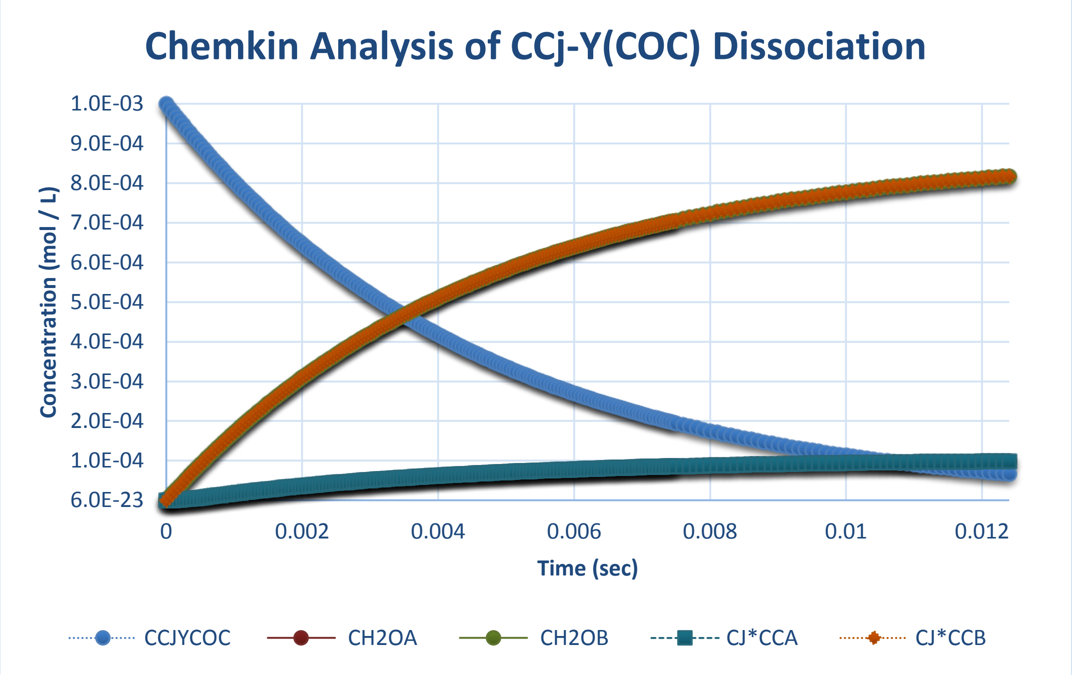

Figure 5.4 Chemkin modeling of CCj-Y(COC) undergoing oxidation at 1 atm and 800K analyzed at 150 points in 50 microsecond increments, followed by 50 steps at increments of 100 microseconds

In Chemkin, analysis for mole fractions on the fate of the unimolecular reactions of the 2 ethyl oxirane radical CCj-Y(COC) have been determined. The dissociation of the CCj-Y(COC) molecule into the Cj=CC and CH2O species are most favored in this system, where 91.8% of the ethyl oxirane radical concentration is formed during beta-scission. The other two paths that are favorable are the formation of CCj-Y(COC) and CC=COCj, at 6.7% and 1.5% product formation under these conditions.

5.6 Conclusion

The thermochemical properties, including standard enthalpies for stable, radical and transition state structure of ethyl oxirane species, with β scission ring opening and oxidation systems, were determined using ab-initio composite calculations. Several Density Function methods were compared. Ring opening data was compared with previous studies completed by Wang *et al*.[147] and Joshi *et al*.[148]. Data was also compared with literature when available, and bond dissociation energies were compared to values reported by Goldsmith *et al.*[105] and Auzmendi-Murua *et al.*[24]. Results of this study show that the main products in the dissociation of the secondary ethyl oxirane radical are CCj-Y(COC) is Cj=CC and CH_2O under typical peroxy chemistry conditions.

CHAPTER 6
OXIDATION OF THE ETHYL OXIRANE SECONDARY RADICAL: THERMOCHEMISTRY AND KINETICS

6.1 Overview

Substituted cyclic ethers are formed in chemistry of the atmosphere and in combustion oxidation reactions of alkanes. This study is directed towards the reactions of the secondary ethyl radical on ethyl oxirane, with moleculear oxygen $^3O_2$, along with the subsequent isomerization and dissociations for the oxidation of the initially formed peroxy radical complex. Formation steps and unimolecular reactions of the ethyl oxiranyl radical are discussed in the chapter 5. The thermochemical properties, oxidation reaction byproducts and the kinetics of the secondary alkyl radical on ethyl oxirane reacting with molecular oxygen which forms a chemically energized peroxy radical, are evaluated under atmospheric and combustion conditions. The chemical activation comes from the bond energy of the newly formed peroxy radical. Previous research has focused more on reactions of hydrocarbon peroxy radicals and there are few studies on oxiranes and other alkyl species bonded to cyclic ethers. This study describes important reaction paths that occur with the S-ethyloxirane radical reaction with molecular oxygen. Study these peroxy radical reactions on carbon atoms near cyclic ethers is relevant to chemistry in combustion systems[10], auto ignition and atmospheric reactions. The study of ethyl oxirane oxidation should also be relevant to understanding reactions and combustion of bio-fuels which also include a number of cyclic ethers such as furans. There is continued interest in research to understand biofuel oxidation pathways for their applications in varied combustion systems.[14,105]

There are a number of experimental and theoretical studies on the early stages of combustion[31-34], but data on the oxidation and reactions of cyclic ethers under ambient and combustion conditions is limited. Of these studies, Baldwin et al. [35] have shown product formation and kinetics in one of the earliest studies on these reactions. They observed the formation of the three member ring cyclic ether, oxirane as a product of ethyl radicals with oxygen. Dagaut et al. [32, 33] and Yakyaoui et al.[34] have also reported results showing the formation of cyclic ethers in significant concentrations from the oxidation of hydrocarbons from low to moderate temperatures for combustion chemistry. More recent studies using computational chemistry on the formation paths of the three-to five-membered cyclic ethers have been reported by Wijaya et al.[36] and Zadar et al[22].

This study starts with the secondary ethyl radical, a hydrocarbon like radical on ethyl oxirane, reacting with molecular oxygen $^3O_2$ to form a peroxy radical. Hydrogen atom transfer reactions can then occur from the carbons on the ethyl-oxirane forming new alkyl radicals that can further react.

Reactions of conventional hydrocarbon radicals reacting with oxygen have received significant study over the past several decades, due to the need for understanding ignition and combustion chemistry used in modeling for optimization by controlling piston design and fuel inlet speeds[14, 22]. Bio-fuel structures are not limited to alcohols and fatty acid esters, they also include ethers such as substituted furans[14, 23].

The standard enthalpies of formation were calculated for 2-(1-hydroperoxyethyl) oxirane, radicals and intermediates using computational chemistry isodesmic work reactions similar to that in the earlier chapters. Computational chemistry is also utilized to determine the reaction kinetic parameters of the peroxy radical association with O_2 and the intramolecular hydrogen atom transfer and beta scission reactions.

Six computational chemistry methods have been employed, they include the composte methods CBS-APNO, CBS-4M, CBS-QB3 and the density functional methods M062X/6-31G+(d,p), ωB97X/6-31G+(d,p) and B3-LYP/6-31G+(d,p). The ideal gas thermodynamic properties will be determined utilizing frequencies, moments of inertia and molecular geometries. Study will provide data including bond dissociation energies, dominate species and kinetics for reactions which take place.

6.2 Nomenclature

Table 6.1 Nomenclature of the Reactants, Intermediates and Products for Oxirane Peroxy System

Nomenclature	Species	Formula
CC•-Y(COC)	CH3CH-Y[CHOCH2]	C_4H_7O
CCQ-Y(COC)	CH3CH(OOH)-Y[CHOCH2]	$C_4H_8O_3$
CCQ•-Y(COC)	CH3CH(OO)-Y[CHOCH2]	$C_4H_7O_3$
CCQ-Y(COC•)	CH3CH(OOH)-Y[CHOCH]	$C_4H_7O_3$
CCQ-Y(C•OC)	CH3CH(OOH)-Y[CHOCH2]	$C_4H_7O_3$
CC•Q-Y(COC)	CH3C(OOH)-Y[CHOCH2]	$C_4H_7O_3$
C•CQ-Y(COC)	CH2CH(OOH)-Y[CHOCH2]	$C_4H_7O_3$
CCQC(=O)C•	CH3CH(OOH)C(=O)CH2	$C_4H_7O_3$
CC(=O)C(=O)C	CH3CH(=O)CH(=O)CH3	$C_4H_8O_2$
CC•QC(=O)C	CH3C(OOH)C(=O)CH3	$C_4H_7O_3$
CCQC=CO•	CH3CH(OOH)CH=CHO	$C_4H_7O_3$
CC=CC=O	CH3CHCHCH(=O)	C_4H_6O
CC(Q)C•C(=O)	CH3CH(OOH)CHCH(=O)	$C_4H_7O_3$
C-Y(COC)C(=O)	CH3-Y(CHOCH)CH(=O)	$C_4H_6O_2$
C-Y(COC)C•(=O)	CH3-Y(CHOCH)C(=O)	$C_4H_5O_2$
C=COC=C=O	C2=CHOCH=C(=O)	$C_4H_4O_2$
TCY2-[COOH-Y(CCO)]	CH3-Y6[CHOOH-Y(CHOCH)]	$C_4H_7O_3$
CCQC•C=O	CH3CH(OOH)CHCH(=O)	$C_4H_7O_3$

Table 6.1 Nomenclature of the Reactants, Intermediates and Products for Oxirane Peroxy System (Continued)

Nomenclature	Species	Formula
TY2-[(COOHC)-Y(COC)]	Y5(CH2CHOOH)-Y(CHOCH2)	$C_4H_7O_3$
TCY2-[(COOH)-Y(COC)]	CH3-Y5[CH-Y(COCH2)HOO]	$C_4H_7O_3$
TCY2-[(CQ)-C(O)CH]	CH3-Y4[C(OOH)C(=O)CH2H]	$C_4H_7O_3$
TS10	CH3CH(OOH)—C(=O)CH2	$C_4H_7O_3$
TS12	CH3CH(---OOH)CHCH(=O)	$C_4H_7O_3$
TS13	CH3CH(O---OH)CHCH(=O)	$C_4H_7O_3$
VTST9	CH3-Y(CHOCH)---C(=O)	$C_4H_5O_2$
VTST10	CH3-Y(CH---CHO)C(=O)	$C_4H_5O_2$
VTST11	CH3-Y(COC)C---HC(=O)	$C_4H_5O_2$
VTST12	CH3-CHO---CHC(=O)	$C_4H_5O_2$
TS7	CH3CH(OOH)-Y(CH---OCH)	$C_4H_7O_3$
TS9	CH3CH(OOH)-Y(CO---CH2)	$C_4H_7O_3$
TS11	CH3CH(OOH)-Y(C---OCH2)	$C_4H_7O_3$
TS8	CH3CH(---OOH)-Y(COCH2)	$C_4H_7O_3$
C=C=O	CH2=C(=O)	C_2H_2O
CC=O	CH3CH(=O)	C_2H_4O
OH	OH	HO
HO2	HOO	HO_2
H	H	H
CC=C•	CH3CH=CH	C_3H_5
C=O	CH2(=O)	CH_2O
C-Y(COC•)	CH3-Y(CHOCH)	C_3H_5O
C#C	CH#CH	C_2H_2
C•=C=O	CH=C(=O)	C_2HO

6.3 Computational Methods

All calculations were performed using the Gaussian 09 program suite[67]. Lowest energy molecule structures were identified using the B3-LYP methodology with the 6-31G++(d,p) basis set. The B3-LYP method combines the three-parameter Becke exchange functional (B3), with the Lee-Yang-Parr correlation functional (LYP)[123] in order to scan each rotor dihedral angle from zero to 360 degrees in 10-degrees increments. As the scan is performed, energy is calculated at each step, while the rest of the molecule remains optimized. After scanning all of the respected dihedral angles where a rotor is located, the total energy corresponding to the most stable conformation were used as a reference in plots of the potential barriers.

To obtain accurate energy calculations (ΔH°_{f298}), isodesmic work reactions were employed for molecules within the study using composite methods CBS-APNO[124], CBS-4M[125] and CBS-QB3[137], and the M06-2X[130], ωB97X[131], B2P-LYP[123], DFT methods with a 6-31+(G(d,p) basis set.

CBS models are based on a series of calculations made on a defined molecular geometry, combined with a complete basis set of model chemistry corrections for basis set truncation errors. These methods show a good degree of accuracy in structure and energies that require convergence in basis set size and in the degree of correlation. CBS-APNO is a more expensive procedure than other CBS methods. (The acronym APNO stands for atomic pair natural orbital.) The APNO portion of this method allows for accurate extrapolations to the complete basis set limit. This is accomplished with (U)HF/6/311G(d,P) geometry optimization and frequency calculations to obtain enthalpic and free energy corrections. This step is followed by a second geometry optimization at the QCISD(T), MP2(full), HF and MP2 levels, each with different basis sets.

CBS-QB3 is a five-step methodology that employs geometry optimization utilizing the B3-LYP level calculations, frequency calculations to obtain thermal corrections, zero-point vibrational energy, and entropic information. The next steps of the computations are single point calculations at the CCSD(T), MP4SQ and MP2 levels. When all the steps are completed, CBS extrapolation then computes the final energies[41].

CBS-4M method is a complete basis-set method that is parameterized to the original CBS-4 method, where M referrs to the use of minimal population localization. This method also includes empirical corrections[124].

M062x is a hybrid meta exchange-correlation functional that is a high nonlocality functional with double the amount of nonlocal exchange[61].

ωB97X is a long range corrected functional created by Head-Gordon and coworkers, which includes empirical dispersion[63].

B2P-LYP[123] is a double hybrid density functional that expands the DFT exchange correlation energies by a combination of mixing Gradient-Corrected (GCA) functional and exact exchange. The sum of these terms derived from GCA functions and correlation energies is calculated with second order perturbation theory.

Data from the methods mentioned above allowed for the determination of entropy and heat capacity values as a function of the following parameters: optimized structure, moments of inertia, vibrational frequencies, internal rotor potentials, molecular symmetry, electron degeneracy, number of optical isomers and the mass of each molecule with respect to temperature. This calculation used a standard formulas from statistical mechanics for the contributions of translational, vibrational, and external rotation (TVR) using the SMCPS (Statistical Mechanics−Heat Capacity, and Entropy) program[87]. SMCPS utilizes the rigid-rotor harmonic oscillator approximation from the vibrational frequencies of individual chemical species with moments of inertia from the optimized structure at the B3-LYP/6- 31G(d,p) level.

Several transition-state structures do not follow the same calculation procedures as other species. This occurs because the transition state structure does not exhibit a maxima (saddle point). in the reaction path Variational transition state theory (VTST) is implemented when there is no saddle point. This method is for determination of rate constants for barrier-less reactions. The variational transition state analysis is accomplished by running a scan along the cleaving bond of interest. The bond distance is increased (lengthened) by one Angstrom at each point and calculating the energy and optimized structure. Then from each optimized structure, the vibrational frequencies were calculated. Rate constants are calculated at each point from the reactant to a complete bond separation point (TST_i): $A+B \rightarrow TST_i$ (k_i). The distances that possess the minimum rate constant at each corresponding bond length are then reported with respect to the temperature(s) at which they were evaluated. The variational rate constant is then determined from the fit of these rate constants to the modified Arrhenius equation:

$$k = A\ T^n\ \exp(-Ea/RT)$$

Kinetic parameters for bimolecular chemical activation reactions, stabilization of chemically energized adducts, and unimolecular thermal dissociation reactions of the stabilized isomers were calculated using a mutli-frequency quantum Rice-Ramsperger-Kassel (qRRK) analysis for k(E). Steady state analysis was used for treatment of initial concentration on the chemically activated energized adducts.

Reaction kinetic parameters for the association reaction forming the chemically activated peroxy radical are reported for each of the stabilized product channels, as a function of pressure and temperature. Reaction kinetic parameters of stabilized intermediates are calculated to adducts and products that are adjacent to the stable intermediate. The current version of the qRRRK computer code utilizes a reduced set of three vibrational frequencies that accurately reproduce the heat capacity of each species to calculate the density of states.

Group Additivity, (GA) which is known as second order approximation method, developed by Benson[21], was utilized for comparison to our calculated values in order to provide added validation of the ΔH°_f 298, S°(T), and C (T) values. This method utilizes additivity of the central atom groups composing the molecule. GA is based on the knowledge of the contributions of representative groups in similar molecules and their properties in linear consistency in thermochemical properties. Thermodynamic properties of larger species, such as those in this study, were accurately approximated based on the sum of smaller representative groups, where there are corrections for rotors, symmetry, electron degeneracy, optical isomers, and gauche and other interactions. The group additivity, Density Functional Theory and composite method values are compared.

6.4 Results and Discussion

Isodesmic reactions were utilized in order to calculate the standard Enthalpies of formation $\Delta H^\circ_{f\ (298)}$ values listed in Table 6.2. 2-(1-hydroperoxyethyl) oxirane, plus the radicals, products and intermediates. These specie enthalpies were all calculated using the composite methods CBS-APNO, CBS-4M, CBS-QB3, and the DFT methods M062X/6-31G+(d,p), ωB97X/6-31G+(d,p), B2PLYP/6-31G+(d,p). Nomenclature for species identification and molecular formulas are listed in Table 6.2. Evaluating the thermochemical enthalpies of the reactants, intermediates and transition states using the different calculation methods and several different isodesmic reactions provides a reinforcement of accuracy and consistency of the data. The isodesmic reactions utilized have been averaged for each calculation method, and the averages of the six methods for each respected species are reported. The standard deviation (STD) is listed for each species. The smallest STD in a set of reactions is 0.1 and the largest is 3.8.

Table 6.2 Standard Enthalpies of Formation used as Reference Species in Isodesmic Reactions for Oxirane Peroxy System

Species	$\Delta H^{\circ}_{f\,298}$ (kcal mol^{-1})	Error Values	Reference
H	52.103	± 0.001	9
O_2	0.0	± 0.0	105
CC=C	4.6	±0.3	105
YCOC	-12.4	±0.6	105
YCOCJ	40.0	±0.6	105
CDCDO	-11.7	±0.1	105
C	-17.6	±0.3	105
C(=O)OH	-90.5	±0.1	105
C=C	12.5	±0.1	105
C=O	-26.2	±0.1	105
CC	-20.0	±0.1	105
CC=O	-39.6	±0.1	105
C=CCj=O	23.2	±0.9	105
CC=C=O	-15.1	±0.9	105
C(=O)Oj	-30.2	±0.9	105
C=CC=O	-15.5	±0.9	105
C=CCC	0.0	±0.1	105
C=CCOH	-30.1	±0.9	105
C=CCOj	23.7	±0.9	105
C=CQ	-9.2	±0.9	105
C2CC	-32.0	±0.4	105
CC(OH)C	-65.4	±0.3	105
CC=CC (trans)	-2.7	±0.2	105
CC=CC (cis)	-1.5	± 0.2	105
CCC(=O)	-45.0	±0.9	105
Cj=O	10.2	±0.9	105
Y(CCC)	13.0	±0.4	105
Y(CjCC)	69.9	±0.9	105
CCCC	-30.0	±0.1	105
C3C	-32.0	±0.4	105
CCC(OH)C	-70.1	±0.35	140
CC(=O)Cj	-6.9	±0.9	105
C2-Y(COC)	-33.74	-	140
C3Cj	17.8	±0.9	105
CC(=O)C	-52	±0.9	105
CCC(=O)C	-57.02	±0.2	134
C=COH	-29.9	±0.6	105

[a] Species do not have uncertainty values available during the time of this study

Table 6.2 Standard Enthalpies of Formation used as Reference Species in Isodesmic Reactions for Oxirane Peroxy System (continued)

Species	$\Delta H°_{f\ 298}$ (kcal mol^{-1})	Error Values	Reference
C=CCQ	-11.9	±0.9	105
CjC=O	4.4	±0.9	105
CCCj=O	-6.9	±0.9	105
CC(Q)=O	-78.2	±0.4	149
CCQj	-6.7	-	142
C=COCC	-33.5	±0.24	150
CCQ	-39.48	-	142
CCj(OH)C	-22.9	±0.9	105
CCCQ	-44.0	-	142
CCCCOH	-65.65	±0.07	106
CCJCC	16.6	±0.9	105
CCJCOH	-13	±0.4	105
CCCC=O	-50.61	±0.22	151
CQ	-31.8	-	142
CQj	2	-	142
CCJCCOH	-18.73		143
CY(COC)	-22.3	±0.9	105
C-Y(COC)-C	-32.76	-	105
CQ(OH)	-75.3	±0.2	105
CQj(OH)	-39.5	±0.2	105
CJCCC	19.3	±0.9	105
CJCCOH	-11.5	±0.9	105
CjCC=O	6.6	±0.9	105
CCJC(OH)C	-22.58	±0.9	105
Cj-Y(COC)-C-C	13.59	-	140
Cj2-Y(COC)	13.35	-	140
C2-Y(COCj)	18.39	-	140
C-Y(CjOC)-C	17.76	-	140
C=COC=C	-3.03	±0.2	150
CCC=OH	-42.23	-	152
CCOH	-56.4	±0.4	105
C=CCQ	-11.9	±0.4	105
CCC(=O)	-45.0	±0.9	105
CCOj	-39.6	±0.4	105
C=C=C	45.1	±0.5	105
C=C=C(=O)	31.2	±0.9	105
CCCOH	-56.4	±0.4	105

[a] Species do not have uncertainty values available during the time of this study

The work reactions in table 6.3 are from both the composite, and the DFT methods, which use the 6-31G++(d,p) basis set. Each species is analyzed using three to five isodesmic reactions, where the reference species react and yield a molecule with the number of each bond type conserved in products and reactants. This leads to the cancellation of systemic errors in the molecular orbital calculations[145] and improved accuracy. Work reactions that are not present in table 6.3 are located in Appendix E.

Optimized geometries, symmetry values, moments of inertia, vibrational frequencies and internal rotor potentials for each species from B3-LYP/6-31G+(d,p) level of theory are present in Appendix E.

Table 6.3 Isodesmic Reactions of Species in Oxirane Peroxy Study

							CBS-APNO	CBS-4M	CBS-QB3	m062x	wb97x	B2-LYP
CCj-Y(COC)	+	CCCOH	=	CC-Y(COC)	+	CCjCOH	19.4	18.4	17.9	18.6	18.4	18.1
CCj-Y(COC)	+	CCCC	=	CC-Y(COC)	+	CCjCC	18.9	17.8	17.1	17.7	17.7	17.3
CCj-Y(COC)	+	CCCQ	=	CC-Y(COC)	+	CCjCQ	20.0	19.1	18.6	20.2	19.0	18.9
CCj-Y(COC)	+	CCCCOH	=	CC-Y(COC)	+	CCjCCOH	19.5	18.0	17.5	18.3	18.2	17.9
CCj-Y(COC)	+	CCC(OH)C	=	CC-Y(COC)	+	CCjC(OH)C	19.1	18.0	17.5	18.3	18.0	17.8
						average	19.4	18.2	17.7	18.6	18.3	18.0
						st. dev.	0.4	0.5	0.6	0.9	0.5	0.6
CDC-Y(COC)	+	CC	=	C=CCC	+	Y(COC)	2.6	2.0	1.7	2.7	2.6	2.1
CDC-Y(COC)	+	C2CC	=	C=CCC	+	C2-Y(COC)	2.1	1.3	1.6	1.5	2.0	1.8
CDC-Y(COC)	+	CCCC	=	C=CCC	+	C-Y(COC)-C	2.5	1.9	2.3	1.9	2.6	2.4
						average	2.4	1.7	1.9	2.0	2.4	2.1
						st. dev.	0.3	0.4	0.4	0.6	0.4	0.3
CCQ-Y(COC)	+	CC	=	CC-Y(COC)	+	CCQ	-49.1	-51.1	-49.5	-50.2	-49.8	-49.7
CCQ-Y(COC)	+	C	=	CC-Y(COC)	+	CQ	-48.6	-50.9	-49.0	-50.0	-49.6	-49.4
CCQ-Y(COC)	+	CC=C	=	CC-Y(COC)	+	C=CCQ	-47.7	-49.7	-47.7	-48.5	-48.2	-48.2
CCQ-Y(COC)	+	CC=CC (c)	=	CC-Y(COC)	+	CC=CCQ	-42.6	-44.9	-42.9	-43.8	-43.6	-43.3
CCQ-Y(COC)	+	CC=CC (t)	=	CC-Y(COC)	+	CC=CCQ	-44.44	-46.6	-44.3	-45.1	-44.8	-44.7
						average	-46.5	-48.7	-46.7	-47.5	-47.2	-47.1
						st. dev.	2.8	2.8	2.9	2.9	2.9	2.9
CCQj-Y(COC)	+	CCQ	=	CCQ-Y(COC)	+	CCQj	-14.1	-13.9	-13.8	-13.6	-13.5	-13.6
CCQj-Y(COC)	+	CQ	=	CCQ-Y(COC)	+	CQj	-13.3	-13.2	-13.5	-13.3	-13.3	-13.4
CCQj-Y(COC)	+	CQ(OH)	=	CCQ-Y(COC)	+	CQj(OH)	-13.1	-11.6*	-13.2	-13.0	-13.2	-13.0
						average	-13.5	-13.5	-13.5	-13.3	-13.3	-13.3
						st. dev.	0.5	0.5	0.3	0.3	0.2	0.3

Table 6.3 Isodesmic Reactions of Species in Oxirane Peroxy Study (Continued)

							CBS-APNO	CBS-4M	CBS-QB3	m062x	wb97x	B2-LYP
CjCQ-Y(COC)	+	CCCOH	=	CCQ-Y(COC)	+	CjCCOH	4.3	4.4	4.9	5.7	4.7	4.6
CjCQ-Y(COC)	+	CCCC	=	CCQ-Y(COC)	+	CjCCC	3.6	3.8	3.8	4.0	3.6	3.6
CjCQ-Y(COC)	+	C-Y(COC)-C	=	CCQ-Y(COC)	+	cj-y(coc)-c	1.4	2.7	3.2	3.1	2.2	2.6
CjCQ-Y(COC)	+	C2-Y(COC)	=	CCQ-Y(COC)	+	cj2-Y(COC)	1.8	2.5	3.2	2.9	2.2	2.6
						average	2.8	3.3	3.8	3.9	3.2	3.4
						st. dev.	1.4	0.9	0.8	1.3	1.2	1.0
CCQ-Y(CjOC)	+	Y(COC)	=	CCQ-Y(COC)	+	Y(COCj)	3.3	1.3	1.7	2.7	2.8	3.0
CCQ-Y(CjOC)	+	Y(CCC)	=	CCQ-Y(COC)	+	Y(CjCC)	5.5*	3.8	1.2	3.3	2.6	2.6
CCQ-Y(CjOC)	+	CY(COC)c	=	CCQ-Y(COC)	+	c-y(cjoc)-c	3.5	1.4	2.26	2.9	2.9	3.4
CCQ-Y(CjOC)	+	C3C	=	CCQ-Y(COC)	+	C3Cj	5.6*	3.9	2.6	3.2	3.3	3.4
CCQ-Y(CjOC)	+	CC(OH)C	=	CCQ-Y(COC)	+	CCj(OH)C	4.2	4.6	2.8	3.4	3.4	3.3
						average	3.6	2.8	2.1	3.1	3.0	3.1
						st. dev.	0.5	1.3	0.7	0.3	0.4	0.4
CCQ-Y(COCj)	+	Y(COC)	=	CCQ-Y(COC)	+	Y(COCj)	5.5	5.5	5.7	5.8	5.8	5.7
CCQ-Y(COCj)	+	C2-Y(COC)	=	CCQ-Y(COC)	+	C2-Y(COCj)	5.6	5.7	6.1	6.1	6.0	6.1
CCQ-Y(COCj)	+	CY(COC)c	=	CCQ-Y(COC)	+	c-y(cjoc)-c	5.7	5.7	6.3	6.0	5.9	6.1
CCQ-Y(COCj)	+	CY(COC)	=	CCQ-Y(COC)	+	CY(COCj)	5.2	5.3	5.6	5.6	5.7	5.6
						average	5.5	5.5	5.6	5.8	5.9	5.9
						st. dev.	0.2	0.2	0.3	0.2	0.2	0.3
CCQCCDO	+	C	=	CC=O	+	CCCQ	-70.5	-75.0	-72.1	-73.4	-72.1	-71.1
CCQCCDO	+	CC	=	CCCC=O	+	CCQ	-72.3	-75.6	-73.8	-74.0	-73.6	-73.0
CCQCCDO	+	CC=C	=	CCCC=O	+	C=CCQ	-71.0	-74.1	-72.0	-72.3	-71.9	-71.4
						average	-71.3	-74.9	-72.7	-73.2	-72.5	-71.8
						st. dev.	0.9	0.7	1.0	0.9	0.9	1.0

Table 6.3 Isodesmic Reactions of Species in Oxirane Peroxy Study (continued)

							CBS-APNO	**CBS-4M**	**CBS-QB3**	**m062x**	**wb97x**	**B2-LYP**
CCQCjCDO	+	CCC=O	=	CCQCCDO	+	CCjC=O	-30.6	-30.5	-32.0	-31.3	-31.4	-31.7
CCQCjCDO	+	CC=O	=	CCQCCDO	+	CjC=O	-31.0	-37.4*	-28.0	-27.6	-27.2	-26.1
CCQCjCDO	+	CCCC	=	CCQCCDO	+	CCjCC	-33.2	-40.1*	-34.3	-34.0	-33.2	-32.7
						average	-31.6	-	-31.4	-31.0	-30.6	-30.2
						st. dev.	1.4	-	3.2	3.2	3.1	3.6
CCQCDOC	+	CC	=	CCC(=O)C	+	CCQ	-77.2	-79.4	-77.2	-78.2	-77.6	-77.6
CCQCDOC	+	C	=	CCQ	+	CCC(=O)	-76.0	-79.7	-77.0	-79.0	-78.2	-77.8
						average	-76.6	-79.6	-77.1	-78.6	-77.9	-77.7
						st. dev.	0.8	0.2	0.1	0.6	0.4	0.2
CCQCDOCj	+	CC=O	=	CCQCDOC	+	CjC=O	-34.3	-40.1*	-27.9	-28.4	-28.1	-27.0
CCQCDOCj	+	CCC(=O)	=	CCQCDOC	+	CjCC=O	-33.9	-39.3*	-33.2	-33.0	-32.8	-32.2
CCQCDOCj	+	CC(=O)C	=	CCQCDOC	+	CC(=O)Cj	-33.2	-33.0	-34.1	-34.2	-33.5	-34.0
						average	-33.8	-	-31.7	-31.9	-31.4	-31.1
						st. dev.	0.6	-	3.3	3.1	2.9	3.6
CC(=O)C(=O)C	+	CC	=	CCC(=O)C	+	CC=O	-78.7	-82.5	-79.1	-78.2	-78.1	-78.2
CC(=O)C(=O)C	+	C	=	CCC(=O)C	+	C=O	-78.4	-82.3	-79.8	-78.6	-78.8	-78.6
CC(=O)C(=O)C	+	CCQ	=	CCC(=O)C	+	CC(Q)=O	-75.4	-80.0	-73.0	-73.2	-72.9	-74.0
						average	-77.5	-81.6	-77.3	-76.7	-76.6	-76.9
						st. dev.	1.8	1.4	3.8	3.0	3.2	2.5
CCQC=C=O	+	C	=	CCQ	+	CC=C=O	-42.3	-44.0	-43.8	-44.7	-44.1	-44.3
CCQC=C=O	+	C	=	CCCQ	+	C=C=O	-39.7	-41.4	-41.7	-42.6	-41.4	-42.0
						average	-41.0	-42.7	-42.7	-43.6	-42.7	-43.2
						st. dev.	1.8	1.8	1.5	1.5	1.9	1.7

Table 6.3 Isodesmic Reactions of Species in Oxirane Peroxy Study (continued)

							CBS-APNO	**CBS-4M**	**CBS-QB3**	**m062x**	**wb97x**	**B2-LYP**
CC=CC=O	+	C	=	CC=C	+	CC=O	-24.2	-25.5	-25.8	-25.0	-24.9	-25.9
CC=CC=O	+	C	=	CC=CC (c)	+	C=O	-25.5	-26.7	-26.9	-25.4	-25.7	-26.7
CC=CC=O	+	C	=	CC=CC (t)	+	C=O	-25.0	-26.2	-26.7	-25.4	-25.7	-26.4
CC=CC=O	+	C	=	CCC=C	+	C=O	-24.9	-25.7	-27.4	-25.7	-26.0	-26.7
CC=CC=O	+	CC	=	CC=C	+	CCC(=O)	-25.0	-24.7	-26.4	-25.2	-25.3	-26.5
						average	-24.9	-25.8	-26.6	-25.3	-25.5	-26.4
						st. dev.	0.5	0.7	0.6	0.2	0.4	0.3
C=COC=C=O	+	CC	=	C=COCC	+	C=C=O	268.8*	-11.9	-12.5	-11.0	-11.5	-11.8
C=COC=C=O	+	C=C	=	C=COC=C	+	C=C=O	-267.9*	-13.2	-10.8	-11.2	-11.3	-11.6
C=COC=C=O	+	C	=	C=COC=C	+	C=O	-10.9	-17.5*	-15.2	-12.6	-12.6	-12.0
						average	-	-12.6	-12.8	-11.6	-11.8	-11.8
						st. dev.	-	0.9	2.2	0.9	0.7	0.2
C-Y(COC)C=O	+	C	=	CY(COC)	+	CC=O	-48.7	-50.4	-49.7	-49.4	-49.0	-49.5
C-Y(COC)C=O	+	CC	=	CY(COC)	+	CCC(=O)	-49.5	-49.6	-50.2	-49.5	-49.4	-50.2
C-Y(COC)C=O	+	CC	=	CCCC=O	+	Y(COC)	-50.5	-50.5	-51.7	-50.5	-50.5	-51.5
						average	-49.6	-50.2	-50.5	-49.8	-49.7	-50.4
						st. dev.	0.9	0.5	1.0	0.6	0.8	1.0
C-Y(COC)-Cj=O	+	C=O	=	C-Y(COC)C=O	+	Cj=O	-10.8	-10.6	-11.0	-10.9	-11.0	-10.9
C-Y(COC)-Cj=O	+	CCC(=O)	=	C-Y(COC)C=O	+	CCCj=O	-10.0	-9.5	-10.7	-10.4	-10.1	-10.1
C-Y(COC)-Cj=O	+	C=CC=O	=	C-Y(COC)C=O	+	C=CCj=O	-9.7	-8.9	-10.9	-10.9	-10.7	-10.7
						average	-10.2	-9.6	-10.9	-10.7	-10.6	-10.6
						st. dev.	0.6	0.9	0.1	0.3	0.4	0.4

Table 6.3 Isodesmic Reactions of Species in Oxirane Peroxy Study (continued)

							CBS-APNO	CBS-4M	CBS-QB3	m062x	wb97x	B2-LYP
CCQC=COH	+	CC	=	CCC=COH	+	CCQ	-65.3	-70.1	-67.8	-67.8	-67.5	-67.6
CCQC=COH	+	C	=	CCC=COH	+	CQ	-64.8	-69.9	-67.3	-67.7	-67.3	-67.2
CCQC=COH	+	C=C	=	CCC=COH	+	C=CQ	-65.7	-69.7	-65.0	-66.0	-65.6	-66.4
CCQC=COH	+	CC=C	=	CCC=COH	+	C=CCQ	-63.9	-68.7	-66.0	-66.1	-65.9	-66.0
						average	-64.9	-69.6	-66.6	-66.9	-66.5	-66.8
						st. dev.	0.8	0.6	1.3	1.0	1.0	0.7
CCQC=COj	+	C(=O)OH	=	CCQC=COH	+	C(=O)Oj	-32.3	-27.7	-33.8	-37.1	-37.6	-36.6
CCQC=COj	+	C=COH	=	CCQC=COH	+	C=COj	-31.1	-29.8	-33.9	-33.6	-33.2	-32.3
CCQC=COj	+	C=CCOH	=	CCQC=COH	+	C=CCOj	-28.9	-22.7*	-33.1	-33.1	-33.6	-32.5
CCQC=COj	+	CCOH	=	CCQC=COH	+	CCOj	-28.3	-21.0	-31.3	-32.4	-33.1	-31.7
						average	-30.1	-28.7	-33.0	-34.1	-34.4	-33.3
						st. dev.	1.9	1.5	1.2	2.1	2.1	2.2
CCOC=C=O	+	C=C	=	C=COCC	+	C=C=O	-45.1	-45.0	-44.5	-43.6	-44.1	-45.0
CCOC=C=O	+	C=C=C	=	C=COCC	+	c=c=c=o	-48.7	-46.1	-44.6	-46.8	-47.1	-44.4
						average	-46.9	-45.6	-44.5	-45.2	-45.6	-44.7
						st. dev.	2.6	0.8	0.1	2.3	2.1	0.4
ccjoc=c=o	+	CCCOH	=	CCOC=C=O	+	CCjCOH	1.1	0.8	-0.8	-0.4	-0.6	-0.3
ccjoc=c=o	+	CCCC	=	CCOC=C=O	+	CCjCC	0.6	0.2	-1.6	-1.2	-1.3	-1.1
ccjoc=c=o	+	CCCCOH	=	CCOC=C=O	+	CCjCCOH	1.3	0.3	-1.2	-0.7	-0.8	-0.5
ccjoc=c=o	+	CCC(OH)C	=	CCOC=C=O	+	CCjC(OH)C	0.6	0.1	-1.4	-0.9	-1.2	-0.8
						average	0.9	0.4	-1.2	-0.8	-1.0	-0.7
						st. dev.	0.3	0.3	0.3	0.3	0.3	0.3

6.4.1 Heat of Formation $\Delta H^\circ_{f\,298}$

The standard enthalpy of formation values ($\Delta H^\circ_{f\,298}$) averaged over the different computational methods from the isodesmic reactions, are listed in Table 6.3 and summarized in Table 6.4. ThisTable lists the average enthalpy of formation ($\Delta H^\circ_{f\,298}$) for species from the different computational methods utilized and over the varied work reactions. Error limits are also listed in Table 6.4 from calculated standard deviation values over the calculated standard enthalpy of formation ($\Delta H^\circ f_{298}$) data. The uncertainty in the reference species is also considered in the error analysis. The standard deviation data over the reactions and methods show an average standard deviation of 1.06 kcal mole^{-1}. These standard deviations are comparable to the average standard deviations, on a per work reaction basis, determined in Table 6.3. Values in Table 6.4 are recommended.

Table 6.4 Summary of Average Heat of Formation $\Delta H^\circ_{f\,298}$ and Literature Values for Oxirane Peroxy System

	Heat of Formation (kcal/mol)	
Species	**Calculated Enthalpy of Formation (kcal mole^{-1})**	**Literature**
CCJ-Y(COC)	18.3 ± 0.8	This Study
C=C-Y(COC)	2.1 ± 0.4	This Study
CCQ-Y(COC)	-47.3 ± 2.7	This Study
CCQ•-Y(COC)	-13.4 ± 0.3	This Study
CCQ-Y(COC•)	5.8 ± 0.3	This Study
CCQ-Y(C•OC)	2.8 ± 0.9	This Study
CC•Q-Y(COC)	***	This Study
C•CQ-Y(COC)	3.4 ± 1.1	This Study
CCQC(=O)C•	-32.9 ± 3.5	This Study
CC(=O)C(=O)C	-77.8 ± 2.9	This Study
CC•QC(=O)C	***	This Study
CCQC=CO•	-32.1 ± 3.5	This Study
CCQC•C(=O)	-30.9 ± 2.5	This Study
CC=CC(=O)	-25.8 ± 0.8	This Study
C-Y(COC)C(=O)	-50.0 ± 0.8	This Study
C-Y(COC)C• (=O)	-10.4 ± 0.6	This Study
C=COC=C=O	-12.01 ± 1.1	This Study

6.4.2 Carbon-Hydrogen Bond Dissociation Energies

The secondary carbon located on the ethyl substituent of ethyl oxirane, labeled C_2 is the more favorable site for loss of a Hydrogen atom and radical formation, as described in chapter 5; it has the lowest bond energy. Oxygen, ($^3O_2$) which is present in the atmosphere in high concentrations and is a diradical will to undergo association, bonding, at the C_2 carbon site during the association step. This association reaction is exothermic by 34 kcal mol^{-1}. Figure 6.1, illustrates the stable species structure of 2-(1-hydroperoxyethyl) oxirane with all the possible bonding sites. Carbon—Hydrogen bond dissociation energies (BDEs) were evaluated at C_1, C_3, C_4 and O_1 bond sites to determine the R—H bond dissociations energy for each site. The BDEs were calculated using the following equation,

$$\Delta H_{reaction} = \Sigma\Delta H_{product} - \Sigma\Delta H_{reactants}$$

$\Delta H_{reaction}$ corresponds to the bond dissociation energy, $\Sigma\Delta H_{product}$ represents the enthalpy of formation of the radical species being observed and eh enthalpy of a hydrogen atom, which has a $\Delta H_f^{\circ}{}_{298}$ of 52.103 kcal mole^{-1}. $\Sigma\Delta H_{reactants}$ corresponds to the parent molecule CCQ-Y(COC) in this case. The 2-(1-hydroperoxyethyl) oxirane specie has five bonding sites, which hydrogen atoms could be abstracted as shown below in Figure 6.1. All BDE values calculated are located in Table 6.5, where they are also compared with literature values.

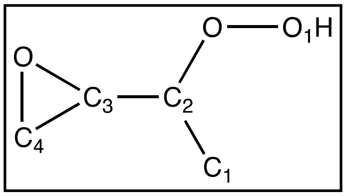

Figure 6.1: Possible radical site positions for 2-(1-Hydroperoxyethyl) oxirane

Table 6.5 Bond Dissociation Energy (BDE) of 2-(1-Hydroperoxyethyl) Oxirane

Reaction					Bond Dissociation Energies (kcal mol^{-1})	
CCQ-Y(COC)	=	CJCQ-Y(COC)	+	H		
-47.3		3.4		52.103	102.8 ± 1.1	101.3 [146]
CCQ-Y(COC)	=	CCQ-Y(CJOC)	+	H		
-47.3		2.8		52.103	102.2 ± 0.9	103.1 [24]
CCQ-Y(COC)	=	CCQ-Y(COCJ)	+	H		
-47.3		5.8		52.103	105.1 ± 0.3	104.8 [24]
CCQ-Y(COC)	=	CCQJ-Y(COC)	+	H		
-47.3		-13.4		52.103	86.0 ± 0.3	84.4 [105]

Hf in units kcal mol^{-1}

The newly formed radical at the C_2 carbon will rapidly react with an oxygen molecule, which is an initial step in oxidation, under both atmospheric and combustion conditions. Figure 3 illustrates the molecular structure of the stable species 2-(sec-Butyl) oxirane and possible carbon-hydrogen and oxygen-hydrogen bonding sites. BDE values are evaluated at the primary carbon-hydrogen site, C_1, the tertiary carbon-hydrogen sites C_3 and C_4, and the oxygen-hydrogen site labeled O_1. Carbon-hydrogen bonds at the C_1, C_3 and C_4 binding sites are reported to have BDE of 102.8, 102.2 and 105.1 kcal/mol, respectively. Primary carbon, C_1, has an observed BDE for the carbon-hydrogen bond that is in good agreement with the primary carbon-hydrogen bond calculated for ethyl oxirane as well as values reported by Hudzik et al[146]. Carbon-hydrogen bonds for carbons C_3 and C_4 agree with the literature values reported for the ethyl oxirane species in addition to studies performed by Auzmendi-Murua et al.[24]. The peroxide oxygen-hydrogen bonding site, labeled O_1, has been determined in this study to have a BDE of 86.0 kcal/mol. This value shows good agreement in comparison to species reported in the study performed by Goldsmith et al.[105]. Where similar species have calculated BDE values of 84.4 kcal/mol on average. In the 2-(sec-Butyl)oxirane species, a radical site cannot be formed at the carbon-hydrogen bond located at the C_2 carbon, due to the instability of the molecule. If a radical is formed at the C_2 site, the molecule will dissociate very rapidly, cleaving the oxygen-oxygen bond resulting in the formation of a carbonyl group (-C=O), which is a ketone for this non terminal carbon, plus the release of a hydroxyl radical. Hydrogen bond dissociation energies values calculated are located in Table 6.5 and data includes comparison to literature.

6.4.3 Internal Rotors

Potential energy curves for internal rotations in the ethyl oxirane radical and peroxide and perocy radical species are calculated using the B3-LYP/6-31G(d,p) level of theory and relaxed scans at 10 degree intervals are used to determine the lowest energy geometries. If a lower energy conformation is found, previous scans are re-run and re-evaluated to insure the lowest energy conformation is located. These potential energy curves are also used to determine thermochemical properties such as entropy, heat capacity and internal rotational contributions. These potential energy curves are presented in Appendix E.

6.4.4 Entropies (S(T)) and Heat Capacities (C_p(T))

Entropies and heat capacities were calculated utilizing the SMCPS computer code. SMCPS **(**Statistical Mechanics−Heat Capacity, and Entropy) applies the rigid-rotor harmonic oscillator (HO) approximation. The subtraction of R ln(σ) for the three fold symmetry of primary methyl groups is included when the symmetry is entered to the program input file. torsion frequencies. Table 6.6 presents the calculated entropies and heat capacities for parent, radical and intermediate species.

Table 6.6 Entropies and Heat Capacities for Parent, Radical and Intermediate Species Oxirane Peroxy System

Transition State	Hf	S	Cp300	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CCJ-Y(COC)	18.3	71.00	19.09	24.43	29.52	33.94	40.90	46.04	54.06
C=C-Y(COC)	2.1	67.01	16.55	22.05	27.43	32.28	40.47	47.11	58.66
CCQ•-Y(COC)	-13.4	79.47	25.14	31.72	37.75	42.87	50.75	56.42	65.11
CCQ-Y(COC•)	5.8	82.38	26.66	33.02	38.84	43.77	51.32	56.76	65.17
CCQ-Y(C•OC)	2.8	78.80	25.28	31.75	37.70	42.79	50.62	56.26	64.92
C•CQ-Y(COC)	3.4	81.79	27.09	33.47	39.26	44.16	51.61	56.96	65.23
CCQC(=O)C•	-32.9	81.05	27.69	34.05	39.69	44.44	51.75	57.04	65.28
CC(=O)C(=O)C	-77.8	76.40	22.26	27.19	31.81	36.01	43.29	49.35	60.01
CCQC•C(=O)	-30.9	78.70	25.97	32.52	38.41	43.41	51.09	56.63	65.15
CC=CC(=O)	-25.8	71.52	20.14	24.60	28.94	32.82	39.10	43.82	51.18
C-Y(COC)C(=O)	-50.0	74.85	22.13	27.43	32.48	36.91	43.89	48.99	56.77
C-Y(COC)C• (=O)	-10.4	72.61	19.84	24.69	29.19	33.08	39.17	43.59	50.31
C=COC=C=O	-10.0	75.78	21.32	25.98	29.99	33.32	38.40	42.06	47.66
TCY2-[COOH-Y(COC)]	33.94	77.03	24.63	31.75	38.21	43.65	51.87	57.61	66.08
TY2-[(COOHC)-Y(COC)]	39.33	79.44	24.74	31.85	38.33	43.77	51.94	57.63	66.04
TCY2-[(COOH)-Y(COC)]	40.57	79.62	25.42	32.08	38.27	43.57	51.69	57.44	65.97
TCY2-[(CQ)-C(O)CH]	31.18	87.13	29.71	35.72	41.14	45.77	52.95	58.13	66.07
TS7	22.69	80.51	25.95	32.32	38.21	43.24	50.98	56.53	65.07
TS8	24.95	86.33	29.63	36.05	41.65	46.29	53.33	58.4	66.24
TS9	21.94	81.03	28.77	35.67	41.52	46.29	53.42	58.51	66.32
TS10	-30.14	81.43	27.78	34.12	39.74	44.48	51.78	57.06	65.28
TS11	37.89	83.84	26.85	33.19	38.99	43.92	51.5	56.96	65.35
TS12	-7.03	87.43	29.01	34.93	40.32	44.92	52.07	57.28	65.42
TS13	36.04	84.34	29.86	36.72	42.47	47.13	54.1	59.08	66.72

Hf in units kcal mol^{-1}

6.4.5 Group Additivity

The group additivity (GA) method, as designed by Benson[91] is a rapid estimation method for the calculation of $\Delta H°$ *f 298*, *S° 298*, and *Cp(T)* of stable species. Group additivity is based on the knowledge of the representative groups contributions in similar molecules. Experimental data has shown that there is linear consistency observed in thermochemical properties such as heat capacity and enthalpy values determined by use of group additivity.

This study utilizes group additivity terms values to compare calculated enthalpies of formation for 2-(1-hydroperoxyethyl)oxirane and radicals to compare and validate accuracy with the calculated values. The group terms employed can be utilized to estimate enthalpy values to compare calculated enthalpy of formation values calculated from computational and experimental studies. Table 6.7 list the groups that are employed in group additivity methodology.

Table 6.7 Group contribution Terms Used in the Calculation of Species

Group	HF	S_{298}	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
C/C/H3[91]	-10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C2/H2[91]	-5.00	9.40	5.50	6.95	8.25	9.36	11.07	12.34	14.20
C/C2/H/O[91]	-7.20	-11.00	4.80	6.64	8.10	8.73	9.81	10.40	11.51
O/C2[91]	-23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.60	-
P[91]	101.10	2.61	-0.77	-1.36	-1.91	-2.40	-3.16	-3.74	-4.66
RJCOC[91]	102.32	1.23	0.48	-0.11	-0.76	-1.36	-2.36	-3.11	-4.21
T[91]	96.50	5.24	-0.78	-2.48	-3.55	-4.15	-4.75	-5.02	-5.39
S[91]	98.45	4.44	-1.50	-2.33	-3.10	-3.39	-3.75	-4.45	-5.20
C/CD/H3[91]	-10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
CD/C/H[91]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
C/CD/H2/O[91]	-6.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.40
O/C/J[91]	-37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
ALKOXY[91]	104.06	-1.46	-0.98	-1.30	-1.61	-1.89	-2.38	-2.80	-3.59
O/C/D[91]	-23.73	9.70	3.91	4.31	4.60	4.84	5.32	5.80	-
CD/H2[91]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19

Comparisons are completed using the sum of the group present in each species with the calculated enthalpy of formation are presented in Table 6.8.

Table 6.8 Comparison of heat of formations with methods and group additivety

	Heat of Formation (kcal/mol)								
Species	CBS-APNO	CBS-4M	CBS-QB3	M062X	Wb97X	B2-LYP	Hf$_{AVERAGE}$	Lit,	G.A.
CCj-Y(COC)	19.4	18.2	17.7	18.6	18.3	18.0	18.3	This Study	19.6
CDC-Y(COC)	2.4	1.7	1.9	2.0	2.4	2.1	2.1	This Study	0.8
CCQ-Y(COC)	-46.5	-48.7	-46.7	-47.5	-47.2	-47.1	-47.3	This Study	-50.9
CCQj-Y(COC)	-13.5	-13.5	-13.5	-13.3	-13.3	-13.3	-13.4	This Study	-16.7
CjCQ-Y(COC)	2.8	3.3	3.8	3.9	3.2	3.4	3.4	This Study	-1.9
CCQ-Y(CjOC)	3.6	2.8	2.1	3.1	3.0	3.1	2.8	This Study	-4.5
CCQ-Y(COCj)	5.5	5.5	5.6	5.8	5.9	5.9	5.8	This Study	-1.9
CCQCCDO	-71.3	-74.9	-72.7	-73.2	-72.5	-71.8	-72.7	This Study	-73.2
CCQCjCDO	-31.6	-30.5	-31.4	-31.0	-30.6	-30.2	-30.9	This Study	-26.9
CCQCDOC	-76.6	-79.6	-77.1	-78.6	-77.9	-77.7	-77.9	This Study	-79.5
CC(=O)C(=O)C	-77.5	-81.6	-77.3	-76.7	-76.6	-76.9	-77.8	This Study	-78.4
CCQC=C=O	-41.0	-42.7	-42.7	-43.6	-42.7	-43.2	-42.7	This Study	-47.6
CC=CC=O	-24.9	-25.8	-26.6	-25.3	-25.5	-26.4	-25.8	This Study	-28.2
C=COC=C=O	-10.9	-12.6	-12.8	-11.6	-11.8	-11.8	-12.0	This Study	-14.4
C-Y(COC)C=O	-49.6	-50.2	-50.5	-49.8	-49.7	-50.4	-50.0	This Study	-48.9
C-Y(COC)-Cj=O	-10.2	-9.6	-10.9	-10.7	-10.6	-10.6	-10.4	This Study	-6.0
CCQC=COH	-64.9	-69.6	-66.6	-66.9	-66.5	-66.8	-66.9	This Study	-66.6
CCQC=COj	-30.1	-28.7	-33.0	-34.1	-34.4	-33.3	-32.1	This Study	-32.5
CCOC=C=O	-46.9	-45.6	-44.5	-45.2	-45.6	-44.7	-45.4	This Study	-52.3
CCjOC=C=O	0.9	0.4	-1.2	-0.8	-1.0	-0.7	-0.4	This Study	-9.4
CCQCDOCj	-33.8	-33.0	-31.7	-31.9	-31.4	-31.1	-32.9	This Study	-30.5

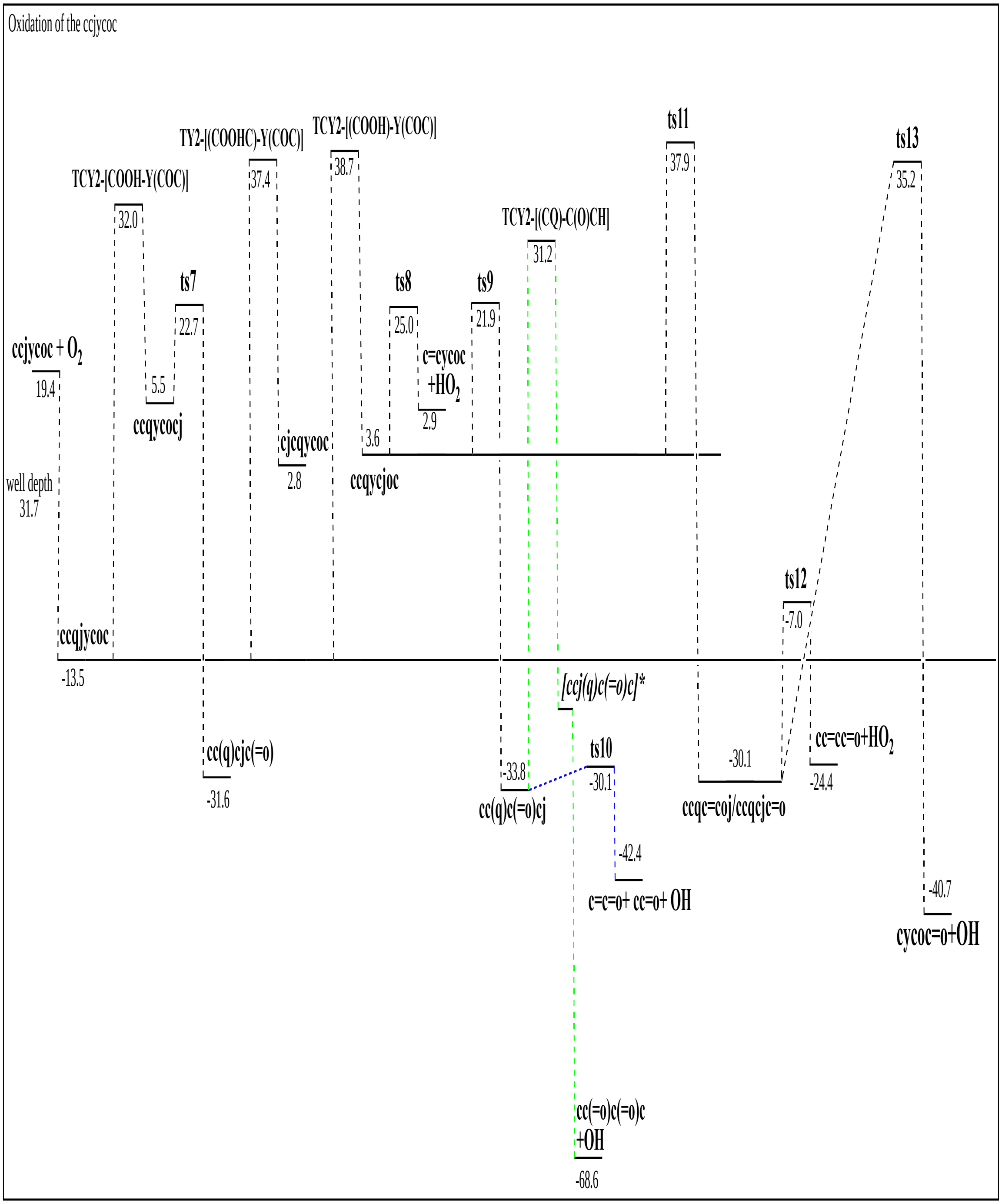

Figure 6.2 Potential energy diagram of CC•Y(COC)+ O_2 oxidation and further reactions of the peroxy adduct CC(OOJ)•Y(COC) = CC(Q)•Y(COC).

6.4.6 Reactions

The reactions that take place can be divided into different reaction classes:

- ROO Stabilization
- Intramolecular hydrogen transfer from the carbon sites to the peroxy radical site
- Intramolecular Ring opening
- Hydrogen atom elimination (beta scissions)
- Molecular elimination (beta scissions)
- HO_2 molecular elimination

This study describes important reaction paths that occur with the S-ethyloxirane radical reaction with molecular oxygen. The potential energy diagram is shown in Figure 6.2. The Thermochemical properties are presented in the above tables.

6.4.6.1 Oxidation of CCJ-Y(COC). The oxidation of CCj-Y(COC) occurs with O_2 association with secondary carbon forming a new bond to the carbon radical with 31.8 kcal mol-1 of new energy in the molecule resulting from the new bond formed.. The energetics of this reaction can be observed in figure 6.3. Literature reported by Zador et al.[1] reports well depths for the formation of alkyl peroxy radicals ($R+O_2$ reactions) to typically have bond energy values of 30-35 kcal mole^{-1} depending on the nature of the alkyl radical. This addition of oxygen is a barrier-less reaction and required accurate computational methodology referred to as the variational transition state theory to calculate the kinetic parameter of this association step. The potential energy scan in figure 5 was completed with the in B3-LYP method using 6-31G++(d,p) basis set. This potential energy scan is accomplished by analyzing the dissociation of CCQ•Y(COC) to form CC•-Y(COC) and an oxygen molecule.

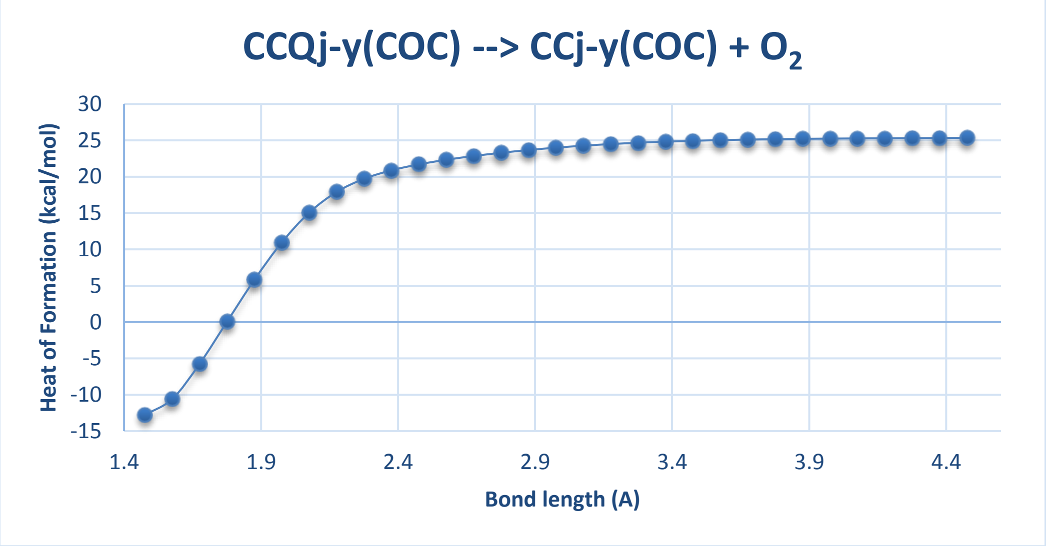

Figure 6.3 VTST of CCQ•Y(COC)→ CC•Y(COC) + O_2.

Similar to the reaction types described in the dissociation of the CCj-Y(COC) species, the same type of reactions will be employed for this system.

6.4.6.2 Intramolecular Hydrogen Atom Transfers in CCQJ-Y(COC). This peroxy radical can undergo hydrogen transfer reactions from each of the four carbon sites to the peroxy radical site – four intra-molecular transfer reactions.

The CCQj-Y(COC) molecule can undergo a number of intramolecular hydrogen atom transfer reactions. A hydrogen atom can transfer from the C_1 carbon to the peroxy oxygen radical site through a five-member ring transition state structure TY2-[(COOHC)-Y(COC)]. This reaction has an activation energy of 52.1 kcal/mol from the stabilized peroxy radical and the product is 16.8 kcal/mol higher in energy than the reactant; this is an endothermic reaction.

A hydrogen atom can transfer form a the C2 carbon to the peroxy oxygen radical forming a radical on the C2 carbon and a hydropeoxide on the C2 carbon, this radical is unstable, the C2 carbon radical immediately forms a π bond (80 kcal/mol bond formed) with the oxygen atom bonded to it, which results in cleavage of the RO—OH bond (45 kcal/mol), with no barrier to form CC(=O)-YCOC + OH.

A hydrogen atom can also transfer from the C_3 carbon to the peroxy oxygen, via a five-member ring transition state structure TCY2-[(COOH)-Y(COC)]. This reaction has an activation energy to the CY2-[(COOH)-Y(COC)] transition structure of 54.0 kcal $mole^{-1}$. This atom movement through TCY2-[(COOH)-Y(COC)] to form CCQ-Y(C•OC) which is 38.7 kcal mol-1 below the TST.

A Hydrogen atom transfer can occur from the C_4 carbon site via the six member ring TCY2-[COOH-Y(COC)] transition state structure, The C4 hydrogen atom bonds to the peroxy oxygen. This reaction had an activation energy of 46.8 kcal/mol and results in the formation of the chemical species CCQ-Y(COCj) (reminder Q = OOH). The formation of CCQ-Y(COCj) is an endothermic reaction with an enthalpy change of 19.2 kcal/mol.

6.4.6.3 Ring Opening Reactions of the three stable radical intermediates formed by the Intramolecular H Atom Transfer Reactions

CCQ-Y(COC•) C_4H_7O [Q equals -OOH]

The radical intermediates that are formed from the hydrogen transfers from the carbon atoms to the peroxy radical site can undergo further reactions. The CCQ-Y(COC•) radical can undergo two ring opening reactions; one cleaving the C3-Oxygen bond, and one cleaving the C—C bond in the ring. These are similar to the reactions described above in the reactions for CCj-Y(COC), where the C_3 and C4 carbon – oxygen bonds are cleaved.

In the opening of the C_3-O bond, this bond is stretched while the C_4-O bond shortens. The reaction proceeds through a saddle point transition state structure tst7. Figure 6.4 shows the reaction path described in this process.

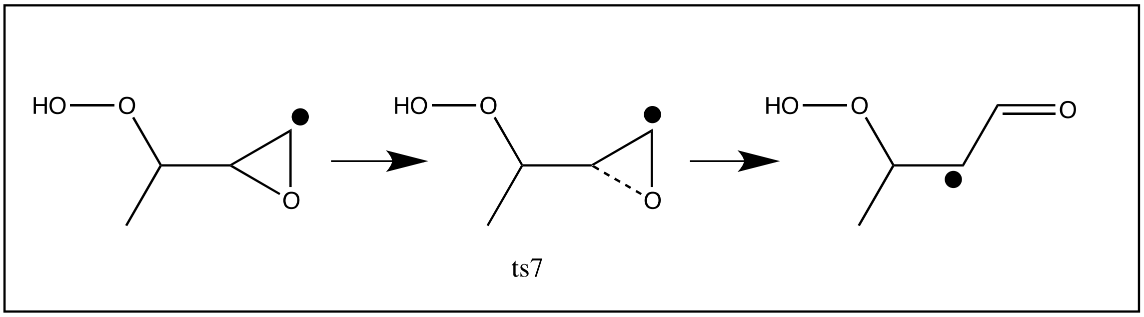

Figure 6.4 Ring opening reactions observed cleaving C_3-O bond of CCQ-Y(COC•).

It is noted that the addition of O_2 to the secondary radical forming a peroxy radical to the CC(OOj)-Y(COC) modifies the bond angle of the ring to be slightly larger than 89 degrees when analyzing the cleavage of the C_3-O bond. This value show reasonable agreement to the non-substituted oxirane study of Wang *et al.*[39], where the reaction was reported as exothermic, with a release of 36.9 kcal/mol. The calculated value in this study for a very slightly different (ethyl substituted oxiranyl radical) reaction has a value of 36.7 kcal/mol. The CCQ-Y(COC•) species can also undergo a ring opening reaction via cleavage forming CCQ-COC• as a product. This reaction was not thoroughly studied in this work but is outline in Figure 6.5. Here there is resonance between the oxygen and the terminal carbon atom, which has sp2 bonding.

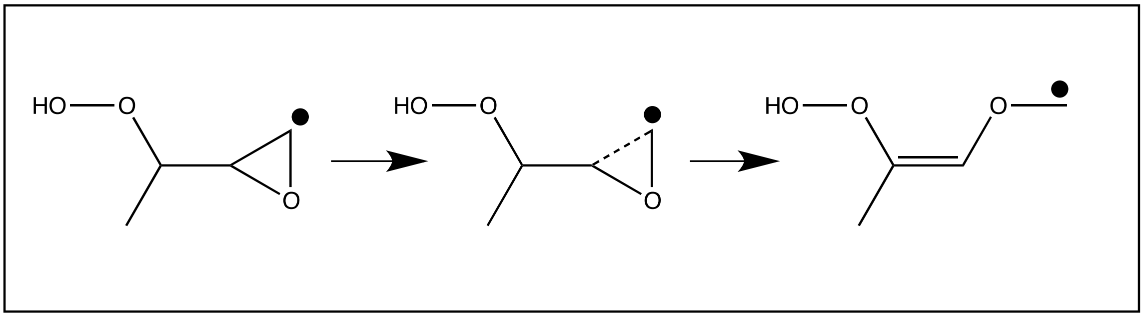

Figure 6.5 Ring opening reactions observed cleaving C_3-C_4 bond of CCQ-Y(COC•)

The final product that can be formed during ring opening reactions from the CCQ-Y(COC•) species is CCQC(=O)C•. This reaction occurs when the C_4-O bond is cleaved. This reaction was not studied in detail during this study but is shown in Figure 6.6.

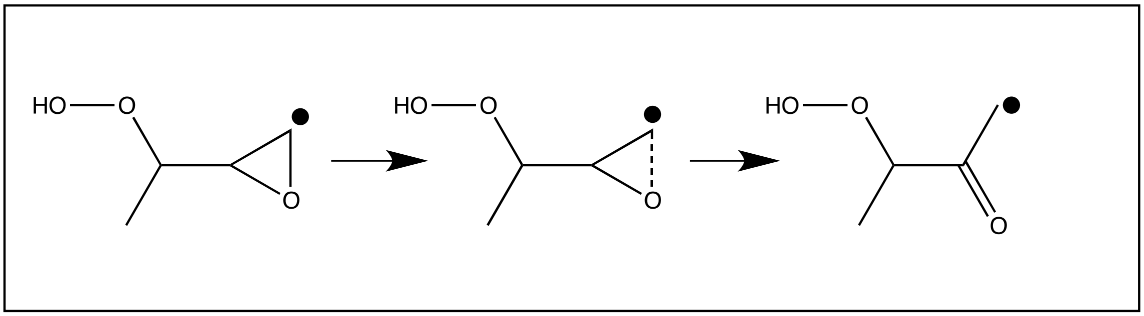

Figure 6.6 Ring opening reactions observed cleaving C_4-O bond of CCQ-Y(COC•)

6.4.6.4 CCQ-Y(C•OC) C_4H_7O Ring Opening Reactions. CCQ-Y(C•OC) can also undergo ring opening reactions similar to the reactions that occur in the CCQ-Y(COC•). The cleavage of the C—C bond in the ring results in a shorting of the C_3-O bond and the C_4-O bond is lengthened. This reaction forms a resonantly stabilized isomer CCQC(=O)C• = CCQC(-O•)=C This reaction has an activation energy of 18.7 kcal/mol and is exothermic, releasing 30.1 kcal/mol.. The resonance between the two structures above accounts for the lower activation energy relative to CCQ-Y(COCj).

CCQ-Y(C•OC) can undergo a ring opening reaction forming a C3-C4 double bond and cleaving the C3--O bond in the ring with formation of the CCQ-(CCO•) radical. This reaction is exothermic and releases 33.7 kcal mole^{-1} of energy with an energy barrier of 35.1 kcal/mol. It is noted that because the carbons are all sp3 in this structure there is no resonance in the CCQ-Y(CCO•) radical and the energetics are higher than when the C_3—C_4 bond in the ring is cleaved.

- **Reactions of the intermediate products, formed in the ring opening reactions of the hydroperoxide oxirane radicals just above.**

CCQC(=O)C• will react to form two different product sets. One reaction path is a beta scission forming [CC•Q] + C=C=O. This [CC•Q] radical is however, not stable and it immediately reacts to CC=O + OH. The overall reaction is acetaldehyde plus ketene plus OH.

CCQC(=O)C• => [CC•Q] + C=C=O => CC=O + OH + C=C=O.

This reaction had a total energy release of 10.0 kcal mole^{-1}, after an activation energy of 2.8 kcal/mol through the transition state structure 5, (tst5).

The second path involves a transition state structure from [$C_1C_2QC_3$(=O)C_4•], where a hydrogen atom from C_2, transfers to C_4, forming a radical on C_2 in [$C_1C_{\bullet 2}QC_3$(=O)C_4j]. The radical on C2 immediately forms a strong (~80 kcal mol-1) π bond with the peroxy oxygen bonded to the C2 carbon and this cleaves the weak (45 kcal mol-1) RO—OH bond. As this reaction occurs, a hydroxyl molecule is cleaved from the peroxy group, leading to the formation of CC(=O)C(=O)C + OH as products.

This hydrogen transfer step reaction has a barrier of 67.0 kcal/mol to achieve the saddle point transition state, tst7, and is exothermic, with a 55. kcal/mol energy released.

6.4.6.5 HO_2 Molecular Elimination Reaction. The secondary peroxy radical of ethyl oxirane CCQ●-Y(COC) can undergo HO_2 molecular elimination – loss of a HO_2 radical from the C_1 and C_2 carbons and forming a new π bond between the C1 and C2 carbons, C=C-(COC)2 (vinyloxirane) + HO_2. This reaction has saddle point barrier of 22.2 kcal $mole^{-1}$ and is overall endothermic by 6.2 kcal/mol.

The CCQ-Y(CjOC) radical undergoes a β scission reaction between the radical site and the C_2 carbon (β-Carbon) with the loss of a HO_2 and formation of a π bond between the C_2 and C_3 carbons, 2-vinyloxirane. The reaction has a barrier 22.2 kcal $mole^{-1}$ and an endothermic reaction energy of 6.2 kcal/mol. CC(OOH)Y(CjOC) => C=CY(C•OC) + HO_2.

CCQC=COj == CCQCjC=O (resonant structures)

There are two reaction paths for resonance forms of CCQC=COj == CCQCjC=O. The lowest energy path involves the beta scission from the carbon radical of the CCQCjC=O to eliminate the a HO_2 peroxy radical with formation of CC=CC=O + HO_2. This reaction has an activation energy of 23.9 kcal/mol to the saddle point, transition state structure, tst6, and is endothermic by 8.1 kcal $mole^{-1}$.

The second path involves formation of a new oxirane ring and elimination of an OH group (hydroxyl). This in an interesting path as the carbon radical site on CCQC•C=O site (C3) bonds to the oxygen on the peroxide carbon (C2), while simultaneously the peroxide RO—OH bond is cleaving. The bonding to the peroxy oxygen allows the molecule to form a different (new) oxirane ring, creating the product CY(COC)C=O + OH. This reaction has a barrier of 67.0 kcal/mol to the saddle point transition state, tst7, and is overall, exothermic, with an energy release of 10.2 kcal/mol.

6.4.6.5 HO_2 Molecular Elimination Reaction. The secondary peroxy radical of ethyl oxirane CCQ●-Y(COC) can undergo HO_2 molecular elimination – loss of a HO_2 radical from the C_1 and C_2 carbons and forming a new π bond between the C1 and C2 carbons, C=C-(COC) 2-(vinyloxirane) + HO_2. This reaction has saddle point barrier of 22.2 kcal mole^{-1} and is overall endothermic by 6.2 kcal/mol.

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6.4.6.6 Reaction Paths of C-Y(COC)Cj=O. The C-Y(COC)C•=O radical is an important product in this reaction system. The reaction paths of the C-Y(COC)C•=O are illustrated in figure 6.7. One of the pathways involves the formation of a carbon monoxide and a methyl oxirane radical. The -C•=O radical forms a triple bond in carbon monoxide (C≡O and cleaves from the carbon in the oxirane ring. The products are CO and a methyl oxirane radical. The reaction has an activation energy of 14.3 kcal mole^{-1} to tst9. The total energy required is 14.2 kcal mole^{-1} with an enthalpy of reaction of 13.8 kcal mole^{-1}.

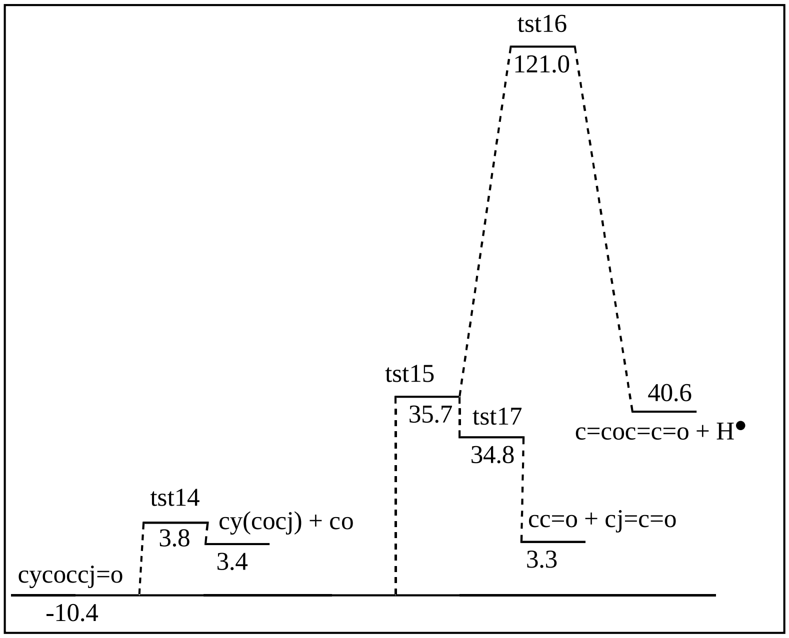


Figure 6.7 Potential energy diagram of C-Y(COC)CCj=O.

A second reaction needing consideration is double bond formation by the carbon C4 radical site to the oxirane ring carbon. This will occur with opening of the ring system over a barrier of 46.1 kcal mole^{-1}, illustrated by tst10. Here a double bond, π bond, is starting to form between the carbon radical site and the adjacent carbon on the oxirane ring at the transition state structure, forming a new π bond and opening the ring. One continuing reaction from tst10 forms acetaldehyde with a ketenyl molecule through tst12, which is 0.9 kcal mol^{-1} below vtst10. The further reaction through tst12 is downhill releasing 32.4 kcal/mol from tst12 to form ketene + acetaldehyde (ethenal) CC=O + C=C=O.

A second reaction from tst10 is to a H atom plus C=COC=C=O. This reaction has an activation energy of 85.3 kcal mole^{-1}. This reaction releases 80.9 kcal/mol from the TS11 saddle point.

6.5 Kinetics

Many of the reactions have high barriers and do not occur under atmospheric or initiation of combustion reactions in the systems described above. The high pressure limit elementary rate constant parameters are listed in Table 6.9. These are high pressure limit rate constants, which are the input data for the QRRK calculations. The QRRK calculations determine the reaction rate constants as a function of pressure. Rate constants here are reported for conditions of one atmosphere and and 800 K.

The association of CCj-Y(COC) with molecular oxygen is the next channel. The pre-exponential constant for this reaction was observed to be 7.27×10^{-11} cm^3/mol*sec. This value is consistent with association values report in studies by Zador et al.[1] The forward rate constant for this reaction is $10^{11.6}$ sec^{-1}. The dissociation rate constant from CCQj-Y(COC) to CCj-Y(COC) + O_2 is observed to be $10^{7.0}$ sec^{-1}.

Table 6.9 High Pressure-Limit Elementary Rate Parameters for Dominate Specie Formation for Oxirane Peroxy System

Reactions	k=A T^n $\exp^{(-Ea/RT)}$		
	A(cm^{3}molecules^{-1} s^{-1})	n	Ea (kcal/mol)
CCJYCOC → CC=COCJ	2.27E+09	1.53	12.01
CC=COCJ → CCJ-Y(COC)	5.26E+09	1.28	42.91
CCJ-Y(COC) → CC=CCOJ	2.64E+10	1.17	4.71
CC=CCOJ → CCJ-Y(COC)	1.21E+10	1.27	68.51
CCDCCOJ → CJ=CC+CH2O	6.83E+09	1.93	31.82
CCDCOCJ → CJ=CC+CH2O	2.00E+10	1.80	35.00
CCJ-Y(COC)+O2 → CCQJ-Y(COC)	8.81E+07	2.12	23.84
CCQJ-Y(COC) → CCJ-Y(COC)+O2	3.82E-02	3.89	-8.63
CCQJ-Y(COC) → CJCQ-Y(COC)	1.01E+08	1.74	52.09
CJCQ-Y(COC) → CCQJ-Y(COC)	3.48E+09	1.03	35.66

The reaction from CCQj-Y(COC) to CjCQ-Y(COC) has a forward and reverse rate constant of $10^{3.47}$ and $10^{5.7}$ sec^{-1}. Figure 6.8 shows the rate constant plot as a function of temperature, ranging from 298 K to 1200K, where the rate constants are plotted versus 1000/T at one atmosphere.

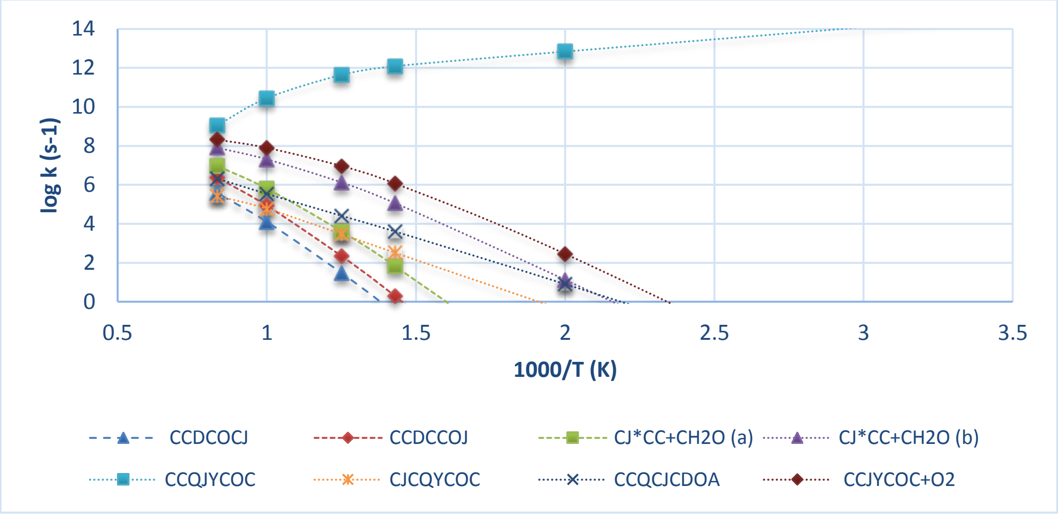


Figure 6.8 Rate constant plot as a function of temperature, ranging from 298 K to 1200K at one atmosphere.

Figure 6.9 shows that the reaction of CCj-Y(COC) + O2 (initial oxidation) goes directly into equilibrium forming the stable adduct CCQj-Y(COC) and that the major product is an equilibrium system with the stable secondary ethyloxirane peroxy radical, which is some 7.5 times lower than the separated products of CCj-Y(COC) + O2 at 800K. As a result, the formation of CCj-Y(COC) + O2 product set dominates this reaction system under conditions of combustion temperatures, at 88.0% formation, and CCQj-Y(COC) is 11.9%.

At room temperature and at atmospheric pressure the peroxy radical formation is complete, there is no further isomerization of unimolecular dissociation reaction of consequence. There will be further reactions in the atmosphere with species such as NO, nitric oxide and with OH, HO_2 and other active species.

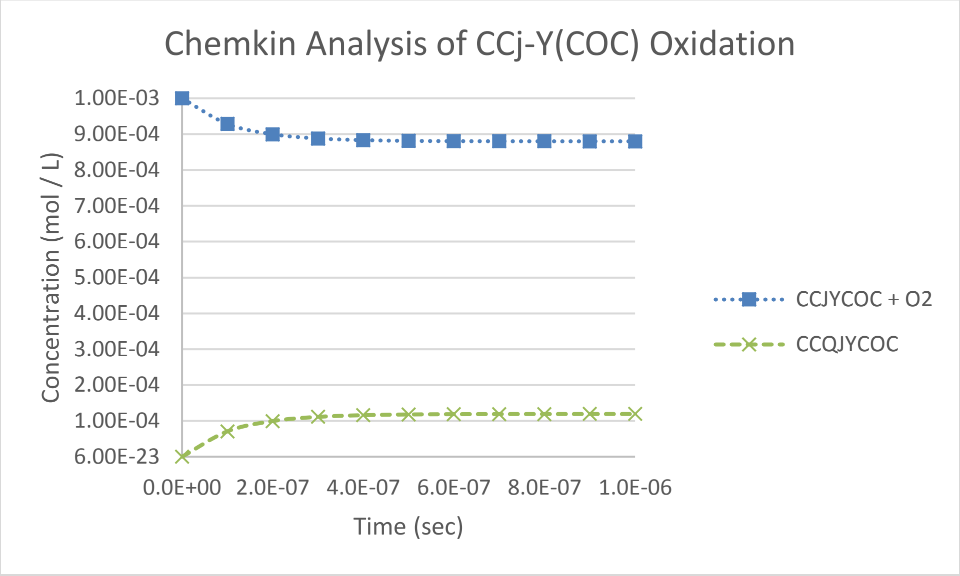


Figure 6.9 Chemkin modeling of CCQj-Y(COC) undergoing oxidation at 1 atm and 800K.

6.6 Conclusion

The thermochemistry, the bond dissociation energies and reaction paths of secondary ethyl oxiranyl radical CCj-Y(COC) under atmospheric and oxidation conditions have been established. The weakest R—H bond present in the CCQ-Y(COC) molecule is the ethyl bonded carbon-H radical in the oxiranyl ring CC•-Y(COC) species,. The reaction of $^3O_2$ association with this secondary radical of ethyl oxirane forms CCQ•-Y(COC), which does not undergo significant further, unimolecular reaction under conditions of atmospheric chemistry. The resulting the ethyl oxirane peroxy radical (CCQj-Y(COC)) has a well depth of 31.7 kcal mol^{-1} below the ethyl oxirane radical and molecular oxygen ((CCj-Y(COC) + O_2) entrance channel. Under combustion conditions (higher temperatures) the reverse reaction CC•-Y(COC) + $^3O_2$ is dominant. The unimolecular reactions of CC•-Y(COC) described, will be most important under combustion conditions. In atmospheric chemistry the stabilized peroxy radical will react with NO to form NO2 and an alkoxy radical CCO•-

Y(COC). This alkoxy radical will further react by reaction paths similar to that of CC•-Y(COC).

CHAPTER 7

THERMOCHEMISTRY AND KINETICS OF OXIDATION OF THE DIETHYL ETHER SECONDARY RADICAL

7.1 Overview

Ethers are widely used as solvents, and as fuel additives for Diesel and Homogeneous Charge Compression Ignition (HCCI) engines. As a result of their use in such applications, ethers and other organic compounds are present in the atmosphere resulting in the formation of photochemical aerosols or smog[37, 38]. Ethers are also important intermediates in isoprene and other pinene molecule oxidation reactions in the atmosphere where aerosols and partially oxygenated hydrocarbons initial to the formation of Peroxy Aceto- Nitrates (PANs) are formed. As the hazards of organic peroxides are relatively well studied, oxidation mechanisms of peroxidizable compounds like ethers reported in the literature are limited. For literature that is present, studies are typically based on experiments under atmospheric and combustion conditions.

Diethyl ether (DEE) is being considered as promising fuel; it is gaining an increasing level of recognition for its safe and cost-effective way of reducing levels of soot and particulate emissions due to its good ignition properties[153]. However, storage of ethers under improper conditions, such as exposure to oxygen in air, for an extended period of time, is known to result in the formation of peroxide bearing intermediates that have the ability to form explosive peroxides[17-19]. DEE is also known to form unstable peroxides during distillation, evaporation and concentration processes which are considered to be a primary factor in laboratory accidents[17-19]. As a result the DEE molecule will be the focal point of this study, where a large emphasis will be placed on evaluating the oxidation of the secondary carbon radical site.

The dimethyl ether has been widely studied from experimental as well as theoretical perspectives[42-47] with specific studies on combustion[29], pyrolysis[48], or atmospheric chemistry[49, 50]. For DEE there is more limited data on mechanistic studies on the oxidation kinetics than there is for the more widely used dimethyl ether diesel additive.

The chemistry of the oxidation of branched ethers has been compared and suggested to have similarities in comparison to the more well-known alkanes[25-28]. There are detailed mechanistic studies in both dimethyl ether[29] as well as diethyl ether[30]. It is accepted that ethers undergo the oxidation that is initiated by a hydroxyl radical under atmospheric conditions[49, 53, 54]. Studies by Di Tommaso et al. [29, 30] show that the ether radicals can undergo beta scission reactions, intramolecular isomerization (hydrogen atom transfers), or reactions $^3O_2$ to form an energized peroxy radical[29, 30]. The peroxy radical is formed with the added energy of the R-OO bond and this chemically energized peroxy radical can undergo reactions before stabilization, where these reactions play a central role in further oxidation reactions of hydrocarbons as well as ethers.

A detailed study of the secondary DEE radical oxidation mechanism has been performed in order to understand the kinetics of the oxidation steps initiated by this peroxy radical formation. Detailed chemical kinetics are developed to characterize and understand the reaction paths with specific attention to the exothermicity and the chain branching paths,; both of which are important to ignition. The most probable reactions paths involved in the oxidation process are determined.

There are two components in this study: (i.) an in-depth study on the oxidation of DEE by a series of reactions involving the initial oxygen molecule association to the secondary radical of diethyl ether – the reactions of this chemical energized system. The second component is the thermochemistry and kinetics of a second oxygen radical addition to a secondary radical site in the 2-diethyl hydroperoxide molecule. Results are presented using a theoretical study based on DFT calculations that provide accurate thermochemical data in addition to providing a theoretical investigation that will help identify possible reaction paths. The oxygen addition to the secondary site results in an energized species. Reaction of this energized peroxy radical, before it is stabilized by collisions with the bath gas, are termed chemical activation reactions. Both the chemical activation and the thermal reactions of the ether peroxides can include intermolecular hydrogen atom transfers from other carbons of the diethyl ether moiety to this newly formed secondary peroxy radical. This creates new carbon radical sites, which can undergo further reactions with the O2 molecules present.

A detailed mechanistic study of the reactions involved in this process is developed and further used to create a kinetic model and the use of Chemkin[163] to describe the reaction paths and products as a function of time and temperature. A Chemkin reaction mechanism is generated for initial unimolecular reactions and the oxidation of this initial secondary ether radical and the formation of its initial products as well as new hydroperoxy carbon radicals on the ether. The mechanism also includes reaction of molecular oxygen to the secondary carbon radical of the CCQOC•C diethyl ether hydroperoxy radical.

The Chemkin program calculates species concentrations at selected temperature, species concentrations and pressure, versus reaction time. The Chemkin program calculates kinetics of species for each reaction in the mechanism, using both forward and reverse reaction rate constants and paths. The reverse reaction rate constants are from the developed thermochemistry.

7.2 Nomenclature

Table 7.1 Nomenclature of the reactants, intermediates and products for Diethyl Ether System

Nomenclature	Species	Formula
CCOCC	$CH_3CH_2OCH_2CH_3$	$C_4H_{10}O$
CC•OCC	$CH_3CHOCH_2CH_3$	C_4H_9O
CCQ•OCC	$CH_3CH(OOJ)OCH_2CH_3$	$C_4H_9O_3$
CCQOC•C	$CH_3CH(OOH)OCHCH_3$	$C_4H_9O_3$
C•CQOCC	$CH_2CH(OOH)OCH_2CH_3$	$C_4H_9O_3$
TC-Y2[COOH]OCC	$CH_3C\text{-}y(OOH)OCH_2CH_3$	$C_4H_9O_3$
TC-Y2[COOHCCO]	$CH_3C\text{-}y(OOHCH_2CH_2O)$	$C_4H_9O_3$
TC-Y2[COOHCO]C	$CH_3CH\text{-}y(OOHCHO)CH_3$	$C_4H_9O_3$
TY2[COOH]OCC	$y(CH_2CHOOH)\text{-}OCH_2CH_3$	$C_4H_9O_3$
CCOC(=O)C	$CH_3CH_2OC(=O)CH_3$	$C_4H_8O_2$
CC=O	$CH_3CH(=O)$	C_2H_4O
CCQ•OCQC	$CH_3CH(Qj)OCH(Q)CH_3$	$C_4H_9O_5$
C•CQOCQC	$CH_2CH(Q)OCH(Q)CH_3$	$C_4H_9O_5$
CC•QOCQC	$CH_3C(Q)OCH(Q)CH_3$	$C_4H_9O_5$
CCO•OC(=O)C	$CH_3CH(Oj)OC(=O)CH_3$	$C_4H_7O_3$
TC-Y8[COOHOOCCO]	$C\text{-}y(CHOCH(Q)CH_2)$	$C_4H_9O_5$
TC•CQOCQC	$CH_2C(Q)OCH(Q)CH_3$	$C_4H_9O_5$
TC-Y2[C(Q)OCCOH]C	$CH_3\text{-}C(Q)y(OCOOH)CH_3$	$C_4H_9O_5$
TCCQOC-Y2[C(OOH)]C	$CH_3CH(Q)OC\text{-}y(OOH)CH_3$	$C_4H_9O_5$
Y(COC)OCQC	y(CH2OCH)-OCH(OOH)CH3	$C_4H_8O_4$
CCQOC=C	$CH_3CH(OOH)OCHCH_2$	$C_4H_8O_4$
CCQOC(=O)C	$CH_3CH(OOH)OC(O)CH_3$	$C_4H_8O_3$
CCOCCQ	$CH_3CH_2OCH_2CH_2(OOH)$	$C_4H_{10}O_3$
CCOC•CQ	$CH_3CH_2OCjHCH_2(OOH)$	$C_4H_9O_3$
CC•OCCQ	$CH_3CjHOCH_2CH_2(OOH)$	$C_4H_9O_3$
C•COCCQ	$CjH_2CH_2OCH_2CH_2(OOH)$	$C_4H_9O_3$
CCOCCQ•	$CH_3CH_2OCH_2CH_2(OOj)$	$C_4H_9O_3$
CC(OH)OCC	$CH_3CH_2(OH)OCH_2CH_3$	$C_4H_{10}O_2$
CC(O•)OCC	$CH_3CH_2(Oj)OCH_2CH_3$	$C_4H_9O_2$

7.3 Computational Methods

The Gaussian 09 Program (G09)[67] was used in the calculation of electronic structural parameters, vibration frequencies, zero point vibrational and thermal energies. Rotational conformers related to the peroxide group in this study were investigated to determine the conformation of each molecule which gave the lowest energy. The Internal rotor potential was also utilized for calculating both entropy and heat capacity contributions. The estimate potential energies for internal Rotator potentials were computed using MOPAC2009[154] using PM3 methodology to scan each dihedral angle where a rotator was located between 0 and 360 degrees in steps of 10 degrees. As this scan calculated the energy at each step, the rest of the molecule remained optimized. After scanning the dihedral angles corresponding to internal rotors, the total energy corresponding to the most stable conformation was calculated and used as a reference in plots of the potential barriers. Internal rotor potentials for the molecules were then calculated at the M062X[130] density function theory (DFT) with the 6-31+ G(d,p) basis set respectively.

Isodesmic work reactions for molecules and radicals were used to obtain accurate calculations for $\Delta H°_{f298}$. The DFT methods M06-2x, ωB97X[131], B2-LYP[123], and B3-LYP with the 6-13+(G(d,p) basis set were used for the stable molecules and radicals. The B3LYP method combines the three parameter Becke exchange functional, B3, with the Lee-Yang-Parr correlation functional, LYP[39]. The M06-2x is a hybrid meta exchange-correlation functional that is a high nonlocality functional with double the amount of nonlocal exchange[61]. The ωB97X is a long-range corrected functional created by Head-Gordon and coworkers which includes empirical dispersion[63].

Isodesmic reactions were used to calculate standard enthalpy of formation; these reactions conserve the number of types of bonds and reaction schemes with similar bonding on both product and reaction sides of the chemical equation. This provides a cancellation of systemic error that can occur in the quantum chemistry calculations, which can result from incomplete calculation of the electron correlation energies[155, 156]. The calculated ΔH298rxn of each work reaction is then used to calculate the Δ_fH°298 of the target reactant, where the two products and one reactant were the reference molecules that have known, evaluated ΔfH° (298) from literature.

Entropy and heat capacity values were calculated as a function of temperature from the optimized structures, moments of inertia, vibration frequencies, internal rotor potentials, symmetry, electron degeneracy, number of optical isomers and the mass of each molecule. This calculation uses a standard formula from statistical mechanics for the contributions of translation, vibrations, and external rotation (TVR) using the SMCPS (Statistical Mechanics−Heat Capacity, and Entropy) program[87]. SMCPS utilizes the rigid rotor-harmonic oscillator approximation from the frequencies, as well as moments of inertia from the optimized B3-LYP/6- 31G(d,p) level. Variational Transition State Theory (VTST) was employed to determine rate constants for barrierless reactions in order to determine enthalpy and entropy values for the transition state structures that do not have saddle points. This was accomplished by running a scan along the selected bond of interest at intervals of 0.1Angstrom. Frequencies, moments of inertia, and enthalpies were determined for each of the 1 Ao interval in the vicinity of the minima of the rate constant calculations.

The group additivity method, developed by Benson[43], was used as a comparison for determined parent ΔH°f 298, S°(T), and C (T) values. This method is based on the knowledge of the contributions of representative groups in similar molecules and their properties in linear consistency in thermochemical properties. Thermodynamic properties of larger species, such as those in this study, were accurately approximated based on the sum of smaller representative groups where there were corrections for rotors, symmetry, electron degeneracy, optical isomers, and gauche and other interactions. The group additivity and calculated Density Functional Theory values were compared.

High-pressure rate constants, k(T), are calculated for the 300−2000 K temperature range using canonical transition state theory (CTST):

$$\mathrm{k(T)}^{n} = \frac{k_b T}{h}\ \mathrm{exp}(^{\frac{\Delta S_c^{\ddagger}}{R}})\mathrm{exp}(^{\frac{-\Delta H^{\ddagger}}{RT}})(\frac{RT}{P^0})^{\ \Delta n^{\ddagger}}$$

Degeneracy is accounted for in the symmetry of reactants and products. These rate constants are then used to determine elementary rate parameters (A, n, Ea) using a modified form of the Arrhenius equation:

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

For the variational transition state calculation of rate constant CCjOCC + O_2 adduct, bond length scans are performed with calculation of optimized structure, energy, and vibration frequencies at each 0.1 Å step. A complete set of thermochemical properties are calculated for the different transition-state structures at each step.

Rate constants are calculated from the reactant to each structure at temperatures of 298 to 2000 K. The minimum rate constant is taken across the temperature−bond length data set, for each temperature. The minimum set of rate constants over the temperature range is fit to modified Arrhenius rate constant form. Temperature and pressure-dependent rate constants are calculated using the multichannel, multifrequency quantum Rice−Ramsperger−Kassel (qRRK) analysis for k(E) with master equation for falloff and stabilization as implemented in the CHEMASTER code[161, 162]. Energy dependence of the rate constant, k(E), must be considered to correctly account for product distribution from chemically activated reactions. The steady-state assumption is applied to the energized adduct where both forward and reverse reaction paths are calculated. In comparison, the formation of products is not reversible, and only adjacent product formation is considered; subsequent dissociation needs to be handled separately. The required input for CHEMASTER includes temperature and pressure ranges of interest, the mass of the species, the Lennard-Jones transport parameters for the collider molecule, the third body bath gas, and reactants, and a reduced set of three representative vibrations and their degeneracies.

7.4 Results and Discussion

Diethyl Ether is an ether and it is noted that the carbon atoms adjacent to carbonyl groups in ketones and adjacent to the oxygen atom in ethers, have significantly lower carbon–hydrogen bond dissociation energies than C--H bond energies on alkanes.

Crounse et al.[51] have shown that the atmospheric oxidation of 3-pentanone proceeds via a set of consecutive reactions starting with the radical site formation via OH radical abstraction, where the H atom is removed from a resonantly stabilized C-H bond adjacent to the carbonyl group.

The C-H bond dissociation energy is lower than a conventional secondary bond by 5 kcal mol^{-1} due to the resonance of the carbon radical site with the carbonyl group.

OH + $CH_3CH_2C(=O)CH2CH3$ → HOH + $CH_3CH\bullet C(=O)CH_2CH_3$

(∆Hrxn - 24 kcal mol-1)

Secondary radical site on ketone

This carbon radical adjacent to a carbonyl group undergoes association reaction with $^3O_2$ to form a peroxy radical with a well depth of 30 kcal mol-2, approximately 12 kcal mol^{-1} deeper than a resonantly stabilized allyl radical. The peroxy radical formed then abstracts the similarly weakly bound hydrogen atom from the corresponding secondary carbon just across the carbonyl to form a hydroperoxide and a new resonance-stabilized alkyl radical.

$CH_3CH_2(C=O)CH^{\bullet}CH_3 + O_2 \rightarrow CH_3CH_2(C=O)CH(OO^{\bullet})CH_3 \rightarrow$

$CH_3CH^{\bullet}(C=O)CH(OOH)CH_3$

$^3O_2$ then adds to this new carbon radical site, forming a RC(OOH)-C=O-(COO•)R' hydroperoxide – peroxy radical. The new peroxy radical undergoes an identical H atom abstraction from the hydroperoxide carbon; this forms a radical site on a carbon with a hydroperoxde group.

$CH_3CH\bullet C=OCH(OOH)CH_3 + O_2 \rightarrow CH_3CH(OO^{\bullet})C=OCH(OOH)CH_3 \rightarrow$

$CH_3CH(OOH)C=OC\bullet(OOH)CH_3$*

The product hydroperoxide carbon radical, (*) is not stable; it immediately undergoes electron rearrangement forming a strong (~ 80 kcal mol-1) RC=O Π bond (a carbonyl) and cleaving the weak (~ 45 kcal mol^{-1} RO—OH).

$[CH_3CH(OOH)C=OC^{\bullet}(OOH)CH_3]^* \rightarrow CH_3CH(OOH)C=OC(=O)CH_3$ + OH

(dHrxn – 35 kcal mol-1)

This last step is ~35 kcal mol^{-1} exothermic, as the newly formed Π bond contributes approximately 80 kcal mol^{-1} of new energy while the cleaved RO—OH bond is only 45 kcal mol-1. Crounse et al. showed that this overall process is dominant over other reaction paths in the 3-pentanone oxidation. They also state that it will be important in the atmospheric oxidation of systems that form similar ketones, such as isoprene.

Our data show that this decrease in C—H bond dissociation energy is also present in cyclic ethers (Auzumendi-Murua and J W Bozzelli – J Phys Chem A 2014). Moreover, our work shows that the significant exothermicity of the ether carbon radical + $^3O_2$ association reactions is similar to that of the ketones of the Crounse et al. data. The carbonyl study further compares the isomerization rates of the carbonyl in ketones with those of comparable structures in alkanes. They show the significant amplification in kinetics with the ketones. The present study illustrates that the same favorable thermodynamics apply in cyclic ethers, and we suggest that ether oxidation in the atmosphere will also undergo this reaction set.

Example: **CCOCC + OH** **=** CC•OCC + H_2O
CC•OCC + O_2 → CCQ•OCC
CCQ•OCC → CCQOC•C
CCQOC•C + O_2 → CCQ•OCQC
CCQ•OCQC → [CC•QOCQC]*
[CC•QOCQC]* → CCQOC(=O)C + OH

Overall : CCOCC + OH + 2O_2 → **CCQOC(=O)C + OH + H_2O**
(OH regeneration)

Under some conditions, further reaction can occur from the chemically activated adduct formed by the O_2 association reactions, resulting in branching. Each O_2 association reaction initially forms a chemically activated adduct with ~ 32 kcal mol-1 energy from the new bond formed.

The $CH_3CH(OOH)OC\bullet(=O)CH_3^*$ has approximately up to 50 kcal mol^{-1} chemical activation energy (resulting from energy of the new π bond formed) in reaction through the transition state. This energy is sufficient to dissociate the RCO—OH bond (only 45 kcal mol-1 is needed) on the remaining CO—OH hydroperoxide group. Conditions for branching depend on temperature, pressure, and rates of the intramolecular reactions above. Some of the energized $CH_3CH(OOH)OC(=O)CH_3*$ will further dissociate to yield an alkoxy radical plus a second OH radical $CH_3CH(O^\bullet)OC(=O)CH_3$ + OH (chain branching). If this occurs in ethers as it does in ketones as Crounse indicates, the overall reaction is chain branching.

7.4.1 Standard Enthalpy (Heat) of Formation $\Delta H°_{f\,298}$

The isodesmic work reactions were used in the process in the analysis of reference species $\Delta H°_{f\,(298)}$ values listed in Table 7.2. DEE enthalpies of formation, along with radicals and products, formed through oxidation using the M062X, ωB97X, B2PLYP DFT methods. Nomenclature for species identification and molecular formulas are listed in Scheme 1. Evaluating the thermochemical enthalpies of the reactants, intermediates, and transition states using three different calculation methods provides a reinforcement of the accuracy and shows consistency of the data. The isodesmic reactions that were utilized have been averaged for each calculation method and were reported as method averages of the three methods. The standard deviation was listed for each species. The smallest standard deviation for a set of molecules was 0.22 and the largest value was 2.44.

Table 7.2 Standard Enthalpies of formation used as Reference Species in Isodesmic Reaction for Diethyl Ether System

Species	**$\Delta H^{\circ}_{f\,298}$ (kcal mol^{-1})**	**Error Values**	**Reference**
H	52.103	± 0.001	9
C (CH4)	-17.78	± 0.07	157
CC	-20.04	± 0.07	158
CCC	-25.02	± 0.12	158
CCOH	-56.21	± 0.5	103
C•COH	-5.9	± 0.4	105
CCO•	-3.1	± 0.4	105
CCOCC	-60.4	± 0.47	61
CCCOH	-60.97	± 0.7	159
CCC•OH	-17.60	± 0.9	105
CCCO•	-8.1	± 0.9	105
CCOC	-51.9	± 0.9	105
C•COC	-1.30	± 0.9	105
CCOC•	-7.30	± 0.9	105
COC	-43.99	± 0.12	105
C•OC	0.8	± 0.9	105
CQ	-31.0		142
CQ•	2.4		142
CCQ	-39.0		142
CCQ•	-6.2		142
CCCQ	-44.0		142
CCCQ•	-11.4		142
C3C	-32.07	± 0.15	158
C3CQ	-58.77		66
COCQ	-70.3		105
C(=O)	-26.2	± 0.1	105
CC•OH	-13	± 0.3	105
CC•OC	-8.6	± 0.9	105

The values determined by the different work reactions and different calculation methods for the enthalpy values of the parent molecules and radicals in this diethyl ether system were highly consistent and support accuracy in the enthalpy values. This data was compared with group additivity calculations and with literature data in Table 7.4. A trend was observed with the B2PLYP method, where the standard enthalpy values calculated by B2PLYP were consistently low by about 0.36 kcal mol^{-1}.

Table 7.3 Work Reactions and Heats of Formation for CCOCC, CCQOCC and CCQOCQC radicals and products

								$\Delta H^\circ_{f\,298}$ (kcal/mol)		
Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
CCOCC	+	C	=	CCOC	+	CC		-60.7	-60.8	-61.0
CCOCC	+	CC	=	CCOC	+	CCC		-61.3	-61.4	-61.8
CCOCC	+	CCOH	=	CCOC	+	C2COH		-61.2	-61.7	-62.1
CCOCC	+	COC	=	CCOC	+	CCOC		-62.3	-62.5	-62.8
CCOCC	+	C2COC	=	CCOC	+	C3COC		-60.7	-61.7	-63.0
CCOCC	+	CCOC	=	CCOC	+	C2COC		-60.3	-60.8	-61.1
							average	-61.1	-61.5	-62.0
							st. dev.	0.7	0.6	0.8
CC•OCC	+	CCOH	=	CCOCC	+	CC•OH		-17.2	-17.0	-17.4
CC•OCC	+	CCOH	=	CCOCC	+	C•COH		-16.9	-17.4	-17.0
CC•OCC	+	CCOH	=	CCOCC	+	CCC•OH		-17.3	-17.2	-17.4
CC•OCC	+	CCOC	=	CCOCC	+	C•COC		-16.2	-16.8	-16.6
CC•OCC	+	COC	=	CCOCC	+	C•OC		-16.2	-16.9	-16.6
CC•OCC	+	CCOC	=	CCOCC	+	CC•OC		-17.4	-17.3	-17.2
							average	-16.8	-17.1	-17.0
							st. dev.	0.5	0.2	0.4
C•COCC	+	C	=	CCOCC	+	CH_3		-9.8	-10.2	-9.3
C•COCC	+	CC	=	CCOCC	+	C•C		-10.0	-9.8	-9.5
C•COCC	+	COC	=	CCOCC	+	C•OC		-9.8	-9.1	-8.9
C•COCC	+	CCOC	=	CCOCC	+	C•COC		-8.7	-8.6	-8.3
C•COCC	+	CCOH	=	CCOCC	+	C•COH		-9.3	-9.1	-8.8
C•COCC	+	CCCOH	=	CCOCC	+	C•CCOH		-8.9	-9.0	-8.7
							average	-9.4	-9.3	-8.9
							st. dev.	0.6	0.6	0.4

Table 7.3 Work Reactions and Heats of Formation for CCOCC, CCQOCC and CCQOCQC radicals and products (continued)

								$\Delta H^\circ_{f\,298}$ (kcal/mol)		
Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
CCQOC•C	+	CCOH	=	CCQOCC	+	CC•OH		-46.6	-46.2	-46.5
CCQOC•C	+	CCOC	=	CCQOCC	+	CC•OC		-47.2	-46.9	-47.1
CCQOC•C	+	CCOH	=	CCQOCC	+	C•COH		-46.3	-46.5	-46.1
CCQOC•C	+	CCCOH	=	CCQOCC	+	CCC•OH		-46.8	-46.3	-46.5
CCQOC•C	+	CCOC	=	CCQOCC	+	CCOC•		-45.6	-46.0	-45.7
CCQOC•C	+	COC	=	CCQOCC	+	C•OC		-46.8	-46.5	-46.3
							average	-46.5	-46.4	-46.4
							st. dev.	0.6	0.3	0.5
CCQOCC•	+	CCOH	=	CCQOCC	+	C•COH		-39.6	-38.8	-38.5
CCQOCC•	+	CCOC	=	CCQOCC	+	C•COC		-38.9	-38.2	-38.1
CCQOCC•	+	CCOCOH	=	CCQOCC	+	C•COCOH		-44.0	-43.4	-43.2
CCQOCC•	+	COC	=	CCQOCC	+	C•OC		-40.1	-38.7	-38.7
CCQOCC•	+	CCCOH	=	CCQOCC	+	C•CCOH		-39.2	-38.6	-38.5
							average	-40.4	-39.5	-39.4
							st. dev.	1.9	2.0	1.9
CCQ•OCC	+	CQ	=	CCQOCC	+	CQ•		-52.2	-52.3	-52.5
CCQ•OCC	+	CCQ	=	CCQOCC	+	CCQ•		-52.6	-52.8	-52.9
CCQ•OCC	+	CCCQ	=	CCQOCC	+	CCCQ•		-53.5	-53.6	-53.7
							average	-52.8	-52.9	-53.0
							st. dev.	0.7	0.6	0.6
CCOC(=O)C	+	C	=	CCOCC	+	C(=O)		-106.9	-107.5	-106.5
CCOC(=O)C	+	CC	=	CCOCC	+	CC(=O)		-106.7	-106.9	-106.1
CCOC(=O)C	+	CCC	=	CCOCC	+	CCC(=O)		-107.7	-107.7	-107.2
							average	-107.1	-107.4	-106.6
							st. dev.	0.6	0.4	0.6

Table 7.3 Work Reactions and Heats of Formation for CCOCC, CCQOCC and CCQOCQC radicals and products (continued)

Isodesmic Work Reaction								$\Delta H^{\circ}_{f\,298}$ (kcal/mol)		
								M06-2x	WB97x	B2PLYP
CCQOCQC	+	C	=	CCQOCC	+	CQ		-122.1	-120.7	-119.5
CCQOCQC	+	CC	=	CCQOCC	+	CCQ		-122.1	-120.7	-121.1
CCQOCQC	+	C3C	=	CCQOCC	+	C3CQ		-122.6	-122.1	-121.1
CCQOCQC	+	COC	=	CCQOCC	+	COCQ		-122.7	-121.3	-120.5
							Average	-122.4	-121.2	-120.2
							st. dev.	0.3	0.7	0.7
CCQ•OCQC	+	CQ	=	CCQOCQC	+	CQ•		-84.7	-84.9	-85.4
CCQ•OCQC	+	CCQ	=	CCQOCQC	+	CCQ•		-85.1	-85.4	-85.8
CCQ•OCQC	+	CCCQ	=	CCQOCQC	+	CCCQ•		-85.9	-86.2	-86.6
							average	-85.2	-85.5	-85.9
							st. dev.	0.65	0.63	0.59
CCQOCQC•	+	CCOH	=	CCQOCQC	+	C•COH		-70.7	-70.5	-70.4
CCQOCQC•	+	CCOC	=	CCQOCQC	+	C•COC		-70.1	-70.0	-70.0
CCQOCQC•	+	CCOH	=	CCQOCQC	+	CC•OH		-71.0	-70.1	-70.7
CCQOCQC•	+	COC	=	CCQOCQC	+	C•OC		-71.2	-70.4	-70.6
CCQOCQC•	+	CCCOH	=	CCQOCQC	+	C•CCOH		-70.3	-70.3	-70.4
							average	-70.7	-70.3	-70.4
							st. dev.	0.5	0.2	0.3
CC(=O)OCQC	+	COC	=	CCOC(=O)C	+	COCQ		-133.9	-133.0	-132.4
CC(=O)OCQC	+	C3C	=	CCOC(=O)C	+	C3CQ		-133.8	-133.9	-133.0
CC(=O)OCQC	+	CC	=	CCOC(=O)C	+	CCQ		-133.4	-132.5	-131.7
CC(=O)OCQC	+	CCC	=	CCOC(=O)C	+	CCCQ		-132.8	-132.3	-131.4
							average	-133.5	-132.9	-132.1
							st. dev.	0.5	0.7	0.7

Table 7.3 Work Reactions and Heats of Formation for CCOCC, CCQOCC and CCQOCQC radicals and products (continued)

								$\Delta H^\circ_{f\,298}$ (kcal/mol)		
Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
C=COCQC	+	CC	=	C=COCC	+	CCQ		-62.9	-62.2	-62.0
C=COCQC	+	CCC	=	C=COCC	+	CCCQ		-62.3	-62.0	-61.7
C=COCQC	+	C3C	=	C=COCC	+	C3CQ		-63.4	-63.6	-63.3
C=COCQC	+	COC	=	C=COCC	+	COCQ		-63.5	-62.7	-62.7
							average	-63.0	-62.6	-62.3
							st. dev.	0.5	0.7	0.7
Y(COC)OCQC	+	C	=	Y(COC)OCC	+	CQ		-102.6	-102.0	-101.2
Y(COC)OCQC	+	CC	=	Y(COC)OCC	+	CCQ		-102.6	-102.0	-101.4
Y(COC)OCQC	+	C3C	=	Y(COC)OCC	+	C3CQ		-103.1	-103.4	-102.7
Y(COC)OCQC	+	COC	=	Y(COC)OCC	+	COCQ		-103.2	-102.5	-102.1
							average	-102.9	-102.5	-101.8
							st. dev	0.3	0.7	0.7
CC(OH)OCC	+	CCC	=	CCOCC	+	CC(OH)C		-106.7	-106.4	-105.9
CC(OH)OCC	+	CCCC	=	CCOCC	+	CC(OH)CC		-106.6	-106.2	-105.8
CC(OH)OCC	+	Y(CCC)	=	CCOCC	+	Y(CCC)OH		-106.5	-105.7	-105.5
CC(OH)OCC	+	CCQ	=	CCOCC	+	C(OH)CQ		-106.3	-105.7	-105.7
							average	-106.5	-106.0	-105.7
							st. dev	0.2	0.4	0.2
CC(O•)OCC	+	CCOH	=	CC(OH)OCC	+	CCO•		-52.5	-52.7	-52.3
CC(O•)OCC	+	CCCOH	=	CC(OH)OCC	+	CCCO•		-52.7	-52.9	-52.5
CC(O•)OCC	+	C(OH)C(OH)	=	CC(OH)OCC	+	C(OH)C(O•)		-52.3	-52.5	-52.7
CC(O•)OCC	+	CC(OH)C	=	CC(OH)OCC	+	CC(O•)C		-52.4	-52.7	-52.8
							average	-52.5	-52.7	-52.6
							st. dev	0.2	0.2	0.2

Table 7.3 Work Reactions and Heats of Formation for CCOCC, CCQOCC and CCQOCQC radicals and products (continued)

Isodesmic Work Reaction								ΔH°$_{f\,298}$ (kcal/mol)		
								M06-2x	WB97x	B2PLYP
CCOCCQ	+	C	=	CCOCC	+	CQ		-78.5	-78.2	-78.1
CCOCCQ	+	CC	=	CCOCC	+	CCQ		-78.5	-78.3	-78.3
CCOCCQ	+	CCC	=	CCOCC	+	CCCQ		-77.9	-78.1	-78.0
CCOCCQ	+	COC	=	CCOCC	+	COCQ		-79.1	-78.8	-79.0
							average	-78.5	-78.3	-78.4
							st. dev	0.5	0.3	0.5
CCOCCQ•	+	CQ	=	CCOCCQ	+	CQ•		-45.5	-45.3	-45.0
CCOCCQ•	+	CCQ	=	CCOCCQ	+	CCQ•		-45.8	-45.6	-45.3
CCOCCQ•	+	CCCQ	=	CCOCCQ	+	CCCQ•		-46.4	-46.1	-45.8
							average	-45.9	-45.7	-45.4
							st. dev	0.5	0.4	0.4
CCQOC(OH)C	+	CCC	=	CCQOCC	+	CC(OH)C		-137.5	-137.7	-137.4
CCQOC(OH)C	+	CQ	=	CCQOCC	+	CQOH		-137.1	-137.0	-137.2
CCQOC(OH)C	+	CC	=	CCQOCC	+	CCOH		-138.0	-137.8	-137.5
CCQOC(OH)C	+	CCC	=	CCQOCC	+	C2COH		-137.9	-138.1	-137.9
							average	-137.6	-137.6	-137.5
							st. dev	0.4	0.5	0.23
CCQOC(O•)C	+	CCOH	=	CCQOC(OH)C	+	CCO•		-82.4	-82.6	-82.1
CCQOC(O•)C	+	CCCOH	=	CCQOC(OH)C	+	CCCO•		-82.7	-82.8	-82.3
CCQOC(O•)C	+	C(OH)C(OH)	=	CCQOC(OH)C	+	C(OH)C(O•)		-82.3	-82.3	-82.5
CCQOC(O•)C	+	CC(OH)C	=	CCQOC(OH)C	+	CC(O•)C		-82.3	-82.6	-82.6
							average	-82.4	-82.6	-82.4
							st. dev	0.2	0.2	0.2

Table 7.4 Calculated $\Delta H^\circ_{f\,298}$ Comparison to Literature and Group Additivity for Diethyl Ether System

	Heat of Formation (kcal/mol)					
Species	M06-2X	WB97X	B2PLYP	Average	Literature (Reference)	GA
CCOCC	-61.1	-61.5	-62.0	-61.5	-60.4 [63]	-59.80
CC•OCC	-17.2	-17.0	-17.4	-17.0	-17.9[30]	-16.89
C•COCC	-9.5	-9.3	-8.5	-8.8	-11.8 [30]	-9.25
CCQOCC	-88.9	-88.1	-88.3	-88.4	-91.7 [30]	-89.50
CCQOC•C	-46.5	-46.4	-46.4	-46.4	-44.0 [30]	-46.59
CCQOCC•	-40.4	-39.5	-39.4	-39.8	-36.1 [63]	-38.95
CC•QOCC	-	-	-	-	-	-46.59
C•CQOCC	-37.9	-37.8	-37.4	-37.7	-33.2 [63]	38.95
CCQ•OCC	-52.8	-52.9	-53.0	-52.9	-54.5[63*]	-55.30
CCOCCQ	-78.5	-78.3	-78.4	-78.4	-74.7[63*]	-79.05
C•COCCQ	-29.7	-29.3	-29.4	-29.5	This work	-28.95
CC•OCCQ	-33.8	-34.0	-33.5	-33.8	This work	-35.60
CCOC•CQ	-35.9	-36.2	-36.8	-36.3	This work	-35.60
CCOCCQ•	-45.9	-45.7	-45.4	-45.6	-44.1[63*]	-45.30
CCOCC•Q	-	-	-	-	-	-28.95
CC(OH)OCC	-106.5	-106.0	-105.7	-106.1	This work	-105.20
CC(O•)OCC	-52.5	-52.7	-52.6	-52.6	-58.9 [160]	-53.24
CCOC(=O)C	-107.1	-107.4	-106.6	-107.0	-106.5 [103]	-105.67
CCQOCQC	-122.4	-121.2	-120.2	-121.3	This work	-119.20
CCQ•OCQC	-85.2	-85.5	-85.9	-85.4	-81.2 [160]	-85.00
CCQOCQC•	-70.7	-70.3	-70.4	-70.5	This work	68.45
CC(=O)OCQC	-133.5	-132.9	-132.1	-132.9	This work	-135.37
C=COCQC	-63.0	-62.6	-62.3	-62.7	This work	-62.84
Y(COC)OCQC	-102.9	-102.5	-101.8	-102.7	This work	-91.67
CC(O•)OC(Q)C	-84.3	-84.4	-84.1	-84.3	91.3 [159]	-83.34
CC(=O)OC(=O)	-125.0	-124.7	-124.7	-124.8	This work	-123.48

*Values obtained from experimental studies in aqueous solution

Enthalpies, entropies, heat capacities for groups are listed in section 7.4.5.

7.4.2Bond Dissociation Energies of Diethyl Ether Species

C-H bonds on the primary and secondary carbon sites and the peroxide O-H bond dissociation energies located in Table 7.5. Bond dissociation energies were computed from a bond cleavage reaction using, the heat of formation recorded for a parent molecule and the corresponding radical, and the $\Delta H_f{}^{\circ}{}_{298}$ of Hydrogen atom; which is52.103 kcal mole^{-1}. The data calculated was consistent with BDE values reported for alkanes having primary and secondary BDE of 101.3 and 98.5 kcal/mol[52], respectively, where the respective primary and secondary radical carbon sites of the DEE radical have a an average BDE of 102.3 and 96.1 kcal/mol. Moreover, when comparing peroxy radical sites in the systems studied it was observed in this particular system that the average BDE was 86.8 kcal/mol. This is similar to that of alkanes containing peroxides at 85.0 kcal/mol[142]. The BDE of the molecules that have gone through its first oxygen addition step the BDE for the primary carbon of DEE-Q the bond dissociation energies were for molecules (a- primary site on the other side of the peroxide, b- primary site on the same side as the peroxide) 100.8 (a) for CCQOCC•, 102.8 (b) for C•CQOCC, and secondary and peroxy sites for molecules CCQOC•C, CCQ•OCC were 94.1 and 87.6 kcal/mol, respectively. When comparing BDE of CCOCCQ and its radicals the secondary site for DEE-Q the dissociations were molecules (c- secondary site on the other side of the peroxide, d- primary site on the same side as the peroxide) it was observed that species C•COCCQ, (c) CCOC•CQ, (d) CC•OCCQ and CCOCCQ• have BDE values of 101.0, 94.1, 96.7 and 84.9 kcal/mol, respectively. Where C•CQOCC bond was 0.3 kcal/mol greater than (a) CCQOCC• and 1.8 kcal/mol lower than (b) C•CQOCC. CCQOC•C has a BDE that was 0.1, 2.6 kcal/mol less than (c) CCOC•CQ and (d) CC•OCCQ, respectively. The final comparison between peroxy radicals CCQ•OCC was 2.8 kcal/mol greater than that of CCOCCQ•. Whereas, species that have undergone two steps of oxidation have observed BDE at the primary site of C•CQOCQC and the peroxy site of CCQ•OCQC was 96.3 and 81.3, respectively.

Table 7.5 Bond Dissociation Energy (BDE) Values for Diethyl Ether System

Reaction					Bond Dissociation Energies (kcal mol^{-1})	
CCOCC	=	CC•OCC	+	H		
-60.4		-17.0		52.103	95.5	96.2 [30]
CCOCC	=	C•COCC	+	H		
-60.4		-8.8		52.103	103.7	104.6 [30]
CCQOCC	=	C•CQOCC	+	H		
-88.4		-37.7		52.103	102.8	110.6 [159*]
CCQOCC	=	CCQOC•C	+	H		
-88.4		-46.4		52.103	94.1	104.1 [159*]
CCQOCC	=	CCQOCC•	+	H		
-88.4		-39.8		52.103	100.8	107.7 [159*]
CCQOCC	=	CCQ•OCC	+	H		
-88.4		-52.9		52.103	87.6	89.3 [30]
CCOCCQ	=	C•COCCQ	+	H		
-78.4		-29.5		52.103	101.4	This work
CCOCCQ	=	CC•OCCQ	+	H		
-78.4		-33.8		52.103	96.7	This work
CCOCCQ	=	CCOC•CQ	+	H		
-78.4		-36.3		52.103	94.2	This work
CCOCCQ	=	CCOCCQ•	+	H		
-78.4		-84.9		52.103	84.9	82.7 [30]
CCQOCQC	=	CCQ•OCQC	+	H		
-121.3		-85.4		52.103	88.0	This work
CCQOCQC	=	C•CQOCQC	+	H		
-121.3		-70.5		52.103	102.9	This work

*Values obtained from experimental studies in aqueous solution

7.4.3 Internal Rotors

Properties for all species including optimized structure parameters, symmetry, moments of inertia, vibration frequencies and internal rotor potentials were calculated using B3-LYP with the basis set of 6-31+G(d,p) methodology with scans performed at each dihedral angle in intervals of 10 degree for 37 steps to achieve the lowest energy conformation after an intial scan using MOPAC. When completed with this step, a list was compiled of results giving the $\Delta H°_{f\,298}$ values for the parent as well as the radicals of species from the methods of M06-2x, ωB97x and B2PLYP. The work reactions in Table 2 are from the noted DFT methods and 6-31G+ (d,p) basis set. Data is in supporting information, including stable species, radicals and transition states.

7.4.4 Entropies (S(T)) and Heat Capacities (C_p(T))

Transition States Structures these are structures that exist for maybe 1x10^{-14} seconds they are not stable items

A transition state is a first-order saddle point on a potential energy surface. The vibration spectrum of a transition state is characterized by one imaginary (negative) frequency. This means that in one direction in the nuclear configuration space, the energy has a maximum, but at the same time all orthogonal directions have a vibrational frequency analysis at the same method level as that of the geometry optimization.

Once the transition state had been identified, the enthalpy was obtained from the calculated energy of the structure. This value was then utilized to calculate the differences between the transition state structure and the products and reactants to obtain the reaction barrier. Table 7.6 lists the transition states and their enthalpies of formation. M062x, wB97x, and B2-LYP, with the basis set 6-31+G (d,p) were used to gather this data. The enthalpies of formation were calculated with the average values obtained from the three methods results. Frequencies and moments of inertia to calculate the entropy and heat capacities ranging from 298K to 1500K were completed by using M062x/6-31+G(d,p) methodology. The thermochemical properties of the transition states were then placed into the NASA polynomial format of the species were converted for further analysis using Chemkin.

Table 7.6 Heat of Formations, Entropy and Heat Capacity for Transition State Structures for Diethyl Ether System

Transition State	Hf	S	Cp300	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
TY2[COOHC]OCC	-17.7	79.38	29.23	37.53	44.87	50.96	60.14	66.63	76.31
TC-Y2[COOH]OCC	-17.9	86.35	30.58	38.10	44.95	50.79	59.79	66.28	76.08
TC-Y2[COOHCO]C	-36.2	81.11	29.66	37.52	44.63	50.64	59.82	66.37	76.17
TC-Y2[COOHCCO]	-31.7	83.41	29.53	37.61	44.84	50.87	60.01	66.51	76.24
TCCQO-Y2[COOHC]	-54.2	96.81	37.37	46.65	54.66	61.19	70.83	77.53	87.52
TC-Y8[COOHOOCCO]	-66.3	92.90	37.04	46.46	54.56	61.15	70.87	77.61	87.60
TCCQOC-Y2[COOH]C	-52.7	92.24	37.48	46.45	54.25	60.69	70.36	77.17	87.36
TC-Y2[C(Q)OCCOH]C	-71.9	91.97	37.53	46.45	54.28	60.76	70.47	77.27	87.41
TCY5OCQC	-57.7	95.43	38.97	47.58	55.03	61.19	70.53	77.18	87.28

Hf in units kcal mol^{-1}

7.4.5 Group Additivity

The group additivity (GA) method, as designed by Benson[38] is a rapid estimation method for the calculation of $\Delta H°_f$ *298*, $S°$ *298*, and $Cp(T)$ of stable species. Group additivity methodology is based on the knowledge of the representative groups contributions in similar molecules. Experimental data also illustrates linear consistency observed in thermochemical properties such as heat capacity and enthalpy values.

This study utilizes group additivity terms values to compare calculated enthalpies of formation for 2-(1-hydroperoxyethyl)oxirane and radicals. The group terms employed can be utilized to estimate enthalpy values to compare calculated enthalpy of formation values calculated from computational and experimental studies. Tables 7.7 list the groups that are employed in group additivity methodology.

Table 7.7 Group Contribution Terms Used for Group Addivitiy

Group	Hf	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
C/C/H3	-10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
CD/H2	6.26	17.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
C/C/H2/O	-8.10	9.80	4.99	6.85	8.30	9.43	11.11	12.33	
O/C2	-23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.61	
O/C/O	-5.25	8.54	3.90	4.31	4.60	4.84	5.32	5.80	
O/H/O	-16.30	27.83	5.21	5.72	6.17	6.66	7.15	7.61	8.43
C/C/H/O2	-16.00	-12.07	5.25	7.10	8.81	9.55	10.31	11.05	
O/C/H	-37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
C/CO/H3	-10.08	30.41	6.19	7.84	9.40	70.79	13.02	14.77	17.58
O/CO2	-46.20	10.26	3.20	3.83	4.09	4.25	4.28	4.32	
CO/C/O	-35.10	10.04	6.10	6.70	7.40	8.02	8.87	9.36	
O/C/CO	-42.19	8.40	3.91	4.31	4.60	4.84	5.32	5.80	
CD/H/O	2.03	6.20	4.75	6.46	7.64	8.35	9.10	9.56	10.46
O/C/CD	-23.73	9.70	3.91	4.31	4.60	4.84	5.32	5.80	
P	101.10	2.61	-0.77	-1.36	-1.91	-2.40	-3.16	-3.74	-4.66
S	98.45	4.44	-1.50	-2.33	-3.10	-3.39	-3.75	-4.45	-5.20
ALKOXY	104.06	-1.46	-01.98	-1.30	-1.61	-1.89	-2.38	-2.80	-3.59
ALPEROX	88.2	0.22	-2.05	-2.84	-3.55	-4.09	-4.72	-4.97	-5.08

Table 7.7 list all of the group contribution terms that are used in the calculation of species using group additivity. Comparisons are completed using the sum of the groups present in each species with the calculated enthalpy of formation are presented in Table 7.8.

Table 7.8 Calculated $\Delta H^\circ_{f\ 298}$ Comparison to Literature and Group Additivity

	Heat of Formation (kcal/mol)					
Species	M06-2X	WB97X	B2PLYP	Average	Literature (Reference)	GA
CCOCC	-61.1	-61.5	-62.0	-61.5	-60.4 [49]	-59.80
CC•OCC	-17.2	-17.0	-17.4	-17.0	-17.9[30]	-16.89
C•COCC	-9.5	-9.3	-8.5	-8.8	-11.8 [30]	-9.25
CCQOCC	-88.9	-88.1	-88.3	-88.4	-91.7 [30]	-89.50
CCQOC•C	-46.5	-46.4	-46.4	-46.4	-44.0 [30]	-46.59
CCQOCC•	-40.4	-39.5	-39.4	-39.8	-36.1 [50]	-38.95
C•CQOCC	-37.9	-37.8	-37.4	-37.7	-33.2 [50*]	38.95
CC•QOCC	-	-	-	-	-	-46.59
CCQ•OCC	-52.8	-52.9	-53.0	-52.9	-54.5[30*]	-55.30
CCOCCQ	-78.5	-78.3	-78.4	-78.4	-74.7[30*]	-79.05
C•COCCQ	-29.7	-29.3	-29.4	-29.5	This work	-28.95
CC•OCCQ	-33.8	-34.0	-33.5	-33.8	This work	-35.60
CCOC•CQ	-35.9	-36.2	-36.8	-36.3	This work	-35.60
CCOCCQ•	-45.9	-45.7	-45.4	-45.6	-44.1[30*]	-45.30
CCOCC•Q	-	-	-	-	-	-28.95
CC(OH)OCC	-106.5	-106.0	-105.7	-106.1	This work	-105.20
CC(O•)OCC	-52.5	-52.7	-52.6	-52.6	-58.9 [51]	-53.24
CCOC(=O)C	-107.1	-107.4	-106.6	-107.0	-106.5 [38]	-105.67
CCQOCQC	-122.4	-121.2	-120.2	-121.3	This work	-119.20
CCQ•OCQC	-85.2	-85.5	-85.9	-85.4	-81.2 [51]	-85.00
CCQOCQC•	-70.7	-70.3	-70.4	-70.5	This work	68.45
Y(COC)OCQC	-102.9	-102.5	-101.8	-102.7	This work	-91.67
CC(O•)OC(Q)C	-84.3	-84.4	-84.1	-84.3	91.3 [51]	-83.34
CC(=O)OC(=O)	-125.0	-124.7	-124.7	-124.8	This work	-123.48

Q represents the –OOH group on the adjacent carbon , example CCQ = CCOOH

7.4.6 Reaction Paths

Similar to that of alkane's auto ignition mechanisms, oxidation begins with an initiation step where a radical (R•) is produced as a result. The reaction responsible for DEE oxidation begins with the loss (abstraction) of a hydrogen atom from the neutral molecule, brought about by an initiator. A typical initiator of this reaction is a hydroxyl radical.

The radicals formed can decompose in the absence of oxygen by beta scission reactions, but this requires an energy barrier that limits this dissociation under atmospheric conditions. Another pathway that can result in chain propagation is where the radical (R•) interacts (associates) with an oxygen molecule forming a ROO• peroxy radical species.

This scheme was further complicated by the possible decomposition of the hydroperoxide radicals that represent the stoichiometric products of the ideal chain propagating cycle. These channels were β-scission, isomerization and hydro-peroxide formation. To carry out the reaction mechanism that was covered in the "Important Reactions of Ethers in Atmospheric and Combustion Environments" portion of this article, isomerization by hydrogen transfer from the secondary carbon of the di-ethyl ether secondary peroxy radical was the focus of this study.

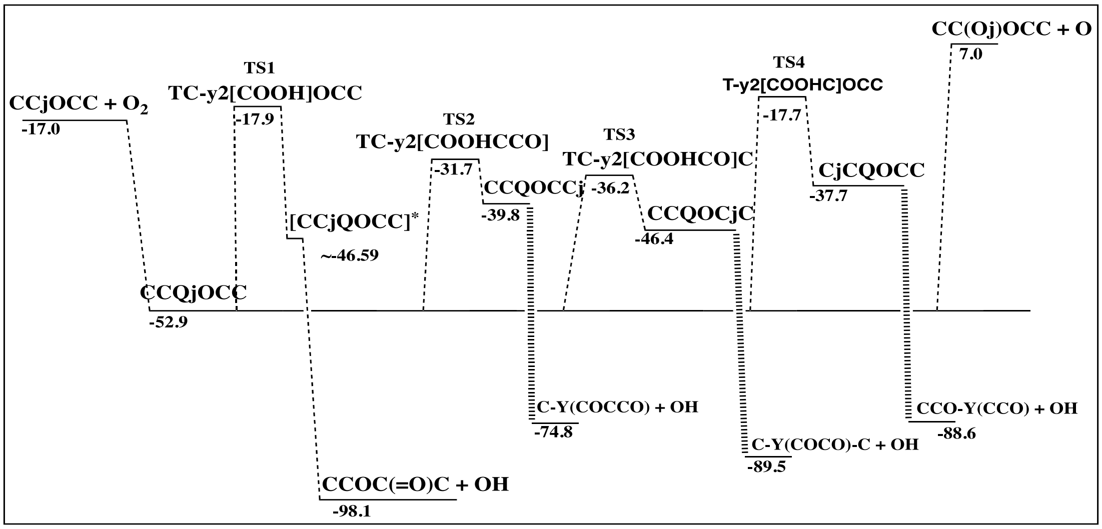


Figure 7.1 Potential energy diagram of CC•OCC+ O_2 oxidation.

Molecular oxygen can be a possible initiator but these reactions are highly endothermic and prohibitive under atmospheric conditions. The reactions involve a barrier-less path involving the $^3O_2$ molecule abstracting a hydrogen from the ether or hydrocarbon and forming HO2 plus the alkyl radical. The CC•OCC radical when formed will react further with $^3O_2$. This reaction analysis uses VTST to determine the pre-exponential factor for the reaction, where there is effectively no barrier. Reaction of the secondary radical with O2 is highly exothermic and was calculated to have a well depth of 35.9 kcal/mol. A study by S. Di Tommaso[30] has shown that the CCQ•OCC peroxy radical is the important peroxy in this diethyl ether system, and that the intramolecular hydrogen atom transfer reaction pathways are important. The fate of this CCQ•OCC species in this study involves hydrogen transfer, OH elimination, and oxygen (atom and O_2) elimination reactions. There are four sites that hydrogen could be transferred from to form a new radical structure. To help describe the reactions the carbon positions are labeled a, b, c and d ($C_aC_{b(}$Q•)OC_cC_d). The most favorable hydrogen transfer site, is from the secondary carbon c to the peroxy oxygen radical. This is a result of the lower energy needed to break the bond of a hydrogen located on a primary carbon. The reaction barrier of this reaction was 14.3 kcal/mol with an overall reaction energy of 6.1 kcal/mol. C_a and C_d are both primary sites. Transfer from the C_a carbon has an activation energy of 34.7 kcal/mol and a total reaction energy of 15.2 kcal/mol. Transfer from the C_d has anactivation energy of 19.5 kcal/mol and a total reaction energy of 13.1 kcal/mol. Transfer from the C_b resulting in hydroxyl elimination with an activation energy of 34.7 kcal/mol; but has an exothermicity of 45.2 kcal/mol. One other important reaction for this peroxy radical, CCQjOCC, is oxygen elimination reaction (

ROO• = RO + O, which is chain branching. This reaction has an endothermic reaction energy of 59.9 kcal/mol.

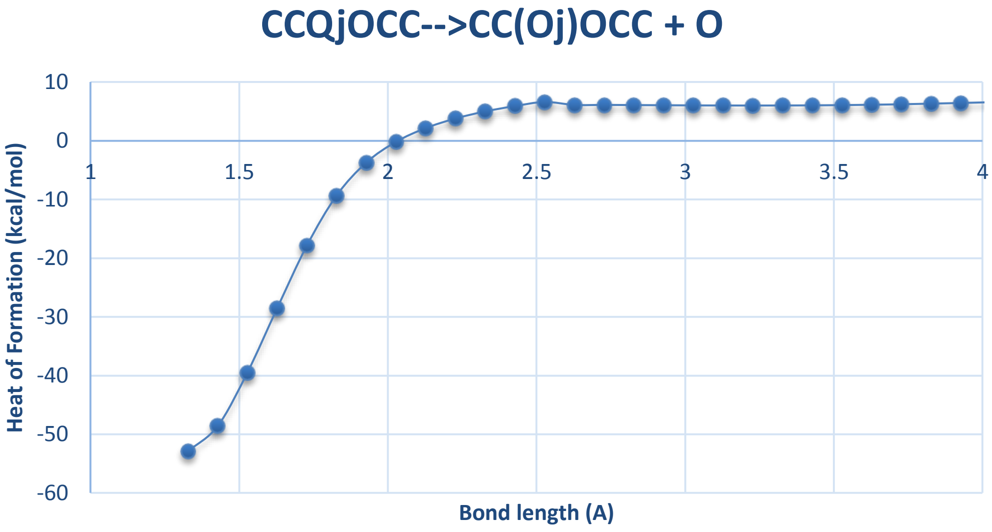


Figure 7.2 Energy scan of CCQ•OCC→ CC(O•)OCC+O.

This study will review this initial hydrogen atom step and move to the second oxidation – the molecular oxygen addition to the secondary carbon of CCQOC•C.

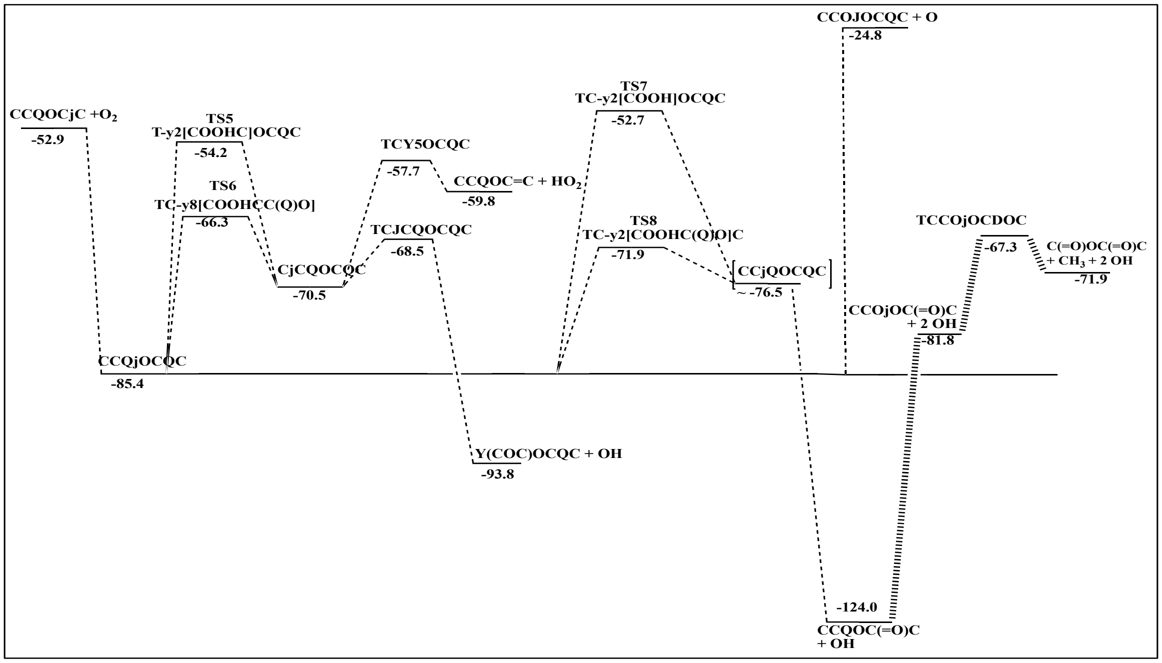


Figure 7.3 Potential energy diagram of CCQOC•C+ O_2 oxidation

A similar O_2 association will occur for the secondary radical produced from the previous low energy hydrogrn transfer, CCQOC•C + O_2. This is barrier-less reaction similar to that of the first oxidation of CC•OCC + O_2 with a well depth of 35.9 kcal/mol. This is consistent with studies performed by Zador *et al.*[54] that show that 30 – 38 kcal/mol are typical for O_2 association with alkyl radicals.

The O_2 association potential energy scan for a second O_2 association was completed with the B3LYP/6-31G+(d,p) method. Here the CCQOC•C combines with a second O_2 to form CCQOCQ•C – a di peroxide system. The scan diagram is in Figure 7.4.

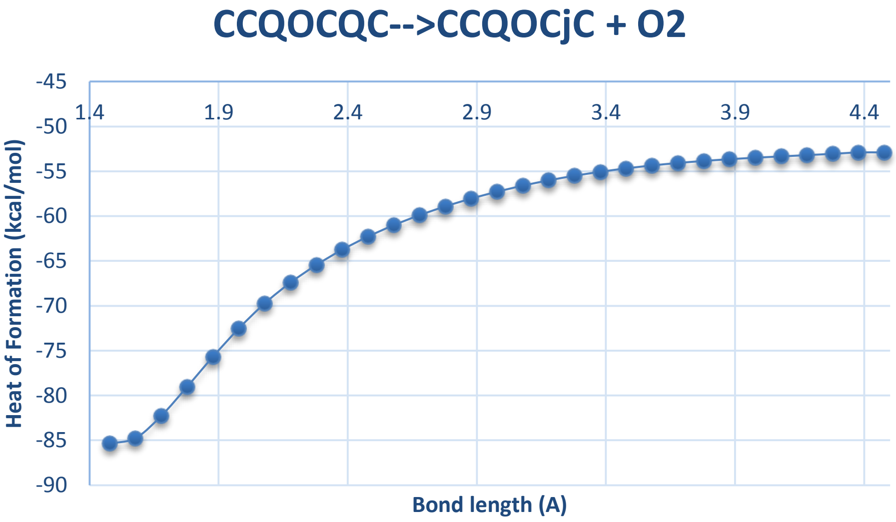


Figure 7.4 VTST of CCQ•OCQC→ CCQOC•C+O_2

This new diperoxy adduct (CCQOCQ•C) can further react via intramolecular isomerizations, as above. The CCQOCQ•C peroxy radical can undergo intramolecular hydrogen transfer reactions similar to the non hydroperoxide formed above CCQ•OCC. These reaction paths are illustrated below in Figure 7.5. CCQ•OCQC can react to C•CQOCQC via two reaction paths: through transition state structures TS5 (TCCQO-Y2[COOHC]) and TS6 (TC-Y2[COOHOOCCO]). Transition state TS6 is the lower energy and more likely path, with an activation energy that is 19.1 kcal/mol, some 12.1 kcal/mol lower than .TS5, which has a barrier of 31.2 kcal/mol. These paths are shown in Figure 7.5. These reactions occur through cyclic transition state structures, where the seven-membered cyclic rings have lower reaction energies a five-membered ring. It is noted that the reactions with larger ring structure, have lower pre-exponential factors.

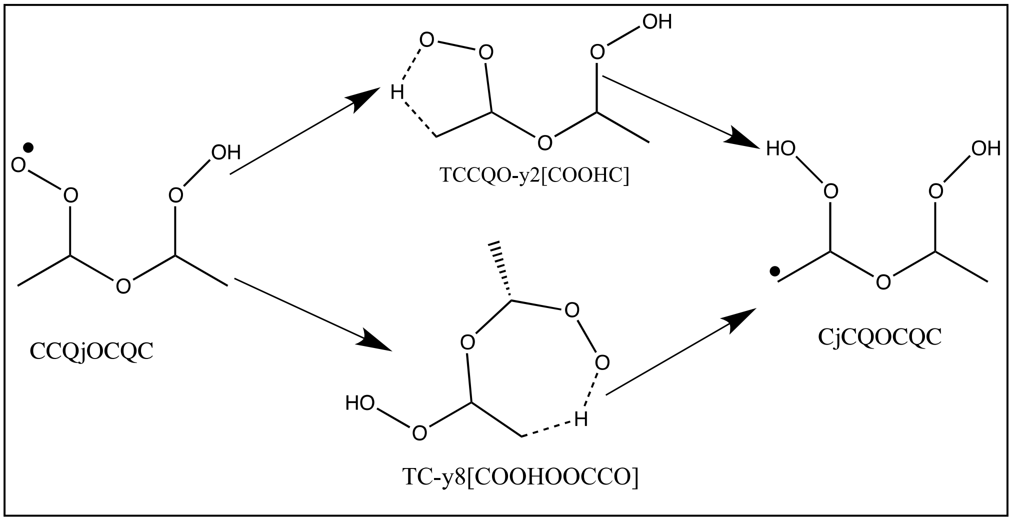


Figure 7.5 Intramolecular hydrogen atom from secondary carbon site.

When this isomerization occurs, the C•CQOCQC moiety has access to a number of further reaction channels. It can undergo HO2 or OH elimination. The OH elimination occurs via the carbon radical site attacking the oxygen atom on the carbon of the hydroperoxide group forming a 3 member oxirane ring, and cleaving of the RO—OH bond. This transition state, TCjCQOCQC has a barrier of 2 kcal/mol and an endothermicity of 23.3 kcal/mol. Kinetics of this reaction are from the literature[30].

There are two intramolecular hydrogen atom transfer sites; one was from the secondary carbon bonded hydroperoide. The newly formed radical site from this H transfer, is unstable and the hydroperoxide carbon radical site dissociates to CCQOC(=O)C + OH. This TC-Y[C(Q)OCCOH]C (TS8) has an activation energy of 13.1 kcal/mol, There is also an IPSO hydrogen transfer from the newly formed peroxy carbon site; this has the higher kcal mole^{-1} barrier for and TCCQOC-Y[COOH]C (TS7) has an activation energy of 32.7 kcal/mol.

The CC(OOj)OCQC to CCQOC(=O)C + OH has an exothermic reaction energy of 38.6 kcal/mol.

TC-Y[C(Q)OCCOH]C (TS8) is the reaction that would be most favored to react under atmospheric conditions because the barrier was lower than that of TCCQOC-Y[COOH]C.

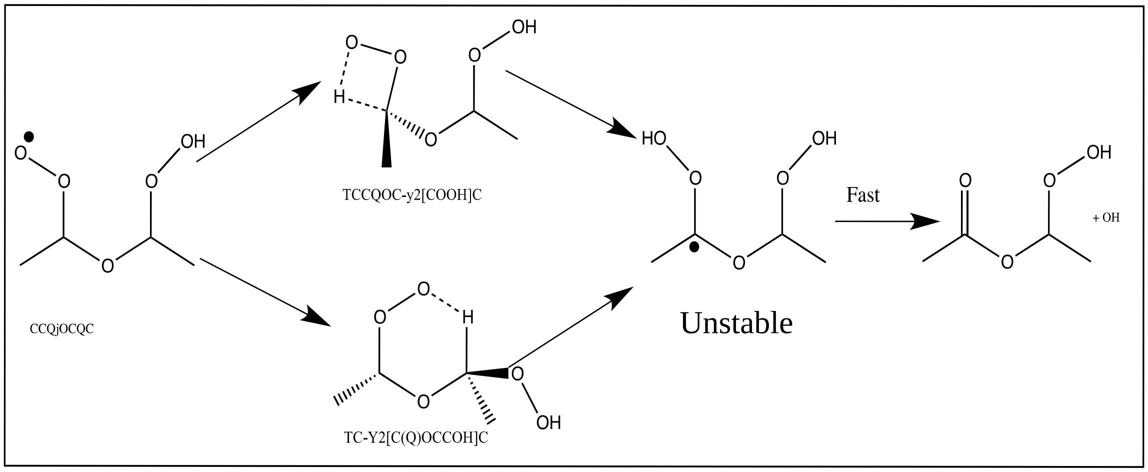


Figure 7.6 Structure of TC-Y2[C(Q)OCCOH]C and TCCQOC-Y2[COOH]C.

The C•CQOCQC radical can also pass through an HO_2 elimination path, this is transition state TCY5OCQC which has a barrier of 34.43 kcal/mol.

One other chain branching reaction that is evaluated is the simple dissociation reaction ROO● = RO● + O● of CCQ•OCQC producing CC(O•)-OCQC + O. This is illustrated in Figure 7.7. This reaction is endothermic by 40.03 kcal/mol above that of the stabilized peroxy radical; but only 26.x kcal/mol above the newly formed – chemically activated peroxy radical.

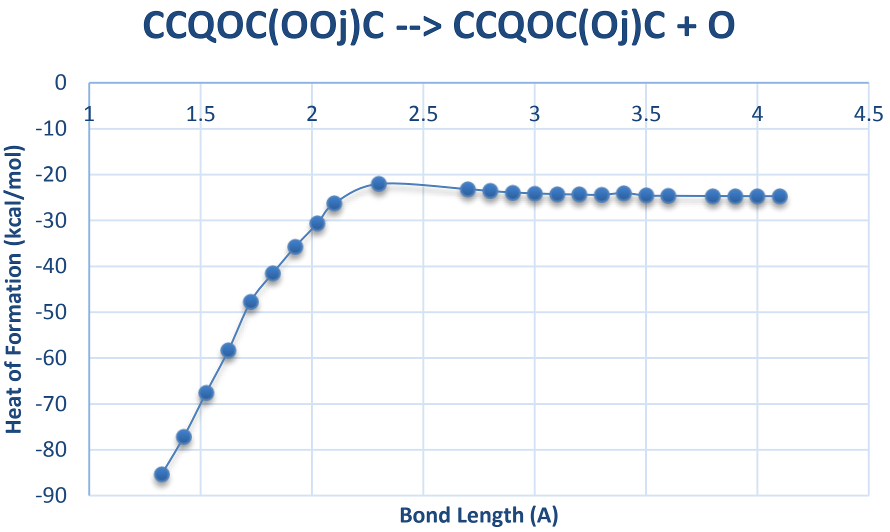


Figure 7.7 Energy Scan of CC(OOH)OC(OO•)C→ CC(OOH)OC(O---O•)C→ CCQOCO•C+O.

The CC(Oj)OC(=O) radical can undergo a beta scission reaction to eliminate a methyl radical and from a new carbonyl π bond. This reaction is CC(Oj)OC(=O) reacts to C(=O)OC(=O)C plus a CH_3. This reaction has a barrier of 14.7 kcal/mol. This reaction was what we would have liked to have seen to see if it were a reaction path that were possible if the formation of CC(Q)OC(=O)C was a dominate species. In Figure 7.7 is the saddle point transition state data that was used to determine the barrier of this path.

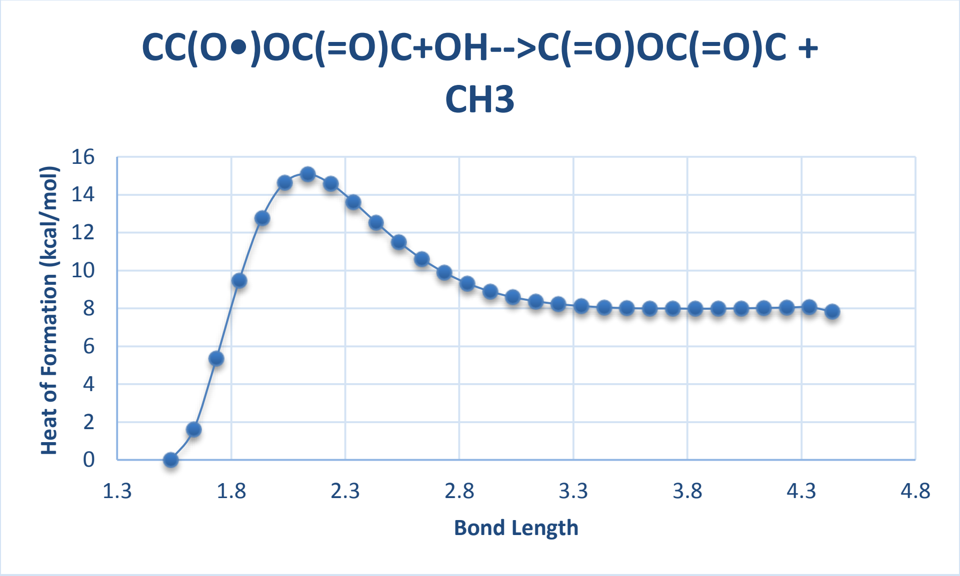


Figure 7.8 Energy scan of CC(O•)OC(=O)C→ CC(=O)OC(=O) + CH3

The secondary carbon was the most stable site for this hydrogen transfer from the carbon to the peroxy radical site to occur, based on calculations done for BDE's. This isomerization path with the lowest activation energy began with the abstraction of a hydrogen atom from the -CH_2- methylene group adjacent to the ether oxygen. The transition state in this reaction involves a six-membered ring and the reaction is only slightly endothermic by 8.9 kcal/mol. After this hydrogen transfer completed, the carbon radical could then decompose by forming a new π bond and eliminating the OH radical. These products lead to the formation of two acetaldehyde molecules.

Chemical activation reaction analysis on this system showed the following paths were important: for CC●OCC + O_2.

- Stabilization or peroxy radical CC(OO●)OCC
- Beta scission of C●CQOCC
- Intramolecular H transfer peroxy group OH elimination CC(OOH)OC•C

- Molecular Elimination CCQOC=C +HO_2

In the absence of further oxidation the formed CC(OOH)OC•C can undergo unimolecular dissociation. This occurrs when the CC•(OOH) molecule was formed after beta scission. In the presence of oxidation of CC(OOH)OC•C the main products were these reactions, CC(OOH)OC(=O)Ca + OH, CCQOC=Cb +HO_2 and CCQOC=Ca +HO_2. The main product was CC(OOH)OC(=O)Ca + OH from CC(OO•)OC(OOH)C. The next important product was elimination of HOI2 radicla (hydroperoxide radical) to CCQOC=Ca + HO_2 from C•C(OOH)OC(OOH)C. A third pathway was peroxy elimination, where a double bond was formed from CC(OO•)OC(OOH)C => CC(OOH)OC(=O)C + OH.

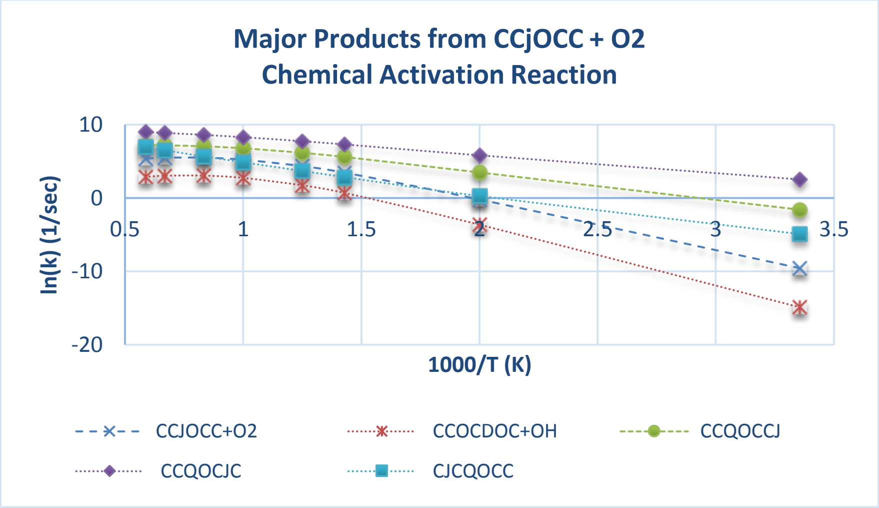


Figure 7.9 Chemical Activations of Dominant Species in CCjOCC Oxidation at 1 atm

In this study only the important species are illustrated shown; all other species concentrations are more than five orders of magnitude below the stabilized adduct. The di ethyl ether peroxy radical can dissociate into an ethyl radical plus an aldehyde, or to CCOC=C plus a hydrogen atom. The three main paths for this diethyl ether radical O2 system are β-scission, isomerization and OH elimination. These reactions occur via a hydrogen transfer from the secondary and primary carbons to the peroxy group.

Unimolecular Reaction of CC(OOH)OC•C

CC(OOH)OC•C dissociates in the absence of further reaction with a second O2, (oxidation) to two aldehydes and a hydroxyl radical. This occurs when the CC•(OOH) moiety on the molecule was formed after beta scission reaction: CC(OOH)OC•C => within the molecule and goes through a fast intermediate step in the presence of oxidation:

CC(OOH)OC•C = CC•(OOH) + CC(=O)

Then CC•(OOH) immediately dissociates to CC=O + OH

Reaction of CC(OOH)OC●C with second O_2

Molecular oxygen is present in high concentrations in combustion environments and in atmospheric chemistry. Under these common conditions the secondary radical CC(OOH)OC●C hydroperoxide will react with O2 via association, with no barrier, to form a hydroperoxide peroxy radical with the peroxy systems on the two secondary carbon sites CC(OOH)OCOO●C*. The * indicates that the adduct is initially formed energized, in this system with some 49.7 kcal mol^{-1} excess energy (relative to thermal conditions) from the new bond formed.

The study by S. Di Tommasso, has noted that CCOC(=O)C + OH is an important channel in liquid phase reactions. After completing a full mechanism of reaction, the data indicated that there are three reaction paths that are in the reaction.

The main products are CC(OOH)OC(=O)C + OH, formed by CC(OO•)OC(OOH)C. The next product was a hydroperoxy radical elimination form CCQOC=C + HO_2, which is formed via a beta scission reaction of the C•C(OOH)OC(OOH)C radical. The third and final pathway is ketone formation and OH elimination where a double bond was formed from CC(OO•)OC(OOH)C via an ipso intramolecular H atom transfer. Table 7.9 lists high-pressure limits for elementary rate parameters used as input data for the QRRK calculations at one atmosphere, and rate constants are reported.

Table 7.9 High Pressure-Limit Elementary Rate Parameters for Dominate Specie Formation

Reactions	k=A T^n exp$^{(-Ea/RT)}$			
	A(cm^{3}molecules^{-1} s^{-1})	n	Ea (kcal mol^{-1})	k (sec^{-1})*
CCQJOCC → CCJOCC+O2	3.55x10^{56}	-14.01	42.93	1.42 x10^{4}
CCQJOCC →CCOCDOC+OH	1.33 x10^{65}	-17.08	51.53	2.90 x10^{1}
CCQJOCC → CCQOCCJ	2.67 x10^{31}	-6.55	24.05	6.92 x10^{5}
CCQJOCC → CCQOCJC	2.13 x10^{21}	-3.23	15.81	4.30 x10^{7}
CCQJOCC → CJCQOCC	5.13 x10^{-2}	3.22	16.34	3.94 x10^{3}
CCQOCCJ → CCQJOCC	6.85 x10^{24}	-4.21	12.59	1.49 x10^{9}
CCQOCJC → CCQJOCC	1.32 x10^{35}	-7.33	17.00	1.58 x10^{9}
CJCQOCC → CCQJOCC	2.21 x10^{69}	-17.1	40.41	4.59 x10^{8}
CCQJOCQC → CCQOCJC + O2	5.88 x10^{48}	-11.75	25.45	5.07 x10^{7}
CCQJOCQC → CCQOCDOC^{A} + OH	1.01 x10^{45}	-10.42	22.81	3.33 x10^{8}
CCQJOCQC → CCQOCDOC^{B} + OH	4.08 x10^{63}	-17.33	42.59	4.64 x10^{1}
CCQJOCQC → CDCOCQC + HO2	7.83 x10^{63}	-17.48	44.19	1.19 x10^{1}
CCQJOCQC → CCQOCOJC + O	4.34 x10^{62}	-17.77	47.64	1.09 x10^{-2}
CCQJOCQC → CJCQOCQCB	2.42 x105	2.00	17.55	2.49 x106
CJCQOCQCA → CCQOCDCA + HO2	3.69 x1011	-0.31	2.87	7.65 x109
CJCQOCQC → YCOCOCQC + OH	4.44 x10-7	3.02	21.37	3.79 x10-4
CJCQOCQCA → CCQJOCQC	3.15 x10-51	16.4	10.38	1.87 x10-6
CJCQOCQCB → CCQOCDCB + HO2	1.00 x10-7	5.86	-3.67	1.04 x1011
CJCQOCQCB → CCQJOCQC	2.83 x10-9	5.19	15.57	1.84 x102
CCQJOCQC → CJCQOCQC^{A}	1.84 x10^{-5}	4.53	18.92	1.77 x10^{3}

*rate constant are observed at 800K and one atmosphere

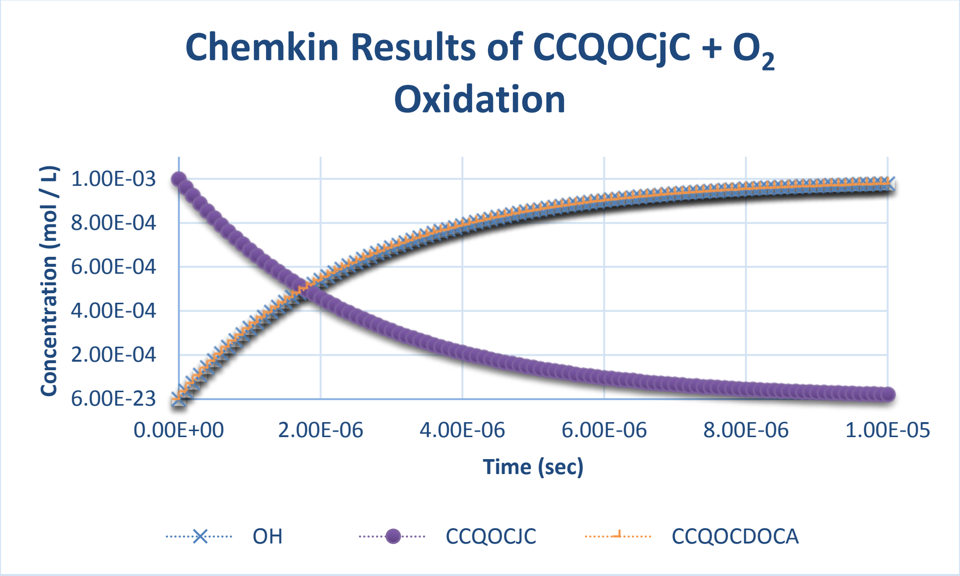


Figure 7.10 Chemkin Results of CCQOCjC + O2 oxidation at 800K and 1 atm.

7.6 Conclusion

The thermochemistry and reaction kinetics of diethyl ether, secondary diethyl ether peroxide, secondary diethyl ether hydroperoxide–secondary radical and secondary diethyl ether hydroperoxide– secondary peroxy radical have been studied. Reaction kinetics predicts that the secondary diethyl ether peroxy radical and the secondary diethyl ether hydroperoxide –secondary peroxy radical are important products from the oxidation reactions.

The mechanism suggests that ether oxidation in the atmosphere will also undergo this reaction set below. During the completion of this reaction, the formation of the CCQOCCj radical dominated the over the secondary bond radical, CCQOCjC.

Example:

$$\begin{array}{lll}
& CH_3CH_2OCH^{\bullet}CH_3 + O_2 & \rightarrow & CH_3CH_2OCH(OO^{\bullet})CH_3 \\
& CH_3CH^{\bullet}OCH(OOH)CH_3 & \rightarrow & CH_3CH{\bullet}OCH(OOH)CH_3 + O_2 \\
& CH_3CH{\bullet}OCH(OOH)CH_3 + O_2 & \rightarrow & CH_3CH(OO^{\bullet})OCH(OOH)CH_3 \\
& CH_3CH(OO^{\bullet})OCH(OOH)CH_3 & \rightarrow & [CH_3CH(OOH)OC{\bullet}(OOH)CH_3]^* \\
& [CH_3CH(OOH)OC^{\bullet}(OOH)CH_3]^* & \rightarrow & CH_3CH(OOH)OC(=O)CH_3 + OH \\
\hline
\textbf{Overall :} & \mathbf{CH_3CH_2OCH_2H_3 + OH + 2O_2} & \rightarrow & \mathbf{CH_3CH(OOH)OC(=O)CH_3 + OH}
\end{array}$$

(OH Regeneration)

Under some conditions, further reactions can occur from the chemically activated adduct formed by the O_2 association reactions, resulting in branching. Each O_2 association reaction initially forms a chemically activated adduct with ~ 32 kcal mol-1 energy from the new bond formed.

$CH_3CH(OOH)OC{\bullet}(=O)CH_3^*$ has approximately up to 50 kcal mol^{-1} activation energy from the transition state as it was formed. This energy was sufficient to dissociate the RCO—OH bond on the CO—OH hydroperoxide group, where only 45 kcal mol-1 was needed. Conditions for branching depend on temperature, pressure and rates of the intramolecular reactions above. Some of the energized $CH_3CH(OOH)OC(=O)CH_3^*$ will further dissociate to yield an alkoxy radical plus a second OH radical $CH_3CH(O^{\bullet})OC(=O)CH_3 + OH$ (chain branching). If this occurs in ethers as it does in ketones as Crounse indicates, the overall reaction was chain branching.

APPENDIX A

CALCULATION OF HEATS OF FORMATIONS AND BOND DISSOCIATION ENERGIES

This appendix contains sample calculations for enthalpies of formations, dH f298, and carbon hydrogen bond dissociation energies (C-H BDE). An example of the work reactions used to calculate the dHf298 for unknown target species, CFC(=O), is presented in Table A.1. These reactions relate the calculated energies for all four species to known literature dHf298 values for the non-targer species using Hess's Law, see equations 2.13 and 2.14. Due to the error cancelling in these isodesmic reactions, accurate dHf298 values are calculated.

Table A.1 Example of the Work Reactions Used to Calculate the dHf298 using CFC(=O)

Isodesmic Work Reaction	CFC(=OC)	+	CH4	>	CC(=O)	+	CH3F
H298 wb97x/6-31G(d,p) (Hartree)	-292.249		-40.457381		-193.028052		-139.673045
dHf_{298} (kcal mol^{-1})	X		-17.78		-52.23		-56.3
dH_{rxn} (kcal mol^{-1})	3.11						
dHf_{298} (kcal mol^{-1})	-93.86						

Bond Dissociation Reaction			CFC(=O)C	=	CjFC(=O)C	+	H
dHf_{298} (kcal mol^{-1})			-94.39		-57.47		52.10
C-H Bond Dissociation Energy (kcal mol-1)	89.02						

Based on the example in Table A.1, all of the species are first optimized using the same method and basis set, B3-LYP/6-31G(d,p). Enthalpies, H_{298}, are calculated in Gaussian 09 according to equations in A.1 as the sum of the total electronic energy, E, and thermal enthalpy corrections, H_{corr}, in units of Hatrees.

$$H_{298} = E + H_{Corr} \tag{A.1}$$

$$H_{Corr} = E_{Corr} + k_B T$$

$$E_{Corr} = E_{Trans} + E_{Rot} + E_{Vib} + E_{Elec} + E_{ZPVE}$$

H_{Corr} includes the sum of an energy correction, E_{Corr}, and the product of Boltzmann's constant and the temperature in Kelvin. E_{Corr} includes corrections from translational (E_{Trans}), rotational (E_{Rot}), vibrational (E_{Vib}), and electronic (E_{Elec}) motions along with the zero-point vibration energy (E_{ZPVE}). These quantities are derived from the molecular partition functions using standard statistical mechanics.

The difference in the H_{298} energies for the products and reactants, ΔH°_{rxn}, is calculated using Hess's Law and reported in units of kcal mol^{-1} using the conversion of one Hartree equal 627.509 kcal mol^{-1}. Combining the ΔH°_{rxn} with the known literature $\Delta H^{\circ}_{f\ 298}$ values generates the $\Delta H^{\circ}_{f\ 298}$ value for the target species.

The C–H bond dissociation reaction has the parent species and sets it equal to the radical and H atom. The difference between the literature $\Delta H^{\circ}_{f\ 298}$ value for the parent, CFC(=O)C, species and the H atom with the previously calculated $\Delta H^{\circ}_{f\ 298}$ value for radical, CjFC(=O)C, species determines the energy needed to remove a H atom from CFC(=O)C to generate CjFC(=O)C. Similar types of bond dissociation reactions can also be utilized to determine fluorine-carbon (C-F), oxygen-hydrogen (O–H) and oxygen-oxygen (O–O) BDEs.

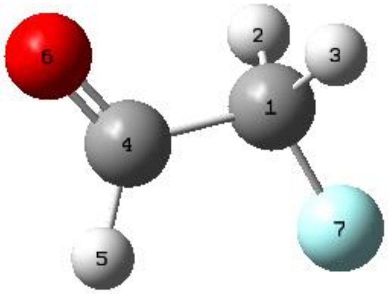
APPENDIX B

THERMOCHEMISTRY OF C2-C3 FLUOROALDEHYDES

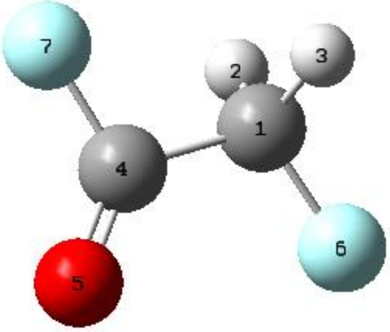
This appendix contains the optimized geometries with corresponding Gaussian atom numbering and symmetry values in parenthesis, moments of inertia, vibrational frequencies internal rotor potential energy graphs, entropies and heat capacities for all of the parent and radical species from B3-LYP/6-31G(d,p) level of theory.

Figure B.1 C2-C3 Fluoroaldehyde Optimized Species.

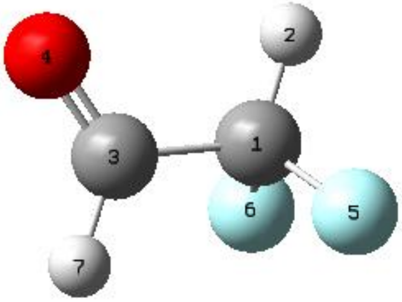
CFC(=O)



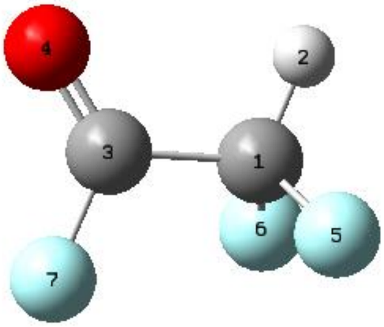
CFCF(=O)



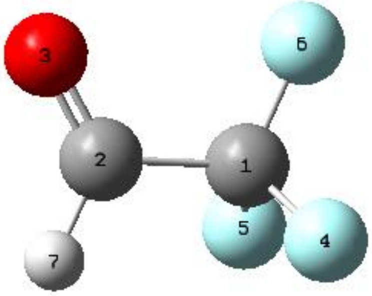
CF2C(=O)C



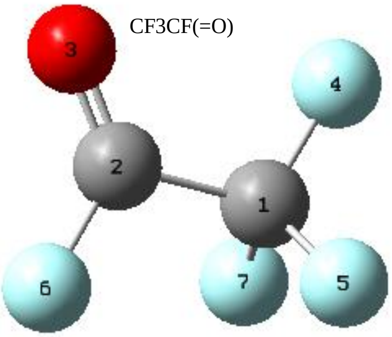
CF2CF(=O)



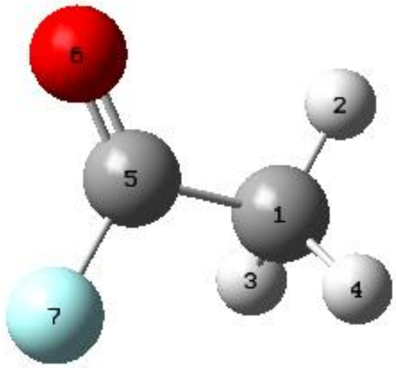
CF3C(=O)



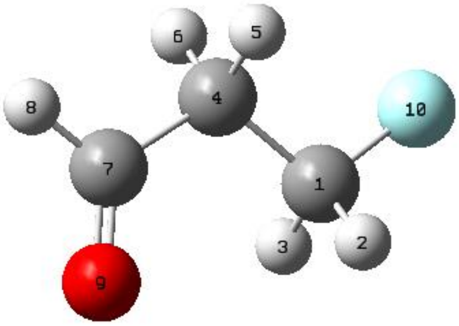
CF3CF(=O)



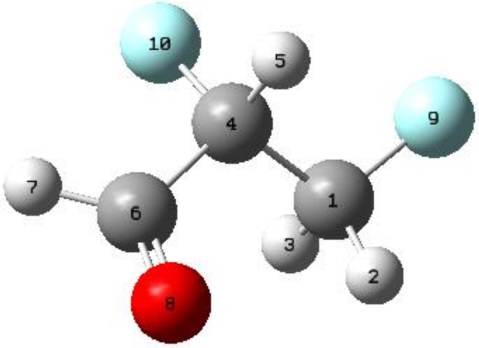
CCF(=O)



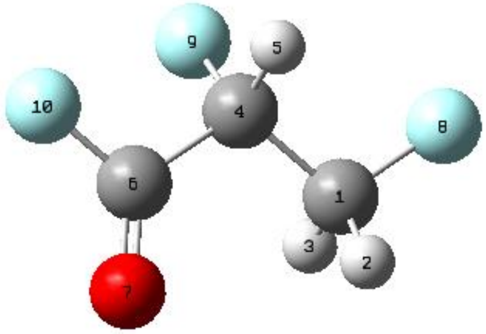
CFCC(=O)



CFCFC(=O)



CFCFCF(=O)



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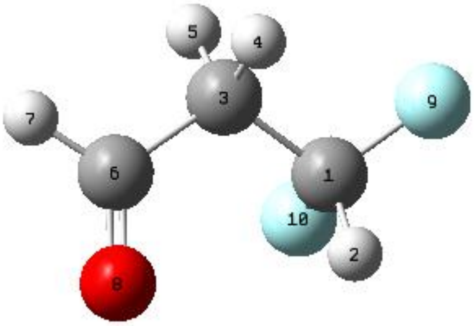
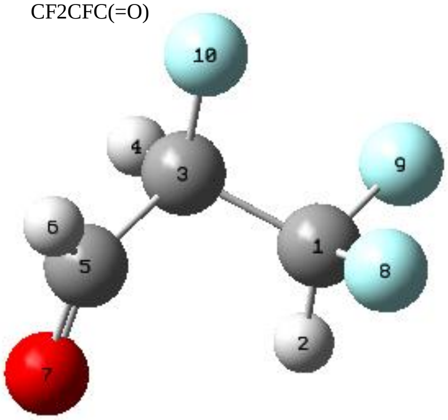


CF2CFC(=O)



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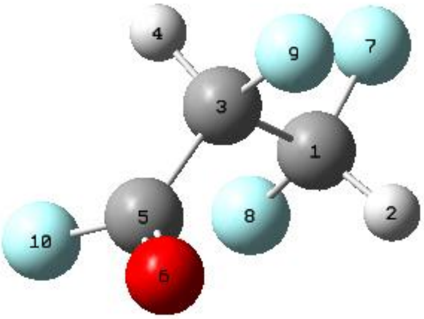

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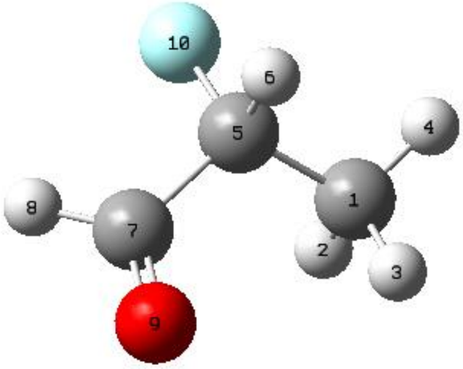

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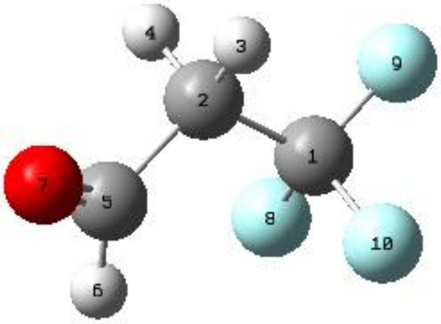
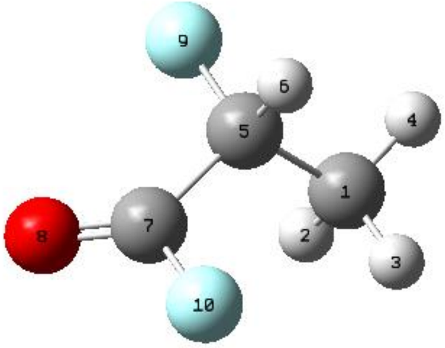
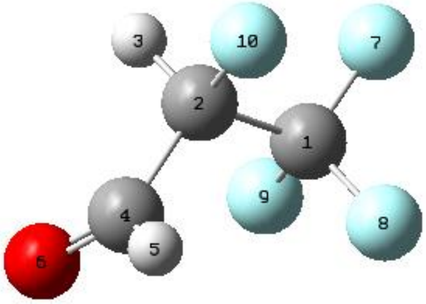


CCFCF(=O)



CF3CFC(=O)



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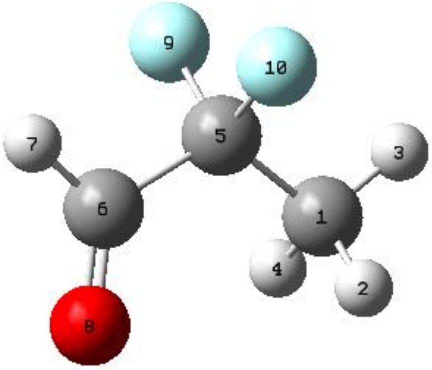
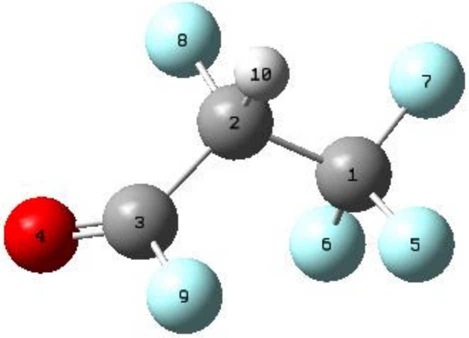
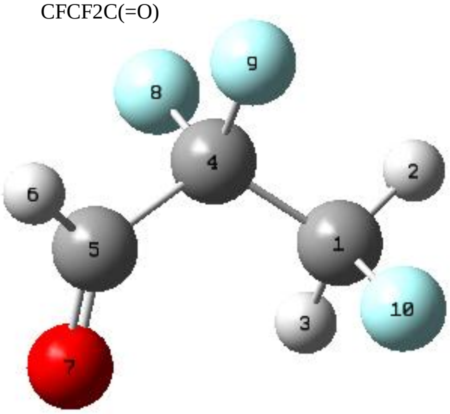


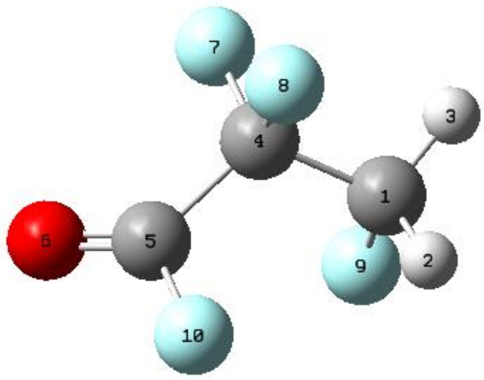
CF3CFCF(=O)



CFCF2C(=O)



CFCF2CF(=O)



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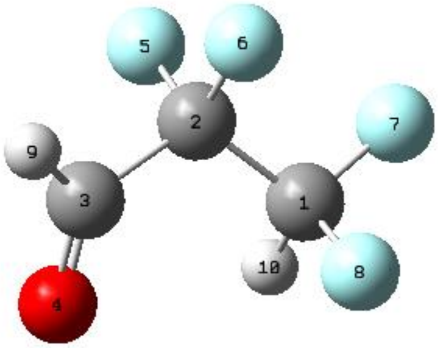

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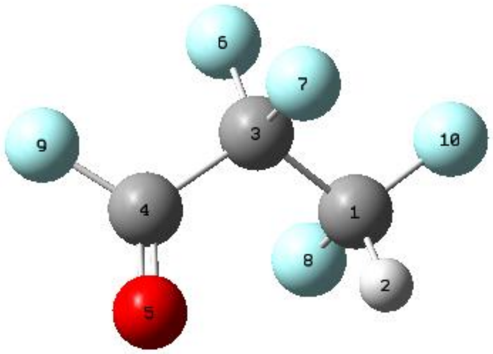

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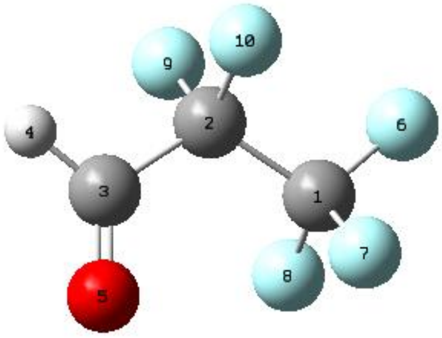

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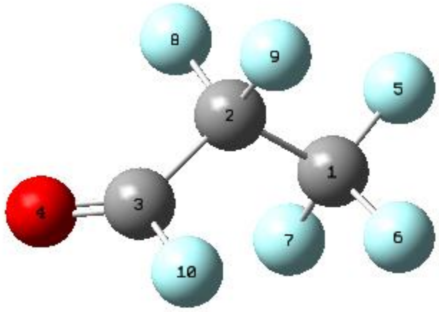
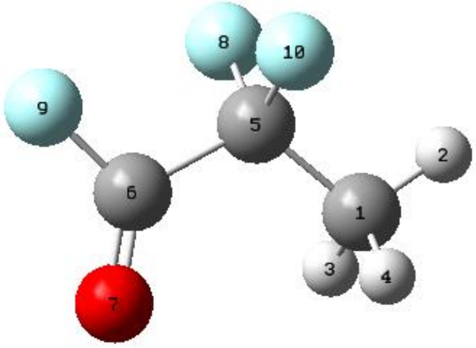
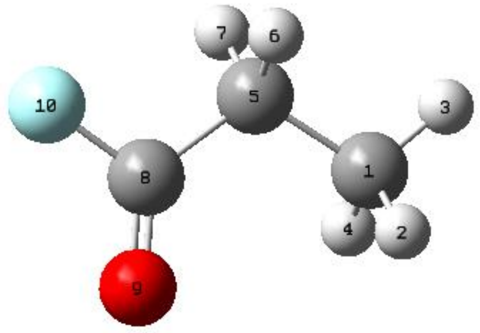


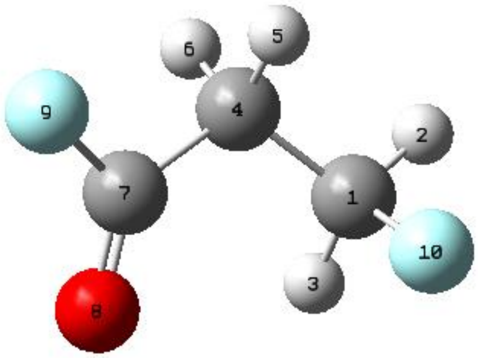
CCF2CF(=O)



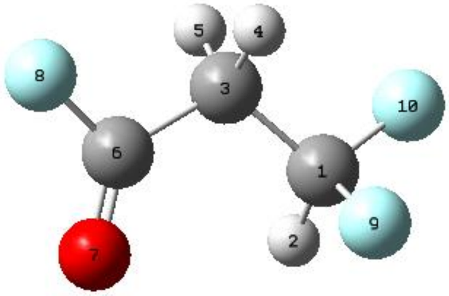
CCCF(=O)



CFCCF(=O)



CF2CCF(=O)



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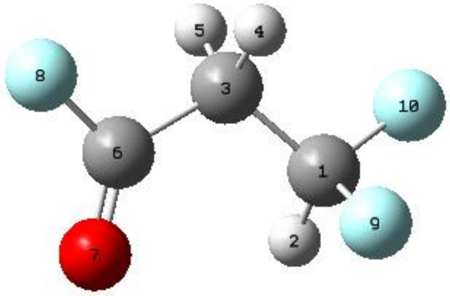


Table B.1: Moments of Inertia for Fluoroaldehydes

Species	Moments of Inertia (GHZ)		
CFC(=O)	40.69451	4.41395	4.08355
CFCF(=O)	10.91093	3.94734	2.95181
CF2C(=O)	9.68005	3.95909	3.08492
CF2CF(=O)	5.73793	2.80597	2.80313
CF3C(=O)	5.66731	3.07312	3.01687
CF3CF(=O)	3.98260	2.55667	2.11882
CCF(=O)	11.49155	9.84067	5.47903
CFCC(=O)	16.87791	2.61430	2.32803
CFCFC(=O)	5.77480	2.53469	1.85520
CFCFCF(=O)	4.55706	1.83842	1.41492
CF2CC(=O)	7.37794	2.33798	2.01134
CF2CFC(=O)	3.93944	2.04958	1.72469
CF2CFCF(=O)	3.07711	1.65727	1.21852
CF3CC(=O)	5.35362	1.62669	1.60961
CF3CFC(=O)	2.90282	1.85045	1.43482
CF3CFCF(=O)	2.51708	1.40953	1.12688
CCFC(=O)	8.56635	4.05910	2.94890
CCFCF(=O)	5.27786	3.20002	2.25663
CCF2C(=O)	5.06446	3.00024	2.85434
CFCF2C(=O)	2.95681	2.74330	1.96887
CFCF2CF(=O)	2.41497	1.92528	1.69376
CF2CF2C(=O)	2.70718	1.93897	1.54068
CF2CF2CF(=O)	2.55087	1.36083	1.17170
CF3CF2C(=O)	2.12827	1.69143	1.39693
CF3CF2CF(=O)	1.94992	1.19796	1.12894
CCF2CF(=O)	3.74784	2.50290	2.05666
CCCF(=O)	10.36711	3.80225	2.87904
CFCCF(=O)	7.39453	2.20490	1.97678
CF2CCF(=O)	5.67843	1.52158	1.35061
CF3CCF(=O)	4.06244	1.33103	1.21799

Table B.2 Vibrational Frequencies for Fluoroaldehydes

Species	Frequencies (cm^{-1})		
CFC(=O)	80.9110	353.5044	575.6218
	791.4528	1128.3223	1192.8684
	1230.0885	1364.8865	1469.5354
	1538.8532	1605.5402	2022.1571
	3131.7593	3222.3258	3278.3691
CFCF(=O)	126.9503	273.0645	497.3571
	595.8890	718.1166	968.4888
	1143.8357	1239.7364	1286.2801
	1384.2389	1574.5425	1611.2553
	2144.4897	3227.4037	3279.0402
CF2C(=O)	85.9190	357.2560	412.6740
	469.6095	667.4027	1091.3380
	1199.1611	1249.1458	1255.0447
	1454.1299	1516.0301	1550.3813
	2046.5086	3155.5491	3321.9441
CF2CF(=O)	52.5848	262.4294	269.5396
	454.8770	640.8866	781.1135
	859.3191	963.6748	1248.5328
	1266.4594	1424.4990	1526.6023
	1537.9290	2136.5095	3335.7959
CF3C(=O)	86.4237	280.7402	350.2083
	475.9267	581.5911	584.6993
	776.4381	929.9044	1096.8352
	1349.6493	1354.3947	1472.7534
	1534.0699	2066.8930	3178.7749
CF3CF(=O)	55.9016	249.6474	267.3353
	420.9664	472.2900	570.9096
	652.9081	769.6088	867.8604
	898.6149	1238.4066	1371.3055
	1426.5837	1520.1506	2165.2339
CCF(=O)	147.4358	444.8425	632.6635
	661.1312	929.6313	1106.0939
	1173.9561	1339.8275	1538.0897
	1584.5342	1592.9796	2106.7078
	3195.3137	3260.4224	3308.7473
CFCC(=O)	108.6714	181.2204	212.2706
	409.8286	741.6247	750.5973
	966.0733	972.8370	1156.9357
	1175.2648	1249.3811	1346.1389
	1417.4736	1452.9664	1532.9696
	1567.5805	1597.7975	1645.8836
	2002.1083	3106.3620	3174.3993
	3202.6802	3237.0391	3291.4187
CFCFC(=O)	96.1751	117.8265	224.6601
	303.7535	474.1930	501.3029
	657.7607	906.9080	998.3510
	1173.4184	1198.0524	1231.0776
	1240.8656	1392.7479	1423.4637
	1472.3062	1529.0479	1582.7467
	1628.4826	2017.9093	3147.9212
	3225.4701	3235.2547	3303.1950
CFCFCF(=O)	70.2423	104.5705	210.3643
	278.9885	377.0926	439.0884
	550.2939	702.2146	793.2839
	986.0543	1029.3148	1193.4790
	1215.0998	1245.3497	1309.9410
	1394.7045	1437.7782	1533.9400
	1581.2121	1630.6407	2142.8161
	3232.0470	3246.7299	3296.3855
CF2CC(=O)	85.1793	149.8506	192.0497
	384.8226	481.7624	607.8138
	755.1936	800.3721	985.4780
	1058.5662	1214.5140	1233.9101
	1257.2644	1356.0825	1452.5007
	1531.0965	1539.7573	1560.7114
	1601.9277	2011.9605	3117.8596
	3189.2051	3230.8313	3324.0705
CF2CFC(=O)	84.6467	95.9036	200.4461
	258.5658	296.7492	495.5229
	581.5826	634.9793	799.7785
	924.9229	1066.5922	1179.6994
	1229.5942	1261.8214	1306.0228
	1424.0912	1467.4472	1529.7207
	1545.3645	1569.4056	2021.3892
	3164.7189	3243.9762	3314.6932
CF2CFCF(=O)	51.1946	74.0282	167.0945
	279.2661	323.3382	407.1398
	437.6464	552.1380	638.0336
	755.1418	804.9914	1032.6011
	1196.7886	1241.6420	1256.7706
	1274.0751	1311.5515	1421.7937
	1503.8241	1546.9515	1584.7551
	2136.1135	3274.4616	3304.3918
CF3CC(=O)	62.0825	101.9330	197.1501
	377.9742	411.6575	484.7772
	584.0222	611.5726	721.1580
	835.1507	942.0397	1104.3043
	1139.1973	1272.3969	1320.1605
	1405.1629	1427.4284	1505.6213
	1556.0292	1583.5849	2020.1243
	3143.6784	3209.7550	3283.3948
CF3CFC(=O)	57.3057	86.6775	208.1261
	247.6503	300.2365	414.4298
	480.2010	561.4744	594.2733
	645.8385	751.2695	909.0886
	1092.8230	1173.7892	1237.2606
	1315.9042	1384.6762	1421.1799
	1442.5301	1516.3603	1545.3635
	2037.3844	3164.5077	3282.9028
CF3CFCF(=O)	38.5970	81.2312	169.2880
	244.2997	286.5265	372.2999
	394.0783	526.0405	573.9974
	610.6446	682.8970	744.3931
	835.8880	972.3753	1039.2857
	1261.6143	1289.3819	1344.1784
	1390.2820	1436.6669	1523.3631
	1540.4025	2150.3434	3265.8867
CCFC(=O)	65.5784	245.2440	277.0534
	414.9568	471.4170	601.4537
	907.5296	994.5346	1044.5308
	1207.7609	1248.4778	1252.2660
	1459.6891	1473.6573	1518.1420
	1540.9341	1602.3704	1615.1245
	2018.3475	3131.3482	3184.2264
	3214.5792	3256.3182	3272.1105
CCFCF(=O)	78.4428	241.3389	251.1340
	324.6343	424.1511	526.8933
	686.3301	801.4251	892.4670
	1012.6624	1157.4946	1219.9516
	1248.2172	1309.3182	1473.0061
	1527.1877	1543.3886	1606.2587
	1617.3779	2136.1288	3188.1696
	3233.8144	3265.6789	3273.4519
CCF2C(=O)	85.3491	238.5914	266.7975
	351.8649	433.7052	471.5802
	515.8687	682.4877	843.0871
	1050.0140	1073.2169	1102.7508
	1317.8568	1340.1504	1412.3004
	1516.0946	1566.9826	1596.1142
	1599.7511	2044.2916	3152.7101
	3202.1681	3282.4008	3289.8817
CFCF2C(=O)	75.2385	121.2151	204.1007
	300.9173	336.6148	459.0244
	485.7747	568.2499	692.9154
	878.3664	1056.0740	1092.6433
	1210.0692	1286.7111	1319.0158
	1391.5866	1435.7860	1516.1193
	1581.4716	1624.6406	2045.8338
	3165.9293	3248.4177	3317.7837
CFCF2CF(=O)	63.8129	95.4541	189.6795
	252.7954	307.7982	403.0838
	444.9668	546.8152	607.3049
	682.0203	849.8918	863.9917
	1059.5841	1206.5054	1224.1958
	1301.7264	1354.4088	1398.3512
	1480.4523	1572.5708	1630.8719
	2160.2813	3251.6971	3319.3515
CF2CF2C(=O)	79.5678	90.0723	174.1007
	259.8987	305.6763	334.3230
	460.0495	496.9107	584.6640
	689.7622	737.3403	919.0988
	1086.1314	1250.2055	1280.3854
	1296.9418	1346.4359	1397.4921
	1514.3214	1530.3475	1595.7524
	2044.7488	3173.7417	3334.1055
CF2CF2CF(=O)	33.8799	89.9720	164.8605
	249.8732	269.7622	306.6014
	381.9667	462.1437	480.2135
	628.0345	677.5649	799.4252
	865.8777	925.6357	1146.9885
	1266.2339	1293.4942	1307.9539
	1422.2792	1483.9980	1526.5563
	1587.6073	2132.8443	3335.0689
CF3CF2C(=O)	87.1247	90.2164	171.2316
	232.6790	305.8565	343.4726
	383.7516	468.4569	475.2054
	568.7991	648.1574	655.1868
	760.6276	853.7429	1093.5929
	1226.6504	1324.9745	1349.2037
	1394.6845	1409.7657	1492.1056
	1582.9557	2058.0692	3167.0577
CF3CF2CF(=O)	32.1450	72.9381	156.1501
	231.2411	262.0606	311.6665
	387.5731	407.5201	416.6027
	547.2245	596.8251	638.5379
	676.4608	776.1869	845.8088
	867.4686	1133.5149	1268.6175
	1381.9727	1396.4391	1402.6132
	1469.2971	1529.5588	2158.5699

CCF2CF(=O)	51.4505	242.9349	242.9799
	276.5560	380.3113	417.5332
	462.7157	622.6159	690.1334
	852.3901	865.6622	1020.7481
	1069.9125	1252.0833	1329.4806
	1377.1592	1478.3046	1564.2191
	1596.9990	1600.0226	2128.5533
	3205.2834	3287.7792	3293.5514
CCCF(=O)	90.6031	235.8660	263.0800
	496.8277	599.6573	683.5573
	879.4517	900.4962	1073.5209
	1181.8275	1215.5424	1262.8286
	1392.7585	1517.5467	1553.4983
	1583.4700	1611.1605	1618.6325
	2097.6360	3181.9013	3189.4301
	3218.1241	3249.1362	3257.4243
CFCCF(=O)	61.1457	119.0324	262.8466
	379.5423	552.9503	615.8726
	688.8207	898.1291	969.0256
	1085.6288	1180.6971	1203.2516
	1270.5240	1347.7980	1398.7367
	1533.1013	1570.4505	1574.0340
	1638.3646	2107.1946	3192.6688
	3231.9080	3249.7084	3291.3414
CF2CCF(=O)	61.0984	99.8766	179.3491
	379.3117	387.9549	566.4008
	592.2436	636.4366	732.9544
	984.1302	996.1282	1173.6414
	1210.8566	1256.1440	1297.1136
	1352.4854	1476.9122	1542.5019
	1570.2394	1603.1028	2106.8215
	3213.9802	3263.1369	3319.7586
CF3CCF(=O)	59.2603	106.3842	164.9540
	356.9108	378.1735	379.0010
	570.7080	583.2456	634.2291
	699.0596	776.9898	944.3462
	996.5488	1038.6657	1228.5571
	1275.8401	1355.3941	1423.7944
	1451.2143	1564.8185	1587.1008
	2127.1758	3228.2095	3274.9325

Trends in change in enthalpy with substitution of a fluorine atom for a hydrogen atom in fluorinated acetaldehydes and propanals

CC(=O) Primary methyl group only

The replacement of a hydrogen atom on the methyl group of acetaldehyde, $CH_3CH=O$, with a fluorine atom, results in a decrease in standard enthalpy of 40 kcal mol^{-1}. A second and a third fluorine atom substitution on this methyl group decrease the enthalpy by 50 and 55 kcal mol^{-1}, respectively.

Aldehyde => fluoroaldehyde $\Delta\ \Delta_f H^o_{298}$ H atom => F atom:

ch3cho => ch2fcho => chf2cho => cf3cho

-40 -50 -55

Compare to alkane fluorocarbons.

Alkane Fluorocarbons $\Delta\ \Delta_f H^o_{298}$ H atom => F atom:

ch3ch3 => ch2fch3 => chf2ch3 => cf3ch3

-45 -55 -59

The above trend shows that the addition of a fluorine atom to the primary methyl group ($-CH_3$) neighboring a carbonyl oxygen group results in a near consistent ~ 5 kcal mol^{-1} smaller decrease in enthalpy per fluorine for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon.

CCf(=O) Primary methyl group with fluorine on carbonyl

Substitution of a fluorine atom for a hydrogen on the carbonyl C(=O) carbon: the enthalpy of formation decrease is 66.1 kcal mol^{-1} from acetyl aldehyde to acetyl fluoride. From fluoroaldehyde to fluoroacetyl fluoride the enthalpy of formation decrease is 63.2 kcal mol^{-1}; the enthalpy of formation decreases to ~ 60.2 kcal mol^{-1} from difluoroaldehyde to difluoroacetyl fluorid and from trifluoroaldehyde to trifluoroacetyl fluoride.

Alkane fluorocarbons $\Delta\ \Delta_f H^o_{298}$ H atom => Fatom:

ch3ch3 => ch2f ch3 => chf2ch3 => cf3ch3

-45. -55. -59.

Acetyl fluoride and fluoro acetyl fluorides

Aldehydes Ch3cho => ch3cfo => ch2fcfo => chf2cfo => cf3cfo

-66.1 -63.2 -60.1 -60.4

Propanal to 3-fluoropropanal … 3,3 tri fluoro propanal

CCC(=O) Primary methyl group only

Substitution of a fluorine for a hydrogen on a primary methyl (CH_3-) group of propanal to 3fluoropropanal, the enthalpy of formation decreases 43.0 kcal mol^{-1}; from 3-fluoropropanal to 3,3-difluoropropanal the enthalpy of formation decreases 53.7 kcal mol^{-1}; from 3,3-difluoropropanal to 3,3,3-trifluoropropanal the enthalpy of formation decreases 40.7 kcal mol^{-1}.

Alkane fluorocarbons $\Delta\,\Delta_f H^o_{298}$ H atom => Fatom:

ch3ch2ch3 => ch2fch2ch3 => chf2ch2ch3 => cf3ch2ch3
-46. -55.6 -59.7

Propanal =>fluoropropanal $\Delta_f H^o_{298}$ H atom => F atom:

ch3ch2cho => ch2fch2cho => chf2ch2cho => cf3ch2cho
-43.0 -53.7 -40.7

The addition of a fluorine atom to the primary methyl group (-CH3) neighboring a secondary methyl group (-CH2-) bonded to a carbonyl group results in a consistent ~ 2-4 kcal mol^{-1} smaller lowering of enthalpy per fluorine for hydrogen substitution for the first two substitutions, relative to a fluorine atom substitution on an alkane carbon. The third addition of a fluorine atom shown for 3,3-difluoropropanal to 3,3,3-trifluoropropanal shows a significantly smaller decrease.

Substitution of a fluorine atom for a hydrogen on the carbonyl C(=O) carbon for 3 fluoro, 3,2 di fluoro and 3,3 tri fluoro propanoyl fluorides

The enthalpy of formation decrease is 66.3 kcal mol^{-1} from propanal to propanoyl fluoride. From propanoyl fluoride to 3-propanoyl fluoride the enthalpy of formation decrease is 42.4 kcal mol^{-1}; the enthalpy of formation decreases 53.6 kcal mol^{-1} from 3-propanoyl fluoride to 3,3-dipropanoyl fluoride; from 3,3-dipropanoyl fluoride to 3,3,3-tripropanoyl fluoride, the enthalpy of formation decreases 55.8 kcal mol^{-1}.

Alkane fluorocarbons $\Delta\,\Delta_f H$ H atom => F atom:

ch3ch2ch3 => ch2f ch2ch3 => chf2 ch2ch3 => cf3 ch2ch3
46.7 -55.6 -59.7
Ch3ch2cho => Ch3ch2cfo => ch2fch2cfo => chf2ch2cfo => cf3ch2cfo
-66.3 -42.4 -53.6 -55.8

The above trend shows that the addition of a fluorine atom to the carbonyl group is consistent to values reported in the fluorine addition in fluoroaldehyde to fluoroacetyl fluoride with a decrease of enthalpy of formation of ~66 kcal mol^{-1}. The addition of a fluorine atom to the primary methyl group (-CH3) bond to a carbonyl oxygen group results in a near consistent ~2-4 kcal mol^{-1} smaller, lowering of enthalpy per fluorine for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon.

Substitution of an F atom on the secondary carbon of propanal

Substitution of a fluorine for a hydrogen on the secondary methyl ($-CH_2-$) group of propanal: the enthalpy of formation decreases 45.5 kcal mol^{-1}; from 2-fluoropropanal to 2,2-fluoropropanal the enthalpy of formation decreases 53.5 kcal mol^{-1}.

Alkane fluorocarbons $\Delta\,\Delta_f H$ H atom => Fatom:

ch3ch2ch3 => ch3chfch3 => ch3cf2ch3
-46.4 -58.0

Propanal =>fluoropropanal $\Delta \Delta_f H$ H atom => Fatom:

ch3ch2cho => ch3chfcho => ch3cf2cho
-45.5 -53.5

The above trend shows that the addition of a fluorine atom to the secondary methyl group (-CH2-) bond to a carbonyl oxygen and primary methyl group results in a near consistent ~1 kcal mol^{-1} smaller lowering of enthalpy for one fluorine atom being substituted for a hydrogen and ~4 kcal mol^{-1} for two fluorine atoms being present for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon.

Substitution of a fluorine atom for a hydrogen on the carbonyl C(=O) carbon of propanal

The enthalpy of formation decrease is 66.3 kcal mol^{-1} from propanal to propanoyl fluoride. From propanoyl fluoride to 2-propanoyl fluoride the enthalpy of formation decrease is 42.4 kcal mol^{-1}; the enthalpy of formation decreases 53.6 kcal mol^{-1} from 2-propanoyl fluoride to 2,2-dipropanoyl fluoride.

Alkane fluorocarbons $\Delta \Delta_f H$ H atom => Fatom:

ch3ch2ch3 => ch3chfch3 => ch3cf2ch3
-46.4 -58.0

Ch3ch2cho => Ch3ch2cfo => ch3chfcfo => ch3cf2cfo
-66.3 -41.9 -51.3

The above trend shows that the addition of a fluorine atom to the carbonyl group is consistent to values reported in the fluorine addition in fluoroaldehyde to fluoroacetyl fluoride and propanal to propanoyl fluoride, with a decrease of enthalpy of formation of ~66 kcal mol^{-1}. The addition of a fluorine atom to the secondary methyl group (-CH2-) bond to a carbonyl oxygen group results in an enthalpy of formation 4.5 kcal mol^{-1} smaller when one fluorine is bond to the secondary methyl group and 6.7 kcal mol^{-1} smaller when two fluorine atoms are bonded to the same group, relative to a fluorine atom substitution on an alkane carbon.

2-fluoropropanal and 2,3-difluoropropanal and substitution of a fluorine for a hydrogen on a primary methyl (CH_3-) group of 2-fluoropropanal: the enthalpy of formation decreases 40.7 kcal mol^{-1}; from 2,3-difluoropropanal to 2,3,3-trifluoropropanal the enthalpy of formation decreases 51.2 kcal mol^{-1}; from 2,3,3-trifluoropropanal to 2,3,3,3-tetrafluoropropanal the enthalpy of formation decreases 38.6 kcal mol^{-1}.

Alkane fluorocarbons $\Delta \Delta_f H$ H atom => Fatom:

ch3chfch3 => ch2fchfch3 => chf2chfch3 => cf3chfch3
-34.5 -54.9 -56.4

Propanal =>fluoropropanal Δ Δ_fH H atom => Fatom:

ch3chfcho => ch2fchfcho => chf2chfcho => cf3chfcho

-40.7 -51.2 -38.6

The above trend shows that the addition of a fluorine atom to the primary methyl group (CH3-) bond to a secondary methyl group with a fluorine atom bond (-CHF-) present results in a consistent trend as observed in the primary fluorine-hydrogen substitution on the primary methyl group is ~6 kcal mol^{-1} smaller lowering the enthalpy for one fluorine atom being substituted for a hydrogen and ~4 kcal mol^{-1} for two fluorine atoms being present for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon. Fully saturated primary group has a decrease of ~18 4 kcal mol^{-1}.

Substitution of a fluorine atom for a hydrogen on the carbonyl C(=O) carbon: the enthalpy of formation decrease is 62.7 kcal mol^{-1} from 2-fluoropropanal to 2-propanoyl fluoride. From 2-propanoyl fluoride to 2,3-dipropanoyl fluoride: the enthalpy of formation decreases 39.7 kcal mol^{-1}; from 2,3-dipropanoyl fluoride to 2,3,3-trifluoropropanoyl fluoride the enthalpy of formation decreases 50.5 kcal mol^{-1}; from 2,3,3-trifluoropropanoyl fluoride to 2,3,3,3-tetrapropanoyl fluoride the enthalpy of formation decreases 39.9 kcal mol^{-1}.

Alkane fluorocarbons Δ Δ_fH H atom => Fatom:

ch3chfch3 => ch2fchfch3 => chf2chfch3 => cf3chfch3

-34.5 -54.9 -56.4

ch3chfco => ch3chfcfo => ch2fchfcfo => chf2chfcfo => cf3chfcfo

-62.7 -39.7 -50.5 -39.9

The above trend shows that the addition of a fluorine atom to the carbonyl group is consistent to values reported in the fluorine addition is similar to other species, with a decrease of enthalpy of formation of ~63 kcal mol^{-1}. The addition of a fluorine atom to the secondary methyl group (-CHF-) bond to a carbonyl oxygen group results in an enthalpy of formation of ~5 kcal mol^{-1} smaller for the substitution of one or two fluorine atoms on the primary methyl group and ~16 kcal mol^{-1} smaller when two fluorine atoms are bond to the same group, relative to a fluorine atom substitution on an alkane carbon.

2,2-difluoropropanal and 2,2,3-trifluoropropanal and substitution of fluorine for hydrogen on the primary methyl (CH_3-) group of 2,2-difluoropropanal: the enthalpy of formation decreases 38.4kcal mol^{-1}; from 2,2,3-trifluoropropanal to 2,2,3,3-tetrafluoropropanal the enthalpy of formation decreases 49.3 kcal mol^{-1}; from 2,2,3,3-tetrafluoropropanal to 2,2,3,3,3-pentafluoropropanal the enthalpy of formation decreases 99.8 kcal mol^{-1}.

Alkane fluorocarbons Δ Δ_fH H atom => Fatom:

ch3cf2ch3 => ch2fcf2ch3 => chf2cf2ch3 => cf3cf2ch3

41.8 -53.0 -51.2

Propanal => fluoropropanal Δ Δ_fH H atom => Fatom:

ch3cf2cho => ch2fcf2cho => chf2cf2cho => cf3cf2cho

-38.4 -49.3 -99.8

The above trend shows that the addition of a fluorine atom to the primary methyl group (CH3-) bond to a secondary methyl group with two fluorine atoms bond (-CF2-) present results in a consistent trend as observed in the primary fluorine-hydrogen substitution on the primary methyl group is ~3 kcal mol^{-1} smaller lowering the enthalpy for one fluorine atom being substituted for a hydrogen and ~4 kcal mol^{-1} for two fluorine atoms being present for hydrogen substitution, relative to a fluorine atom substitution on an alkane carbon. Fully saturated primary and secondary methyl groups has an observed decrease of ~45 kcal mol^{-1} in comparison to the corresponding fluoroalkane.

Substitution of a fluorine atom for a hydrogen on the carbonyl C(=O) carbon: the enthalpy of formation decrease is 60.9 kcal mol^{-1} from 2,2-difluoropropanal to 2,2-dipropanoyl fluoride. From 2,2-dipropanoyl fluoride to 2,2,3-tripropanoyl fluoride: the enthalpy of formation decreases 38.1 kcal mol^{-1}; from 2,2,3-tripropanoyl fluoride to 2,2,3,3-tetrapropanoyl fluoride the enthalpy of formation decreases 47.9 kcal mol^{-1}; from 2,2,3,3-tetrapropanoyl fluoride to 2,2,3,3,3-pentapropanoyl fluoride the enthalpy of formation decreases 54.8 kcal mol^{-1}.

Alkane fluorocarbons Δ Δ_fH H atom => Fatom:

ch3cf2ch3 => ch2fcf2ch3 => chf2cf2ch3 => cf3cf2ch3

-41.8 -53.0 -51.2

ch3cf2cho => ch3cf2cfo => ch2fcf2cfo => chf2chfcfo => cf3chfcfo

-60.9 -38.1 -47.9 -54.8

The above trend shows that the addition of a fluorine atom to the carbonyl group is consistent to values reported in the fluorine addition is similar to other species, with a decrease of enthalpy of formation of ~61 kcal mol^{-1}.

The addition of a fluorine atom to the secondary methyl group (-CH2-) bonded to a carbonyl oxygen group results in an enthalpy of formation of ~5 kcal mol^{-1} lower for the substitution of one or two fluorine atoms on the primary methyl group and ~16 kcal mol^{-1} lower when two fluorine atoms are bond to the same group, relative to a fluorine atom substitution on an alkane carbon.

Table B.3 Change in Enthalpy of formation Compared to Parent Hydrocarbons CH3CH(=O) and CH3CH2CH(=O) upon substitution of fluorine atoms for hydrogen atoms

Species	$\Delta H^{\circ}_{f\ 298}$ (kcal/mol)[a]	Difference Calculated from Corresponding Nonfluorinated Species	Difference Calculated from Substituting Carbon-Hydrogen Bond with a Carbon-Fluorine Bond
CFCH(=O)	-80.4	-40.7 [a]	-40.7[a]
CF2CH(=O)	-130.0	-90.3 [a]	-49.6[c]
CF3CH(=O)	-185.4	-145.7 [a]	-55.4[d]
CCFH(=O)	-105.8	-66.1 [a]	-66.1[a]
CFCFH(=O)	-143.6	-103.9 [a]	-63.2[c]
CF2CFH(=O)	-190.1	-150.4 [a]	-60.1[d]
CF3CFH(=O)	-245.8	-206.1 [a]	-60.4[e]
CFCCH(=O)	-87.4	-43.1 [b]	-43.1[b]
CF2CCH(=O)	-141.1	-96.7 [b]	-53.6[f]
CF3CCH(=O)	-198.9	-154.5 [b]	-57.8[g]
CCFCH(=O)	-89.9	-45.6 [b]	-89.9[b]
CCF$_2$CH(=O)	-143.4	-99.0 [b]	-53.4[h]
CFCFCH(=O)	-129.0	-84.6 [b]	-41.5[f]
CFCF2CH(=O)	-181.4	-137.0 [b]	-38.0[i]
CF2CFCH(=O)	-181.8	-137.4 [b]	-40.7[g]
CF3CFCH(=O)	-220.4	-176.1 [b]	-21.6[e]
CF2CF2CH(=O)	-262.5	-218.1 [b]	-80.7[j]
CF3CF2CH(=O)	-330.5	-286.1 [b]	-110.0[k]
CCCF(=O)	-203.9	-159.5 [b]	-159.5[b]
CFCCF(=O)	-110.7	-66.3 [b]	-23.2[f]
CF2CCF(=O)	-153.1	-108.7 [b]	-12.0[g]
CF3CCF(=O)	-206.7	-162.4 [b]	-7.9[e]
CCFCF(=O)	-152.6	-108.3 [b]	-62.7[h]
CCF2CF(=O)	-344.7	-300.4 [b]	-201.4[k]
CFCFCF(=O)	-192.3	-147.9 [b]	-63.3[i]
CF2CFCF(=O)	-235.7	-191.3 [b]	-53.9[j]
CF3CFCF(=O)	-282.5	-238.1 [b]	-62.1[k]
CFCF2CF(=O)	-242.0	-197.7 [b]	-60.6[l]
CF2CF2CF(=O)	-230.7	-186.3 [b]	31.8[m]
CF3CF2CF(=O)	-289.9	-245.5 [b]	40.6[n]

a represents acetaldehyde, b propanal, c represents fluoroacetaldehyde, d represents difluoroacetaldehyde, e represents 3,3,3-trifluoropropanal, f represents 3-fluoropropanal, g represents 2,2-difluoropropanal, h represents 2-fluoropropanal, i represents 2,3-difluoropropanal, j represents 2,3,3-trifluoropropanal, k represents 2,2,3-trifluoropropanal, l represents 2,2,3,3-tetrafluoropropanal, m represents 2,2,3,3-tetrapropanoyl fluoride, n represents 2,2,3,3,3-pentafluoropropanal. molecules excluded from the calculation.

Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes

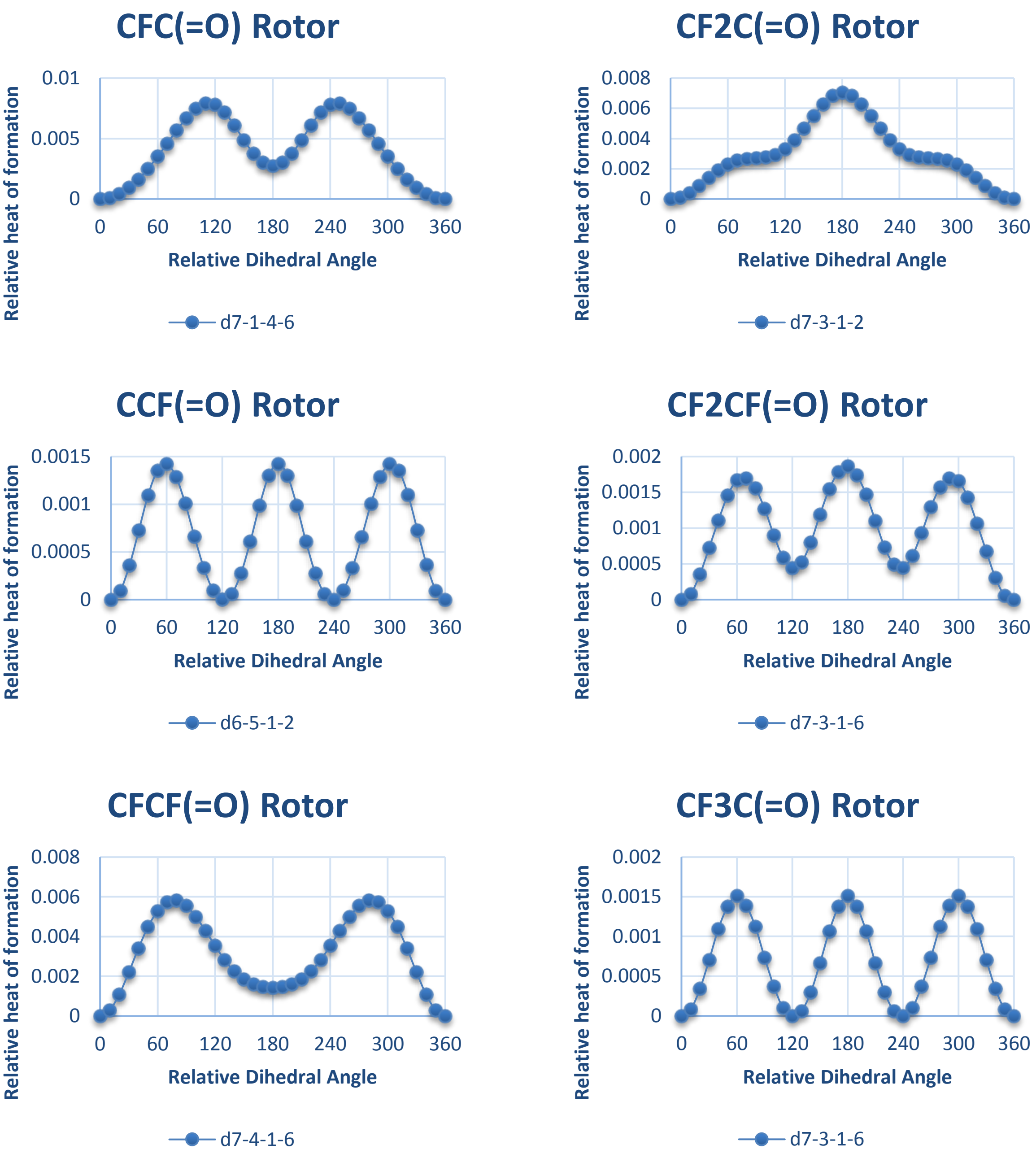


Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)

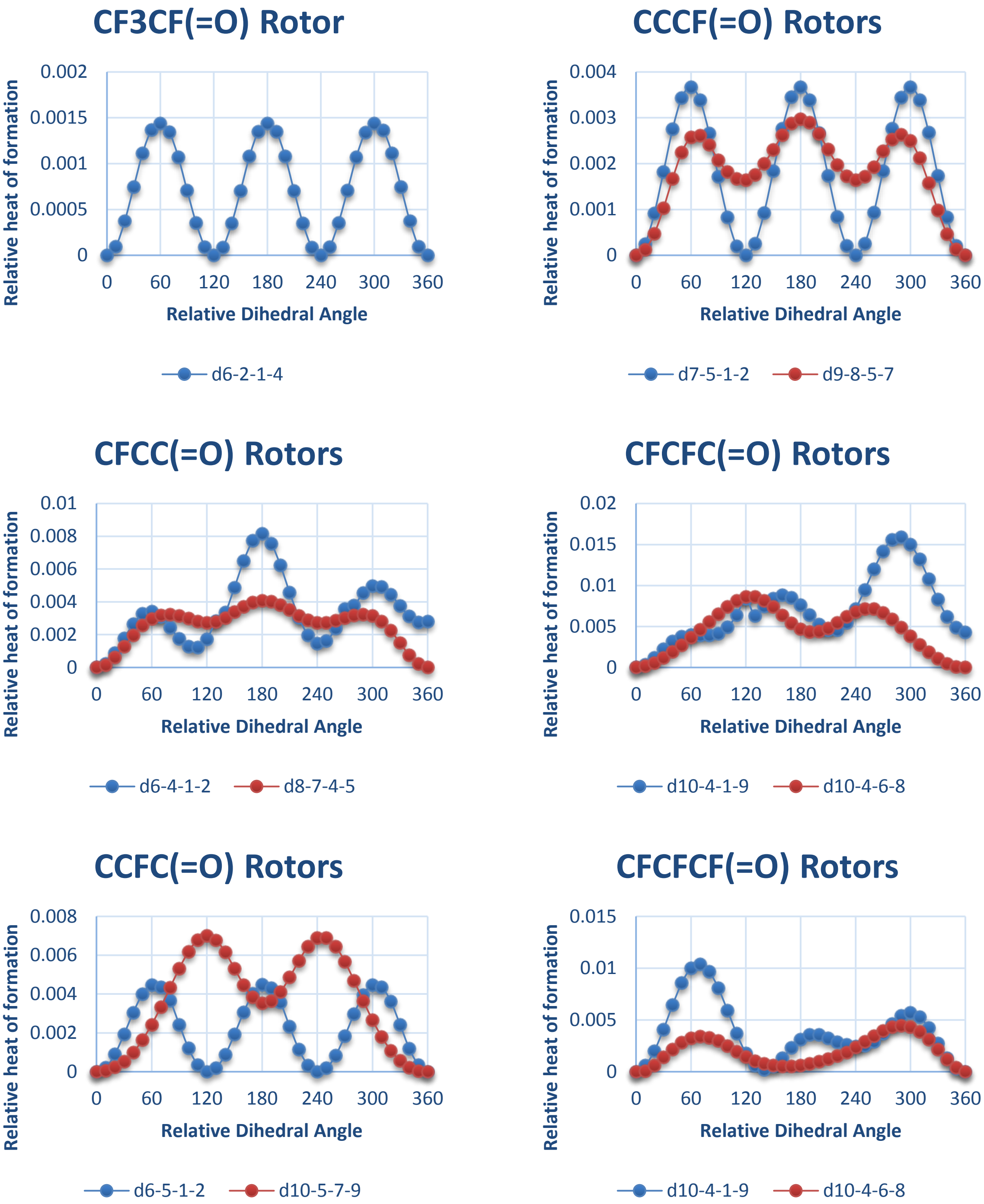
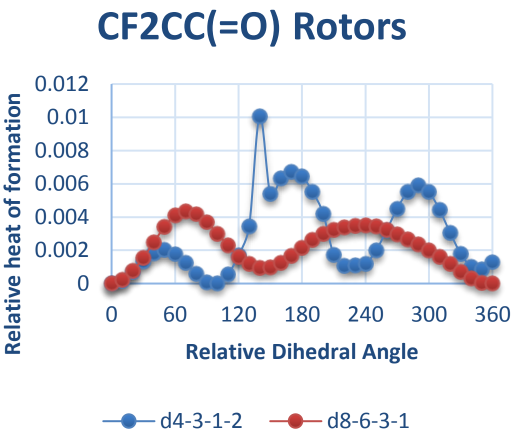
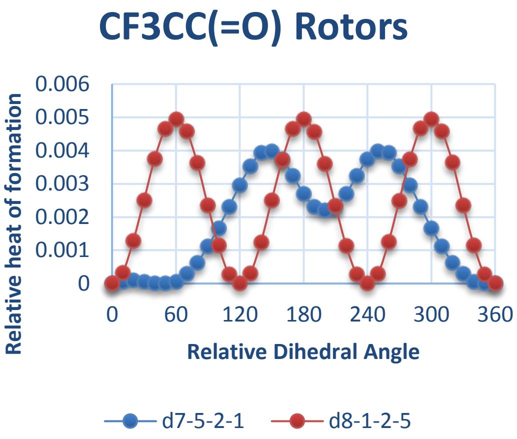
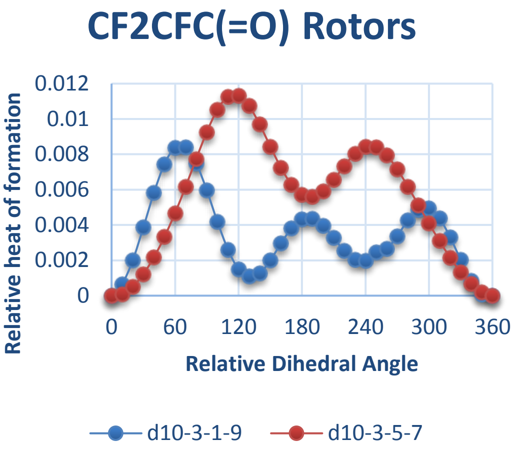
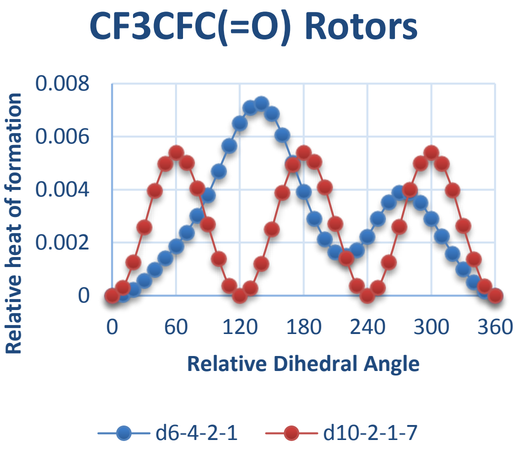


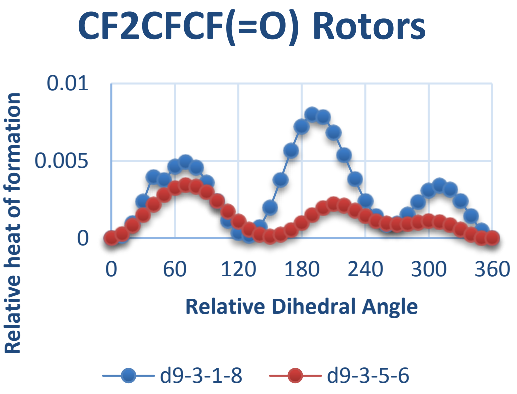
Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)











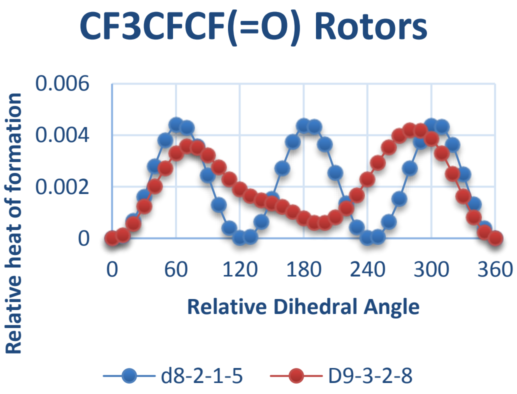


Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)

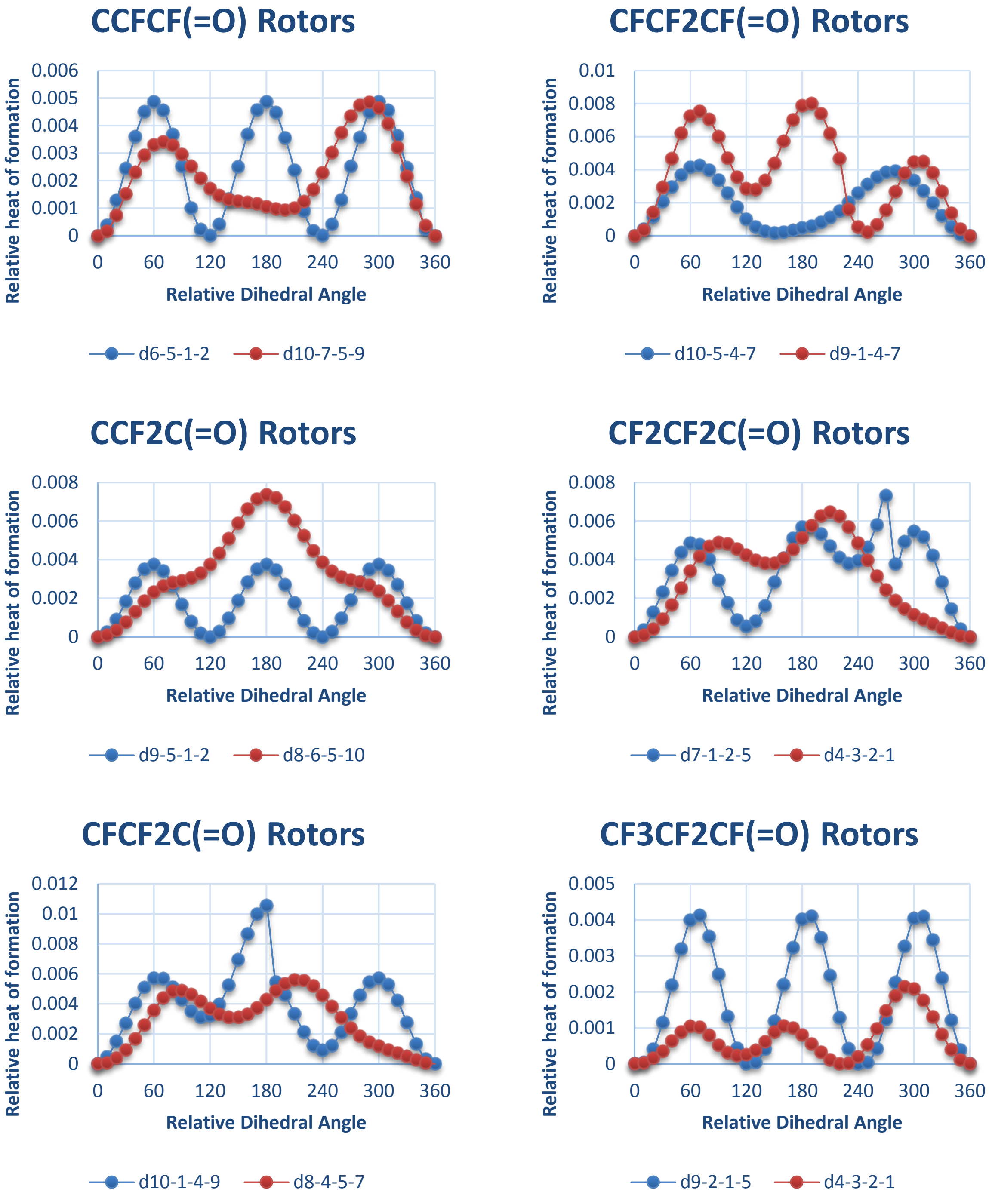


Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)

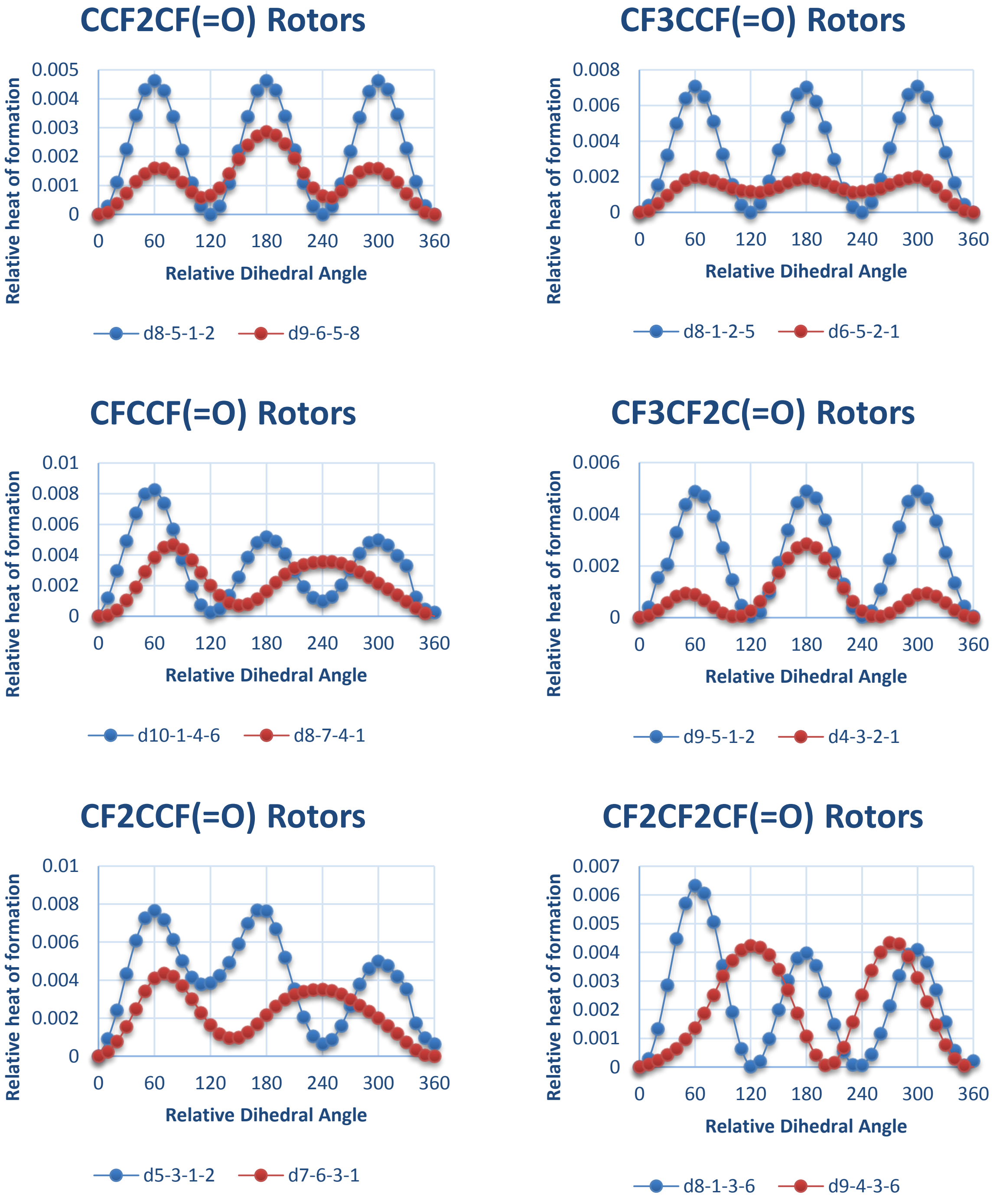


Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)

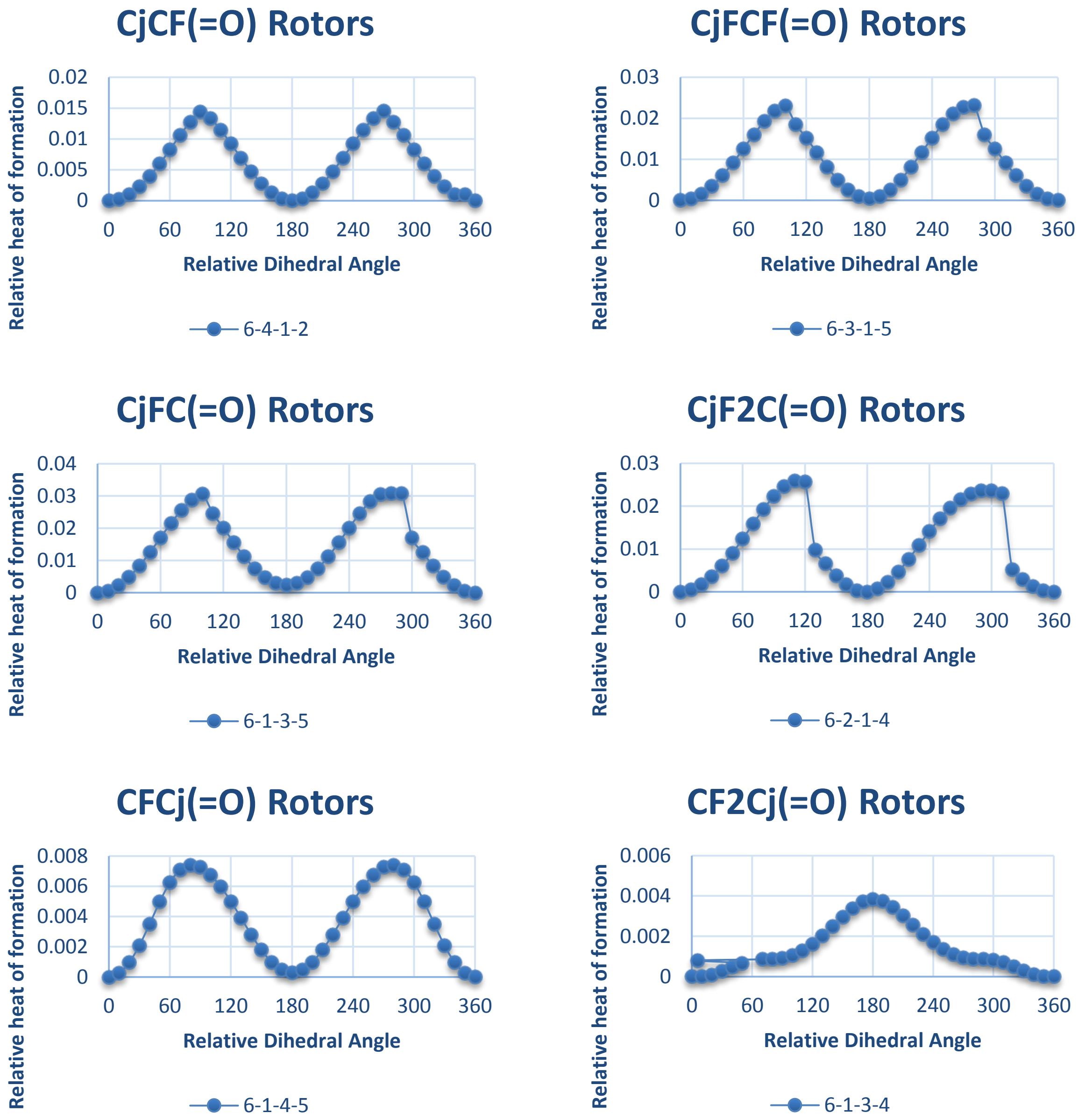
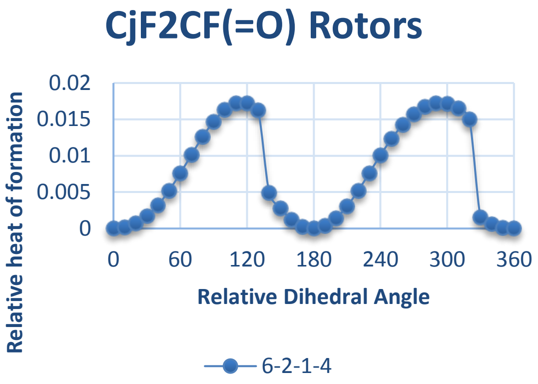


Figure B.2 Potential Energy Profiles of C2-C3 Fluoroaldehydes (Continued)



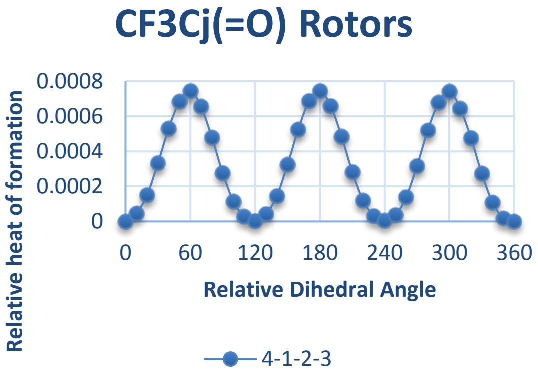


Table B.4 Isodesmic Reactions Calculations for Fluoroaldehydes

CF2CF2CF(=O)							**mo62x**	**m06**	**wb97x**	**b3plyp**	**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**G-2**	**G-3**	**G-4**	**W1U**
CF2CF2CF(=O)	+	C(=O)	=	CF2CF2C(=O)	+	CF(=O)	-287.15	-287.47	-286.52	-286.47	-286.85	-286.11	-287.13	-287.78	-287.77	-289.17	-287.2
CF2CF2CF(=O)	+	CH4	=	CF2CF2C(=O)	+	CH3F	-287.54	-288.59	-287.7	-286.48	-286.62	-288.06	-290.34	-289.04	-289.01	-293.06	-289.42
CF2CF2CF(=O)	+	CC	=	CF2CF2C(=O)	+	CFC	-288.04	-288.76	-287.91	-286.92	-287.26	-288.15	-290.15	-289.63	-289.63	-293.29	-289.68
CF2CF2CF(=O)	+	CFCFC(=O)	=	CF2CF2C(=O)	+	CFCFCF(=O)	-287.26	-287.48	-287.37	-287.13	-287.02	-285.96	-287.11	-287.6	-287.6	-287.84	-287.24
CF3CF2CF(=O)																	
CF3CF2CF(=O)	+	CH2F2	=	CF2CF2CF(=O)	+	CHF3	-342.4	-342.35	-341.76	-341.76	-341.38	-341.93	-342.29	-342.05	-342.05	-343.99	-342.25
CF3CF2CF(=O)	+	CCCF2	=	CF2CF2CF(=O)	+	CF3CC	-341.13	-341	-340.78	-341.11	-340.4	-338.61	-341.67	-341.07	-341.07	-343.04	-341.76
CF3CF2CF(=O)	+	CF2C(=O)	=	CF2CF2CF(=O)	+	CF3C(=O)	-345.37	-345.29	-345.14	-345.26	-345.17	-345.01	-345.62	-345.7	-345.71	-346.44	-345.56
CF3CF2C(=O)																	
CF3CF2C(=O)	+	CFC(=O)	=	CF2CFCF(=O)	+	CFCF(=O)	-330.84	-329.41	-329.03	-328.1	-331.85	-334.63	-327.88	-334.81	-334.81	-330.18	-327.56
CF3CF2C(=O)	+	CF2C(=O)	=	CF2CFCF(=O)	+	CF2CF(=O)	-330.13	-328.61	-328.28	-327.52	-331.26	-334.73	-327.43	-333.51	-333.51	-328.72	-326.9
CF3CF2C(=O)	+	CC(=O)	=	CF2CFCF(=O)	+	CCF(=O)	-330.47	-329.2	-328.3	-327.72	-331.18	-332.66	-328.16	-334.14	-334.14	-331.25	-327.87
CF3CF2C(=O)	+	CFCFC(=O)	=	CF2CFCF(=O)	+	CFCFCF(=O)	-330.53	-329.17	-328.77	-327.72	-331.74	-334.18	-327.47	-334.48	-334.48	-329.42	-327.13
CCF2CF(=O)																	
CCF2CF(=O)	+	CFC(=O)	=	CCF2C(=O)	+	CFCF(=O)	-202.19	-202.13	-202.2	-201.92	-201.96	-201.82	-201.66	-202.71	-202.7	-202.68	-201.88
CCF2CF(=O)	+	CF2C(=O)	=	CCF2C(=O)	+	CF2CF(=O)	-201.48	-201.32	-201.44	-201.34	-201.37	-201.92	-201.21	-201.41	-201.41	-201.22	-201.22
CCF2CF(=O)	+	CC(=O)	=	CCF2C(=O)	+	CCF(=O)	-201.82	-201.91	-201.46	-201.54	-201.29	-199.85	-201.94	-202.04	-202.04	-203.75	-202.19
CCF2CF(=O)	+	CFCFC(=O)	=	CCF2C(=O)	+	CFCFCF(=O)	-201.88	-201.88	-201.94	-201.54	-201.85	-201.37	-201.24	-202.38	-202.37	-201.92	-201.45
CCCF(=O)																	
CCCF(=O)	+	C(=O)	=	CCC(=O)	+	CF(=O)	-108.89	-109.05	-108.59	-108.4	-109.38	-111.04	-108.26	-109.54	-109.53	-108.44	-108.16
CCCF(=O)	+	CH4	=	CCC(=O)	+	CH3F	-109.28	-110.17	-109.77	-108.42	-109.16	-112.99	-111.47	-110.81	-110.77	-112.33	-110.38
CCCF(=O)	+	CC	=	CCC(=O)	+	CFC	-109.78	-110.34	-109.98	-108.85	-109.8	-113.08	-111.29	-111.4	-111.39	-112.56	-110.64

Table B.4 Isodesmic Reactions Calculations for Fluoroaldehydes (continued)

CFCCF(=O)							**mo62x**	**m06**	**wb97x**	**b3plyp**	**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**G-2**	**G-3**	**G-4**	**W1U**
CFCCF(=O)	+	C(=O)	=	CCCF(=O)	+	CF(=O)	-151.62	-151.07	-150.9	-151.9	-152.27	-150.83	-149.96	-151.12	-151.12	-149.36	-150.37
CFCCF(=O)	+	CH4	=	CCCF(=O)	+	CH3F	-152.02	-152.2	-152.08	-151.91	-152.05	-152.78	-153.16	-152.38	-152.36	-153.25	-152.59
CFCCF(=O)	+	CC(=O)	=	CCCF(=O)	+	CCF(=O)	-151.67	-151.11	-151.28	-152.56	-151.88	-149.16	-150.64	-150.6	-150.61	-149.86	-151.14
CF2CCF(=O)																	
CF2CCF(=O)	+	CFC(=O)	=	CFCCF(=O)	+	CFCF(=O)	-204.42	-203.46	-204.03	-203.99	-205.16	-206.21	-203.07	-205.69	-205.69	-202.77	-203.00
CF2CCF(=O)	+	CC(=O)	=	CFCCF(=O)	+	CFC(=O)	-204.56	-204.31	-204.07	-203.34	-204.49	-206.65	-205.13	-205.94	-205.95	-206.45	-204.62
CF2CCF(=O)	+	CCC(=O)	=	CF2CC(=O)	+	CCCF(=O)	-205.41	-205.44	-205.32	-205.38	-205.22	-204.43	-205.65	-205.37	-205.38	-206.1	-205.74
CF2CCF(=O)	+	CCF(=O)	=	CCCF(=O)	+	CF2CF(=O)	-205.53	-205.71	-205.63	-205.41	-205.72	-209.37	-204.97	-204.68	-204.68	-203.2	-204.8
CF3CCF(=O)																	
CF3CCF(=O)	+	CCC(=O)	=	CF3CC(=O)	+	CCCF(=O)	-261.84	-261.21	-261.56	-261.54	-261.76	-261.23	-262.24	-262	-262.01	-263.11	-262.19
CF3CCF(=O)	+	CC(=O)	=	CF3CC(=O)	+	CCF(=O)	-260.66	-260.17	-260.41	-260.48	-260.64	-260.48	-261.06	-260.91	-260.91	-261.93	-261.01
CF3CCF(=O)	+	C(=O)	=	CF3CC(=O)	+	CF(=O)	-260.61	-260.14	-260.03	-259.83	-261.02	-262.15	-260.38	-261.42	-261.42	-261.43	-260.23
CF2CF2C(=O)																	
CF2CF2C(=O)	+	CFCC(=O)	=	CFCF2C(=O)	+	CF2CC(=O)	-229.21	-229.3	-228.99	-229.01	-228.99	-227.97	-229.09	-229.68	-229.69	-230.41	-229.42
CF2CF2C(=O)	+	CH3F	=	CFCF2C(=O)	+	CH2F2	-229.36	-229.65	-228.93	-228.72	-228.73	-229.66	-229.17	-229.96	-229.96	-231.06	-229.22
CF2CF2C(=O)	+	CFC(=O)	=	CFCF2C(=O)	+	CF2C(=O)	-229.44	-229.92	-229.15	-228.91	-229.16	-230.06	-228.9	-229.74	-229.73	-230.16	-229.25
CF2CF2C(=O)	+	CFCF(=O)	=	CFCF2C(=O)	+	CF2CF(=O)	-228.74	-229.12	-228.39	-228.33	-228.57	-230.16	-228.45	-228.44	-228.44	-228.7	-228.59
CjCF(=O)																	
CjCF(=O)	+	CH4	=	CCF(=O)	+	CH3J	-59.50	-60.00	-59.99	-60.74	-58.53	-62.49	-60.92	-59.44	-59.42	-61.49	-60.76
CjCF(=O)	+	CC	=	CCF(=O)	+	CJC	-59.80	-58.77	-59.58	-60.22	-60.18	-64.28	-60.30	-60.90	-60.90	-60.85	-60.06
CjCF(=O)	+	CCCC	=	CCF(=O)	+	CJCCC	-59.93	-59.43	-58.87	-59.93	-59.89	-64.10	-60.02	-60.65	-60.64	-60.58	-59.79
CjFC(=O)																	
CjFC(=O)	+	CH3F	=	CFC(=O)	+	CJH2F	-44.36	-45.17	-44.31	-45.61	-44.17	-51.34	-45.49	-45.12	-45.12	-46.33	-45.66
CjFC(=O)	+	CFC	=	CFC(=O)	+	CJFC	-43.54	-43.63	-43.29	-44.30	-44.13	-51.57	-44.68	-44.74	-44.74	-45.20	-44.51
CjFC(=O)	+	CFCF	=	CFC(=O)	+	CJFCF	-42.26	-42.58	-41.86	-42.63	-43.74	-51.28	-43.37	-44.29	-44.29	-44.30	-43.21
CjFC(=O)	+	CF2CF	=	CFC(=O)	+	CF2CJF	-45.77	-46.18	-45.30	-46.11	-46.81	-55.00	-46.73	-47.26	-47.27	-47.31	-46.50
CjFC(=O)	+	CF3CF	=	CFC(=O)	+	CF3CJF	-46.74	-47.21	-46.16	-46.96	-47.64	-56.17	-47.46	-47.94	-47.94	-47.89	-47.25

Table B.4 Isodesmic Reactions Calculations for Fluoroaldehydes (continued)

			CFCj(=O)				**mo62x**	**m06**	**wb97x**	**b3plyp**	**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**G-2**	**G-3**	**G-4**	**W1U**
CFCj(=O)	+	C(=O)OH	=	CFC(=O)	+	Cj(=O)OH	-42.19	-41.84	-42.02	-42.02	-41.59	-39.07	-42.18	-41.19	-41.19	-42.00	-42.07
CFCj(=O)	+	CC(=O)	=	CFC(=O)	+	CCj(=O)	-41.86	-41.78	-41.76	-42.16	-40.71	-38.93	-42.26	-40.39	-40.39	-42.74	-42.44
CFCj(=O)	+	CC=C	=	CFC(=O)	+	CCj=C	-40.72	-37.93	-40.90	-40.75	-33.72	-30.11	-41.50	-32.59	-32.60	-41.71	-41.34
CFCj(=O)	+	CCC(=O)	=	CFC(=O)	+	CCCj(=O)	-41.94	-41.82	-41.73	-42.05	-40.72	-39.20	-42.43	-40.33	-40.34	-42.81	-42.50
			CjFCF(=O)														
CjFCF(=O)	+	CH3F	=	CFCF(=O)	+	CJH2F	-103.80	-104.72	-104.01	-105.01	-101.72	-105.54	-104.60	-102.67	-102.67	-105.45	-104.84
CjFCF(=O)	+	CFC	=	CFCF(=O)	+	CJFC	-102.98	-103.18	-102.99	-103.70	-101.67	-105.77	-103.80	-102.29	-102.29	-104.31	-103.69
CjFCF(=O)	+	CFCF	=	CFCF(=O)	+	CJFCF	-101.70	-102.13	-101.56	-102.03	-101.28	-105.48	-102.49	-101.83	-101.84	-103.42	-102.39
CjFCF(=O)	+	CF2CF	=	CFCF(=O)	+	CF2CJF	-105.21	-105.73	-105.00	-105.51	-104.35	-109.20	-105.85	-104.81	-104.81	-106.42	-105.68
CjFCF(=O)	+	CF3CF	=	CFCF(=O)	+	CF3CJF	-106.18	-106.76	-105.86	-106.36	-105.18	-110.37	-106.58	-105.49	-105.49	-107.01	-106.43
			CjF2C(=O)														
CjF2C(=O)	+	CF2C	=	CF2C(=O)	+	CJF2C	-91.56	-93.38	-91.10	-92.17	-89.70	-99.26	-93.27	-89.85	-89.84	-94.97	-93.52
CjF2C(=O)	+	CF2CF	=	CF2C(=O)	+	CJF2CF	-89.95	-91.80	-89.23	-90.11	-89.24	-100.05	-91.57	-89.59	-89.59	-93.20	-91.50
CjF2C(=O)	+	CF2CF2	=	CF2C(=O)	+	CJF2CF2	-94.70	-96.54	-93.97	-94.85	-93.68	-104.96	-96.33	-93.82	-93.82	-97.60	-96.21
			CF2Cj(=O)														
CF2Cj(=O)	+	C(=O)OH	=	CF2C(=O)	+	Cj(=O)OH	-90.34	-90.15	-90.02	-89.87	-90.28	-88.43	-90.25	-90.60	-90.59	-90.60	-90.17
CF2Cj(=O)	+	CC(=O)	=	CF2C(=O)	+	CCj(=O)	-90.00	-90.09	-89.76	-90.01	-89.40	-88.29	-90.33	-89.81	-89.80	-91.34	-90.54
CF2Cj(=O)	+	CC=C	=	CF2C(=O)	+	CCj=C	-88.87	-86.25	-88.90	-88.60	-82.40	-79.47	-89.57	-82.01	-82.01	-90.31	-89.43
CF2Cj(=O)	+	CCC(=O)	=	CF2C(=O)	+	CCCj(=O)	-90.09	-90.13	-89.73	-89.90	-89.41	-88.56	-90.50	-89.75	-89.74	-91.41	-90.59
			CjF2CF(=O)														
CjF2CF(=O)	+	CF2C	=	CF2CF(=O)	+	CJF2C	-148.01	-149.98	-147.92	-148.90	-144.64	-150.67	-149.99	-144.11	-144.55	-150.64	-149.98
CjF2CF(=O)	+	CF2CF	=	CF2CF(=O)	+	CJF2CF	-146.41	-148.40	-146.05	-146.84	-144.18	-151.45	-148.29	-143.85	-144.29	-148.86	-147.97
CjF2CF(=O)	+	CF2CF2	=	CF2CF(=O)	+	CJF2CF2	-151.16	-153.14	-150.79	-151.58	-148.62	-156.36	-153.05	-148.09	-148.52	-153.26	-152.68

Table B.4 Isodesmic Reactions Calculations for Fluoroaldehydes (continued)

CF3Cj(=O)							mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
CF3Cj(=O)	+	C(=O)OH	=	CF3C(=O)	+	Cj(=O)OH	-144.93	-144.60	-144.91	-144.64	-144.72	-141.83	-144.89	-145.13	-145.12	-145.18	-144.77
CF3Cj(=O)	+	CC(=O)	=	CF3C(=O)	+	CCj(=O)	-144.59	-144.54	-144.65	-144.79	-143.84	-141.69	-144.96	-144.33	-144.33	-145.92	-145.14
CF3Cj(=O)	+	CC=C	=	CF3C(=O)	+	CCj=C	-143.46	-140.70	-143.79	-143.37	-136.85	-132.87	-144.21	-136.53	-136.54	-144.89	-144.03
CF3Cj(=O)	+	CCC(=O)	=	CF3C(=O)	+	CCCj(=O)	-144.68	-144.58	-144.62	-144.67	-143.85	-141.96	-145.13	-144.27	-144.28	-145.99	-145.19

Table B.5 Entropy and Heat Capacities for Fluoroaldehyde Species

Species	**$S°_{298}$**	**C_P300**	**C_P 400**	**C_P 500**	**C_P 600**	**C_P 800**	**C_P 1000**	**C_P 1500**	**Rotors**
CF2CF2CF(=O)	87.79	27.70	32.52	36.56	39.81	44.44	47.40	51.27	
	8.52	0.99	0.99	0.99	0.99	0.99	0.99	0.98	
	8.22	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	104.53	**29.69**	**34.51**	**38.55**	**41.80**	**46.43**	**49.39**	**53.24**	
CF3CF2CF(=O)	90.72	30.22	35.36	39.41	42.56	46.85	49.44	52.58	
	8.80	0.99	0.99	0.99	0.99	0.99	0.99	0.93	
	8.28	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	107.80	**32.21**	**37.35**	**41.40**	**44.55**	**48.84**	**51.42**	**54.50**	
CF3CF2C(=O)	85.80	28.35	33.23	37.22	40.40	44.90	47.78	51.50	
	8.70	0.99	0.99	0.99	0.99	0.99	0.99	0.95	
	7.38	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	101.88	**30.34**	**35.22**	**39.21**	**42.39**	**46.89**	**49.76**	**53.44**	
CCF2CF(=O)	78.96	23.86	28.45	32.40	35.69	40.63	44.07	49.08	
	5.77	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.03	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	92.75	**25.85**	**30.44**	**34.39**	**37.68**	**42.62**	**46.06**	**51.07**	
CCCF(=O)	71.25	18.99	23.22	27.19	30.67	36.23	40.36	46.73	
	5.77	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	7.62	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	84.64	**20.98**	**25.21**	**29.18**	**32.66**	**38.22**	**42.35**	**48.72**	
CFCCF(=O)	76.03	20.45	24.90	29.00	32.53	38.00	41.91	47.75	
	7.97	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	8.12	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	92.12	**22.44**	**26.89**	**30.99**	**34.52**	**39.99**	**43.90**	**49.74**	
CF2CCF(=O)	79.85	22.63	27.29	31.43	34.90	40.12	43.72	48.91	
	8.42	0.99	0.99	0.99	0.99	0.99	0.99	0.98	
	8.17	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	96.44	**24.62**	**29.28**	**33.42**	**36.89**	**42.11**	**45.71**	**50.89**	

[a] Units cal mol-1 K-1. [b] No rotors. Use of torsion frequencies for rotor contributions without reduction (correction) in entropy for equivalent hydrogen atoms in CH3 groups. [c] Only methyl rotors. [d] All internal rotors.

Table B.5 Entropy and Heat Capacities for Fluoroaldehyde Species (Continued)

Species	**S°_{298}**	**C_P300**	**C_P 400**	**C_P 500**	**C_P 600**	**C_P 800**	**C_P 1000**	**C_P 1500**	**Rotors**
CF3CCF(=O)	82.43	25.04	30.05	34.24	37.62	42.51	45.75	50.20	
	8.63	0.99	0.99	0.99	0.99	0.99	0.99	0.96	
	8.25	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	99.31	**27.03**	**32.04**	**36.23**	**39.61**	**44.50**	**47.74**	**52.15**	
CF2CF2C(=O)	83.44	25.82	30.41	34.39	37.68	42.51	45.75	50.20	
	8.46	0.99	0.99	0.99	0.99	0.99	0.99	0.98	
	7.41	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
	99.31	**27.81**	**32.40**	**36.38**	**39.67**	**44.50**	**47.74**	**52.18**	
CJFC(=O)	**64.98**	**14.60**	**17.10**	**19.27**	**21.06**	**23.73**	**25.57**	**28.26**	
CJCF(=O)	**64.75**	**15.05**	**17.79**	**19.94**	**21.62**	**24.06**	**25.75**	**28.28**	
CFCJ(=O)	**65.87**	**14.37**	**16.80**	**18.93**	**20.70**	**23.40**	**25.30**	**28.11**	
CJFCF(=O)	**70.59**	**16.93**	**19.62**	**21.74**	**23.39**	**25.71**	**27.22**	**29.28**	
CJF2C(=O)	**70.71**	**16.84**	**19.36**	**21.46**	**23.16**	**25.60**	**27.19**	**29.32**	
CF2CJ(=O)	**72.33**	**16.77**	**19.30**	**21.39**	**23.07**	**25.47**	**27.06**	**29.22**	
CJF2CF(=O)	**76.37**	**19.52**	**22.05**	**24.01**	**25.53**	**27.60**	**28.85**	**30.35**	
CF3CJ(=O)	**75.64**	**19.40**	**22.18**	**24.24**	**25.77**	**27.79**	**28.99**	**30.41**	
CJFC(=O)	**64.98**	**14.60**	**17.10**	**19.27**	**21.06**	**23.73**	**25.57**	**28.26**	

[a] Units cal mol-1 K-1. [b] No rotors. Use of torsion frequencies for rotor contributions without reduction (correction) in entropy for equivalent hydrogen atoms in CH3 groups. [c] Only methyl rotors. [d] All internal rotors.

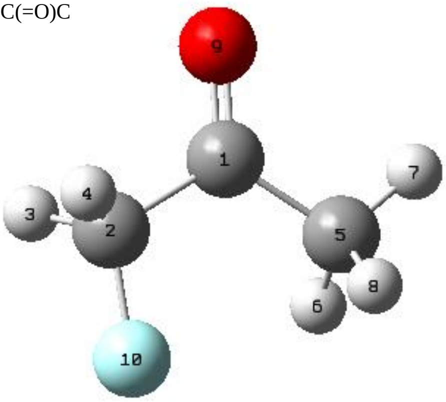
APPENDIX C

THERMOCHEMISTRY AND BOND DISSOCIATION ENERGIES OF KETONES

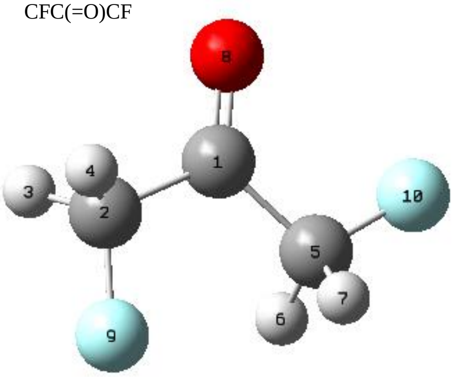
This appendix contains the optimized geometries with corresponding Gaussian atom numbering and symmetry values in parenthesis, moments of inertia, vibrational frequencies, internal rotor potential energy graphs, entropies, and heat capacities for all of the parent and radical species from B3-LYP/6-31G(d,p) level of theory.

Figure C.1 Fluorinated Ketones Species Optimized Structures

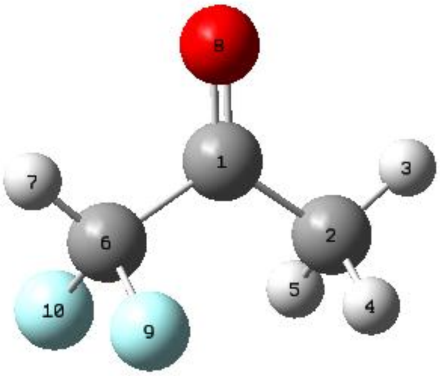
CFC(=O)C



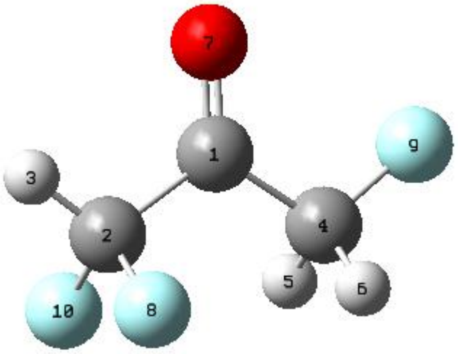
CFC(=O)CF



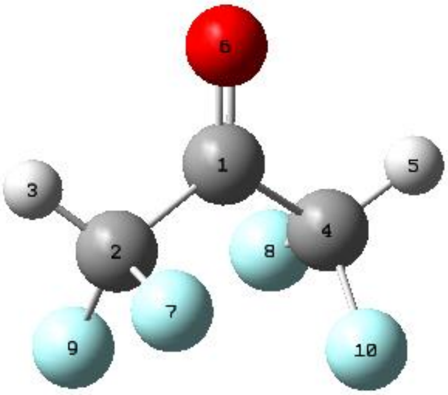
CF2C(=O)C



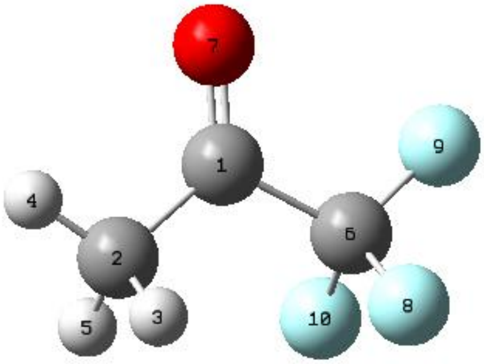
CF2C(=O)CF



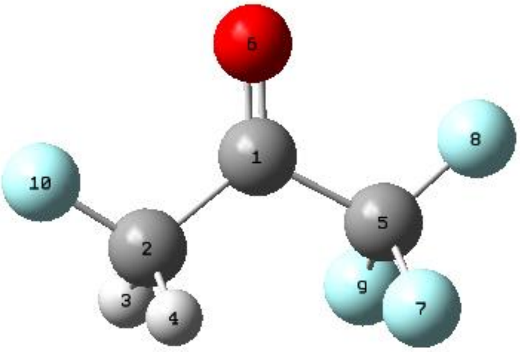
CF2C(=O)CF2



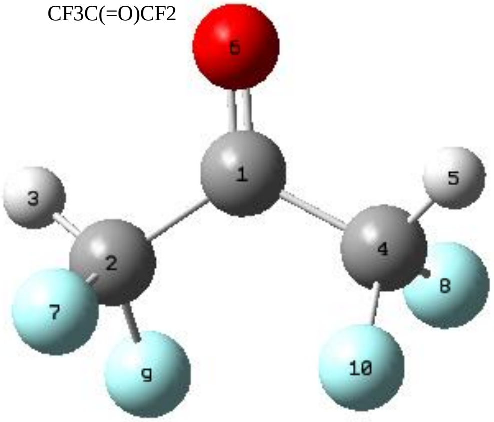
CF3C(=O)C



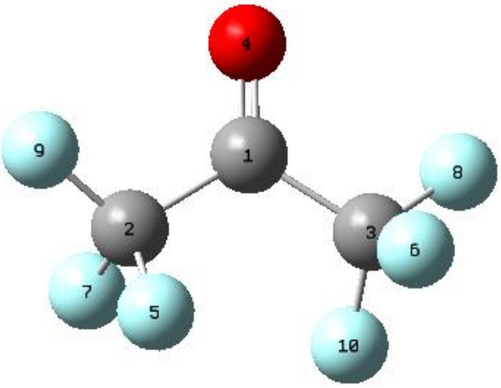
CF3C(=O)CF



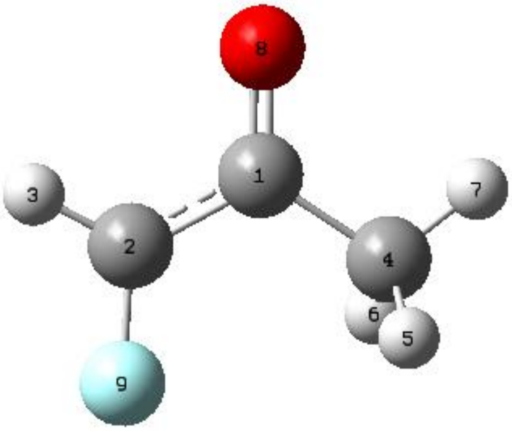
CF3C(=O)CF2



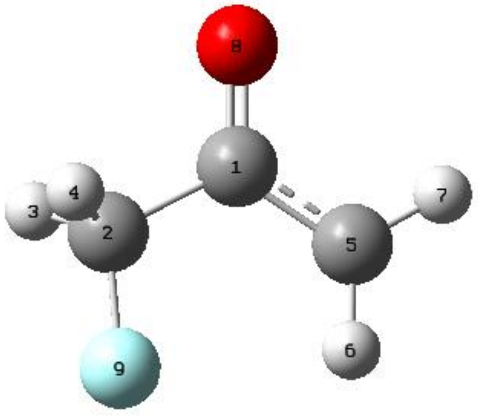
CF3C(=O)CF3



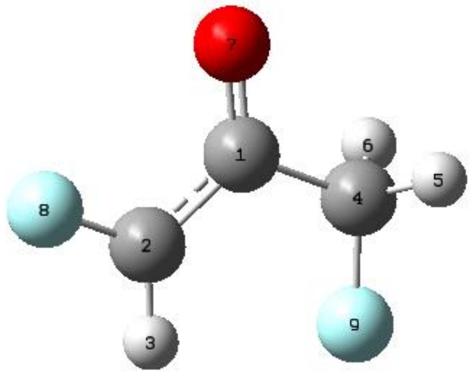
CjFC(=O)C



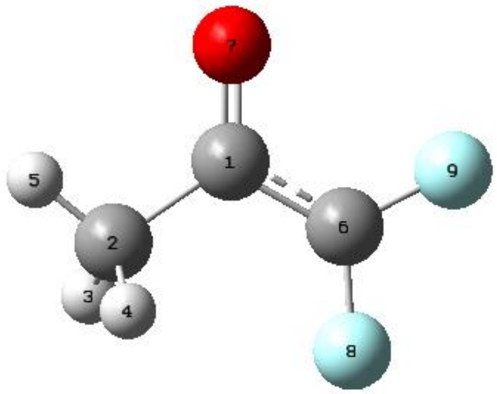
CFC(=O)Cj



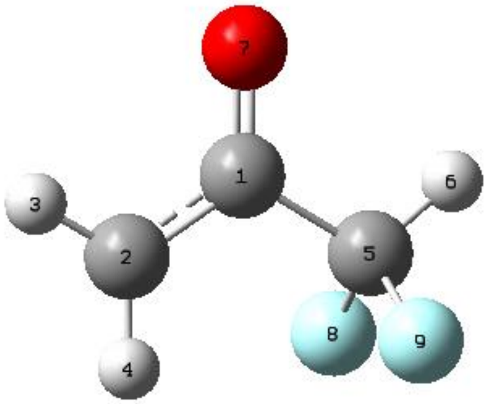
CjFC(=O)CF



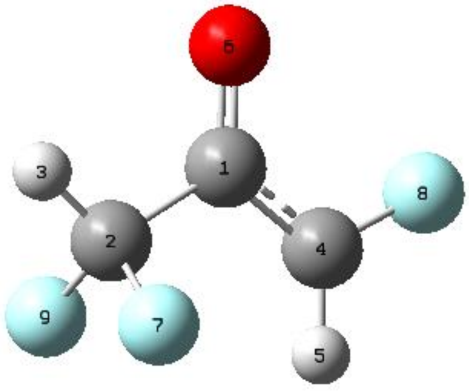
CjF2C(=O)C



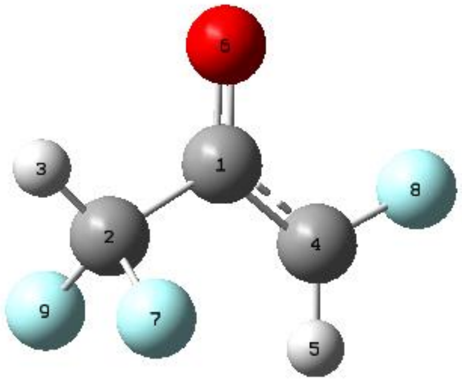
CF2C(=O)Cj



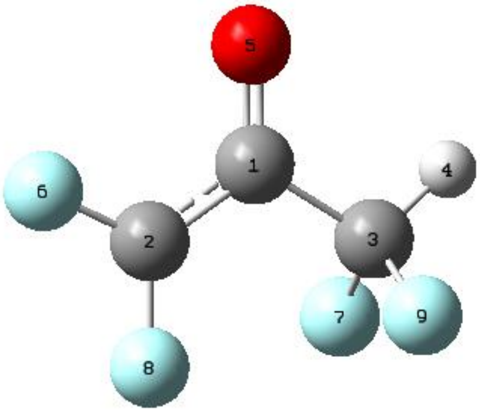
CF2C(=O)CjF



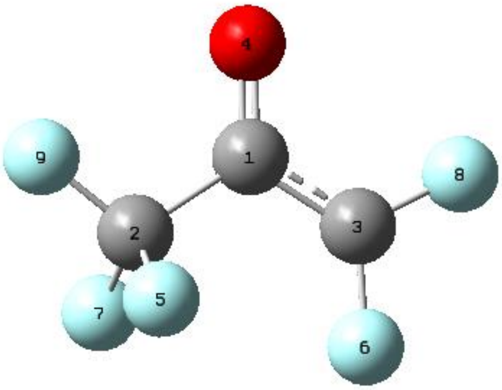
CjF2C(=O)CF



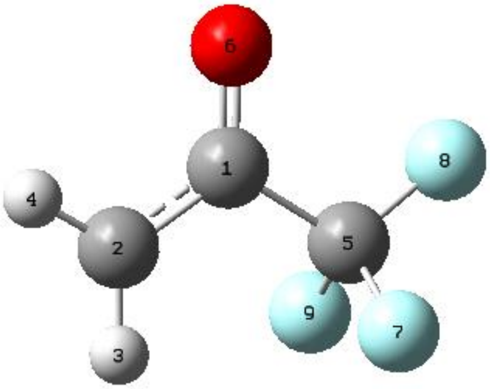
CjF2C(=O)CF2



CjF2C(=O)CF3



CF3C(=O)Cj



CF3C(=O)CjF

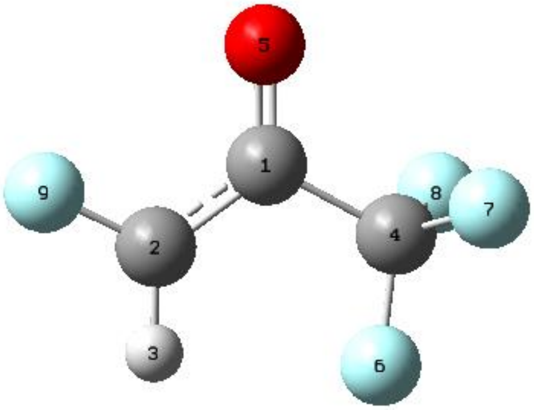


Table C.1 Moments of Inertia for Fluorinated Ketones

Species	Moments of Inertia		
CFC(=O)C	8.60919	3.97239	2.81374
CFC(=O)CF	5.97865	2.41582	1.75887
CF2C(=O)C	4.99435	2.66370	2.59740
CF2C(=O)CF	4.29978	1.63215	1.52567
CF2C(=O)CF2	2.57849	1.70566	1.46931
CF3C(=O)C	3.61361	2.41292	1.98008
CF3C(=O)CF	3.52587	1.35577	1.19771
CF3C(=O)CF2	2.35053	1.30401	1.16842
CF3C(=O)CF3	2.14774	1.01775	0.91853
CjFC(=O)C	9.02495	4.08126	2.86017
CFC(=O)Cj	9.68551	3.97629	2.87046
CjFC(=O)CF	6.06032	2.49047	1.78519
CjF2C(=O)C	5.28469	3.29191	2.05432
CF2C(=O)Cj	5.34248	2.68022	2.65629
CF2C(=O)CjF	4.30993	1.68431	1.55723
CjF2C(=O)CF	3.70097	2.27258	1.49431
CjF2C(=O)CF2	2.96123	1.60786	1.28919
CjF2C(=O)CF3	2.63059	1.27129	1.01288
CF3C(=O)Cj	3.74450	2.47546	2.03387
CF3C(=O)CjF	3.57681	1.39000	1.21892

Table C.2 Vibrational Frequencies for Fluorinated Ketones

CFC(=O)CF	73.3029	111.0198	186.8157
	288.2239	449.8537	489.2260
	583.7689	816.0035	835.4585
	1052.8757	1071.1114	1094.5222
	1178.9895	1234.6672	1261.7595
	1371.0988	1405.3836	1462.6652
	1469.4087	1823.8503	3050.0033
	3070.8504	3096.2122	3128.9293
CF2C(=O)C	40.8525	113.8763	225.2731
	245.4798	406.2198	519.9997
	601.3622	602.5852	797.4140
	1023.5434	1024.8817	1071.0929
	1109.6813	1256.7134	1350.9847
	1362.7296	1398.0466	1470.2755
	1472.7577	1815.8573	3053.2093
	3117.3585	3141.6850	3170.0903
CF2C(=O)CF	32.3187	80.8475	183.2612
	221.9012	292.3865	404.3633
	570.0294	572.2986	665.2929
	810.2490	993.3898	1065.4291
	1107.1629	1109.9217	1200.0897
	1259.9827	1346.7849	1360.1873
	1409.8566	1472.0144	1839.6924
	3053.5653	3102.0973	3144.4594
CF2C(=O)CF2	49.1650	49.6974	146.4534
	184.1117	262.7256	349.9126
	431.8328	458.9163	564.9769
	630.8319	777.3278	855.7495
	1062.9495	1096.4513	1106.2417
	1150.1261	1265.9652	1339.9160
	1359.7513	1370.6554	1375.4243
	1837.7084	3127.0244	3128.9826
CF3C(=O)C	28.7615	106.9576	226.3273
	229.9627	357.2356	411.4698
	486.9734	548.6265	612.2842
	618.8203	752.6762	971.0071
	1038.7472	1117.5590	1137.8080
	1212.4022	1320.2096	1400.2691
	1469.8432	1472.6231	1840.4271
	3054.5252	3119.3358	3172.4365
CF3C(=O)CF	16.9281	80.1560	171.8764
	224.1221	292.5011	338.7018
	409.8757	480.8558	555.2985
	594.8320	706.9362	806.3741
	997.6432	1000.8138	1127.5896
	1139.7349	1205.8388	1260.3346
	1301.5634	1408.0117	1471.5133
	1862.9036	3051.2359	3100.2321
CF3C(=O)CF2	40.1812	54.7926	143.4217
	185.8028	257.9429	274.9643
	362.0997	457.0778	500.1240
	519.3838	579.8028	675.2947
	750.6484	786.4001	1074.0696
	1091.0098	1144.3668	1171.5284
	1218.1983	1311.4756	1359.2963
	1366.3142	1858.7788	3133.1737
CF3C(=O)CF3	37.0551	38.6216	143.2497
	188.1019	253.2137	269.6708
	310.6786	364.1454	457.8617
	491.1356	516.4298	525.2146
	619.2341	702.8966	759.1129
	776.9863	960.5615	1138.3006
	1181.1454	1198.8507	1232.2011
	1259.9919	1319.3509	1879.5233
CjFC(=O)C	59.1316	198.0993	230.5539
	477.5722	483.9023	555.0337
	634.5514	817.3738	999.0185
	1027.9112	1169.8483	1277.7544
	1397.7852	1421.3871	1473.8939
	1478.4274	1600.4278	3049.0771
CFC(=O)Cj	83.5903	256.7198	408.5631
	479.4628	488.4952	504.5992
	793.9425	830.9713	1002.3635
	1007.3123	1055.1422	1244.1286
	1301.1499	1377.2770	1467.3290
	1476.8561	1558.1651	3072.1121
	3128.8481	3176.2411	3295.4120
CjFC(=O)CF	79.8552	194.0955	196.7712
	295.2406	484.1720	496.4681
	618.4720	633.6329	903.9458
	999.6895	1050.4766	1178.3604
	1238.9283	1247.2303	1377.7466
	1474.2159	1486.9280	1591.5677
	3075.4264	3133.3955	3256.1774

Table C.2 Vibrational Frequencies for Fluorinated Ketones (Continued)

CjF2C(=O)C	23.1950	130.1369	205.7333
	215.8000	379.4466	502.7477
	525.3953	569.6624	723.8754
	965.9176	1027.2332	1143.9107
	1327.5598	1399.9993	1465.5232
	1479.7450	1504.0975	1604.7043
	3049.7660	3113.1864	3165.8379
CF2C(=O)Cj	32.1982	230.5580	250.5520
	403.6472	412.6319	514.3759
	606.6775	633.9224	828.8567
	863.2717	1020.7950	1050.1620
	1113.0404	1309.9786	1359.0716
	1361.0240	1479.3843	1578.2386
	3144.9063	3174.0195	3292.0064
CF2C(=O)CjF		146.3155	178.5254
	282.9107	305.1948	402.6509
	574.9635	576.7001	695.4010
	726.6346	902.5379	1049.9161
	1111.8133	1207.4931	1253.8100
	1351.0377	1358.8391	1498.8314
	1599.5534	3146.0615	3238.8974
CjF2C(=O)CF	51.6591	112.6272	174.9556
	248.2878	301.1486	388.6642
	510.1725	540.2233	649.7292
	723.2323	983.6584	1050.0679
	1144.3176	1245.3720	1350.1117
	1386.5016	1489.6718	1518.3843
	1579.1137	3064.5941	3147.0452
CjF2C(=O)CF2	42.4037	102.7232	147.1426
	219.8018	298.0706	339.6410
	373.4109	486.6843	564.0880
	665.9523	684.8040	727.7262
	1064.4820	1098.7225	1174.3026
	1345.4531	1363.8254	1376.8450
	1527.2534	1578.2087	3141.5047
CjF2C(=O)CF3	33.4496	104.2280	144.6848
	223.1050	284.5389	334.3267
	347.2091	373.9477	489.0639
	502.1635	594.1452	657.1870
	675.3559	750.4018	996.6971
	1144.5331	1198.8492	1287.2929
	1378.8092	1526.3682	1584.5517
CF3C(=O)Cj	20.7851	229.5559	234.4261
	364.9921	407.4297	414.1226
	492.5858	553.3622	614.8459
	650.8613	760.2904	830.4334
	1017.9775	1129.1579	1144.7518
	1215.5206	1354.0810	1480.9431
	1586.3292	3176.4508	3294.6708
CF3C(=O)CjF	13.5384	155.8150	194.1803
	286.0817	291.4932	355.1265
	412.3169	491.1897	564.0440
	600.8091	715.9062	732.6255
	866.7646	1068.8574	1164.8773
	1176.1781	1258.5840	1294.3569
	1495.2742	1574.2218	3253.7957

Figure C.2 Potential Energy Profiles of Fluorinated Ketones and Corresponding Radicals

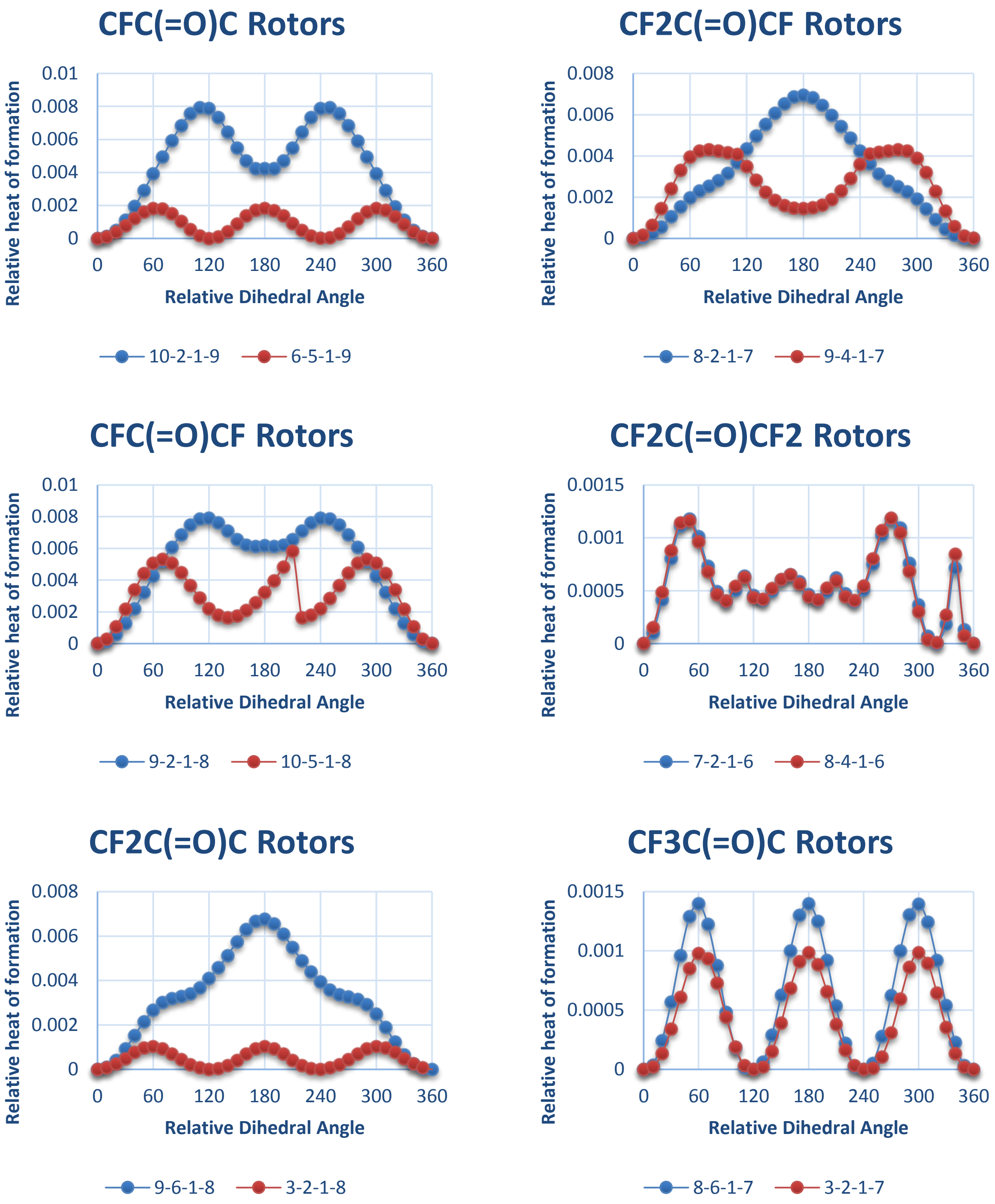


Figure C.2 Potential Energy Profiles of Fluorinated Ketones and Corresponding Radicals (Continued)

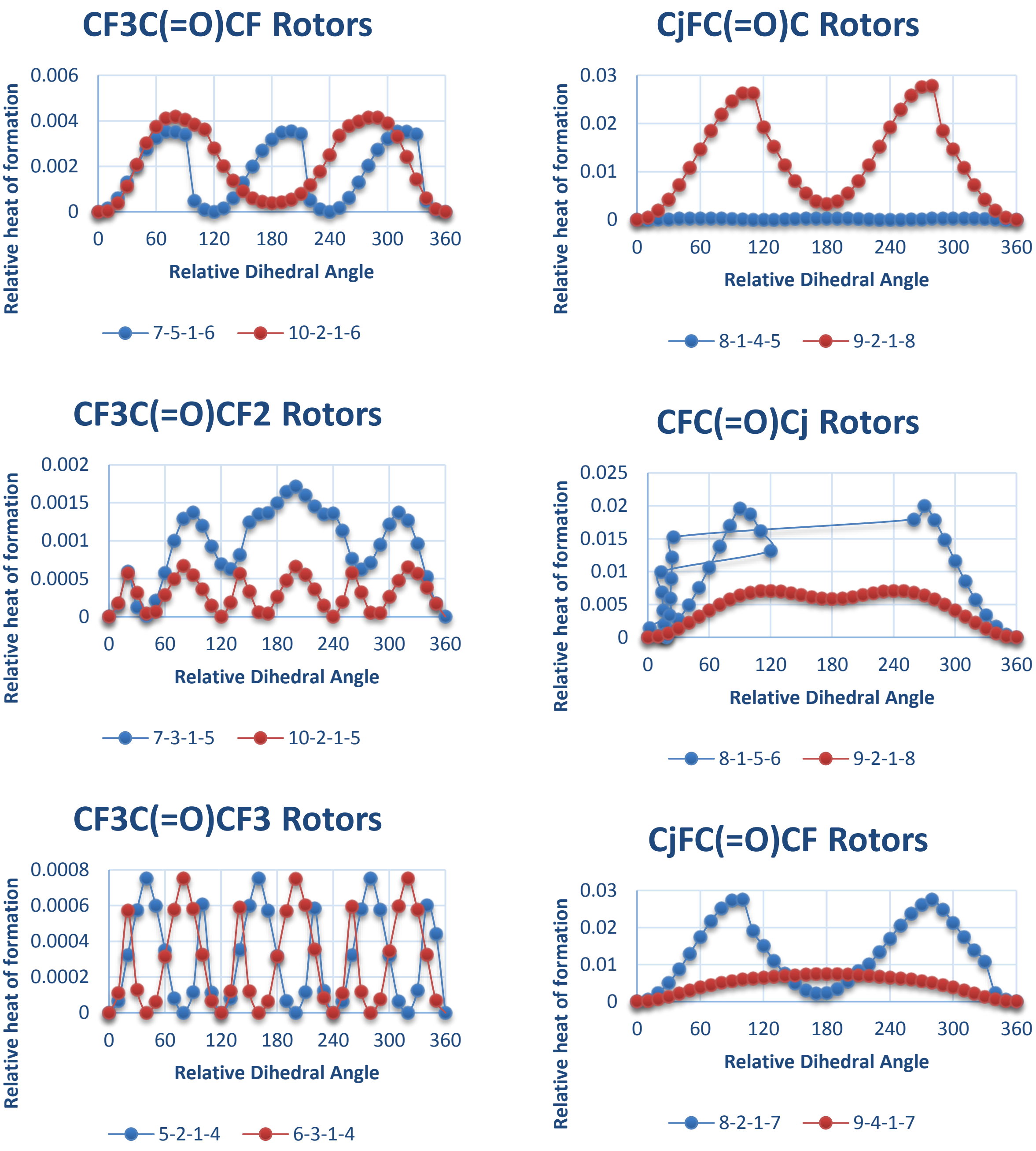


Figure C.2 Potential Energy Profiles of Fluorinated Ketones and Corresponding Radicals (Continued)

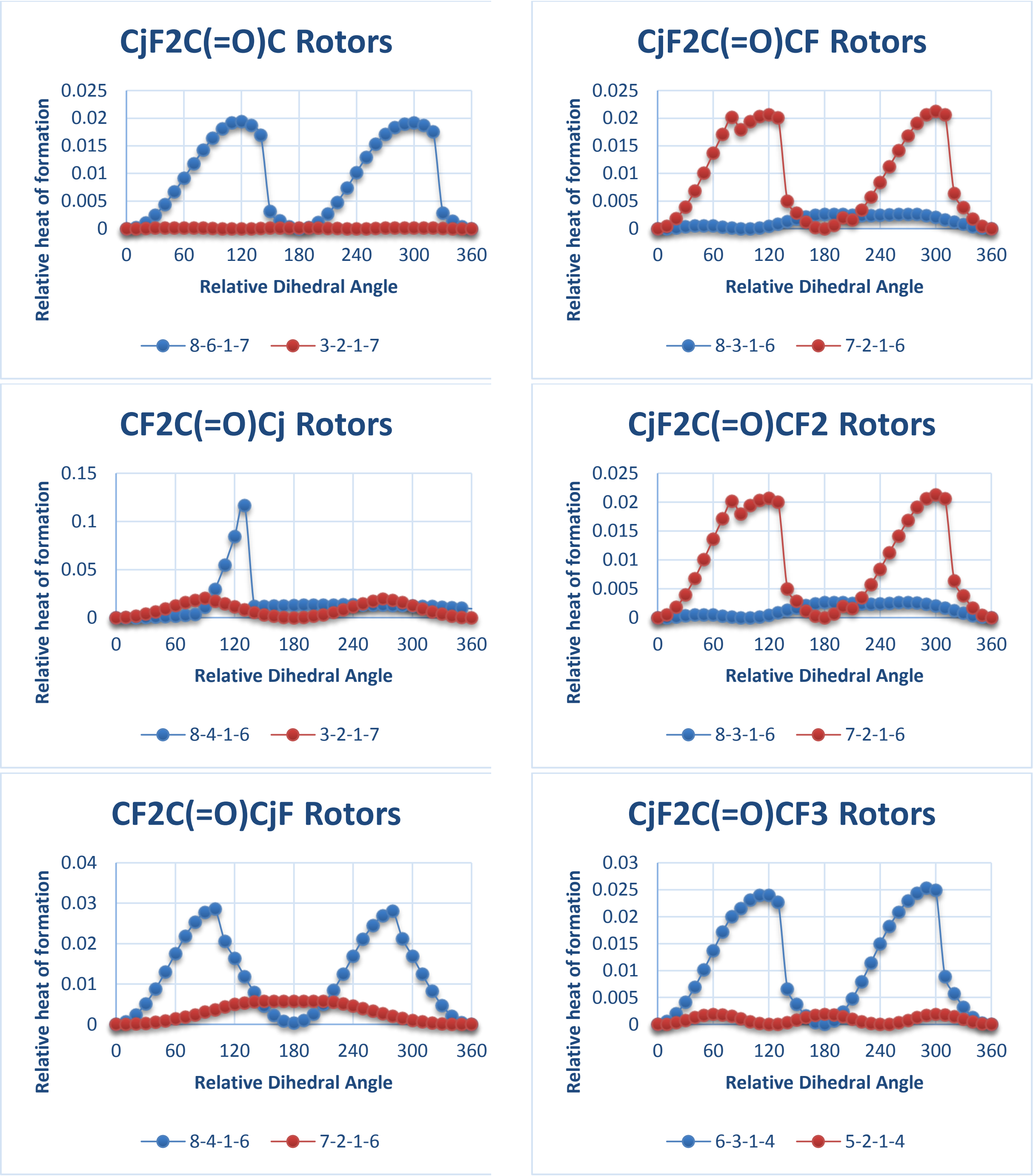
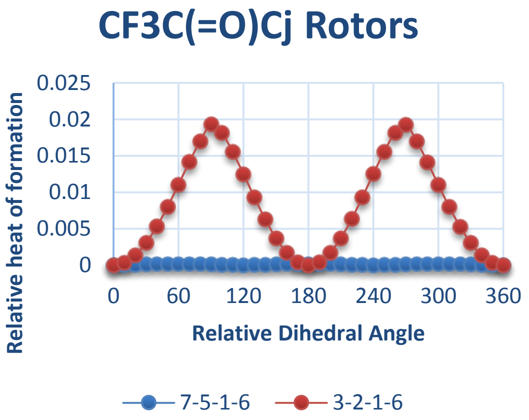


Figure C.2 Potential Energy Profiles of Fluorinated Ketones and Corresponding Radicals (Continued)



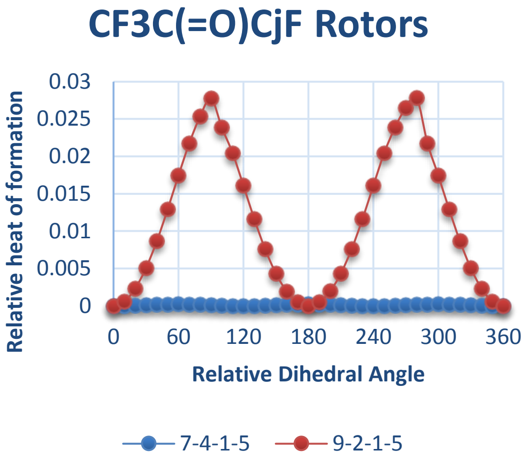


Table C.3 TVR Calculations for Fluorinated Ketones

Species	HF	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
CFC(=O)C	-94.39	73.76	20.63	25.09	29.12	32.55	37.87	41.73	47.61
		7.56	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		5.10	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-94.39	86.42	22.62	27.08	31.11	34.54	39.86	43.72	49.60
CFC(=O)CF	-133.28	78.04	22.33	26.97	31.10	34.54	39.72	43.35	48.67
		7.72	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		7.87	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-133.28	93.63	24.32	28.96	33.09	36.53	41.71	45.34	50.66
CF2C(=O)C	-144.59	79.13	22.91	27.50	31.52	34.86	39.90	43.44	48.68
		7.18	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		5.10	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-144.59	91.41	24.90	29.49	33.51	36.85	41.89	45.43	50.67
CF2C(=O)CF	-182.14	83.82	24.61	29.38	33.49	36.85	41.75	45.06	49.74
		7.29	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		4.06	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-182.14	95.17	26.60	31.37	35.48	38.84	43.74	47.05	51.73
CF2C(=O)CF2	-230.17	87.37	26.95	31.84	35.94	39.19	43.81	46.80	50.83
		7.63	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		7.63	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-230.17	102.63	28.94	33.83	37.93	41.18	45.80	48.79	52.82
CF3C(=O)C	-200.09	82.98	25.63	30.43	34.40	37.59	42.24	45.39	49.89
		8.07	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		5.76	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-200.09	96.81	27.62	32.42	36.39	39.58	44.23	47.38	51.88

Table C.3 TVR Calculations for Fluorinated Ketones (Continued)

Species	HF	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
CF3C(=O)CF	-237.15	88.12	27.33	32.30	36.36	39.56	44.08	47.01	50.96
		8.35	0.99	0.99	0.99	0.99	0.99	0.99	0.99
		8.00	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	-237.15	104.47	29.32	34.29	38.35	41.55	46.07	49.00	52.94
CF3C(=O)CF2	-285.95	90.49	29.64	34.76	38.81	41.92	46.15	48.75	52.04
		8.54	0.99	0.99	0.99	0.99	0.99	0.99	0.98
		8.78	0.99	0.99	0.99	0.99	0.99	0.99	0.93
	-285.95	107.80	31.63	36.75	40.80	43.91	48.14	50.73	53.95
CF3C(=O)CF3	-340.38	90.61	32.35	37.68	41.69	44.65	48.49	50.70	53.25
		8.82	0.99	0.99	0.99	0.99	0.99	0.98	0.92
		8.82	0.99	0.99	0.99	0.99	0.99	0.98	0.92
	-340.38	108.25	34.34	39.67	43.68	46.64	50.47	52.67	55.09
CjFC(=O)C	-57.47	73.55	20.48	24.46	27.88	30.65	34.58	37.06	40.24
		5.747	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936
		7.4400	0.9940	0.9938	0.9937	0.9937	0.9936	0.9936	0.9936
CFC(=O)Cj	-50.32	71.37	20.01	24.31	27.94	30.9	35.33	38.46	43.17
		5.1754	0.9938	0.9937	0.9937	0.9936	0.9936	0.9936	0.9936
		7.5280	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936
	-50.32	84.07	22.00	26.30	29.93	32.89	37.32	40.45	45.16
CjFC(=O)CF	-97.21	76.51	21.98	26.19	29.78	32.71	37	39.93	44.16
		7.7115	0.9938	0.9937	0.9937	0.9936	0.9936	0.9936	0.9936
		7.7458	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936
	-97.21	91.97	23.97	28.18	31.77	34.70	38.99	41.92	46.15

Table C.3 TVR Calculations for Fluorinated Ketones (Continued)

Species	HF	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
CjF2C(=O)C	-104.21	80.65	22.97	26.82	30.16	32.93	37.1	40	44.2
		7.777	0.9938	0.9937	0.9937	0.9937	0.9936	0.9936	0.9936
		5.7505	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936
	-104.21	94.18	24.96	28.81	32.15	34.92	39.09	41.99	46.19
CF2C(=O)Cj	-100.55	77.1	22.32	26.76	30.39	33.26	37.4	40.2	44.27
		8.7171	0.995	0.9944	0.9941	0.9939	0.9932	0.9895	0.9475
		8.7178	0.9938	0.9937	0.9937	0.9936	0.993	0.9894	0.9475
	-100.55	94.53	24.31	28.75	32.38	35.25	39.39	42.18	46.17
CF2C(=O)CjF	-147.18	76.46	22.28	26.64	30.23	33.07	37.08	39.7	43.28
		7.7541	0.994	0.9938	0.9937	0.9937	0.9936	0.9936	0.9936
		8.1268	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9927
	-147.18	92.34	24.27	28.63	32.22	35.06	39.07	41.69	45.27
CjF2C(=O)CF	-142.87	82.15	24.45	28.55	32.02	34.83	38.89	41.56	45.23
		7.1685	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936
		8.1557	0.9939	0.9938	0.9937	0.9936	0.9936	0.9936	0.9925
	-142.87	97.47	26.44	30.54	34.01	36.82	40.88	43.55	47.22
CjF2C(=O)CF2	-142.87	82.15	24.45	28.55	32.02	34.83	38.89	41.56	45.23
		8.2354	0.994	0.9938	0.9937	0.9937	0.9936	0.9936	0.9913
		8.4438	0.9936	0.9936	0.9936	0.9936	0.9936	0.9932	0.9832
	-142.87	98.83	26.44	30.54	34.01	36.82	40.88	43.55	47.20
CjF2C(=O)CF3	-249.56	89.23	29.43	33.93	37.36	39.94	43.32	45.29	47.56
		9.0234	0.9940	0.9938	0.9936	0.9929	0.9860	0.9649	0.8485
		8.6967	0.9936	0.9936	0.9936	0.9936	0.9936	0.9900	0.9518
	-249.56	106.95	31.42	35.92	39.35	41.93	45.30	47.24	49.36

Table C.3 TVR Calculations for Fluorinated Ketones (Continued)

Species	HF	S	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
CF3C(=O)Cj	-156.52	80.99	25.03	29.69	33.27	35.99	39.74	42.16	45.48
		7.9904	0.9936	0.9936	0.9936	0.9936	0.9936	0.9936	0.9934
		5.1786	0.9938	0.9937	0.9937	0.9936	0.9936	0.9936	0.9936
	-156.52	94.16	27.02	31.68	35.26	37.98	41.73	44.15	47.47
CF3C(=O)CjF	-202.37	86.44	26.92	31.52	35.08	37.79	41.42	43.64	46.48
		8.3126	0.9936	0.9936	0.9936	0.9936	0.9936	0.9935	0.9894
		8.3124	0.994	0.9938	0.9937	0.9937	0.9936	0.9935	0.9895
	-202.37	103.07	28.91	33.51	37.07	39.78	43.41	45.63	48.46

Table C.4 Isodesmic Reactions Calculations for Fluorinated Ketones

								mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
CFC(=O)C																		
	CFC(=O)C	+	CH4	=	CC(=O)C	+	CH3F	-93.73	-93.94	-93.86	-93.51	-94.02	-96.22	-94.66	-94.53	-94.51	-95.11	-94.19
	CFC(=O)C	+	CC	=	CC(=O)C	+	CFC	-94.23	-94.11	-94.07	-93.95	-94.65	-96.32	-94.47	-95.13	-95.13	-95.34	-94.45
	CFC(=O)C	+	CC(=O)	=	CC(=O)C	+	CFC(=O)	-92.24	-92.25	-92.18	-92.23	-92.19	-93.36	-92.24	-92.01	-92.02	-92.67	-92.39
	CFC(=O)C	+	CCC(=O)	=	CC(=O)C	+	CFCC(=O)	-96.00	-95.97	-95.97	-95.87	-95.92	-96.56	-95.96	-96.10	-96.10	-96.76	-96.16
CFC(=O)CF																		
	CFC(=O)CF	+	CH4	=	CFC(=O)C	+	CH3F	-133.26	-132.72	-132.35	-132.31	-132.65	-133.96	-133.97	-133.30	-133.27	-134.83	-133.40
	CFC(=O)CF	+	CC	=	CFC(=O)C	+	CFC	-133.75	-132.89	-132.56	-132.74	-133.28	-134.05	-133.78	-133.89	-133.89	-135.06	-133.66
	CFC(=O)CF	+	CC(=O)	=	CFC(=O)C	+	CFC(=O)	-131.77	-131.03	-130.67	-131.02	-130.83	-131.09	-131.55	-130.77	-130.78	-132.38	-131.60
	CFC(=O)CF	+	CCC(=O)	=	CFC(=O)C	+	CFCC(=O)	-135.52	-134.76	-134.46	-134.66	-134.55	-134.30	-135.28	-134.86	-134.86	-136.48	-135.37
CF2C(=O)C																		
	CF2C(=O)C	+	CFCC	=	CFC(=O)C	+	CCCF2	-145.08	-144.58	-144.43	-144.69	-144.38	-143.08	-144.87	-144.74	-144.73	-145.34	-144.87
	CF2C(=O)C	+	CFC	=	CFC(=O)C	+	CF2C	-144.89	-144.54	-144.25	-144.50	-144.19	-143.51	-144.65	-144.62	-144.61	-145.22	-144.66
	CF2C(=O)C	+	CH3F	=	CFC(=O)C	+	CH2F2	-145.24	-145.01	-144.40	-144.43	-144.08	-145.03	-144.67	-144.89	-144.89	-145.51	-144.47
	CF2C(=O)C	+	CFC(=O)	=	CFC(=O)C	+	CF2C(=O)	-145.33	-145.27	-144.61	-144.61	-144.51	-145.44	-144.41	-144.66	-144.65	-144.61	-144.50
	CF2C(=O)C	+	CFCF(=O)	=	CFC(=O)C	+	CF2CF(=O)	-145.04	-144.89	-144.28	-144.45	-144.34	-145.96	-144.37	-143.78	-143.78	-143.57	-144.26
CF2C(=O)CF																		
	CF2C(=O)CF	+	CFCC	=	CFC(=O)CF	+	CCCF2	-181.43	-181.89	-182.19	-182.45	-182.08	-180.34	-182.71	-182.38	-182.37	-183.23	-182.71
	CF2C(=O)CF	+	CFC	=	CFC(=O)CF	+	CF2C	-181.24	-181.85	-182.01	-182.26	-181.89	-180.77	-182.50	-182.26	-182.25	-183.11	-182.50
	CF2C(=O)CF	+	CH3F	=	CFC(=O)CF	+	CH2F2	-181.59	-182.31	-182.16	-182.19	-181.78	-182.30	-182.52	-182.53	-182.52	-183.39	-182.31
	CF2C(=O)CF	+	CFC(=O)	=	CFC(=O)CF	+	CF2C(=O)	-181.68	-182.58	-182.37	-182.37	-182.21	-182.70	-182.25	-182.31	-182.29	-182.49	-182.34
	CF2C(=O)CF	+	CFCF(=O)	=	CFC(=O)CF	+	CF2CF(=O)	-181.39	-182.20	-182.04	-182.21	-182.04	-183.22	-182.22	-181.43	-181.42	-181.46	-182.10

Table C.4 Isodesmic Reactions Calculations for Fluorinated Ketones (Continued)

CF2C(=O)CF2									mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
	CF2C(=O)CF2	+	CFCC	=	CF2C(=O)CF	+	CCCF2		-229.43	-230.12	-229.45	-229.50	-230.02	-228.73	-230.23	-231.34	-231.35	-231.62	-229.99
	CF2C(=O)CF2	+	CFC	=	CF2C(=O)CF	+	CF2C		-229.24	-230.07	-229.26	-229.31	-229.84	-229.16	-230.01	-231.23	-231.23	-231.50	-229.78
	CF2C(=O)CF2	+	CH3F	=	CF2C(=O)CF	+	CH2F2		-229.59	-230.54	-229.42	-229.23	-229.72	-230.69	-230.04	-231.50	-231.50	-231.78	-229.59
	CF2C (=O)CF2	+	CFC(=O)	=	CF2C(=O)CF	+	CF2C(=O)		-229.68	-230.81	-229.63	-229.42	-230.16	-231.09	-229.77	-231.27	-231.27	-230.89	-229.62
	CF2C(=O)CF2	+	CFCF(=O)	=	CF2C(=O)CF	+	CF2CF(=O)		-229.40	-230.42	-229.30	-229.26	-229.99	-231.61	-229.74	-230.39	-230.39	-229.85	-229.38
CF3C(=O)C																			
	CF3C(=O)C	+	CH2F2	=	CF2C(=O)C	+	CHF3		-199.93	-200.08	-200.04	-199.96	-199.58	-200.89	-200.04	-199.70	-199.69	-200.98	-200.10
	CF3C(=O)C	+	CF2C(=O)	=	CF2C(=O)C	+	CF3C(=O)		-199.64	-199.75	-200.14	-200.18	-200.10	-200.69	-200.10	-200.08	-200.08	-200.15	-200.14
	CF3C(=O)C	+	CF2C	=	CF2CC(=O)	+	CF3C		-199.74	-199.92	-200.13	-200.31	-199.72	-199.23	-200.57	-199.82	-199.81	-201.17	-200.66
CF3C(=O)CF																			
	CF3C(=O)CF	+	CH4	=	CF3C(=O)C	+	CH3F		-237.02	-236.77	-236.35	-236.30	-236.36	-236.72	-238.08	-237.55	-236.94	-239.03	-237.57
	CF3C(=O)CF	+	CC	=	CF3C(=O)C	+	CFC		-237.52	-236.94	-236.56	-236.73	-237.00	-236.82	-237.90	-238.15	-237.56	-239.26	-237.82
	CF3C(=O)CF	+	CC(=O)	=	CF3C(=O)C	+	CFC(=O)		-235.53	-235.08	-234.66	-235.01	-234.54	-233.86	-235.66	-235.03	-234.44	-236.58	-235.76
	CF3C(=O)CF	+	CCC(=O)	=	CF3C(=O)C	+	CFCC(=O)		-239.29	-238.81	-238.45	-238.65	-238.26	-237.06	-239.39	-239.12	-238.53	-240.68	-239.54
CF3C(=O)CF2																			
	CF3C(=O)CF2	+	CFCC	=	CF2C(=O)CF2	+	CCCF2		-285.44	-284.60	-285.03	-284.33	-285.46	-287.07	-286.06	-287.01	-287.01	-288.13	-
	CF3C(=O)CF2	+	CFC	=	CF2C(=O)CF2	+	CF2C		-285.26	-284.55	-284.85	-284.14	-285.28	-287.50	-285.84	-286.90	-286.89	-288.01	-
	CF3C(=O)CF2	+	CH3F	=	CF2C(=O)CF2	+	CH2F2		-285.61	-285.02	-285.00	-284.07	-285.16	-289.02	-285.87	-287.17	-287.17	-288.30	-
	CF3C(=O)CF2	+	CFC(=O)	=	CF2C(=O)CF2	+	CF2C(=O)		-285.70	-285.29	-285.21	-284.25	-285.59	-289.43	-285.60	-286.94	-286.93	-287.40	-
	CF3C(=O)CF2	+	CFCF(=O)	=	CF2C(=O)CF2	+	CF2CF(=O)		-285.41	-284.91	-284.88	-284.09	-285.43	-289.95	-285.57	-286.06	-286.06	-286.36	-

Table C.4 Isodesmic Reactions Calculations for Fluorinated Ketones (Continued)

								mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4
CF3C(=O)CF3																	
	CF3C(=O)CF3	+	CH2F2	=	CF3C(=O)CF2	+	CHF3	-340.91	-340.94	-340.51	-340.36	-339.66	-340.39	-340.54	-339.92	-	-	-
	CF3C(=O)CF3	+	CF2C(=O)	=	CF3C(=O)CF2	+	CF3C(=O)	-340.61	-340.61	-340.61	-340.58	-340.18	-340.19	-340.60	-340.30	-	-	-
	CF3C(=O)CF3	+	CCCF2	=	CF3C(=O)CF2	+	CF3CC	-340.66	-340.62	-340.55	-340.73	-339.71	-338.09	-340.94	-339.96	-	-	-
	CF3C(=O)CF3	+	CF2C	=	CF3C(=O)CF2	+	CF3C	-340.72	-340.80	-340.61	-340.74	-339.82	-338.75	-341.10	-340.06	-	-	-
CJC(=O)C																	
	CJC(=O)C	+	CH4	=	CC(=O)C	+	CH3J	-8.12	-8.60	-9.46	-9.58	-8.44	-14.19	-9.09	-9.45	-9.42	-10.08	-9.53
	CJC(=O)C	+	CC	=	CC(=O)C	+	CJC	-8.43	-7.37	-9.05	-9.06	-10.08	-15.98	-8.47	-10.90	-10.90	-9.45	-8.83
	CJC(=O)C	+	CCCC	=	CC(=O)C	+	CJCCC	-8.55	-8.02	-8.34	-8.77	-9.79	-15.80	-8.20	-10.65	-10.64	-9.17	-8.55
CJFC(=O)CF																	
	CJFC(=O)CF	+	CH3F	=	CFC(=O)CF	+	CJH2F	-96.75	-97.42	-96.80	-97.90	-95.52	-101.97	-97.38	-96.54	-96.53	-97.98	-97.60
	CJFC(=O)CF	+	CFC	=	CFC(=O)CF	+	CJFC	-95.93	-95.88	-95.78	-96.58	-95.47	-102.20	-96.57	-96.16	-96.15	-96.85	-96.46
	CJFC(=O)CF	+	CFCF	=	CFC(=O)CF	+	CJFCF	-94.65	-94.83	-94.35	-94.91	-95.08	-101.91	-95.26	-95.70	-95.70	-95.95	-95.16
	CJFC(=O)CF	+	CF2CF	=	CFC(=O)CF	+	CF2CJF	-98.16	-98.43	-97.79	-98.39	-98.15	-105.63	-98.63	-98.68	-98.67	-98.96	-98.45
	CJFC(=O)CF	+	CF3CF	=	CFC(=O)CF	+	CF3CJF	-99.13	-99.47	-98.66	-99.24	-98.98	-106.80	-99.35	-99.36	-99.35	-99.54	-99.20
CF2C(=O)CJ																	
	CF2C(=O)CJ	+	CH4	=	CF2C(=O)C	+	CH3J	-100.63	-101.21	-101.80	-102.72	-101.88	-108.84	-102.48	-102.92	-102.90	-103.54	-102.53
	CF2C(=O)CJ	+	CC	=	CF2C(=O)C	+	CJC	-100.94	-99.98	-101.40	-102.20	-103.53	-110.63	-101.86	-104.38	-104.38	-102.91	-101.83
	CF2C(=O)CJ	+	CCC	=	CF2C(=O)C	+	CJCC	-97.07	-96.96	-97.75	-98.37	-99.71	-106.96	-98.04	-100.61	-100.60	-99.09	-97.99
	CF2C(=O)CJ	+	CCCC	=	CF2C(=O)C	+	CJCCC	-101.53	-101.11	-101.16	-102.39	-103.70	-110.92	-102.06	-104.60	-104.59	-103.10	-102.03
	CF2C(=O)CJ	+	C3C	=	CF2C(=O)C	+	CJ3C	-96.32	-94.41	-95.99	-95.77	-99.78	-108.29	-95.24	-100.27	-100.26	-95.92	-95.20

Table C.4 Isodesmic Reactions Calculations for Fluorinated Ketones (Continued)

CJF2C(=O)C								mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
	CJF2C(=O)C	+	CF2C	=	CF2C(=O)C	+	CJF2C	-102.73	-104.49	-103.01	-104.01	-101.07	-109.02	-105.57	-101.11	-101.11	-107.05	-105.77
	CJF2C(=O)C	+	CF2CF	=	CF2C(=O)C	+	CJF2CF	-101.13	-102.91	-101.14	-101.95	-100.60	-109.80	-103.86	-100.85	-100.85	-105.28	-103.75
	CJF2C(=O)C	+	CF2CF2	=	CF2C(=O)C	+	CJF2CF2	-105.87	-107.65	-105.88	-106.70	-105.04	-114.71	-108.62	-105.09	-105.08	-109.68	-108.47
CF2C(=O)CJF																		
	CF2C(=O)CJF	+	CH3F	=	CF2C(=O)CF	+	CJH2F	-146.25	-147.20	-146.96	-148.12	-145.93	-152.58	-146.73	-146.41	-146.98	-147.90	-147.67
	CF2C(=O)CJF	+	CFC	=	CF2C(=O)CF	+	CJFC	-145.42	-145.66	-145.94	-146.81	-145.89	-152.80	-145.92	-146.03	-146.60	-146.76	-146.52
	CF2C(=O)CJF	+	CFCF	=	CF2C(=O)CF	+	CJFCF	-144.14	-144.61	-144.51	-145.14	-145.50	-152.52	-144.61	-145.58	-146.15	-145.87	-145.22
	CF2C(=O)CJF	+	CF2CF	=	CF2C(=O)CF	+	CF2CJF	-147.65	-148.21	-147.94	-148.62	-148.57	-156.24	-147.97	-148.56	-149.13	-148.87	-148.51
	CF2C(=O)CJF	+	CF3CF	=	CF2C(=O)CF	+	CF3CJF	-148.62	-149.24	-148.81	-149.47	-149.40	-157.41	-148.70	-149.23	-149.80	-149.46	-149.26
CJF2C(=O)CF																		
	CJF2C(=O)CF	+	CF2C	=	CF2C(=O)CF	+	CJF2C	-142.24	-143.54	-141.85	-142.80	-139.95	-148.55	-143.77	-140.34	-140.34	-145.28	-143.74
	CJF2C(=O)CF	+	CF2CF	=	CF2C(=O)CF	+	CJF2CF	-140.64	-141.96	-139.99	-140.75	-139.49	-149.33	-142.06	-140.08	-140.08	-143.50	-141.72
	CJF2C(=O)CF	+	CF2CF2	=	CF2C(=O)CF	+	CJF2CF2	-145.38	-146.70	-144.72	-145.49	-143.93	-154.24	-146.82	-144.32	-144.31	-147.90	-146.43
	CJF2C(=O)CF	+		=	CF2C(=O)CF	+	CF3CJF2	-142.44	-143.88	-141.68	-142.51	-140.60	-150.88	-143.51	-140.82	-140.82	-144.93	-143.40
CJF2C(=O)CF2																		
	CJF2C(=O)CF2	+	CF2C	=	CF2C(=O)CF2	+	CJF2C	-193.70	-194.44	-193.41	-194.52	-190.93	-200.03	-195.02	-190.64	-190.64	-195.92	-195.34
	CJF2C(=O)CF2	+	CF2CF	=	CF2C(=O)CF2	+	CJF2CF	-192.10	-192.86	-191.55	-192.46	-190.46	-200.81	-193.32	-190.38	-190.38	-194.15	-193.32
	CJF2C(=O)CF2	+	CF2CF2	=	CF2C(=O)CF2	+	CJF2CF2	-196.84	-197.60	-196.28	-197.21	-194.90	-205.72	-198.08	-194.62	-194.61	-198.55	-198.03
	CJF2C(=O)CF2	+	CF3CF2	=	CF2C(=O)CF2	+	CF3CJF2	-193.89	-194.78	-193.23	-194.22	-191.57	-202.36	-194.76	-191.12	-191.12	-195.58	-195.01

Table C.4 Isodesmic Reactions Calculations for Fluorinated Ketones (Continued)

								mo62x	m06	wb97x	b3plyp	CBS-APNO	CBS-4M	CBS-QB3	G-2	G-3	G-4	W1U
CF3C(=O)CJ																		
	CF3C(=O)CJ	+	CH4	=	CF3C(=O)C	+	CH3J	-157.40	-157.21	-157.35	-158.22	-157.79	-165.19	-158.07	-159.53	-159.51	-159.16	-158.08
	CF3C(=O)CJ	+	CC	=	CF3C(=O)C	+	CJC	-157.71	-155.98	-156.95	-157.70	-159.44	-166.98	-157.45	-160.99	-160.99	-158.53	-157.38
	CF3C(=O)CJ	+	CCC	=	CF3C(=O)C	+	CJCC	-153.84	-152.96	-153.30	-153.87	-155.62	-163.31	-153.63	-157.22	-157.22	-154.71	-153.55
	CF3C(=O)CJ	+	CCCC	=	CF3C(=O)C	+	CJCCC	-158.30	-157.11	-156.71	-157.88	-159.62	-167.27	-157.65	-161.21	-161.21	-158.72	-157.58
	CF3C(=O)CJ	+	C3C	=	CF3C(=O)C	+	CJ3C	-153.09	-150.41	-151.54	-151.26	-155.70	-164.64	-150.83	-156.88	-156.87	-151.54	-150.75
CF3C(=O)CJF																		
	CF3C(=O)CJF	+	CH3F	=	CF3C(=O)CF	+	CJH2F	-200.82	-202.94	-202.14	-202.79	-201.23	-209.16	-202.12	-201.98	-202.57	-203.02	-202.43
	CF3C(=O)CJF	+	CFC	=	CF3C(=O)CF	+	CJFC	-200.00	-201.40	-201.12	-201.47	-201.19	-209.38	-201.31	-201.60	-202.19	-201.89	-201.29
	CF3C(=O)CJF	+	CFCF	=	CF3C(=O)CF	+	CJFCF	-198.72	-200.35	-199.69	-199.80	-200.80	-209.10	-200.00	-201.15	-201.74	-200.99	-199.99
	CF3C(=O)CJF	+	CF2CF	=	CF3C(=O)CF	+	CF2CJF	-202.22	-203.95	-203.13	-203.29	-203.87	-212.82	-203.37	-204.12	-204.71	-204.00	-203.27
	CF3C(=O)CJF	+	CF3CF	=	CF3C(=O)CF	+	CF3CJF	-203.20	-204.98	-203.99	-204.13	-204.70	-213.99	-204.09	-204.80	-205.39	-204.58	-204.03
CF3C(=O)CJF2																		
	CF3C(=O)CJF2	+	CF2C	=	CF3C(=O)CF2	+	CJF2C	-249.16	-251.21	-248.80	-249.95	-246.84	-256.57	-250.63	-246.58	-246.58	-251.56	-
	CF3C(=O)CJF2	+	CF2CF	=	CF3C(=O)CF2	+	CJF2CF	-247.56	-249.62	-246.94	-247.89	-246.38	-257.35	-248.93	-246.32	-246.32	-249.78	-
	CF3C(=O)CJF2	+	CF2CF2	=	CF3C(=O)CF2	+	CJF2CF2	-252.31	-254.37	-251.68	-252.63	-250.82	-262.26	-253.69	-250.55	-250.55	-254.18	-
	CF3C(=O)CJF2	+	CF3CF2	=	CF3C(=O)CF2	+	CF3CJF2	-249.36	-251.54	-248.63	-249.65	-247.49	-258.90	-250.37	-247.06	-247.05	-251.21	-

APPENDIX D
THERMOCHEMISTRY AND BOND DISSOCIATION

ENERGIES OF ETHYL OXIRANE

This appendix contains the optimized geometries with corresponding Gaussian atom numbering and symmetry values in parenthesis, moments of inertia, vibrational frequencies, internal rotor potential energy graphs, entropies, and heat capacities for all of the parent and radical species from B3-LYP/6-31G(d,p) level of theory.

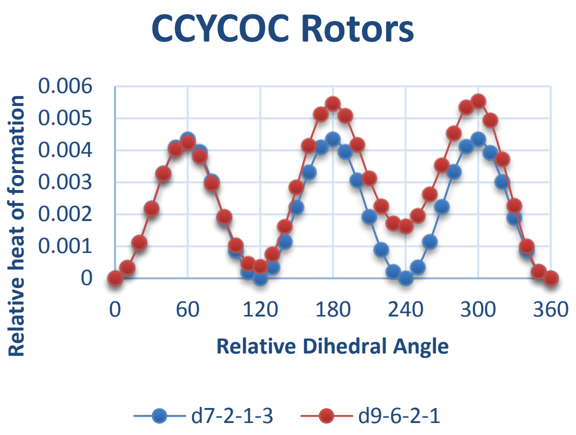
Table D.1 Moments of Inertia for Oxirane Species in System

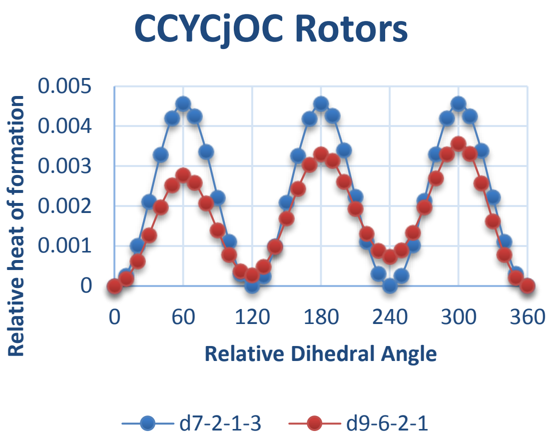
Species	Moments of Inertia (GHZ)		
CC-Y(COC)	13.0111682	3.2945262	2.9665353
CjC-Y(COC)	14.17499	3.44999	3.08457
CCj-Y(COC)	16.68148	2.88013	2.78015
CC-Y(CjOC)	13.5028031	3.3888058	2.9361467
CC-Y(COCj)	12.6814281	3.5173282	3.1183104
CC=COCj	27.8267292	2.2789230	2.1553332
CC=CCOj	21.9829069	2.1641201	2.1038578
C=C-Y(COC)	17.4415442	3.1140827	3.0250335

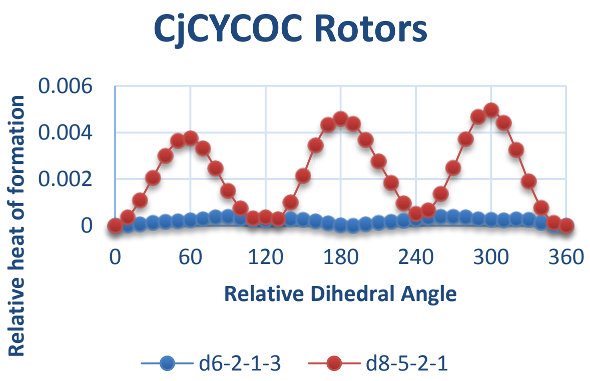
Table D.2 Vibrational Frequencies for Oxirane Species in Sysems

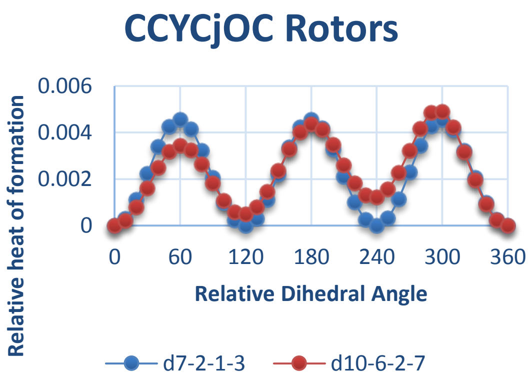
CC-Y(COC)	110.8112	235.2328	260.1972
	430.5874	512.6687	816.6654
	869.7330	954.9749	1018.0076
	1050.0659	1105.7894	1159.9441
	1226.4373	1276.3873	1286.1495
	1296.8269	1400.6835	1402.2654
	1462.4078	1535.4441	1582.9908
	1598.7422	1614.3930	1624.2471
	1674.2738	3158.9794	3164.9978
	3198.8300	3222.3664	3236.8426
	3246.9621	3259.1281	3334.1327
CjC-Y(COC)		176.5104	257.3810
	419.2436	488.6770	537.5740
	802.8913	925.8862	956.7270
	1037.7743	1092.2775	1154.7527
	1176.8583	1222.7165	1285.7684
	1292.0468	1346.1790	1401.8718
	1458.8841	1568.3323	1577.7373
	1591.3579	1672.8830	3129.0842
	3182.1435	3248.4996	3266.9758
	3269.9416	3335.6992	3373.2913
CCj-Y(COC)		71.6105	276.4114
	384.7188	445.5235	568.3778
	812.0889	834.0550	960.0671
	968.8281	989.0712	1090.2888
	1138.5460	1149.8831	1166.6918
	1217.3756	1289.7213	1326.2634
	1416.4537	1474.4518	1480.6311
	1508.8848	1534.9531	3017.9646
	3091.2541	3112.3602	3135.9487
	3150.9567	3207.8696	3224.9955
CC-Y(CjOC)		223.5250	237.4040
	393.4154	499.2954	797.8391
	848.3353	976.3062	1038.3290
	1052.5143	1112.2562	1186.8901
	1213.2502	1243.8189	1300.5993
	1390.3490	1454.0393	1535.8950
	1562.4475	1592.9084	1612.6267
	1622.5835	1676.5780	3131.3272
	3168.8577	3202.3584	3230.9050
	3242.0077	3248.7883	3339.3769
CC-Y(COCj)		235.8082	265.4406
	430.6290	515.2271	809.5347
	888.5144	930.8156	1009.5102
	1042.7635	1119.3247	1166.9141
	1203.7127	1254.3050	1288.5702
	1394.8614	1416.0511	1467.8266
	1536.2551	1595.8209	1609.0112
	1615.5258	1630.4497	3161.1384
	3167.4918	3202.5093	3225.6180
	3238.0802	3274.8824	3305.6461
CC=COCj		211.0989	219.5815
	227.8022	331.7962	482.1804
	538.5235	787.9732	912.5904
	994.9151	1059.5813	1119.9580
	1164.2014	1215.3677	1294.2893
	1385.9243	1414.0907	1465.3703
	1543.8787	1596.2888	1596.7774
	1615.2729	1855.1923	3156.1814
	3202.7809	3226.0514	3253.1457
	3310.0007	3315.0202	3397.4738
CC=CCOj		194.7952	218.8779
	291.3974	460.6633	527.5359
	837.4489	972.9014	1015.2076
	1098.2441	1109.9162	1160.6297
	1172.1105	1201.8109	1307.4458
	1399.7272	1429.0529	1494.6454
	1538.1779	1565.1835	1597.5969
	1607.9995	1858.2265	3122.1385
	3158.1195	3187.3758	3205.3267
	3236.6812	3271.3141	3290.4158
C=C-Y(COC)		310.1323	368.4237
	499.2196	751.1745	882.1273
	961.0939	1044.6025	1065.5371
	1071.7408	1126.4820	1199.7247
	1277.1192	1280.6744	1304.0729
	1390.5977	1413.5818	1498.8257
	1594.8997	1663.9253	1857.0418
	3247.7545	3279.4579	3286.9297
	3307.4706	3336.8722	3367.7270
	1616.2161	1671.3295	3179.8927
	3228.5695	3249.6311	3262.8530
	3266.2928	3360.1423	4096.8174

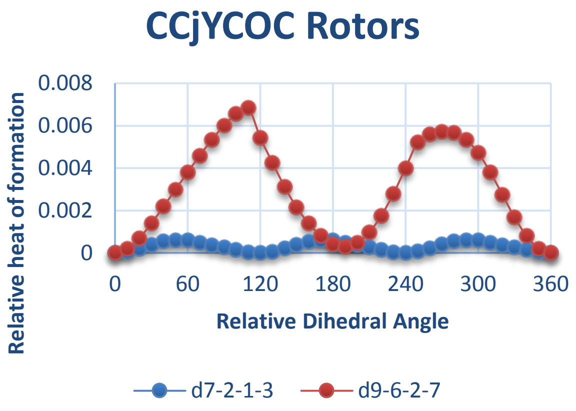
Figure D.1 Potential Energy Profiles of Species in Oxirane System











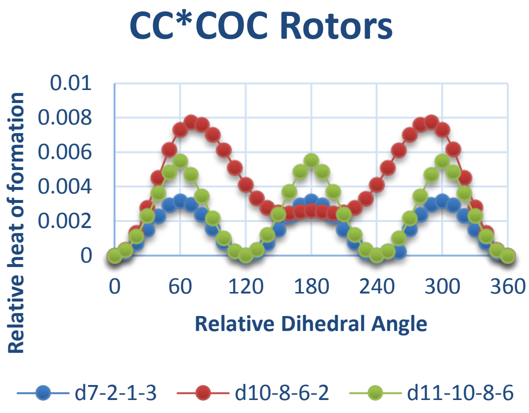


Figure D.1 Potential Energy Profiles of Species in Oxirane System (Continued)

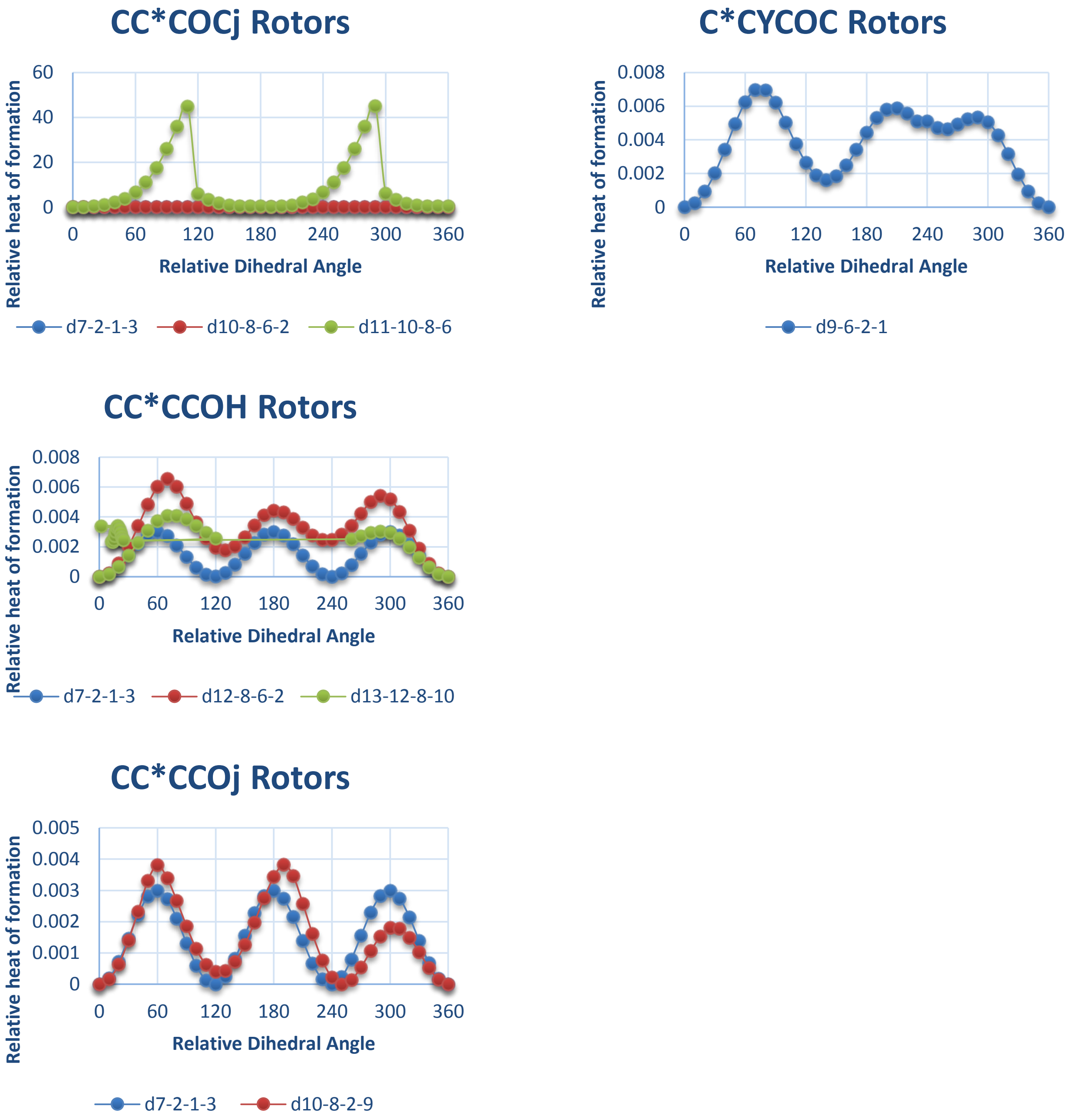


Table D.3 Thermochemical Data for Oxirane Species in Sysems

SPECIES	HF	S°_{298}	C_P300	C_P 400	C_P 500	C_P 600	C_P 800	C_P 1000	C_P 1500
CCJYCOC	18.34	71	19.09	24.43	29.52	33.94	40.9	46.04	54.06
TCY4O	80.54	70.43	19.46	25.19	30.56	35.15	42.22	47.28	54.94
CJCYCOC	21.65	70.1	19.2	24.69	29.81	34.23	41.12	46.19	54.12
TS3	58.71	77.86	21.53	26.89	31.78	35.91	42.28	46.97	54.43
C*C	12.54	52.39	10.46	12.87	15	16.88	19.99	22.38	26.16
H	52.1	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97
CJ*CC	63.76	65.21	15.26	18.51	21.36	23.85	27.92	31.01	35.82
CH2O	-28	52.33	8.47	9.48	10.49	11.48	13.29	14.78	16.96
YCOCJ	40	60.4	11.2	14.2	16.7	18.8	21.8	24	27.3
TCY3YCOC	83.09	73.8	20.44	25.68	30.68	35.05	41.95	46.99	54.74
CCYCJOC	23.57	69.48	18.2	23.51	28.64	33.16	40.34	45.64	53.88
TY3YCOC	71.45	72.2	20.26	25.86	31.01	35.4	42.19	47.12	54.73
TSX	57.66	73.45	21.79	27.5	32.63	36.93	43.44	48.11	55.28
CDCYCOC	2.09	69.52	18.39	23.61	28.5	32.69	39.18	43.89	51.17
CCDCOCJ	-12.54	72.33	20.79	25.76	30.47	34.6	41.22	46.19	54.07
CCDCCOJ	16.13	71.16	19.18	24.3	29.26	33.64	40.64	45.86	54
TS2	48.25	80.56	22.98	27.72	32.18	36.07	42.3	47.01	54.54
CCYCOCJ	25.06	68.99	18.09	23.55	28.77	33.32	40.49	45.77	53.95
TSD	30.52	73.23	21.17	26.4	31.21	35.34	41.85	46.69	54.36
TS1	22.75	82.39	23.75	28.49	32.88	36.68	42.74	47.32	54.68
TSP	23.08	73.52	20.18	25.21	30.08	34.35	41.15	46.2	54.14

Table D.4 Isodesmic Reactions Calculations for Oxirane Species in Sysems

				CCYCOC			**CBS-APNO**	**CBS-4M**	**CBS-QB3**	**m062x**	**wb97x**	**B2-LYP**
CCYCOC	+	Y(CCC)	=	CCY(CCC)	+	Y(COC)	-28.7	-28.7	-28.8	-28.1	-28.2	-28.4
CCYCOC	+	CCCOH	=	CY(COC)	+	CCC(OH)C	-27.6	-27.2	-27.2	-26.6	-26.7	-26.9
CCYCOC	+	CCCOH	=	CY(COC)	+	CCCCOH	-27.1	-27.4	-27.2	-26.9	-26.7	-27.0
CCYCOC	+	Y(CCC)	=	CY(CCC)	+	CY(COC)	-27.9	-28.1	-27.6	-27.6	-27.4	-27.4
CCYCOC	+	CY(CCC)	=	CCY(CCC)	+	CY(COC)	-28.0	-28.3	-28.0	-27.7	-27.7	-27.8
				CjCYCOC								
CjCYCOC	+	CCCOH	=	CCYCOC	+	CjCCOH	22.7	22.7	23.2	23.5	23.2	23.1
CjCYCOC	+	CCCC	=	CCYCOC	+	CjCCC	22.0	22.0	22.1	21.8	22.0	22.1
CjCYCOC	+	CY(COC)c	=	CCYCOC	+	cj-y(coc)-c	19.7	20.9	21.4	20.9	20.6	21.1
CjCYCOC	+	C2-Y(COC)	=	CCYCOC	+	cj2-Y(COC)	20.1	20.8	21.5	20.7	20.6	21.0
				CCjYCOC								
CCjYCOC	+	CCCOH	=	CCYCOC	+	CCjCOH	19.4	18.4	17.9	18.6	18.4	18.1
CCjYCOC	+	CCCC	=	CCYCOC	+	CCjCC	18.9	17.8	17.1	17.7	17.7	17.3
CCjYCOC	+	CCCQ	=	CCYCOC	+	CCjCQ	20.0	19.1	18.6	20.2	19.0	18.9
CCjYCOC	+	CCCCOH	=	CCYCOC	+	CCjCCOH	19.5	18.0	17.5	18.3	18.2	17.9
CCjYCOC	+	CCC(OH)C	=	CCYCOC	+	CCjC(OH)C	19.1	18.0	17.5	18.3	18.0	17.8
				CCYCjOC								
CCYCjOC	+	Y(COC)	=	CCYCOC	+	Y(COCj)	23.0	23.1	22.9	23.2	23.2	23.0
CCYCjOC	+	Y(CCC)	=	CCYCOC	+	Y(CjCC)	25.2	25.6	22.4	23.8	23.0	22.6
CCYCjOC	+	CC(OH)C	=	CCYCOC	+	CCj(OH)C	23.9	25.5	24.0	23.9	23.9	23.3
CCYCjOC	+	CY(COC)c	=	CCYCOC	+	c-y(cjoc)-c	23.2	23.2	23.4	23.4	23.3	23.4
				CCYCOCj								
CCYCOCj	+	Y(COC)	=	CCYCOC	+	Y(COCj)	24.7	24.6	24.5	24.6	24.5	24.5
CCYCOCj	+	Y(CCC)	=	CCYCOC	+	Y(CjCC)	26.9	27.1	24.1	25.2	24.4	24.1
CCYCOCj	+	CC(OH)C	=	CCYCOC	+	CCj(OH)C	25.6	27.0	25.7	25.3	25.2	24.8
CCYCOCj	+	C2-Y(COC)	=	CCYCOC	+	C2-Y(COCj)	24.7	24.7	24.9	24.9	24.8	24.9

Table D.4 Isodesmic Reactions Calculations for Oxirane Species in Sysems (Continued)

				CCDCOC			CBS-APNO	CBS-4M	CBS-QB3	m062x	wb97x	B2-LYP
CCDCOC	+	CC=COH	=	C=COC	+	CCDCCOH	-59.2	-61.4	-61.5	-60.4	-60.4	-59.7
CCDCOC	+	C=CQ	=	C=COC	+	CC=CQ	-57.6	-58.0	-57.7	-58.4	-58.3	-57.3
CCDCOC	+	CC=C	=	CC=CC (CIS)	+	C=COC	-58.0	-58.5	-57.6	-57.4	-57.5	-57.7
CCDCOC	+	CC=C	=	CC=CC (TRANS)	+	C=COC	-57.5	-58.0	-57.4	-57.4	-57.5	-57.4
				CCDCOCj								
CCDCOCj	+	COC	=	CCDCOC	+	CjOC	-12.6	-24.5	-12.2	-11.4	-13.6	-12.5
CCDCOCj	+	COC=O	=	CCDCOC	+	CjOC=O	-11.8	-10.3	-11.8	-10.4	-11.1	-11.4
CCDCOCj	+	CCOC	=	CCDCOC	+	CCOCj	-12.7	-11.7	-12.4	-11.5	-11.8	-12.0
CCDCOCj	+	COCOH	=	CCDCOC	+	CjOCOH	-13.7	-12.9	-14.0	-12.9	-13.3	-13.7
				CCDCCOH								
CCDCCOH	+	CC=C	=	CC=CC (TRANS)	+	C=CCOH	-37.8	-36.8	-37.6	-37.8	-38.1	-38.6
CCDCCOH	+	CC=C	=	CC=CC (CIS)	+	C=CCOH	-38.3	-37.2	-37.7	-37.8	-38.1	-38.8
CCDCCOH	+	C=C	=	CC=C	+	C=CCOH	-37.8	-37.0	-37.6	-37.9	-38.1	-38.7
CCDCCOH	+	C=CQ	=	C=CCOH	+	CC=CQ	-38.0	-36.7	-37.8	-38.8	-38.9	-38.4
				CCDCCOj								
CCDCCOj	+	C(OH)C=O	=	CCDCCOH	+	C(Oj)C=O	17.4	18.0	17.6	16.8	16.8	17.2
CCDCCOj	+	C=CCOH	=	CCDCCOH	+	C=CCOj	15.8	14.9	15.6	15.8	16.0	16.5
CCDCCOj	+	C=C(OH)C	=	CCDCCOH	+	C=C(Oj)C	12.7	6.8	14.7	15.3	17.0	16.8
CCDCCOj	+	CCCOH	=	CCDCCOH	+	CCCOj	16.3	16.4	16.7	17.5	16.5	16.8
CCDCCOj	+	C=COH	=	CCDCCOH	+	C=COj	13.6	7.8	14.7	15.3	16.3	16.6
				CDC-Y(COC)								
CDC-Y(COC)	+	CC	=	C=CCC	+	Y(COC)	2.6	2.0	1.7	2.7	2.6	2.1
CDC-Y(COC)	+	C2CC	=	C=CCC	+	C2-Y(COC)	2.1	1.3	1.6	1.5	1.9	1.8
CDC-Y(COC)	+	CCCC	=	C=CCC	+	CY(COC)c	2.5	1.9	2.3	1.9	2.6	2.4

APPENDIX E

THERMOCHEMISTRY AND BOND DISSOCIATION ENERGIES OF ETHYL OXIRANE PEROXY

This appendix contains the optimized geometries with corresponding Gaussian atom numbering and symmetry values in parenthesis, moments of inertia, vibrational frequencies, internal rotor potential energy graphs, entropies, and heat capacities for all of the parent and radical species from B3-LYP/6-31G(d,p) level of theory.

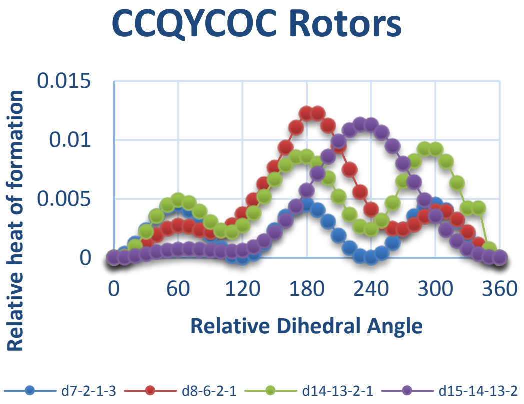
Table E.1 Moments of Inertia for Oxirane Peroxy Species

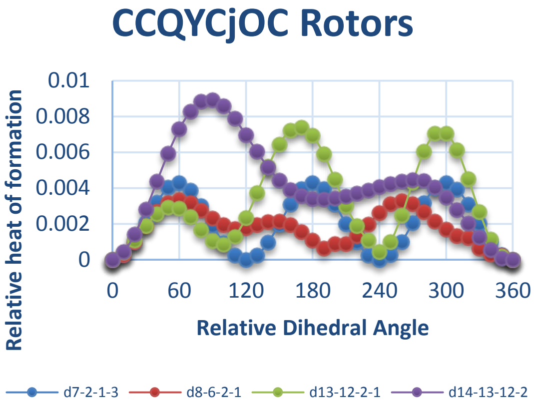
Species	Moments of Inertia (GHZ)		
CCQj-Y(COC)	3.7361514	2.2781436	1.5246008
CjCQ-Y(COC)	3.8030109	2.2477164	1.5115786
CCQ-Y(CjOC)	3.3564734	2.6929913	1.7341016
CCQ-Y(COCj)	3.7778499	2.2196762	1.4911877
CCQCjC(=O)	3.9326900	2.2837814	1.6824240
CC(=O)C(=O)C	5.2643487	3.3574352	2.1032429
CCQC(=O)Cj	3.3250983	2.3625382	1.7185302
CC=CC(=O)	33.4059226	2.1946037	2.0855514
CYCOCC(=O)	10.1275202	2.0433981	1.8635751
CYCOCCj(=O)	10.4242683	2.0801189	1.8822209
C=COC=C(=O)	10.1346543	2.0056039	1.8347666

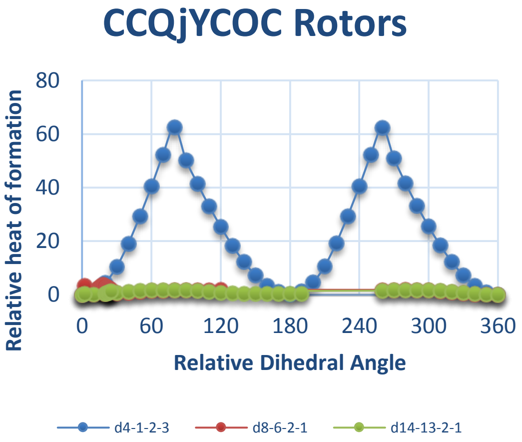
Table E.2 Vibrational Frequencies for Oxirane Peroxy Species in Systems

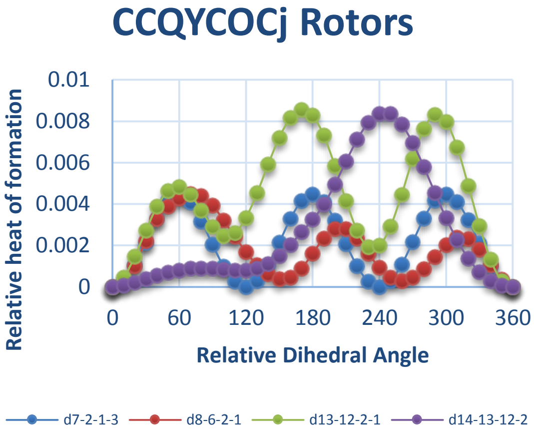
CCQj-Y(COC)		113.7730	215.1907
	252.0308	258.1029	346.4444
	425.2665	486.2108	588.7636
	792.2911	865.0393	926.2411
	942.1466	1015.7974	1087.1175
	1128.0558	1172.1979	1257.0609
	1262.9821	1268.7351	1316.1498
	1326.6780	1434.3610	1467.0038
	1569.2532	1579.8628	1657.1828
	1665.5151	1673.0532	3218.8069
	3278.7749	3296.6211	3300.3950
	3328.2664	3363.5494	3426.0685
CjCQ-Y(COC)		129.8418	179.3461
	201.0753	233.4288	287.0402
	358.6331	427.7075	462.6581
	545.9165	627.9967	908.8892
	972.1140	986.2387	1040.2447
	1143.4837	1161.4756	1199.7181
	1242.1965	1276.1541	1287.5401
	1299.8160	1389.5948	1408.9516
	1462.2715	1550.7076	1560.3557
	1596.0792	1676.5524	3148.5690
	3260.8344	3286.2565	3288.1818
	3351.6233	3403.3462	4147.5617
CCQ-Y(CjOC)		172.0244	219.4651
	234.0722	249.8950	339.8774
	440.6789	474.3329	588.5095
	655.8583	784.3633	951.7378
	1007.5559	1030.6720	1127.8702
	1143.8593	1195.4688	1216.4288
	1245.2068	1274.3065	1303.6207
	1466.6201	1489.9765	1541.9763
	1551.8361	1599.7956	1603.5285
	1616.2161	1671.3295	3179.8927
	3228.5695	3249.6311	3262.8530
	3266.2928	3360.1423	4096.8174
CCQ-Y(COCj)		112.4049	119.5526
	220.7913	250.2338	267.2641
	351.2748	427.1218	493.9568
	578.5973	852.0600	879.0509
	941.7666	988.8554	1021.8653
	1125.7460	1167.5447	1207.8610
	1233.1503	1255.2690	1293.6551
	1333.4303	1435.4491	1459.5744
	1491.3999	1568.6874	1578.2800
	1659.5319	1667.8750	3219.4932
	3277.0757	3298.0892	3305.5334
	3362.8090	3397.0969	3823.2696
CCQCjC(=O)		206.4622	236.6117
	238.9236	273.8891	304.9226
	427.5082	460.6362	585.4568
	650.9091	711.0600	807.8089
	910.4324	987.1818	1033.9337
	1080.3812	1140.6960	1191.3241
	1214.7760	1327.3131	1406.2224
	1431.9835	1505.9697	1532.9811
	1557.2925	1587.6584	1605.4568
	1611.7247	1622.3583	3176.6153
	3184.3491	3191.9886	3245.6575
	3274.5745	3306.2257	4077.4515
CC(=O)C(=O)C		133.3798	133.8399
	257.3581	387.3468	393.4461
	575.6308	588.8274	681.3750
	745.9913	984.2527	1056.9450
	1106.4945	1178.9405	1228.4084
	1409.4483	1519.7078	1534.0893
	1577.7470	1578.0434	1581.9273
	1585.6202	1995.3880	2020.3598
	3187.7597	3188.2372	3251.2335
	3251.4097	3288.8905	3289.4106
	3213.5909	3250.6957	3263.9843
	3306.6930	3426.6378	4140.4542
CCQC(=O)Cj		141.2756	229.9300
	242.9038	244.5811	298.6095
	317.2642	458.5027	518.8044
	535.4473	606.2109	674.8440
	806.1653	839.2636	984.4041
	1068.7541	1121.0545	1173.2672
	1225.5068	1284.7405	1356.0919
	1446.3897	1477.5806	1526.7440
	1535.6323	1555.4846	1595.7081
	1608.5000	1620.6769	3179.6556
	3213.5909	3250.6957	3263.9843
	3306.6930	3426.6378	4140.4542
CC=CC(=O)			
CYCOCC(=O)	115.1052	214.0021	239.3648
	276.1813	437.8914	484.9045
	567.2921	876.4215	950.5856
	1051.6754	1096.2584	1125.3755
	1193.0939	1234.6214	1272.9892
	1303.5909	1361.9336	1440.1563
	1516.0448	1539.7431	1594.4330
	1605.6254	1645.1182	2014.4195
	3122.5102	3173.3806	3235.8435
	3249.1311	3271.0263	3315.8558
CYCOCCj(=O)		213.6378	245.5392
	325.1616	437.2431	480.2227
	572.4448	889.6240	946.3005
	1030.7591	1102.5259	1142.8625
	1167.0808	1263.8129	1305.4065
	1364.7739	1444.1925	1533.4876
	1591.1987	1603.7057	1635.6178
	2132.6177	3174.4554	3237.6868
	3252.2409	3287.3098	3290.7248
C=COC=C(=O)	70.6439	166.5063	299.7499
	314.5946	592.1534	599.7539
	698.5211	761.6446	792.8219
	994.6979	1028.5612	1111.8860
	1114.2980	1250.4581	1350.6627
	1457.9713	1540.9163	1561.0956
	1838.7782	2386.7227	3314.6217
	3366.1539	3375.2446	3404.7447

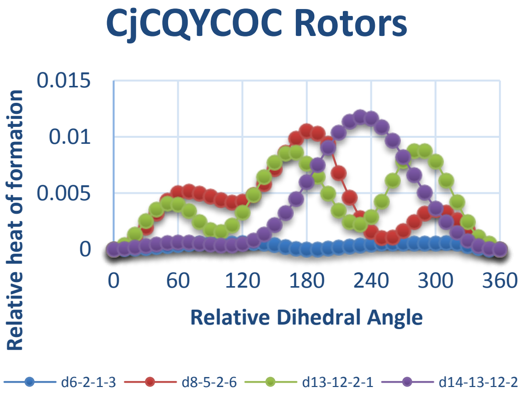
Figure E.1 Potential Energy Profiles of Species in Oxirane Oxidation System











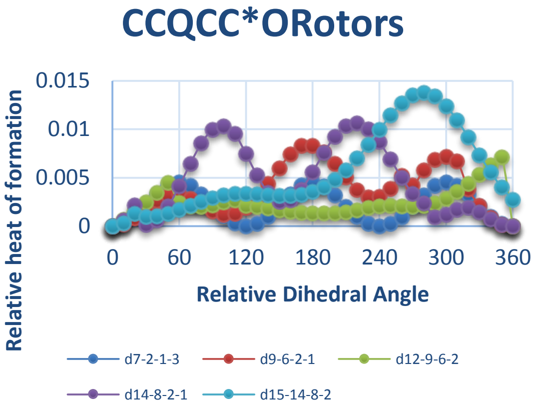


Figure E.1 Potential Energy Profiles of Species in Oxirane Oxidation System (Continued)

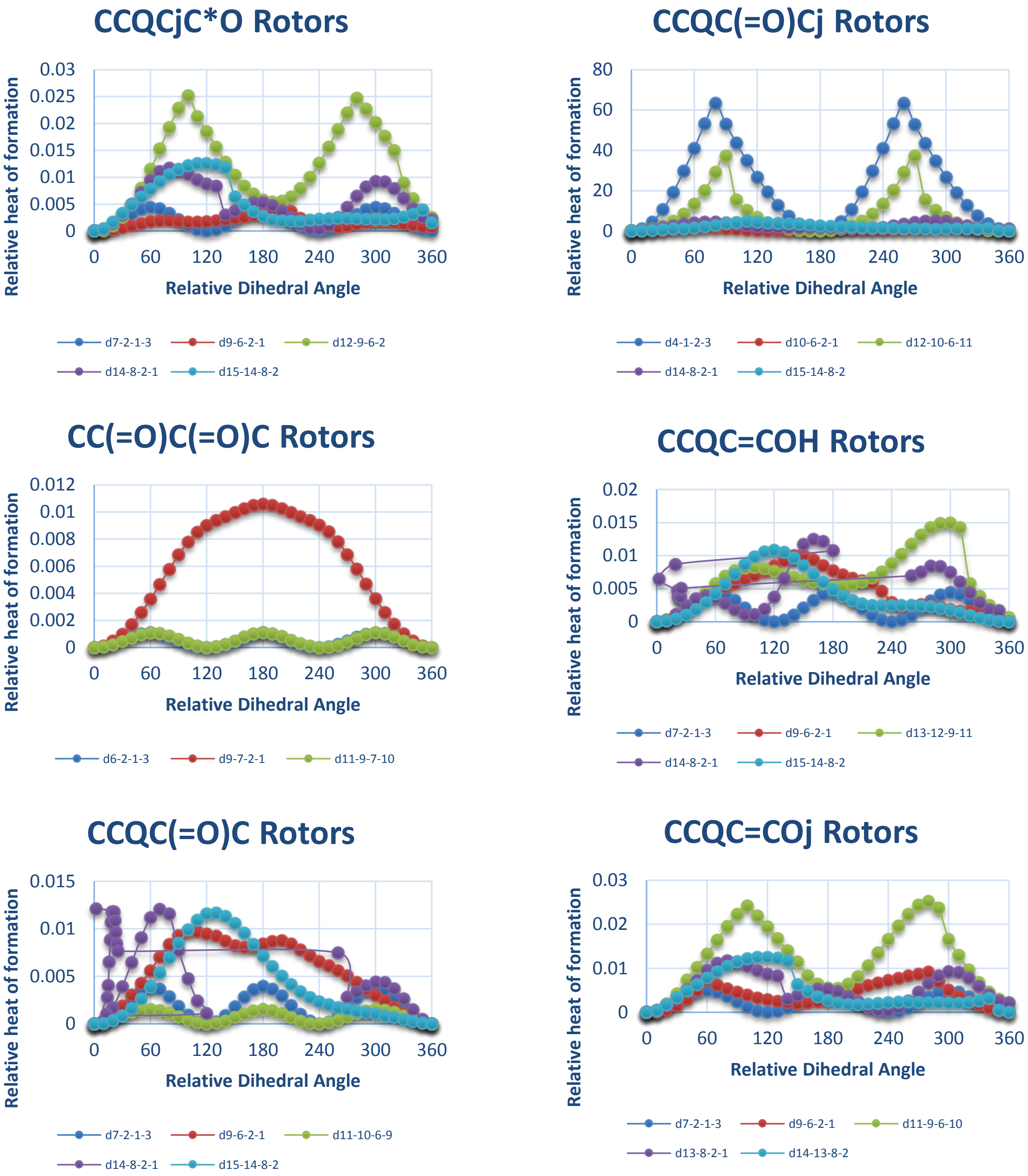


Figure E.1 Potential Energy Profiles of Species in Oxirane Oxidation System (Continued)

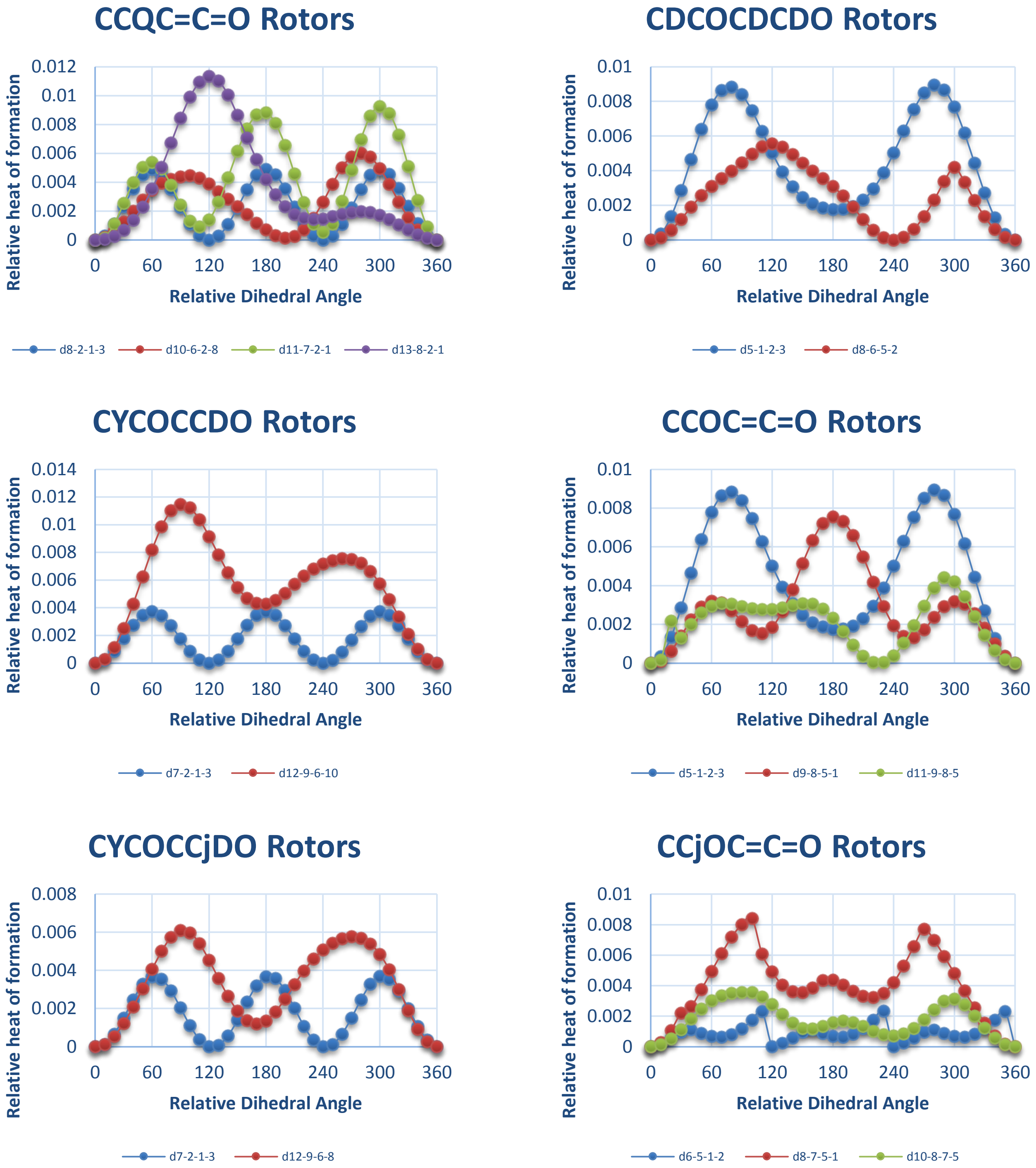


Table E.3 Thermochemical Data for Oxirane Peroxy Species in Systems

Species	Hf_{298}	**$S°_{298}$**	**C_P300**	**C_P400**	**C_P500**	**C_P600**	**C_P800**	**C_P1000**	**C_P1500**
CCQJYCOC	-13.42	79.47	25.14	31.72	37.75	42.87	50.75	56.42	65.11
CCQYCOCJ	5.76	82.38	26.66	33.02	38.84	43.77	51.32	56.76	65.17
CJCQYCOC	3.39	81.79	27.09	33.47	39.26	44.16	51.61	56.96	65.23
CCQYCJOC	2.82	78.8	25.28	31.75	37.7	42.79	50.62	56.26	64.92
CDCYCOC	2.09	67.01	16.55	22.05	27.43	32.28	40.47	47.11	58.66
CCQCDOCJ	-32.9	81.05	27.69	34.05	39.69	44.44	51.75	57.04	65.28
CCDCDOC	-77.76	76.4	22.26	27.19	31.81	36.01	43.29	49.35	60.01
CCQCJCDO	-30.92	78.7	25.97	32.52	38.41	43.41	51.09	56.63	65.15
CYCOCCDO	-50.02	74.85	22.13	27.43	32.48	36.91	43.89	48.99	56.77
CYCOCCJDO	-10.44	72.61	19.84	24.69	29.19	33.08	39.17	43.59	50.31
CDCOCDCDO	-12.01	75.78	21.32	25.98	29.99	33.32	38.4	42.06	47.66
HO2	2.94	54.76	8.35	8.89	9.46	9.99	10.77	11.38	12.48
OH	8.93	43.88	7.16	7.08	7.05	7.05	7.15	7.33	7.87
O2	0	49.01	6.98	7.23	7.46	7.68	8.04	8.33	8.73
C*C*O	-11.4	59.2	12.7	14.65	16.73	17.8	19.5	20.98	23.03
CCDO	-39.6	63	13	15.5	18	20.2	23.8	26.6	30.9
CJ*C*O	42.9	58.8	12	13.1	13.9	14.6	15.7	16.6	17.9
CYCOCJ	29.77	63.17	13.7	17.62	21.37	24.64	29.76	33.52	39.36
TCY6O	33.94	77.03	24.63	31.75	38.21	43.65	51.87	57.61	66.08
TSA	22.69	80.51	25.95	32.32	38.21	43.24	50.98	56.53	65.07
TY5YCOC	39.33	79.44	24.74	31.85	38.33	43.77	51.94	57.63	66.04
TCY5YCOC	40.57	79.62	25.42	32.08	38.27	43.57	51.69	57.44	65.97
TSE	24.95	86.33	29.63	36.05	41.65	46.29	53.33	58.4	66.24
TSB	21.94	81.03	28.77	35.67	41.52	46.29	53.42	58.51	66.32
TCY5DOQ	31.18	87.13	29.71	35.72	41.14	45.77	52.95	58.13	66.07
TS5	-30.14	81.43	27.78	34.12	39.74	44.48	51.78	57.06	65.28
TSC	37.89	83.84	26.85	33.19	38.99	43.92	51.5	56.96	65.35
TS6	-7.03	87.43	29.01	34.93	40.32	44.92	52.07	57.28	65.42
TS7	36.04	84.34	29.86	36.72	42.47	47.13	54.1	59.08	66.72
CO	-26.42	47.21	6.9	7.03	7.17	7.32	7.62	7.89	8.42
TS9	3.83	80.15	22.6	26.89	30.93	34.45	40.05	44.19	50.59
TS10	35.7	77.72	23.89	28.89	33.14	36.64	41.95	45.76	51.57
TS11	121	80.96	28.05	33.17	37.15	40.28	44.87	48.1	52.96
TS12	34.81	75.93	22.39	26.81	30.85	34.38	39.98	44.13	50.55
CCDOCDOC	-77.76	76.4	22.26	27.19	31.81	36.01	43.29	49.35	60.01
CCDCCDO	-25.77	71.52	20.14	24.6	28.94	32.82	39.1	43.82	51.18
CCYCOC	-27.64	71.06	20.22	26.09	31.82	36.88	44.94	50.92	60.24

E.4 Isodesmic Reactions for Oxirane Peroxy Species in System

							CBS-APNO	CBS-4M	CBS-QB3	m062x	wb97x	B2-LYP
CCQ-Y(COC)												
CCQ-Y(COC)	+	CC	=	CC-Y(COC)	+	CCQ	-49.1	-51.1	-49.5	-50.2	-49.8	-49.7
CCQ-Y(COC)	+	C	=	CC-Y(COC)	+	CQ	-48.6	-50.9	-49.0	-50.0	-49.6	-49.4
CCQ-Y(COC)	+	CC=C	=	CC-Y(COC)	+	C=CCQ	-47.7	-49.7	-47.7	-48.5	-48.2	-48.2
CCQ-Y(COC)	+	CC=CC (cis)	=	CC-Y(COC)	+	CC=CCQ	-42.6	-44.9	-42.9	-43.8	-43.6	-43.3
CCQ-Y(COC)	+	CC=CC trans	=	CC-Y(COC)	+	CC=CCQ	-44.4	-46.6	-44.3	-45.1	-44.8	-44.7
CCQj-Y(COC)												
CCQj-Y(COC)	+	CCQ	=	CCQ-Y(COC)	+	CCQj	-14.1	-13.9	-13.8	-13.6	-13.5	-13.6
CCQj-Y(COC)	+	CQ	=	CCQ-Y(COC)	+	CQj	-13.3	-13.2	-13.5	-13.3	-13.3	-13.4
CCQj-Y(COC)	+	CQ(OH)	=	CCQ-Y(COC)	+	CQj(OH)	-13.1	-11.6	-13.2	-13.0	-13.2	-13.0
CjCQ-Y(COC)												
CjCQ-Y(COC)	+	CCCOH	=	CCQ-Y(COC)	+	CjCCOH	4.3	4.4	4.9	5.7	4.7	4.6
CjCQ-Y(COC)	+	CCCC	=	CCQ-Y(COC)	+	CjCCC	3.6	3.8	3.8	4.0	3.6	3.6
CjCQ-Y(COC)	+	CY(COC)c	=	CCQ-Y(COC)	+	cj-y(coc)-c	1.4	2.7	3.2	3.1	2.2	2.6
CjCQ-Y(COC)	+	C2-Y(COC)	=	CCQ-Y(COC)	+	cj2-Y(COC)	1.8	2.5	3.2	2.9	2.2	2.6
CCQ-Y(CjOC)												
CCQ-Y(CjOC)	+	Y(COC)	=	CCQ-Y(COC)	+	Y(COCj)	3.3	1.3	1.7	2.7	2.8	3.0
CCQ-Y(CjOC)	+	Y(CCC)	=	CCQ-Y(COC)	+	Y(CjCC)	5.5	3.8	1.2	3.3	2.6	2.6
CCQ-Y(CjOC)	+	CY(COC)c	=	CCQ-Y(COC)	+	c-y(cjoc)-c	3.5	1.4	2.3	2.9	2.9	3.4
CCQ-Y(CjOC)	+	C3C	=	CCQ-Y(COC)	+	C3Cj	5.6	3.9	2.6	3.2	3.3	3.4
CCQ-Y(CjOC)	+	CC(OH)C	=	CCQ-Y(COC)	+	CCj(OH)C	4.2	3.6	2.8	3.4	3.4	3.3
CCQ-Y(COCj)												
CCQ-Y(COCj)	+	Y(COC)	=	CCQ-Y(COC)	+	Y(COCj)	5.5	5.5	5.7	5.8	5.8	5.7
CCQ-Y(COCj)	+	C2-Y(COC)	=	CCQ-Y(COC)	+	C2-Y(COCj)	5.6	5.7	6.1	6.1	6.0	6.1
CCQ-Y(COCj)	+	CY(COC)c	=	CCQ-Y(COC)	+	c-y(cjoc) c	5.7	5.7	6.3	6.0	5.9	6.1

CCQ-Y(COCj)	+	CY(COC)	=	CCQ-Y(COC)	+	CY(COCj)	5.2	5.3	5.6	5.6	5.7	5.6

CCD-Y(COC)

CCD-Y(COC)	+	CC	=	CC=CC (cis)	+	Y(COC)	9.6	9.7	6.2	8.5	8.1	7.8
CCD-Y(COC)	+	CC	=	CC=CC trans	+	Y(COC)	10.2	10.2	6.4	8.6	8.1	8.1
CCD-Y(COC)	+	CC=O	=	CC=CC (cis)	+	Y(COC)=O	8.1	9.6	9.0	7.1	8.0	8.4
CCD-Y(COC)	+	CC=O	=	CC=CC trans	+	Y(COC)=O	8.6	10.1	9.2	7.2	8.0	8.6

CCQCCDO

CCQCCDO	+	C	=	CC=O	+	CCCQ	-70.5	-75.0	-72.1	-73.4	-72.1	-71.1
CCQCCDO	+	CC	=	CCCC=O	+	CCQ	-72.3	-75.6	-73.8	-74.0	-73.6	-73.0
CCQCCDO	+	CC=C	=	CCCC=O	+	C=CCQ	-71.0	-74.1	-72.0	-72.3	-71.9	-71.4

CCQCjCDO

CCQCjCDO	+	CCC=O	=	CCQCCDO	+	CCjC=O	-30.6	-30.5	-32.0	-31.3	-31.4	-31.7
CCQCjCDO	+	CC=O	=	CCQCCDO	+	CjC=O	-31.0	-37.3	-28.0	-27.6	-27.2	-26.1
CCQCjCDO	+	CCCC	=	CCQCCDO	+	CCjCC	-33.2	-40.1	-34.3	-34.0	-33.2	-32.7

CCQCDOC

CCQCDOC	+	CC	=	CCC(=O)C	+	CCQ	-77.2	-79.4	-77.2	-78.2	-77.6	-77.6
CCQCDOC	+	C	=	CCQ	+	CCC(=O)	-76.0	-79.7	-77.0	-79.0	-78.2	-77.8

CCQCDOCj

CCQCDOCj	+	CC=O	=	CCQCDOC	+	CjC=O	-34.3	-40.1	-27.9	-28.4	-28.1	-27.0
CCQCDOCj	+	CCC(=O)	=	CCQCDOC	+	CjCC=O	-33.9	-39.3	-33.2	-33.0	-32.8	-32.2
CCQCDOCj	+	CC(=O)C	=	CCQCDOC	+	CC(=O)Cj	-33.2	-33.0	-34.0	-34.2	-33.5	-34.0

CC(=O)C(=O)C

CC(=O)C(=O)C	+	CC	=	CCC(=O)C	+	CC=O	-78.7	-82.5	-79.1	-78.2	-78.1	-78.2
CC(=O)C(=O)C	+	C	=	CCC(=O)C	+	C=O	-78.4	-82.3	-79.8	-78.6	-78.8	-78.6
CC(=O)C(=O)C	+	CCQ	=	CCC(=O)C	+	CC(Q)=O	-75.4	-80.0	-73.0	-73.2	-72.9	-74.0

		CCQC=C=O										
CCQC=C=O	+	C	=	CCQ	+	CC=C=O	-42.3	-44.0	-43.8	-44.7	-44.1	-44.3
CCQC=C=O	+	C	=	CCCQ	+	C=C=O	-39.7	-41.4	-41.7	-42.6	-41.4	-42.0
		CC=CC=O										
CC=CC=O	+	C	=	CC=C	+	CC=O	-24.2	-25.5	-25.8	-25.0	-24.9	-25.9
CC=CC=O	+	C	=	CC=CC (cis)	+	C=O	-25.5	-26.7	-26.9	-25.4	-25.7	-26.7
CC=CC=O	+	C	=	CC=CC trans	+	C=O	-25.0	-26.2	-26.7	-25.4	-25.7	-26.4
CC=CC=O	+	C	=	CCC=C	+	C=O	-24.9	-25.7	-27.4	-25.7	-26.0	-26.7
CC=CC=O	+	CC	=	CC=C	+	CCC(=O)	-25.0	-24.7	-26.4	-25.2	-25.3	-26.5
		C=COC=C=O										
C=COC=C=O	+	CC	=	C=COCC	+	C=C=O	268.8	-11.9	-12.4	-11.0	-11.5	-11.8
C=COC=C=O	+	C=C	=	C=COC=C	+	C=C=O	267.9	-13.2	-10.8	-11.2	-11.3	-11.6
C=COC=C=O	+	C	=	C=COC=C	+	C=O	-10.9	-17.5	-15.2	-12.6	-12.6	-12.0
		C-Y(COC)C=O										
C-Y(COC)C=O	+	C	=	CY(COC)	+	CC=O	-48.7	-50.4	-49.7	-49.4	-49.0	-49.5
C-Y(COC)C=O	+	CC	=	CY(COC)	+	CCC(=O)	-49.5	-49.6	-50.2	-49.5	-49.4	-50.2
C-Y(COC)C=O	+	CC	=	CCCC=O	+	Y(COC)	-50.5	-50.5	-51.7	-50.5	-50.5	-51.5
		C-Y(COC)-Cj=O										
C-Y(COC)-Cj=O	+	C=O	=	C-Y(COC)C=O	+	Cj=O	-10.8	-10.6	-11.0	-10.9	-11.0	-10.9
C-Y(COC)-Cj=O	+	CCC(=O)	=	C-Y(COC)C=O	+	CCCj=O	-10.0	-9.5	-10.7	-10.4	-10.1	-10.1
C-Y(COC)-Cj=O	+	C=CC=O	=	C-Y(COC)C=O	+	C=CCj=O	-9.7	-8.9	-10.9	-10.9	-10.7	-10.7
		CCQC=COH										
CCQC=COH	+	CC	=	CCC=COH	+	CCQ	-65.3	-70.1	-67.8	-67.8	-67.5	-67.6
CCQC=COH	+	C	=	CCC=COH	+	CQ	-64.8	-69.9	-67.3	-67.7	-67.3	-67.2
CCQC=COH	+	C=C	=	CCC=COH	+	C=CQ	-65.7	-69.7	-65.0	-66.0	-65.6	-66.4

CCQC=COH	+	CC=C	=	CCC=COH	+	C=CCQ	-63.9	-68.7	-66.0	-66.1	-65.9	-66.0

CCQC=COj

CCQC=COj	+	C(=O)OH	=	CCQC=COH	+	C(=O)Oj	-32.3	-27.7	-33.8	-37.1	-37.6	-36.6
CCQC=COj	+	C=COH	=	CCQC=COH	+	C=COj	-31.1	-29.8	-33.9	-33.6	-33.2	-32.3
CCQC=COj	+	C=CCOH	=	CCQC=COH	+	C=CCOj	-28.9	-22.7	-33.1	-33.1	-33.6	-32.5
CCQC=COj	+	CCOH	=	CCQC=COH	+	CCOj	-28.3	-21.0	-31.3	-32.4	-33.1	-31.7

CCOC=C=O

CCOC=C=O	+	C=C	=	C=COCC	+	C=C=O	-45.1	-45.0	-44.5	-43.6	-44.1	-45.0
CCOC=C=O	+	C=COH	=	C=COCC	+	c(oh)=c=o	-40.7	-40.1	-40.6	-39.5	-39.7	-40.2
CCOC=C=O	+	CC=C	=	C=COCC	+	CC=C=O	-39.8	-38.9	-39.4	-38.7	-39.2	-39.7
CCOC=C=O	+	C=C=C	=	C=COCC	+	c=c=c=o	-48.7	-46.1	-44.6	-46.8	-47.1	-44.4

CCjOC=C=O

CCjOC=C=O	+	CCCOH	=	CCOC=C=O	+	CCjCOH	1.1	0.8	-0.8	-0.4	-0.6	-0.3
CCjOC=C=O	+	CCCC	=	CCOC=C=O	+	CCjCC	0.6	0.2	-1.6	-1.2	-1.3	-1.1
CCjOC=C=O	+	CCCQ	=	CCOC=C=O	+	CCjCQ	1.8	1.5	-0.1	1.2	-0.1	0.5
CCjOC=C=O	+	CCCCOH	=	CCOC=C=O	+	CCjCCOH	1.3	0.3	-1.2	-0.7	-0.8	-0.5
CCjOC=C=O	+	CCC(OH)C	=	CCOC=C=O	+	CCjC(OH)C	0.6	0.1	-1.4	-0.9	-1.2	-0.8

APPENDIX F

THERMOCHEMISTRY AND BOND DISSOCIATION ENERGIES OF DIETHYL ETHER SPECIES

This appendix contains the optimized geometries with corresponding Gaussian atom numbering and symmetry values in parenthesis, moments of inertia, vibrational frequencies, internal rotor potential energy graphs, entropies, and heat capacities for all of the parent and radical species from B3-LYP/6-31G(d,p) level of theory.

Table F.1 Diethyl Ether Species Optimized Structures

Z-Matrix Structures

```
CCOCC
C
 C      1    B1
 H      1    B2   2    A1
 H      1    B3   2    A2   3    D1   0
 H      1    B4   2    A3   3    D2   0
 O      2    B5   1    A4   3    D3   0
 H      2    B6   1    A5   6    D4   0
 H      2    B7   1    A6   6    D5   0
 C      6    B8   2    A7   1    D6   0
 H      9    B9   6    A8   2    D7   0
 H      9    B10  6    A9   2    D8   0
 C      9    B11  6    A10  2    D9   0
 H      12   B12  9    A11  6    D10  0
 H      12   B13  9    A12  6    D11  0
 H      12   B14  9    A13  6    D12  0
  B1      1.51521177
  B2      1.09280512
  B3      1.09347611
  B4      1.09282105
  B5      1.41093321
  B6      1.10212310
  B7      1.10210817
  B8      1.41090280
  B9      1.10216465
  B10     1.10208697
  B11     1.51522512
  B12     1.09281341
B13       1.09348614
B14       1.09280701
A1      110.24305370
A2      110.47032269
A3      110.25199558
A4      108.51184361
A5      110.64123888
A6      110.72357760
A7      112.87619339
A8      109.75778947
A9      109.75414454
A10     108.51102253
A11     110.24619612
A12     110.46877071
A13     110.24886221
D1     -120.18408039
D2      119.64561079
D3      -59.90492625
D4      120.45253035
D5     -120.52239867
D6      179.07921630
D7       59.01269780
D8      -58.86150225
D9     -179.92871220
D10      59.89225444
D11    -179.93154480
D12     -59.75516123
```

```
CjCOCC
C
 C        1      B1
 H        1      B2   2      A1
 H        1      B3   2      A2   3      D1   0
 O        2      B4   1      A3   4      D2   0
 H        2      B5   1      A4   5      D3   0
 H        2      B6   1      A5   5      D4   0
 C        5      B7   2      A6   1      D5   0
 H        8      B8   5      A7   2      D6   0
 H        8      B9   5      A8   2      D7   0
 C        8      B10  5      A9   2      D8   0
 H        11     B11  8      A10  5      D9   0
 H        11     B12  8      A11  5      D10  0
 H        11     B13  8      A12  5      D11  0
B1          1.49062635
B2          1.08408110
B3          1.08282708
B4          1.41464808
B5          1.10223646
B6          1.09945497
B7          1.41495473
B8          1.10250919
B9          1.10024997
B10         1.51482606
B11         1.09298698
B12         1.09357826
B13         1.09287228
A1        119.10568752
```

```
  A2        121.14800509
  A3        113.07540100
  A4        110.42138808
  A5        110.91478613
  A6        113.21395384
  A7        109.41532278
  A8        110.22748836
  A9        108.15875090
  A10        110.24414121
  A11        110.47303477
  A12        110.31788553
```

CCjOCC

```
C
 C         1        B1
 H         1        B2    2        A1
 H         1        B3    2        A2    3        D1    0
 H         1        B4    2        A3    4        D2    0
 O         2        B5    1        A4    5        D3    0
 H         2        B6    1        A5    6        D4    0
 C         6        B7    2        A6    1        D5    0
 H         8        B8    6        A7    2        D6    0
 H         8        B9    6        A8    2        D7    0
 C         8       B10    6        A9    2        D8    0
 H        11       B11    8        A10   6        D9    0
 H        11       B12    8        A11   6        D10   0
 H        11       B13    8        A12   6        D11   0
  B1        1.48628276
  B2        1.10068601
  B3        1.09454232
  B4        1.09260276
  B5        1.36029476
  B6        1.09103236
  B7        1.42054900
  B8        1.09982732
  B9        1.09812785
  B10        1.51384447
  B11        1.09264453
```

CCQOCC

```
C
 H         1        B1
 H         1        B2    2        A1
 H         1        B3    2        A2    3        D1    0
 C         1        B4    2        A3    4        D2    0
 H         5        B5    1        A4    2        D3    0
 H         5        B6    1        A5    2        D4    0
 O         5        B7    1        A6    2        D5    0
 C         8        B8    5        A7    1        D6    0
 H         9        B9    8        A8    5        D7    0
 O         9       B10    8        A9    5        D8    0
 O        11       B11    9        A10   8        D9    0
 H        12       B12   11        A11   9        D10   0
 C         9       B13    8        A12   5        D11   0
 H        14       B14    9        A13   8        D12   0
 H        14       B15    9        A14   8        D13   0
 H        14       B16    9        A15   8        D14   0
  B1        1.09273037
  B2        1.09321963
  B3        1.09317716
  B4        1.51441557
  B5        1.09996549
  B6        1.09783193
  B7        1.42427046
  B8        1.39793505
  B9        1.10108758
  B10        1.41855818
  B11        1.42255811
  B12        0.97088579
  B13        1.51141524
```

```
D1         168.68386285
D2        -149.61458668
D3         123.81744597
D4        -117.52515142
D5          68.23329497
D6          53.15826944
D7         -64.76822664
D8         173.75947019
D9          59.67153412
D10        179.73352466
D11        -59.95529295
```

```
B12          1.09276629
B13          1.09328189
A1         112.11316249
A2         110.39111454
A3         110.33362953
A4         114.25075182
A5         121.08438476
A6         114.92535242
A7         109.06530710
A8         109.05296046
A9         108.30134884
A10        110.30107762
A11        110.43671545
A12        110.22514936
D1        -119.61715808
D2        -119.94461765
D3        -172.97510878
D4        -146.06258157
D5        -178.44099902
D6          58.99719793
D7         -58.86017070
D8         179.91515128
D9          60.13332844
D10        -59.76990919
D11       -179.88063445
```

```
B14          1.09170427
B15          1.09034082
B16          1.09191042
A1         108.75136401
A2         108.33108916
A3         110.35416776
A4         110.84632890
A5         111.22622694
A6         107.98953280
A7         114.07662349
A8         110.70584342
A9         110.48849461
A10        108.52526030
A11        102.17204544
A12        108.73277127
A13        109.35283902
A14        110.04397966
A15        109.58611616
D1        -117.77116472
D2        -121.09129316
D3         -60.83279959
D4         179.15250234
D5          58.53631110
D6         177.51003423
D7          41.83657510
D8         -69.67836015
D9         -66.41484631
D10         74.91452223
D11        165.28656226
D12        -63.87101736
```

```
 D13       56.04361044

CCQjOCC
C
 H         1       B1
 H         1       B2    2      A1
 H         1       B3    2      A2    3       D1    0
 C         1       B4    4      A3    2       D2    0
 H         5       B5    1      A4    4       D3    0
 H         5       B6    1      A5    4       D4    0
 O         5       B7    1      A6    4       D5    0
 C         8       B8    5      A7    1       D6    0
 H         9       B9    8      A8    5       D7    0
 O         9       B10    8      A9    5       D8    0
 O         11      B11    9      A10    8       D9    0
 C         9       B12    8      A11    5       D10    0
 H         13      B13    9      A12    8       D11    0
 H         13      B14    9      A13    8       D12    0
 H         13      B15    9      A14    8       D13    0
  B1       1.09219730
  B2       1.09288551
  B3       1.09110603
  B4       1.52033499
  B5       1.09327121
  B6       1.08977558
  B7       1.44377482
  B8       1.37754149
  B9       1.09573390
  B10       1.49786992
  B11       1.32739827
  B12       1.50730132
  B13       1.09025855

CjCQOCC
C
 H         1       B1
 H         1       B2    2      A1
 H         1       B3    3      A2    2       D1    0
 C         1       B4    4      A3    3       D2    0
 H         5       B5    1      A4    4       D3    0
 H         5       B6    1      A5    4       D4    0
 O         5       B7    1      A6    4       D5    0
 C         8       B8    5      A7    1       D6    0
 H         9       B9    8      A8    5       D7    0
 O         9       B10    8      A9    5       D8    0
 O         11      B11    9      A10    8       D9    0
 H         12      B12    11      A11    9       D10    0
 C         9       B13    8      A12    5       D11    0
 H         14      B14    9      A13    8       D12    0
 H         14      B15    9      A14    8       D13    0
  B1       1.09318105
  B2       1.09314266
  B3       1.09272404
  B4       1.51403587
  B5       1.09977771
  B6       1.09751544
  B7       1.42520819
  B8       1.39759972
  B9       1.10514286
  B10       1.42272137
  B11       1.42282516
  B12       0.97126365
  B13       1.48309797

CCQOCjC
C
 H         1       B1
 H         1       B2    2      A1
 H         1       B3    2      A2    3       D1    0
 C         1       B4    4      A3    3       D2    0
```

```
D14        176.04315493


B14         1.08910477
B15         1.09022847
A1        107.72716561
A2        108.47700193
A3        110.41772761
A4        111.81663572
A5        110.90079965
A6        111.72419623
A7        115.53884333
A8        112.89683012
A9        110.75908061
A10        111.77726601
A11        109.85665383
A12        110.28386129
A13        109.28543722
A14        109.12917290
D1       -117.26970224
D2        122.75133309
D3        179.47974837
D4         58.93213991
D5        -57.38615741
D6        -85.72355933
D7         41.03877332
D8        -69.50078890
D9        -62.22879579
D10        168.64603718
D11        176.72703517
D12         56.27079294
D13        -63.18867293


B14         1.08069069
B15         1.08108985
A1        108.50728911
A2        108.37928197
A3        110.38428534
A4        110.90672266
A5        111.25952388
A6        107.92217752
A7        113.93135170
A8        110.54632669
A9        110.70061715
A10        108.22825694
A11        102.25624468
A12        108.98613361
A13        119.89210929
A14        118.97759058
D1        117.90571083
D2       -121.16142158
D3        -60.74049826
D4        179.00829433
D5         58.52398812
D6        176.69940036
D7         40.49515597
D8        -70.34180927
D9        -67.48694772
D10         71.42168926
D11        164.83764464
D12         -9.43723237
D13        167.43166263


H          5       B5    1      A4    4       D3    0
O          5       B6    1      A5    4       D4    0
C          7       B7    5      A6    1       D5    0
H          8       B8    7      A7    5       D6    0
O          8       B9    7      A8    5       D7    0
```

```
O        10      B10   8     A9   7      D8   0
H        11      B11  10     A10   8      D9   0
C         8      B12   7     A11   5      D10   0
H        13      B13   8     A12   7      D11   0
H        13      B14   8     A13   7      D12   0
H        13      B15   8     A14   7      D13   0
  B1        1.09437877
  B2        1.10039750
  B3        1.09224919
  B4        1.48538836
  B5        1.08845289
  B6        1.36713496
  B7        1.41089628
  B8        1.09996808
  B9        1.41127782
  B10        1.42196766
  B11        0.97281844
  B12        1.50911897
  B13        1.09170471
  B14        1.09178569
  B15        1.09080131
  A1       107.29578967
  A2       108.67298174
  A3       110.34496778
  A4       122.09893926
  A5       114.03936599
  A6       115.92199008
  A7       109.90356826
  A8       110.96179554
  A9       108.67543466
  A10       101.31548291
  A11       107.94683745
  A12       109.40350020
  A13       109.66079398
  A14       109.58802883
  D1      -116.58141015
  D2      -122.56576749
  D3        40.58126176
  D4      -171.37512156
  D5      -170.71954906
  D6        62.61827794
  D7       -48.89615411
  D8       -61.00980503
  D9        86.91463404
  D10      -174.09602822
  D11      -178.41017612
  D12       -58.34945246
  D13        61.68856759
```

```
CCQOCCj
C
H         1      B1
H         1      B2   2     A1
C         1      B3   3     A2   2     D1   0
H         4      B4   1     A3   3     D2   0
H         4      B5   1     A4   3     D3   0
O         4      B6   1     A5   3     D4   0
C         7      B7   4     A6   1     D5   0
H         8      B8   7     A7   4     D6   0
O         8      B9   7     A8   4     D7   0
O        10      B10   8     A9   7      D8   0
H        11      B11  10     A10   8      D9   0
C         8      B12   7     A11   4      D10   0
H        13      B13   8     A12   7      D11   0
H        13      B14   8     A13   7      D12   0
H        13      B15   8     A14   7      D13   0
  B1        1.08385654
  B2        1.08299369
  B3        1.49308970
  B4        1.09281470
  B5        1.09848883
  B6        1.43563917
  B7        1.39733446
  B8        1.10167841
  B9        1.41866234
  B10        1.42123269
  B11        0.97275917
  B12        1.51133061
  B13        1.09170373
  B14         1.09036518
  B15         1.09193151
  A1       118.90700895
  A2       120.86044808
  A3       110.71372021
  A4       110.62267210
  A5       113.05597004
  A6       114.79140411
  A7       110.46865453
  A8       111.68606307
  A9       108.86383837
  A10       101.80995350
  A11       108.32212334
  A12       109.48392081
  A13       109.89941578
  A14       109.45782947
  D1       179.06046969
  D2       149.00094590
  D3        28.65262042
  D4       -93.79381924
  D5        84.95432293
  D6        50.85783115
  D7       -60.57733012
  D8       -66.04352145
  D9        82.18344957
  D10       174.03596028
  D11       -62.19363773
  D12        57.80906577
  D13       177.74596500
```

```
CC(=O)OCC
C
H         1      B1
H         1      B2   2     A1
H         1      B3   3     A2   2     D1   0
C         1      B4   3     A3   2     D2   0
H         5      B5   1     A4   3     D3   0
H         5      B6   1     A5   3     D4   0
O         5      B7   1     A6   3     D5   0
C         8      B8   5     A7   1     D6   0
O         9      B9   8     A8   5     D7   0
C         9      B10   8     A9   5     D8   0
H        11      B11   9     A10   8     D9   0
H        11      B12   9     A11   8     D10   0
H        11      B13   9     A12   8     D11   0
  B1        1.09275352
  B2        1.09273999
  B3        1.09309994
  B4        1.51318006
  B5        1.09416835
  B6        1.09405439
  B7        1.43689302
  B8        1.34512322
  B9        1.20773821
  B10        1.50472443
  B11        1.09292999
  B12        1.09208683
```

```
  B13          1.08843157
  A1         108.51388965
  A2         108.53742797
  A3         110.67749110
  A4         112.15257116
  A5         112.16989935
  A6         107.27551381
  A7         115.80936134
  A8         123.15709053
  A9         111.32846489
  A10         109.37462862
  A11         109.98617802
A12         109.30570827
D1         117.76095714
D2        -121.60107925
D3         -59.12667398
D4         179.42405149
D5          60.14290659
D6         179.45774043
D7          -0.23880381
D8         179.40471350
D9         -64.26207519
D10         53.80711206
D11        175.29315659
```

CCQjOCQC

```
C
 C         1       B1
 H         1       B2    2      A1
 H         1       B3    2      A2    3      D1    0
 H         1       B4    2      A3    3      D2    0
 H         2       B5    1      A4    3      D3    0
 O         2       B6    1      A5    3      D4    0
 O         2       B7    1      A6    7      D5    0
 O         8       B8    2      A7    1      D6    0
 C         7       B9    2      A8    1      D7    0
 C        10       B10    7      A9    2      D8    0
 H        10       B11    7      A10    2      D9    0
 O        10       B12    7      A11    2      D10    0
 O        13       B13   10      A12    7      D11    0
 H        14       B14   13      A13   10      D12    0
 H        11       B15   10      A14    7      D13    0
 H        11       B16   10      A15    7      D14    0
 H        11       B17   10      A16    7      D15    0
  B1         1.51324421
  B2         1.09121010
  B3         1.09166858
  B4         1.09325678
  B5         1.09200399
  B6         1.38015247
  B7         1.47813130
  B8         1.30015084
  B9         1.41857128
  B10         1.50971394
  B11         1.09746811
  B12         1.40623054
  B13         1.42182374
  B14         0.97296487
  B15         1.09007304
B16          1.09157920
B17          1.09166580
A1         108.47146460
A2         111.12782823
A3         109.50619794
A4         112.45361726
A5         117.49310710
A6         108.57494486
A7         111.32509885
A8         118.35817221
A9         107.05796713
A10        110.22739548
A11        111.63829498
A12        109.31329017
A13        101.12026381
A14        109.77958740
A15        109.56134985
A16        109.18685296
D1        -119.70470354
D2         118.59226397
D3         -51.78964143
D4        -176.57276740
D5        -119.70879001
D6         -71.10668594
D7         -37.81408933
D8        -177.44716225
D9          60.56720346
D10        -51.88917625
D11        -67.45095379
D12         95.67643211
D13         58.48202098
D14        -61.69519558
D15        178.38711306
```

YCOCOCQC

```
C
 C         1       B1
 H         1       B2    2      A1
 H         1       B3    2      A2    3      D1    0
 O         2       B4    1      A3    3      D2    0
 O         2       B5    1      A4    5      D3    0
 H         2       B6    1      A5    5      D4    0
 C         6       B7    2      A6    1      D5    0
 C         8       B8    6      A7    2      D6    0
 H         8       B9    6      A8    2      D7    0
 O         8      B10    6      A9    2      D8    0
 O        11       B11    8      A10    6      D9    0
 H        12       B12   11      A11    8      D10    0
 H         9      B13    8      A12    6      D11    0
 H         9      B14    8      A13    6      D12    0
 H         9      B15    8      A14    6      D13    0
  B1         1.45980124
  B2         1.08654693
  B3         1.08670395
  B4         1.41240649
B5           1.37437463
B6           1.09040371
B7           1.41780368
B8           1.51053804
B9           1.09879830
B10          1.40202341
B11          1.42250066
B12          0.97364212
B13          1.09084550
B14          1.09107058
B15          1.09233095
A1         120.64199675
A2         117.36338183
A3          59.86517996
A4         116.90232522
A5         122.29345158
A6         116.32138942
A7         107.46391557
A8         109.24914900
A9         111.92460707
```

```
A10      108.57096612
A11      102.15001718
A12      109.92979670
A13      109.49951343
A14      109.27418755
D1      -154.45887491
D2      -102.18041945
D3      -107.06281118
D4       101.32266355
D5       157.28552067
D6       165.16162804
D7        41.71442952
D8       -78.38981178
D9        78.43838962
D10      -94.58481447
D11     -178.91191125
D12      -58.23458334
D13       61.10113352
```

```
CCQOC(=O)C
C
 H      1    B1
 H      1    B2   2     A1
 H      1    B3   2     A2   3     D1   0
 C      1    B4   2     A3   4     D2   0
 H      5    B5   1     A4   2     D3   0
 O      5    B6   1     A5   2     D4   0
 O      7    B7   5     A6   1     D5   0
 H      8    B8   7     A7   5     D6   0
 O      5    B9   1     A8   7     D7   0
 C     10    B10   5     A9   1     D8   0
 O     11    B11   10    A10   5     D9   0
 C     11    B12   10    A11   5     D10   0
 H     13    B13   11    A12   10    D11   0
 H     13    B14   11    A13   10    D12   0
 H     13    B15   11    A14   10    D13   0
  B1       1.09000898
  B2       1.09161386
  B3       1.09143990
  B4       1.51257000
  B5       1.09215270
  B6       1.39303348
  B7       1.41996287
  B8       0.97805356
  B9       1.45615240
  B10       1.33615929
  B11       1.21434603
  B12       1.50299120
  B13       1.09220080
B14       1.09268001
B15       1.08826167
A1      109.58991610
A2      108.56820049
A3      111.18766984
A4      111.92729599
A5      115.74647567
A6      112.43989020
A7      101.18654064
A8      110.52074553
A9      121.11638732
A10      124.56203665
A11      111.37166058
A12      109.80715070
A13      109.23940528
A14      109.30641626
D1     -119.74593875
D2     -120.12559653
D3     -171.98497178
D4       69.00815948
D5      -27.16784997
D6      -76.52167556
D7     -128.90319257
D8       75.56560036
D9        2.49441405
D10     -177.96828331
D11       56.41851629
D12      -61.48098947
D13      177.86538298
```

```
C=COCQC
C
 C      1    B1
 H      1    B2   2     A1
 H      1    B3   2     A2   3     D1   0
 O      2    B4   1     A3   4     D2   0
 C      5    B5   2     A4   1     D3   0
 C      6    B6   5     A5   2     D4   0
 H      2    B7   1     A6   5     D5   0
 H      6    B8   5     A7   2     D6   0
 O      6    B9   5     A8   2     D7   0
 H      7   B10   6     A9   5     D8   0
 H      7   B11   6    A10   5     D9   0
 H      7   B12   6    A11   5     D10   0
 O     10    B13   6    A12   5     D11   0
 H     14    B14   10    A13   6     D12   0
  B1       1.33350001
  B2       1.08267950
  B3       1.08258464
  B4       1.36458804
  B5       1.40818369
  B6       1.51044962
  B7       1.08560238
  B8       1.09907341
  B9       1.41169281
  B10       1.09154279
  B11       1.09172383
  B12       1.09045721
B13       1.42161949
B14       0.97015528
A1      118.14160406
A2      123.51594002
A3      128.09264180
A4      118.20314448
A5      107.71010132
A6      122.29725230
A7      109.70198872
A8      111.46393725
A9      109.57138190
A10      109.33292276
A11      109.83716290
A12      108.84978146
A13      101.68641294
D1     -178.81843480
D2        2.76544822
D3        9.58700757
D4      168.21639263
D5      179.85019136
D6       45.22474592
D7      -66.89331614
D8      -61.77225817
D9      178.25640026
D10       58.36643201
D11      -64.39541957
D12       91.04734133
```

```
CCQOCOjC
C
 C        1       B1
 H        1       B2    2       A1
 H        1       B3    2       A2    3       D1    0
 H        1       B4    2       A3    4       D2    0
 H        2       B5    1       A4    5       D3    0
 O        2       B6    1       A5    5       D4    0
 O        2       B7    1       A6    7       D5    0
 C        7       B8    2       A7    1       D6    0
 O        8       B9    2       A8    1       D7    0
 H        10      B10    8       A9    2       D8    0
 C        9       B11    7      A10    2       D9    0
 H        9       B12    7      A11    2      D10    0
 O        9       B13    7      A12    2      D11    0
 H        12      B14    9       A13    7       D12    0
 H        12      B15    9       A14    7       D13    0
 H        12      B16    9       A15    7       D14    0
   B1         1.51101395
   B2         1.09148062
   B3         1.09245238
   B4         1.09141567
   B5         1.09825135
   B6         1.40613339
   B7         1.41035364
   B8         1.41192198
   B9         1.42459158
   B10         0.96887257
   B11         1.52950778
   B12         1.11107602
   B13         1.35117361
   B14         1.09010526
   B15           1.09093687
   B16           1.09160905
   A1          110.51515119
   A2          109.42244714
   A3          108.66638483
   A4          112.26034999
   A5          110.23966774
   A6          105.94876716
   A7          115.30903469
   A8          107.07313146
   A9          101.08292855
   A10          107.39984457
   A11          109.49483125
   A12          114.12264164
   A13          109.81699641
   A14          109.04621996
   A15          108.97390840
   D1         -120.67577149
   D2         -118.98994623
   D3           59.21927072
   D4          -63.37197681
   D5         -118.81403492
   D6          133.10080359
   D7         -175.81865792
   D8         -104.76464078
   D9          174.86205925
   D10           55.17351497
   D11          -61.83825296
   D12         -177.20719437
   D13          -56.32424840
   D14           62.51776550
```

```
CC(=O)OCOjC
C
 C        1       B1
 H        1       B2    2       A1
 H        1       B3    2       A2    3       D1    0
 H        1       B4    2       A3    4       D2    0
 O        2       B5    1       A4    5       D3    0
 O        2       B6    1       A5    6       D4    0
 C        7       B7    2       A6    1       D5    0
 C        8       B8    7       A7    2       D6    0
 H        8       B9    7       A8    2       D7    0
 O        8       B10    7       A9    2       D8    0
 H        9       B11    8      A10    7       D9    0
 H        9       B12    8      A11    7      D10    0
 H        9       B13    8      A12    7      D11    0
   B1         1.50275841
   B2         1.09250914
   B3         1.09251113
   B4         1.08834380
   B5         1.20970037
   B6         1.34606520
   B7         1.44351952
   B8         1.53405639
   B9         1.10470442
   B10         1.33464192
   B11         1.09132926
   B12           1.09037575
   B13           1.09156409
   A1          109.61702461
   A2          109.50894670
   A3          109.32481903
   A4          125.50926606
   A5          111.46207735
   A6          116.45514159
   A7          109.78930573
   A8          108.15187339
   A9          109.88377112
   A10          108.39014833
   A11          109.53855908
   A12          109.12195648
   D1         -117.86007070
   D2         -120.99526560
   D3           -0.78719567
   D4         -179.97587628
   D5          178.43332444
   D6           83.19584832
   D7          -36.46316768
   D8         -154.78014368
   D9          -59.08389502
   D10         -179.01015299
   D11           60.75720507
```

```
CC(=O)OC(=O)
C
 C        1       B1
 H        1       B2    2       A1
 H        1       B3    2       A2    3       D1    0
 H        1       B4    2       A3    4       D2    0
 O        2       B5    1       A4    5       D3    0
 O        2       B6    1       A5    6       D4    0
 C        7       B7    2       A6    1       D5    0
 H        8       B8    7       A7    2       D6    0
 O        8       B9    7       A8    2       D7    0
   B1          1.49752789
   B2          1.09271117
   B3          1.09271676
   B4          1.08813383
   B5          1.19959360
   B6          1.38046422
   B7          1.37638357
   B8          1.09562232
```

```
  B9        1.19100179
  A1      109.43543652
  A2      109.43415284
  A3      109.25803109
  A4      126.81958320
  A5      110.16217154
  A6      118.72994136
  A7      113.49468058

YCOCOCC
C
 C          1       B1
 H          1       B2    2      A1
 H          1       B3    2      A2    3      D1    0
 O          2       B4    1      A3    4      D2    0
 O          2       B5    1      A4    5      D3    0
 H          2       B6    1      A5    5      D4    0
 C          6       B7    2      A6    1      D5    0
 C          8       B8    6      A7    2      D6    0
 H          8       B9    6      A8    2      D7    0
 H          9      B10    8       A9    6      D8    0
 H          9      B11    8      A10    6      D9    0
 H          9      B12    8      A11    6      D10    0
 H          8      B13    6      A12    2      D11    0
  B1        1.45877041
  B2        1.08705851
  B3        1.08676632
  B4        1.40909236
  B5        1.37102755
  B6        1.09249995
  B7        1.42637777
  B8        1.51349570
  B9        1.10032829
  B10       1.09320227
  B11       1.09282195

TS1
C
 C          1       B1
 H          1       B2    2      A1
 H          1       B3    2      A2    3      D1    0
 H          1       B4    2      A3    4      D2    0
 O          2       B5    1      A4    4      D3    0
 H          2       B6    1      A5    6      D4    0
 O          2       B7    1      A6    6      D5    0
 C          6       B8    2      A7    1      D6    0
 C          9       B9    6      A8    2      D7    0
 O          8      B10    2       A9    1      D8    0
 H          9      B11    6      A10    2      D9    0
 H          9      B12    6      A11    2      D10    0
 H          10      B13    9      A12    6      D11    0
 H          10      B14    9      A13    6      D12    0
 H          10      B15    9      A14    6      D13    0
  B1        1.50245314
  B2        1.09177782
  B3        1.08987059
  B4        1.09177634
  B5        1.35235408
  B6        1.43783993
  B7        1.43772123
  B8        1.44104275
  B9        1.51274134
  B10       1.44144630
  B11       1.09378176
  B12       1.09382630
  B13       1.09262753

TS2
C
 C          1       B1
```

```
A8        120.07331988
D1       -117.64600540
D2       -121.17638775
D3         -0.01176211
D4       -180.00000000
D5        179.98625423
D6         -0.00177391
D7        179.99581235


B12         1.09262176
B13         1.09710275
A1        120.45874740
A2        117.49341452
A3         59.89378886
A4        118.02874313
A5        121.63266202
A6        112.51985970
A7        107.94155430
A8        109.21173610
A9        110.27624932
A10       110.42941165
A11       110.18740061
A12       109.06365854
D1       -153.96085627
D2        103.44635389
D3       -106.32577295
D4        101.55838430
D5        144.30857385
D6        179.25034940
D7         58.50649153
D8       -179.89180184
D9        -59.70232311
D10        60.14858573
D11       -59.67626395


B14         1.09311471
B15         1.09268823
A1        109.18397593
A2        109.03521249
A3        109.19409566
A4        110.11482459
A5        113.77667619
A6        113.82692971
A7        116.30738284
A8        107.11512015
A9         89.53818616
A10       108.65542645
A11       108.57621558
A12       110.63987271
A13       109.76638141
A14       110.63371728
D1       -120.37767372
D2       -120.37654003
D3        179.96772341
D4       -128.99002010
D5        129.04217717
D6        179.30762484
D7        177.20574088
D8        116.32867254
D9         56.31676700
D10       -61.94754188
D11       -60.71040658
D12       179.49578718
D13        59.71735065


O          2       B2    1      A1
C          3       B3    2      A2    1      D1    0
```

```
C        4     B4   3     A3   2     D2   0
O        2     B5   1     A4   3     D3   0
O        6     B6   2     A5   1     D4   0
H        1     B7   2     A6   3     D5   0
H        1     B8   2     A7   3     D6   0
H        2     B9   1     A8   7     D7   0
H        4     B10  3     A9   2     D8   0
H        4     B11  3     A10  2     D9   0
H        5     B12  4     A11  3     D10  0
H        5     B13  4     A12  3     D11  0
H        5     B14  4     A13  3     D12  0
H        7     B15  6     A14  2     D13  0
  B1       1.54371671
  B2       1.38218754
  B3       1.42595683
  B4       1.51368786
  B5       1.41568761
  B6       1.42412987
  B7       1.09370073
  B8       1.09024686
  B9       1.09826538
  B10      1.09618732
  B11      1.10052090
  B12      1.09304135
  B13      1.09279814
  B14      1.09249738
  B15      1.41371823
```

```
A1       108.04757084
A2       113.89011153
A3       107.82244057
A4       102.97358585
A5       102.96913812
A6       108.64847229
A7       113.75019833
A8       115.34323795
A9       109.23591416
A10      109.07159186
A11      110.20935276
A12      110.48975183
A13      110.16565353
A14      101.31707498
D1       178.92702275
D2      -177.36911596
D3      -120.92991225
D4        28.17675497
D5         4.38221094
D6      -120.98613847
D7      -131.91959789
D8        61.57016436
D9       -56.62898442
D10     -179.77670222
D11       60.04183397
D12      -59.89919069
D13      -49.55120292
```

```
TS3
C
 C       1     B1
 H       1     B2   2     A1
 H       1     B3   2     A2   3     D1   0
 H       1     B4   2     A3   4     D2   0
 O       2     B5   1     A4   5     D3   0
 O       2     B6   1     A5   6     D4   0
 O       7     B7   2     A6   1     D5   0
 H       2     B8   1     A7   7     D6   0
 C       6     B9   2     A8   1     D7   0
 C       10    B10  6     A9   2     D8   0
 H       8     B11  7     A10  2     D9   0
 H       10    B12  6     A11  2     D10  0
 H       11    B13  10    A12  6     D11  0
 H       11    B14  10    A13  6     D12  0
 H       11    B15  10    A14  6     D13  0
  B1       1.50477339
  B2       1.09175871
  B3       1.09160825
  B4       1.09144540
  B5       1.40612522
  B6       1.42014462
  B7       1.41395415
  B8       1.10060616
  B9       1.40599811
  B10      1.50476004
  B11      1.41394963
  B12      1.10061597
  B13      1.09161838
```

```
B14        1.09177835
B15        1.09145779
A1       109.33701721
A2       109.07484551
A3       110.10114668
A4       109.40296202
A5       107.28533727
A6       105.62441316
A7       113.46392275
A8       111.50627629
A9       109.41067492
A10      106.13542221
A11      109.51915722
A12      109.08028836
A13      109.36309084
A14      110.07926791
D1      -119.29023624
D2      -120.07701552
D3       178.82441682
D4      -118.49417688
D5      -179.08541151
D6      -118.95063398
D7      -173.34041265
D8       173.34741590
D9       -70.53839287
D10      -61.70865689
D11       60.37485279
D12      -58.98062544
D13     -179.54887571
```

```
TS4
C
 C       1     B1
 H       1     B2   2     A1
 H       1     B3   2     A2   3     D1   0
 H       1     B4   2     A3   4     D2   0
 O       2     B5   1     A4   4     D3   0
 O       2     B6   1     A5   6     D4   0
 O       7     B7   2     A6   1     D5   0
 H       2     B8   1     A7   7     D6   0
 C       6     B9   2     A8   1     D7   0
```

```
H        10    B10  6     A9   2     D8   0
H        10    B11  6     A10  2     D9   0
C        10    B12  6     A11  2     D10  0
H        8     B13  7     A12  2     D11  0
H        13    B14  10    A13  6     D12  0
H        13    B15  10    A14  6     D13  0
  B1       1.50972782
  B2       1.09200543
  B3       1.09113315
  B4       1.09122085
```

```
B5        1.39721840
B6        1.42049713
B7        1.41495589
B8        1.10071454
B9        1.41462233
B10       1.09701566
B11       1.09413529
B12       1.52161279
B13       1.40262297
B14       1.09735591
B15       1.09355126
A1      109.17223972
A2      109.18787604
A3      110.27010917
A4      108.91211302
A5      105.63127275
A6      108.18169975
A7      112.94083443
A8      114.34228579
A9      109.91858454
A10     107.31273380
A11     112.45607343
A12     106.11325725
A13     109.17732054
A14     110.86764210
D1     -119.34097719
D2     -120.43137701
D3      -60.75995097
D4     -120.62706178
D5     -177.43975235
D6     -117.58340943
D7      171.17173230
D8      -35.65313290
D9     -153.18099693
D10      87.72876164
D11     -94.04687064
D12    -169.75866161
D13      69.68976975
```

TS5

```
C
 C      1    B1
 H      1    B2    2     A1
 H      1    B3    2     A2    3     D1    0
 H      2    B4    1     A3    3     D2    0
 O      2    B5    1     A4    3     D3    0
 O      2    B6    1     A5    6     D4    0
 C      6    B7    2     A6    1     D5    0
 C      8    B8    6     A7    2     D6    0
 H      8    B9    6     A8    2     D7    0
 O      8    B10   6     A9    2     D8    0
 H      9    B11   8     A10   6     D9    0
 H      9    B12   8     A11   6     D10   0
 H      9    B13   8     A12   6     D11   0
 O      7    B14   2     A13   1     D12   0
 O     11    B15   8     A14   6     D13   0
 H     16    B16  11     A15   8     D14   0
 H     15    B17   7     A16   2     D15   0
B1        1.52402097
B2        1.08911349
B3        1.09433717
B4        1.09404098
B5        1.39734505
B6        1.41610983
B7        1.40462821
B8        1.50997198
B9        1.09798923
B10       1.41525458
B11       1.09236621
B12       1.09106085
B13       1.09148484
B14       1.45066842
B15       1.42976579
B16       0.96777116
B17       1.40209993
A1      112.09414936
A2      111.82619768
A3      115.30611626
A4      107.88536311
A5      103.21407805
A6      114.93461505
A7      107.57425008
A8      110.47601163
A9      111.12597006
A10     109.81067892
A11     109.80795817
A12     109.19450402
A13     106.37162250
A14     108.27665720
A15     100.73920937
A16     104.40367081
D1     -127.64544964
D2       94.87432945
D3      -29.81351215
D4     -117.84524426
D5     -175.59563963
D6      179.23419314
D7       56.06715454
D8      -55.38595049
D9      178.76535064
D10      57.74683109
D11     -61.63569835
D12       6.26059936
D13     -61.71421166
D14    -124.79318415
D15      23.21851477
```

TS6

```
C
 C      1    B1
 H      1    B2    2     A1
 H      1    B3    2     A2    3     D1    0
 H      2    B4    1     A3    4     D2    0
 O      2    B5    1     A4    4     D3    0
 O      2    B6    1     A5    6     D4    0
 C      6    B7    2     A6    1     D5    0
 C      8    B8    6     A7    2     D6    0
 H      8    B9    6     A8    2     D7    0
 O      8    B10   6     A9    2     D8    0
 H      9    B11   8     A10   6     D9    0
 H      9    B12   8     A11   6     D10   0
 H      9    B13   8     A12   6     D11   0
O       7    B14   2     A13   1     D12   0
H      15    B15   7     A14   2     D13   0
O      11    B16   8     A15   6     D14   0
H      17    B17  11     A16   8     D15   0
B1        1.53331702
B2        1.09537291
B3        1.09146487
B4        1.09769982
B5        1.40709996
B6        1.39850870
B7        1.40238768
B8        1.50879498
B9        1.10006296
B10       1.41725644
```

```
  B11         1.09113253
  B12         1.09115425
  B13         1.09191449
  B14         1.42314956
  B15         0.97111654
  B16         1.41111726
  B17         1.41258624
  A1        109.13299089
  A2        110.01185377
  A3        111.19184491
  A4        111.92987709
  A5        111.54674630
  A6        115.20400651
  A7        109.12899298
  A8        109.29941546
  A9        111.31759561
  A10       109.28680727
  A11       110.07752257
  A12       109.20785658
  A13       108.54033944
  A14       101.62670308
  A15       108.18267652
  A16       105.85523086
  D1       -120.82172002
  D2       -155.60391528
  D3         80.80153721
  D4       -122.01872920
  D5         87.96051603
  D6        166.83021503
  D7         42.81571498
  D8        -76.73479062
  D9        -62.16278701
  D10       177.56741628
  D11        57.49645941
  D12        61.54888532
  D13        80.91779725
  D14        61.80651347
  D15       -89.77943319
```

```
TS7
C
 C      1    B1
 H      1    B2   2    A1
 H      1    B3   2    A2   3    D1   0
 H      1    B4   2    A3   4    D2   0
 O      2    B5   1    A4   5    D3   0
 O      2    B6   1    A5   6    D4   0
 C      6    B7   2    A6   1    D5   0
 C      8    B8   6    A7   2    D6   0
 H      8    B9   6    A8   2    D7   0
 O      8    B10  6    A9   2    D8   0
 H      9    B11  8    A10  6    D9   0
 H      9    B12  8    A11  6    D10  0
 H      9    B13  8    A12  6    D11  0
 O      7    B14  2    A13  1    D12  0
 O      11   B15  8    A14  6    D13  0
 H      16   B16  11   A15  8    D14  0
 H      15   B17  7    A16  2    D15  0
  B1        1.50294352
  B2        1.09145422
  B3        1.09150903
  B4        1.09049058
  B5        1.34690299
  B6        1.43677370
  B7        1.44541027
  B8        1.51066879
  B9        1.09252450
  B10       1.39649303
  B11       1.09112076
  B12       1.09069017
  B13       1.09264289
  B14       1.44130051
  B15       1.42118077
  B16       0.97299297
  B17       1.44281171
  A1      109.20932112
  A2      109.15338158
  A3      108.87542726
  A4      110.41126668
  A5      113.75762568
  A6      120.24042723
  A7      105.42392997
  A8      109.14418960
  A9      111.17560564
  A10     110.00274481
  A11     109.28907371
  A12     109.42715029
  A13      89.11239006
  A14     110.13680734
  A15     101.77651862
  A16      90.23627412
  D1     -119.58252380
  D2     -120.21337227
  D3     -179.63467001
  D4     -129.84724748
  D5     -175.86805229
  D6      161.47485055
  D7       38.40993691
  D8      -82.03285443
  D9      -57.52193780
  D10    -178.15341900
  D11      62.35056807
  D12    -104.32929193
  D13     100.07962724
  D14     -88.39032314
  D15     -10.43618859
```

```
TS8
 C
 C      1    B1
 H      1    B2   2    A1
 H      1    B3   2    A2   3    D1   0
 H      1    B4   2    A3   4    D2   0
 H      2    B5   1    A4   5    D3   0
 O      2    B6   1    A5   5    D4   0
 O      2    B7   1    A6   7    D5   0
 O      8    B8   2    A7   1    D6   0
 C      7    B9   2    A8   1    D7   0
 C      10   B10  7    A9   2    D8   0
 O      10   B11  7    A10  2    D9   0
 O      12   B12  10   A11  7    D10  0
 H      13   B13  12   A12  10   D11  0
H       11   B14  10   A13  7    D12  0
H       11   B15  10   A14  7    D13  0
H       11   B16  10   A15  7    D14  0
H       9    B17  8    A16  2    D15  0
 B1       1.50382716
 B2       1.09147854
 B3       1.09185720
 B4       1.09145243
 B5       1.09507563
 B6       1.41904406
 B7       1.41706662
 B8       1.41103035
 B9       1.38621825
 B10      1.50461204
```

```
 B11           1.41503811
 B12           1.41640000
 B13           0.97102971
 B14           1.08984977
 B15           1.09101444
 B16           1.09028304
 B17           1.41525871
 A1          109.92160044
 A2          109.52957365
 A3          109.00508185
 A4          113.94893871
 A5          108.47123471
 A6          107.43842142
 A7          105.26853552
 A8          114.16517500
 A9          110.51129818
 A10         104.71653650
 A11         108.72571715
 A12         102.02216926
 A13         109.52925865
 A14         107.79044215
 A15         109.34697754
 A16         106.16218727
 D1         -120.63692046
 D2         -119.47291625
 D3           62.39813250
 D4          -59.93537722
 D5         -117.35734500
 D6         -179.68494069
 D7         -169.91083887
 D8          167.66537162
 D9          -69.32635556
 D10         176.83090566
 D11         -87.39984411
 D12         175.98774457
 D13          56.50976359
 D14         -62.93239358
 D15         -72.17235325
```

```
CCOCCQ
C
 H        1        B1
 H        1        B2    2        A1
 H        1        B3    3        A2    2        D1    0
 C        1        B4    3        A3    4        D2    0
 H        5        B5    1        A4    3        D3    0
 H        5        B6    1        A5    3        D4    0
 O        5        B7    1        A6    3        D5    0
 C        8        B8    5        A7    1        D6    0
 H        9        B9    8        A8    5        D7    0
 H        9        B10   8        A9    5        D8    0
 C        9        B11   8        A10   5        D9    0
 H       12        B12   9        A11   8        D10   0
 H       12        B13   9        A12   8        D11   0
 O       12        B14   9        A13   8        D12   0
 O       15        B15  12        A14   9        D13   0
 H       16        B16  15        A15  12        D14   0
 B1           1.09524583
 B2           1.09433369
 B3           1.09434753
 B4           1.51916783
 B5           1.10240882
 B6           1.10229578
 B7           1.42348752
 B8           1.41828830
 B9           1.10150900
 B10          1.09959197
 B11          1.52543263
 B12          1.09643715
 B13          1.09588652
 B14          1.42435200
 B15          1.46332937
 B16          0.97093461
 A1         108.46939827
 A2         108.33842534
 A3         110.64854799
 A4         110.67862702
 A5         110.69942385
 A6         108.72809211
 A7         113.43284191
 A8         110.93959551
 A9         110.85421118
 A10        106.98282004
 A11        110.90216660
 A12        110.30987662
 A13        112.37288167
 A14        107.12675525
 A15         99.87607260
 D1         117.53872330
 D2         121.48410078
 D3         179.43368144
 D4          60.39612527
 D5         -60.07030410
 D6         179.59751358
 D7          61.41218561
 D8         -58.86251845
 D9        -178.97679631
 D10         58.99968498
 D11        -61.85877652
 D12       -176.67650459
 D13        -69.52071910
 D14       -121.75139268
```

```
CCOCJCQ
C
 H        1        B1
 H        1        B2    2        A1
 H        1        B3    3        A2    2        D1    0
 C        1        B4    4        A3    3        D2    0
 H        5        B5    1        A4    4        D3    0
 H        5        B6    1        A5    4        D4    0
 O        5        B7    1        A6    4        D5    0
 C        8        B8    5        A7    1        D6    0
 H        9        B9    8        A8    5        D7    0
 C        9        B10   8        A9    5        D8    0
 H       11        B11   9        A10   8        D9    0
 H       11        B12   9        A11   8        D10   0
 O       11        B13   9        A12   8        D11   0
 O       14        B14  11        A13   9        D12   0
 H       15        B15  14        A14  11        D13   0
 B1           1.09493498
 B2           1.09402519
 B3           1.09394840
 B4           1.51711194
 B5           1.09852600
 B6           1.09829456
 B7           1.43698298
 B8           1.35560789
 B9           1.08743104
 B10          1.47538641
 B11          1.09607308
 B12          1.09656373
 B13          1.45205616
 B14          1.46934916
 B15          0.97100937
 A1         108.42484954
```

```
 A2          108.49674549
 A3          110.77054283
 A4          111.22805623
 A5          111.29237715
 A6          108.40828471
 A7          116.13955377
 A8          117.82139836
 A9          116.36086441
 A10          110.97863733
 A11          110.90833253
 A12          107.63988255
 A13          106.74854558
 A14          100.16834743
```

```
D1          117.61494193
D2         -121.79103276
D3          -59.19969776
D4          179.85103070
D5           60.28041018
D6         -178.45355370
D7           15.32073673
D8          174.23621113
D9          156.40258395
D10          34.21168016
D11         -85.30060585
D12        -177.67121905
D13        -116.11650254
```

CCjOCCQ

```
 C
 H    1   r21
 H    1   r31          2   a312
 H    1   r41          2   a412         3   d4123         0
 C    1   r51          2   a512         3   d5123         0
 X    5   r65          1   a651         2   d6512         0
 H    5   r75          1   a751         2   d7512         0
 O    5   r85          1   a851         2   d8512         0
 C    8   r98          5   a985         1   d9851         0
 H    9   r109          8   a1098         5   d10985         0
 H    9   r119          8   a1198         5   d11985         0
 C    9   r129          8   a1298         5   d12985         0
 H   12   r1312         9   a13129        8   d131298        0
 H   12   r1412         9   a14129        8   d141298        0
 O   12   r1512         9   a15129        8   d151298        0
 O   15   r1615        12   a161512       9   d1615129       0
 H   16   r1716        15   a171615      12   d17161512      0
   r21           1.096346
   r31           1.102828
   r41           1.097690
   r51           1.470106
   r65           0.955338
   r75           1.088161
   r85           1.347396
   r98           1.421311
   r109          1.103035
   r119          1.111243
   r129          1.537696
   r1312         1.107771
   r1412         1.106640
   r1512         1.393474
```

```
r1615         1.527769
r1716         0.942423
a312        107.982740
a412        108.123522
a512        110.528242
a651        102.518257
a751        124.489679
a851        126.332630
a985        118.006211
a1098       102.492621
a1198       111.857035
a1298       110.528295
a13129      111.067390
a14129      112.293843
a15129      112.816855
a161512     107.934452
a171615      94.566332
d4123      -116.426874
d5123       123.509700
d6512       171.441825
d7512        34.938194
d8512      -137.908138
d9851        -8.155797
d10985      151.246734
d11985       35.370150
d12985      -88.773010
d131298      66.430833
d141298     -54.893789
d151298    -167.067062
d1615129    -75.543605
d17161512  -178.505990
```

CjCOCCQ

```
C
 H              1          B1
 H              1          B2    2          A1
 C              1          B3    3          A2    2          D1    0
 H              4          B4    1          A3    3          D2    0
 H              4          B5    1          A4    3          D3    0
 O              4          B6    1          A5    3          D4    0
 C              7          B7    4          A6    1          D5    0
 H              8          B8    7          A7    4          D6    0
 H              8          B9    7          A8    4          D7    0
 C              8         B10    7          A9    4          D8    0
 H             11          B11    8          A10    7          D9    0
 H             11          B12    8          A11    7         D10    0
 O             11          B13    8          A12    7         D11    0
 O             14          B14   11          A13    8          D12    0
 H             15          B15   14          A14   11          D13    0
   B1          1.08234098
   B2          1.08191949
   B3          1.48908048
   B4          1.09772488
   B5          1.09950245
   B6          1.42806163
```

```
B7            1.42343126
B8            1.09829488
B9            1.09428092
B10            1.52001269
B11            1.09321298
B12            1.09277701
B13            1.42578890
B14            1.47097021
B15            0.96981797
A1          118.82979829
A2          120.89203421
A3          110.99437471
A4          110.71782277
A5          113.36953817
A6          113.38162672
A7          110.52064471
A8          111.23553783
A9          106.35840255
A10          110.94495171
A11          110.46304859
A12          112.01891822
A13          106.31080342
```

```
 A14        99.19852308
 D1       -170.21277980
 D2         89.75262226
 D3        -29.09329103
 D4       -153.25532197
 D5         70.36230018
 D6         60.15323659
 D7        -60.47698145
 D8        179.32916595
 D9         59.44900923
 D10       -61.95769724
 D11      -176.64947186
 D12       -69.03730545
 D13      -124.93554250
```

CCOCCQj

```
C
 H     1     B1
 H     1     B2    2     A1
 H     1     B3    3     A2    2     D1    0
 C     1     B4    3     A3    4     D2    0
 H     5     B5    1     A4    3     D3    0
 H     5     B6    1     A5    3     D4    0
 O     5     B7    1     A6    3     D5    0
 C     8     B8    5     A7    1     D6    0
 H     9     B9    8     A8    5     D7    0
 H     9     B10   8     A9    5     D8    0
 C     9     B11   8     A10   5     D9    0
 H     12    B12   9     A11   8     D10   0
 H     12    B13   9     A12   8     D11   0
 O     12    B14   9     A13   8     D12   0
 O     15    B15   12    A14   9     D13   0
 B1         1.09270158
 B2         1.09161241
 B3         1.09319586
 B4         1.52356687
 B5         1.09076856
 B6         1.09831384
 B7         1.42842202
 B8         1.41849316
 B9         1.09322873
 B10        1.09738168
 B11        1.51761074
 B12        1.09144050
 B13        1.08911141
 B14        1.46088623
 B15        1.32755798
 A1       108.65475128
 A2       108.41892703
 A3       110.42943296
 A4       110.20649828
 A5       110.55204721
 A6       113.77115473
 A7       115.55956130
 A8       108.17430665
 A9       111.28335492
 A10      112.18260475
 A11      111.31540886
 A12      112.20566248
 A13      111.20774113
 A14      110.81298004
 D1       116.50851227
 D2       120.39641505
 D3       -61.36953913
 D4       179.54079814
 D5        55.82829856
 D6        73.65512476
 D7       130.43003677
 D8        11.81739034
 D9      -109.92900489
 D10      174.29186543
 D11       49.24150399
 D12      -66.39036444
 D13      -72.05701326
```

CC(OH)OCC

```
C
 H     1     B1
 H     1     B2    2     A1
 H     1     B3    2     A2    3     D1    0
 C     1     B4    4     A3    2     D2    0
 H     5     B5    1     A4    4     D3    0
 O     5     B6    1     A5    4     D4    0
 C     7     B7    5     A6    1     D5    0
 H     8     B8    7     A7    5     D6    0
 H     8     B9    7     A8    5     D7    0
 C     8     B10   7     A9    5     D8    0
 H     11    B11   8     A10   7     D9    0
 H     11    B12   8     A11   7     D10   0
 H     11    B13   8     A12   7     D11   0
 O     5     B14   1     A13   7     D12   0
 H     15    B15   5     A14   1     D13   0
 B1         1.09343372
 B2         1.09369488
 B3         1.09327959
 B4         1.52175654
 B5         1.09744997
 B6         1.41692504
 B7         1.43475320
 B8         1.09702819
 B9         1.09898442
 B10        1.51997471
 B11        1.09548713
 B12        1.09450476
 B13        1.09447398
 B14        1.42037999
 B15        0.96737080
 A1       109.30637774
 A2       107.96454127
 A3       109.41874381
 A4       110.37204578
 A5       114.82071825
 A6       116.91739526
 A7       109.86852809
 A8       109.78437709
 A9       107.87588797
 A10      110.14277797
 A11      110.68957265
 A12      110.81363947
 A13      106.99569635
 A14      107.90177198
 D1       118.28448317
 D2      -121.06057929
 D3       -55.88805512
 D4      -171.70712617
 D5       -54.62488545
 D6       -45.19705728
 D7        73.71459067
 D8      -166.14796306
 D9      -178.24447122
 D10      -58.36206518
 D11       61.71525372
 D12     -124.38841298
 D13     -176.15896492
```

```
CC(Oj)OCC
C
 H          1        B1
 H          1        B2    2        A1
 H          1        B3    3        A2    2        D1    0
 C          1        B4    3        A3    4        D2    0
 H          5        B5    1        A4    3        D3    0
 H          5        B6    1        A5    3        D4    0
 O          5        B7    1        A6    3        D5    0
 C          8        B8    5        A7    1        D6    0
 H          9        B9    8        A8    5        D7    0
 O          9        B10    8        A9    5        D8    0
 C          9        B11    8        A10    5        D9    0
 H          12        B12    9        A11    8        D10    0
 H          12        B13    9        A12    8        D11    0
 H          12        B14    9        A13    8        D12    0
   B1        1.09525543
   B2        1.09426113
   B3        1.09432956
   B4        1.51886039
   B5        1.10221773
   B6        1.09613032
   B7        1.43349938
   B8        1.40973997
   B9        1.12046781
   B10        1.34720131
   B11        1.54342852
   B12        1.09122688
   B13        1.09239103
   B14        1.09187197
   A1        108.38659870
   A2        108.33653870
   A3        110.57533880
   A4        110.73881852
   A5        111.09975378
   A6        108.17946199
   A7        115.07087712
   A8        109.07953268
   A9        116.39304185
   A10        107.59775802
   A11        109.90075365
   A12        108.99493464
   A13        108.90733872
   D1        117.55080255
   D2        121.75195553
   D3        -179.89424073
   D4        60.22425108
   D5        -60.25461481
   D6        -176.72655579
   D7        64.27077070
   D8        -52.62522432
   D9        -178.44746497
   D10        -174.11976364
   D11        65.66775686
   D12        -53.27643767
```

```
CCQOC(Oj)C
C
 C          1        B1
 H          1        B2    2        A1
 H          1        B3    2        A2    3        D1    0
 H          1        B4    2        A3    4        D2    0
 H          2        B5    1        A4    5        D3    0
 O          2        B6    1        A5    5        D4    0
 O          2        B7    1        A6    7        D5    0
 C          7        B8    2        A7    1        D6    0
 O          8        B9    2        A8    1        D7    0
 H          10        B10    8        A9    2        D8    0
 C          9        B11    7        A10    2        D9    0
 H          9        B12    7        A11    2        D10    0
 O          9        B13    7        A12    2        D11    0
 H          12        B14    9        A13    7        D12    0
 H          12        B15    9        A14    7        D13    0
 H          12        B16    9        A15    7        D14    0
   B1        1.51101395
   B2        1.09148062
   B3        1.09245238
   B4        1.09141567
   B5        1.09825135
   B6        1.40613339
   B7        1.41035364
   B8        1.41192198
   B9        1.42459158
   B10        0.96887257
   B11        1.52950778
   B12        1.11107602
   B13        1.35117361
   B14        1.09010526
   B15        1.09093687
   B16        1.09160905
   A1        110.51515119
   A2        109.42244714
   A3        108.66638483
   A4        112.26034999
   A5        110.23966774
   A6        105.94876716
   A7        115.30903469
   A8        107.07313146
   A9        101.08292855
   A10        107.39984457
   A11        109.49483125
   A12        114.12264164
   A13        109.81699641
   A14        109.04621996
   A15        108.97390840
   D1        -120.67577149
   D2        -118.98994623
   D3        59.21927072
   D4        -63.37197681
   D5        -118.81403492
   D6        133.10080359
   D7        -175.81865792
   D8        -104.76464078
   D9        174.86205925
   D10        55.17351497
   D11        -61.83825296
   D12        -177.20719437
   D13        -56.32424840
   D14        62.51776550
```

Table F.2 Vibrational Frequencies for Diethyl Ether Species in Systems

Vibrational Frequencies

Species	Frequencies (cm^{-1})		
CCOCC	102.0259	110.9764	198.4773
	249.7608	255.1706	437.8580
	448.6385	813.9835	828.6783
	876.2860	960.4232	1088.9621
	1110.9538	1174.4313	1199.0469
	1203.0667	1214.8473	1301.7305
	1313.5761	1387.7956	1406.5038
	1427.1354	1466.9466	1494.2746
	1494.5514	1507.7780	1510.7639
	1524.3833	1543.1286	3002.0073
	3010.8322	3037.1708	3040.4401
	3077.5660	3078.0280	3156.9967
	3157.2212	3167.3107	3167.4759
CjCOCC	86.8023	153.4439	191.9950
	246.0055	289.7327	386.8128
	484.3976	556.7114	827.0679
	863.2408	875.4560	1008.8620
	1079.2666	1125.0652	1157.8295
	1188.3409	1196.8526	1300.4530
	1308.8960	1386.2665	1402.9805
	1442.3284	1472.7732	1488.2768
	1490.5866	1508.2594	1535.0631
	3013.3837	3018.6841	3054.3671
	3058.9235	3072.1787	3152.2414
CCjOCC	81.1715	101.5231	180.6200
	194.3052	243.9079	433.3320
	454.9513	624.4745	810.0138
	878.2012	973.6373	1027.5090
	1109.7798	1130.8688	1182.1878
	1192.7615	1283.7251	1304.3927
	1377.4398	1401.1260	1427.1543
	1465.1802	1473.3962	1492.8000
	1501.9140	1507.7153	1528.7631
	3017.3053	3032.9284	3073.6835
	3076.9272	3099.1392	3143.5515
	3155.6511	3157.2609	3161.6381
CCQOCC	50.2444	99.8056	141.5903
	190.2899	216.0769	253.6264
	290.6670	335.1003	385.3598
	437.7725	561.8301	706.9835
	817.3238	858.6624	907.0918
	975.6760	1010.1329	1109.8774
	1131.2030	1149.6690	1185.5936
	1194.4353	1214.8421	1306.3073
	1364.9810	1378.3706	1406.9120
	1426.5295	1433.0226	1455.0982
	1486.8707	1490.3964	1498.0390
	1507.7823	1537.4234	3039.1332
	3063.8489	3072.4352	3087.1146
	3091.0022	3155.3370	3161.2310
	3171.1714	3190.7134	3782.4483
CCQjOCC	26.9540	98.2266	158.3238
	204.8563	231.3409	287.3849
	322.4017	355.8255	464.7921
	525.6736	706.8572	791.1481
	807.5130	880.4736	959.8572
	1064.3139	1104.0705	1130.2877
	1155.6200	1196.1588	1230.5742
	1258.3558	1343.9835	1381.9616
	1391.8784	1413.3761	1429.7693
	1439.7103	1489.1513	1497.4737
	1500.2375	1502.9016	1523.1321
	3066.7404	3083.6127	3089.5354
	3091.1579	3138.6246	3153.7461
	3163.5311	3180.6965	3187.7310
CjCQOCC	56.7268	100.9360	174.8873
	198.8635	213.7878	245.8583
	274.0057	328.7085	387.0447
	438.3828	460.9721	574.1100
	759.6647	820.7737	885.7283
	914.2164	972.9989	1034.5472
	1108.8716	1135.4964	1182.6100
	1187.8602	1197.4839	1306.3281
	1355.0109	1360.6075	1406.3099
	1435.5010	1440.8798	1465.2266
	1489.6872	1508.7110	1537.9604
	3019.0223	3041.5650	3071.9857
	3095.1845	3155.8904	3159.3708
	3218.8287	3342.4921	3792.0621
CCQOCjC	80.9352	97.6687	154.5321
	185.8315	198.1691	223.3145
	311.7800	372.2049	398.2943
	439.7671	553.5785	587.1858
	715.8986	859.6809	917.4456
	984.5603	1013.7038	1025.8357
	1136.4256	1144.3239	1162.8296
	1201.4512	1261.4220	1351.8269
	1381.8219	1397.9249	1433.2477
	1438.4619	1456.0613	1474.8364
	1486.9975	1495.7793	1500.1910
	3017.0494	3077.2929	3088.2601
	3103.0036	3156.7974	3172.7651
	3184.2053	3192.9842	3748.3402
CC(=O)OCC	41.8826	70.3949	155.2911
	198.2602	268.7952	377.9570
	434.9324	607.3142	650.9286
	805.5599	886.1846	975.3185
	1020.6256	1066.5866	1116.3415
	1155.9896	1185.5939	1299.3877
	1310.7710	1390.5299	1416.2828
	1444.8946	1478.2192	1485.7406
	1498.6876	1507.4109	1528.3165
	1864.6015	3082.2861	3086.6737
	3098.0602	3142.7739	3162.5851
	3164.7545	3171.6911	3206.5096
CCQOCQC	39.9102	136.1067	181.2892
	218.5225	224.1488	248.6708
	252.0733	293.8552	335.3616
	362.0083	440.2215	459.4595
	490.8364	567.8216	631.7011
	671.5038	744.0508	815.8473
	865.8353	924.0769	962.8899
	1004.7543	1014.7408	1118.8516
	1121.9008	1154.7140	1167.2254
	1191.6641	1205.7477	1367.7328
	1376.8355	1380.9492	1419.0010
	1425.7148	1435.2095	1464.9145
	1484.1213	1489.8068	1491.6859
	1499.6381	1506.5814	3085.4161
	3088.9761	3094.0577	3138.4073
	3176.1815	3176.9110	3186.8646
	3190.1929	3676.7866	3737.3895
CjCQOCQC		131.3953	146.8362
	184.7488	219.1963	229.4672
	248.9987	288.7617	332.4081
	360.3663	440.0675	453.8545
	480.1051	512.0173	575.3114
	631.4695	692.1806	804.7411
	833.4390	875.4334	924.3182
	984.8340	1001.8536	1030.8582
	1117.3523	1129.9860	1151.5510
	1182.8716	1192.8087	1352.1026
	1372.6433	1385.3766	1400.0361
	1434.6830	1450.8404	1458.6251
	1485.2622	1490.4625	1500.0861
	3078.2349	3079.6954	3090.7070
	3179.5147	3187.1198	3203.4906
	3329.5009	3664.4895	3734.6336
CCQjOCQC	76.2494	107.0755	132.9280
	184.3129	221.1806	233.7612
	274.6777	292.4971	332.2084
	374.3173	424.0749	446.3988
	487.6981	513.0652	656.9722
	712.7776	841.1931	860.3345
	918.7524	974.5226	1007.2768
	1081.4007	1122.2181	1142.8050
	1157.3702	1208.1303	1263.8861
	1316.4243	1353.1923	1378.8564
	1386.7936	1402.1343	1423.7089
	1440.2449	1459.8350	1489.9159
	1495.6153	1501.3984	1513.7311
	3087.2444	3091.8270	3111.0381
	3168.5288	3174.6502	3179.4320
	3192.4710	3193.0681	3770.8793
YCOCOCQC	76.7401	111.9285	196.3171
	210.2312	219.4722	307.8677
	337.7141	458.8290	513.2698
	556.8745	569.3243	644.3566
	849.5533	895.7136	911.3821
	940.4460	1034.6662	1058.6587
	1101.9143	1134.7481	1155.9399
	1174.8196	1178.6217	1200.4732
	1230.3877	1324.7396	1370.3604
	1391.7656	1428.8236	1443.6417
	1458.8697	1490.2839	1499.2999
	1545.5290	3082.6682	3088.4011
	3141.2824	3164.3843	3177.7660
	3186.1671	3242.9431	3769.9579
CCQOC(=O)C	86.2521	117.4148	130.2530
	209.5659	241.5056	262.5199
	328.1830	351.8525	433.7273
	494.3033	594.8128	618.7506
	634.9977	736.6094	820.1736
	907.7120	945.6324	1017.3791

	1038.9412	1070.5221	1113.9402
	1175.8337	1188.7709	1312.5574
	1379.3679	1405.3612	1428.6522
	1443.4841	1477.9024	1485.3827
	1488.4867	1492.3584	1500.6356
	1833.2531	3092.4832	3092.6887
	3163.8835	3168.8759	3177.4241
	3199.9329	3218.2264	3658.2284
CCQOC=C	79.3031	145.8436	200.7567
	225.6767	229.5079	263.6321
	319.1301	395.0570	461.2756
	640.4906	697.4284	736.9804
	854.5436	898.5374	926.9408
	990.8981	1015.1823	1016.5668
	1124.2550	1145.5158	1192.9121
	1251.9808	1359.4569	1369.3333
	1387.6224	1414.4543	1435.3020
	1448.8152	1490.7495	1501.8727
	1722.3202	3088.0924	3105.0874
	3173.6805	3192.4263	3205.6916
	3233.0439	3302.7809	3819.4725
CCQOC(Oj)C	79.3031	145.8436	200.7567
	225.6767	229.5079	263.6321
	319.1301	395.0570	461.2756
	640.4906	697.4284	736.9804
	854.5436	898.5374	926.9408
	990.8981	1015.1823	1016.5668
	1124.2550	1145.5158	1192.9121
	1251.9808	1359.4569	1369.3333
	1387.6224	1414.4543	1435.3020
	1448.8152	1490.7495	1501.8727
	1722.3202	3088.0924	3105.0874
	3173.6805	3192.4263	3205.6916
	3233.0439	3302.7809	3819.4725
CC(Oj)OC(=O)C	88.6115	101.8724	135.4091
	203.4067	226.0165	330.0684
	432.5168	442.3629	526.5914
	614.4954	644.9525	868.6229
	945.1876	982.3837	1015.8169
	1048.1888	1072.4988	1097.9564
	1164.3399	1220.7149	1299.5897
	1358.3965	1399.9220	1425.1410
	1480.6314	1485.6591	1495.5354
	1497.8856	1853.9363	2998.5789
	3094.4363	3096.5250	3171.1169
	3191.6736	3202.7106	3215.0786
CC(=O)OC(=O)	49.6668	106.4653	129.6551
	229.7448	403.5838	564.0752
	589.0925	651.9848	981.9548
	1006.7100	1061.9497	1069.1474
	1121.4374	1252.6065	1399.4875
	1417.0395	1471.3703	1479.0542
	1899.0793	1926.7364	3089.7839
	3167.5240	3168.5030	3209.7117
YCOCOCC	70.4305	109.6337	199.4732
	257.1510	385.9740	464.1282
	583.7945	825.8145	844.8627
	903.0799	930.1475	1024.9913
	1100.7016	1114.0146	1162.2910
	1180.5250	1183.7985	1190.3606
	1235.6943	1309.9374	1332.8466
	1399.6743	1433.0861	1470.1715
	1494.1283	1512.1247	1533.7110
	1560.5307	3040.7823	3089.9892
	3105.7392	3143.2100	3154.3292
	3179.1332	3182.5478	3250.1364
TS1		51.3791	116.4422
	130.6544	199.7541	207.2073
	247.7093	365.7240	383.1240
	463.0798	569.6859	688.7871
	817.0936	870.6829	922.6288
	943.4823	1010.0070	1070.6155
	1105.6054	1127.2766	1142.3325
	1183.1752	1288.9824	1306.3567
	1318.4626	1402.0863	1412.5823
	1444.3363	1482.3744	1489.7897
	1490.4763	1508.1472	1526.8839
	1967.2829	3069.2701	3072.9061
	3075.9950	3139.6064	3157.6537
	3162.6362	3165.3275	3189.9217
TS2		67.1069	91.6761
	188.4589	207.7252	261.2280
	363.1147	411.7769	465.9047
	579.6637	640.3389	814.3110
	826.8075	885.1375	931.8652
	944.9294	987.0896	1050.7680
	1103.2664	1109.4440	1148.4984
	1176.8992	1184.5434	1226.9096
	1308.8760	1326.4972	1374.6178
	1404.6308	1442.8340	1461.1163
	1489.3206	1507.5441	1532.3123
	1763.2264	3032.2201	3067.7475
	3071.8624	3109.6245	3149.8471
	3155.2716	3161.8656	3254.4798
TS3		124.2444	177.1988
	204.6026	214.0683	283.8292
	319.4723	414.7591	470.3024
	500.2207	570.5795	630.3217
	863.0963	882.8211	898.6624
	979.3114	1074.7291	1111.8954
	1141.3947	1156.1650	1178.2023
	1196.8784	1231.0805	1295.2356
	1355.6550	1377.6288	1395.7453
	1426.6215	1452.8480	1486.0238
	1491.2701	1494.7120	1497.5541
	1661.8040	3064.6852	3073.1136
	3080.5673	3088.5117	3142.1446
	3172.0483	3179.9254	3182.9747
TS4		128.6196	185.8209
	203.2011	289.0704	329.6295
	363.6793	434.4996	539.9925
	566.8330	592.6930	679.5581
	832.2415	865.7838	892.4165
	953.1436	1070.2505	1072.9146
	1090.5063	1130.1287	1160.3731
	1181.7990	1196.9239	1239.0291
	1317.8465	1370.7124	1384.6034
	1412.9227	1436.2533	1444.7103
	1488.1026	1491.7063	1494.5714
	1498.5031	3039.5468	3080.2484
	3087.0068	3099.6198	3126.3357
	3177.3050	3181.8460	3225.4252
TS5		39.6316	76.7415
	130.6798	177.2101	190.5032
	235.7939	250.6331	310.2956
	336.2029	409.5750	436.8555
	527.8840	583.9542	647.4152
	701.4579	823.7461	862.3797
	906.1356	942.2592	953.9042
	984.0846	1011.9997	1059.5558
	1112.3344	1132.6836	1144.1045
	1161.0973	1187.0381	1210.5338
	1331.8092	1359.0369	1381.4426
	1399.6254	1415.6682	1438.7238
	1455.3861	1488.9938	1498.9579
	1755.3226	3082.5014	3122.5483
	3130.5206	3155.4292	3169.6725
	3181.9584	3265.4407	3851.6372
TS6		89.0205	117.3079
	142.0204	190.3740	230.9573
	271.9436	298.8534	359.7556
	375.7672	426.9931	445.4383
	531.8967	577.7127	590.8928
	668.8878	700.3437	870.6671
	894.7378	941.6971	986.8234
	993.3964	1076.8950	1098.9679
	1122.6930	1159.2990	1174.5594
	1179.0013	1202.3648	1230.4002
	1356.3117	1366.9116	1378.6339
	1409.6675	1431.5011	1445.8129
	1451.6113	1481.2429	1491.1514
	1497.4797	3086.0739	3087.2546
	3089.9234	3140.1796	3177.9241
	3184.3243	3247.3458	3797.5464
TS7	-1817.4730	89.0205	117.3079
	142.0204	190.3740	230.9573
	271.9436	298.8534	359.7556
	375.7672	426.9931	445.4383
	531.8967	577.7127	590.8928
	668.8878	700.3437	870.6671
	894.7378	941.6971	986.8234
	993.3964	1076.8950	1098.9679
	1122.6930	1159.2990	1174.5594
	1179.0013	1202.3648	1230.4002
	1356.3117	1366.9116	1378.6339
	1409.6675	1431.5011	1445.8129
	1451.6113	1481.2429	1491.1514
	1497.4797	3086.0739	3087.2546
	3089.9234	3140.1796	3177.9241
	3184.3243	3247.3458	3797.5464
TS8		67.9154	121.0448
	162.3389	207.4575	216.9654
	241.7535	299.6244	313.8290
	336.5939	366.6616	437.1097
	443.6535	545.4585	565.4943
	621.3551	666.9544	873.6833
	901.3049	924.6145	1009.9151
	1050.2788	1068.0290	1102.9543
	1132.3954	1161.9728	1187.6180
	1241.0784	1305.9291	1330.0267
	1382.5690	1386.1455	1413.6744
	1427.8969	1447.3121	1484.9086
	1489.8742	1490.8234	1498.5274
	1646.9925	3073.1154	3092.4909
	3135.5163	3163.6238	3183.4036

	3188.6569	3198.9885	3775.8395
CCOCCQ	51.6373	74.0281	122.9325
	136.7054	169.1479	185.7242
	253.7602	314.7200	382.4897
	445.7456	554.3158	816.5369
	833.6673	864.1102	903.0777
	1036.8032	1053.8286	1095.2112
	1157.9709	1171.8301	1176.0609
	1204.0468	1257.5610	1310.2785
	1318.0672	1343.9076	1366.3479
	1413.5485	1439.0277	1471.8285
	1500.7630	1509.7897	1527.0938
	1543.0268	1558.9941	3017.0933
	3036.1610	3053.9226	3083.5038
	3087.2717	3090.9125	3157.3454
	3162.4036	3172.7024	3798.2026
CCOCjCQ		63.8895	90.2951
	146.5001	201.8012	215.2447
	250.9596	290.5241	344.8951
	435.6269	530.0761	589.5490
	828.7301	857.9216	869.4974
	955.6309	982.6444	1088.4034
	1123.4928	1174.9203	1192.3271
	1248.7091	1282.6315	1312.6590
	1324.7832	1373.4348	1410.5110
	1443.3969	1486.3113	1510.4174
	1521.3449	1527.3440	1544.8033
	3057.6911	3081.7587	3087.3362
	3105.0423	3140.5671	3167.3163
	3178.3617	3209.9463	3795.0246
CCjOCCQ		112.0326	138.4752
	189.1015	243.2308	245.2746
	303.1381	335.4096	379.3732
	491.1846	564.8491	641.4337
	790.6023	897.9627	957.0044
	1024.0770	1053.8084	1083.3531
	1120.2939	1137.1645	1180.4219
	1259.6616	1303.3383	1327.3918
	1345.2271	1387.2150	1417.4084
	1435.4308	1442.6667	1479.4466
	1489.7407	1501.9229	1531.1955
	2996.6549	3088.5276	3093.4137
	3098.9082	3142.3561	3144.7578
	3162.5106	3222.8269	3848.4240
CjCOCCQ		72.6178	138.6311
	176.2393	202.6169	216.8330
	269.6393	347.0116	391.1964
	463.5652	542.4921	550.3040
	818.0180	851.2685	958.3677
	971.8639	1068.2952	1100.2575
	1120.8984	1138.2998	1177.5319
	1198.4360	1260.1599	1298.2153
	1311.6473	1347.8749	1390.0439
	1404.5352	1453.2764	1466.1044
	1485.3368	1488.3534	1534.0922
	3021.1134	3032.6757	3064.4709
	3076.6630	3090.2766	3145.0698

	3188.4943	3302.8086	3836.0621
CCOCCQj		87.2294	123.1432
	170.1775	265.5518	301.5258
	352.4518	466.8629	494.0136
	572.9292	797.0483	832.5396
	880.8127	922.1210	1033.6522
	1069.1502	1102.0004	1130.5076
	1187.6368	1220.6607	1264.1111
	1314.2548	1322.2298	1343.2654
	1384.2555	1399.1357	1417.8639
	1430.6305	1477.2044	1491.0704
	1501.6048	1504.7328	1519.3381
	3035.0536	3050.3263	3057.3219
	3105.9233	3122.5934	3125.4890
	3143.7698	3150.4432	3181.2964
CC(OH)OCC	75.3225	137.5678	226.1221
	266.1391	282.6642	348.0422
	394.8579	445.9802	492.3010
	673.7625	827.9706	846.4051
	920.1043	979.1780	1068.0903
	1096.1416	1144.2468	1162.9295
	1190.8745	1215.0171	1285.5061
	1315.0523	1394.6668	1401.2994
	1416.9472	1440.3898	1466.4114
	1491.2583	1496.4650	1504.8608
	1511.3754	1537.8041	3048.0541
	3068.1390	3084.1215	3094.3292
	3100.7179	3150.6421	3157.4906
	3169.9390	3176.7152	3886.4389
CC(Oj)OCC		124.1797	189.5742
	211.3908	262.9335	341.8948
	407.2323	473.2907	612.7571
	817.4170	863.6603	914.3057
	961.2582	1023.3943	1088.3583
	1116.0547	1183.2342	1187.7441
	1210.6229	1224.8833	1307.0512
	1325.7089	1391.0064	1402.9752
	1446.4555	1488.6556	1493.0206
	1498.8042	1508.9726	1534.4568
	2903.5765	3019.8487	3074.5287
	3089.3753	3093.8915	3158.4300
	3161.2896	3180.8019	3195.4955
CCQOC(Oj)C		69.9115	166.6282
	190.8322	224.2177	232.5093
	272.3629	322.4039	358.3750
	397.3922	467.3081	505.9236
	570.7950	643.8906	865.0607
	904.7001	928.7351	973.5477
	1020.6958	1043.9909	1107.9950
	1135.8312	1167.2250	1194.2501
	1211.2708	1227.5774	1312.0667
	1360.3308	1396.9576	1402.3270
	1418.9652	1454.8406	1486.8829
	1491.1520	1498.1117	1500.9966
	2923.3809	3084.5215	3089.4759
	3092.6862	3175.2238	3181.6420
	3183.1662	3198.9206	3824.8173

Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System

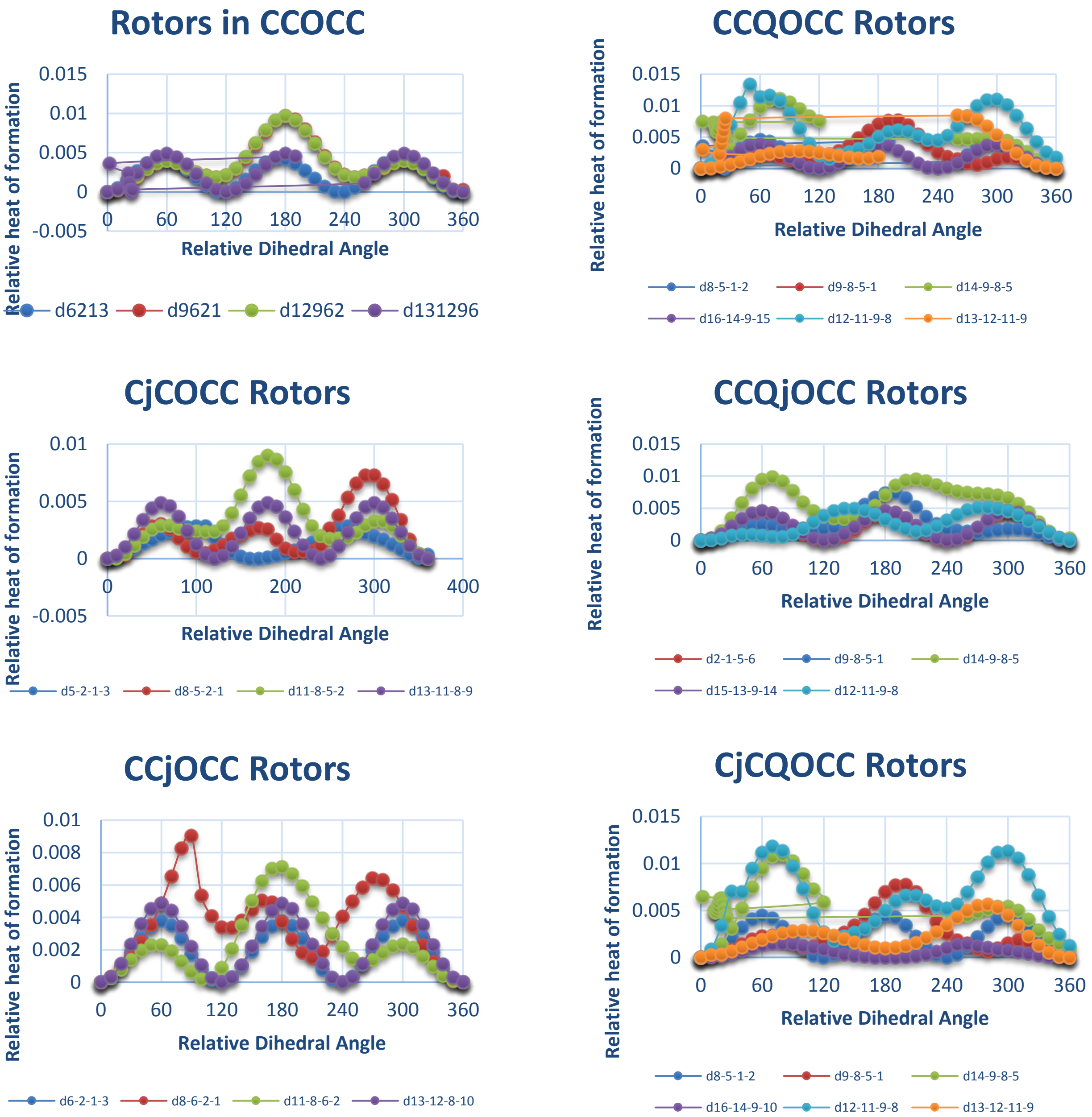


Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System (Continued)

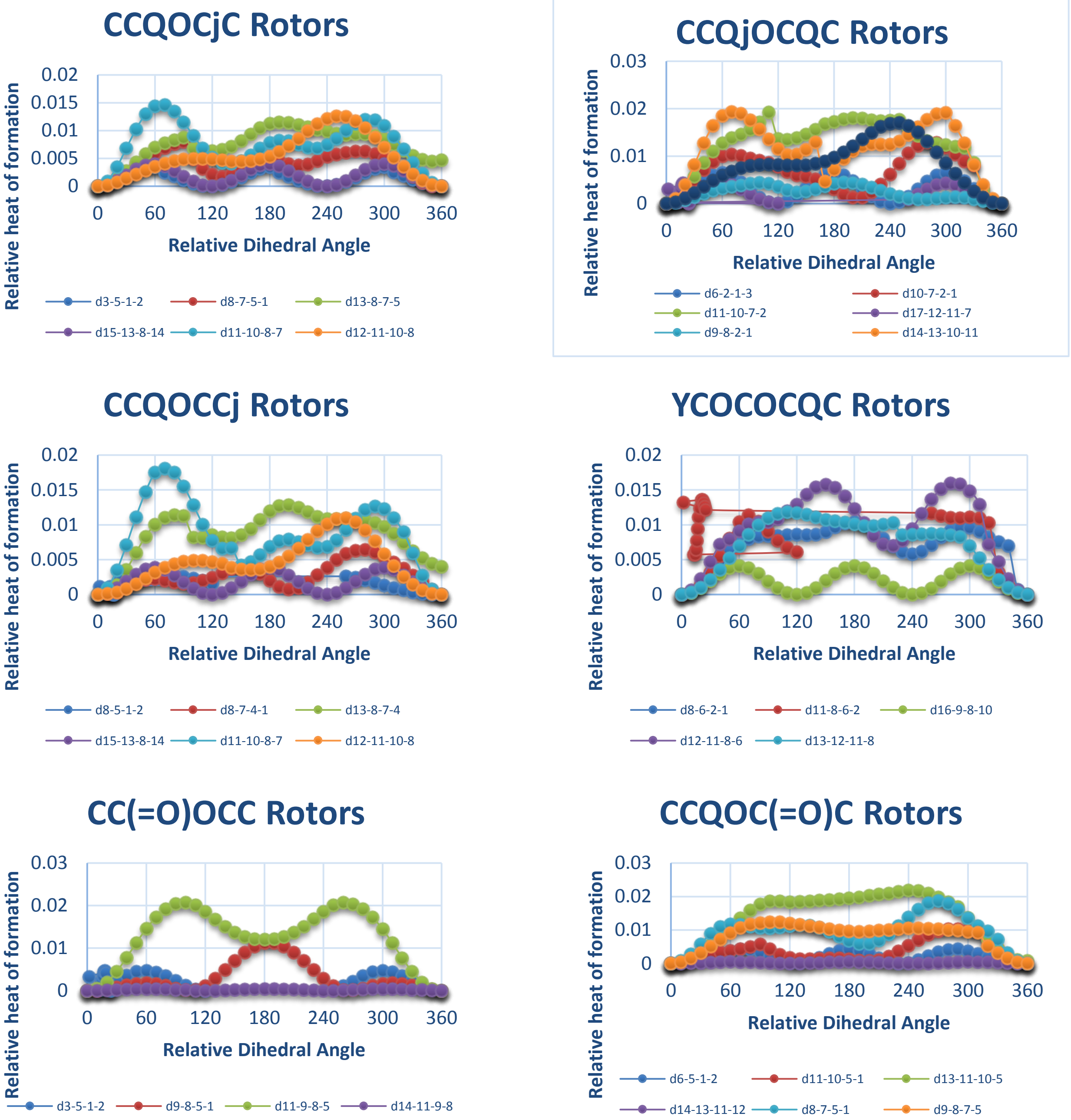
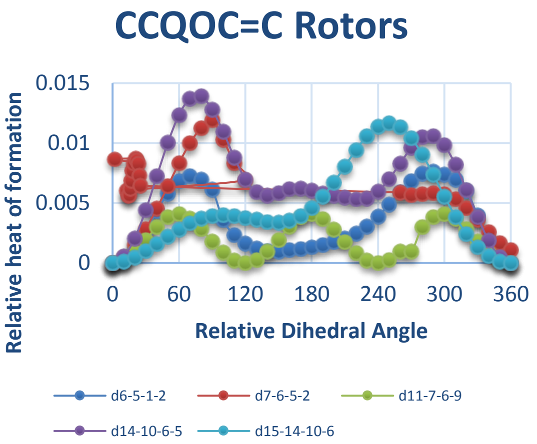
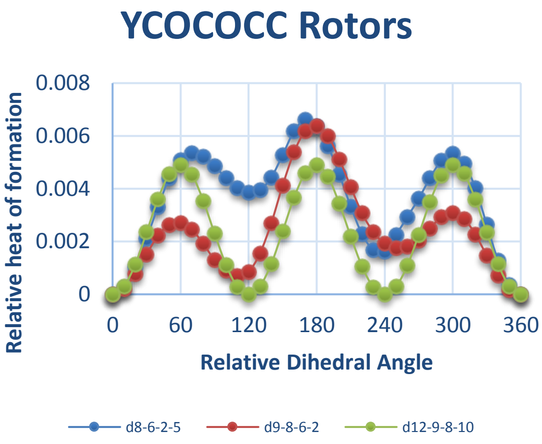
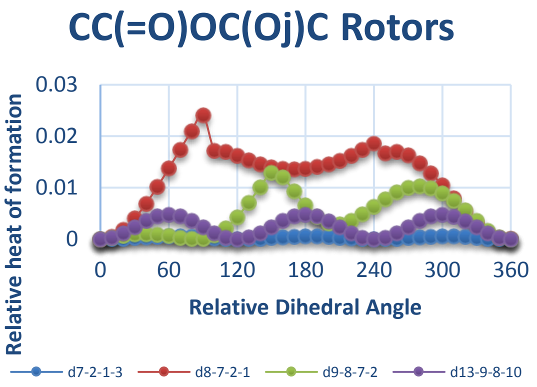
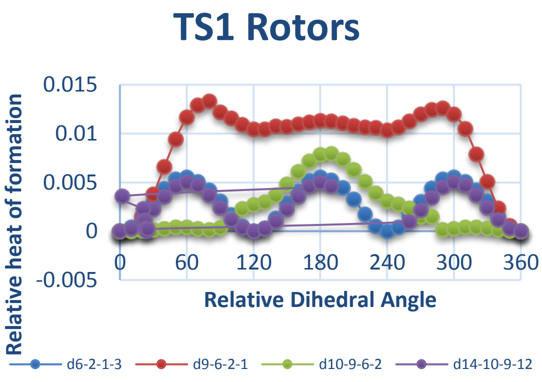


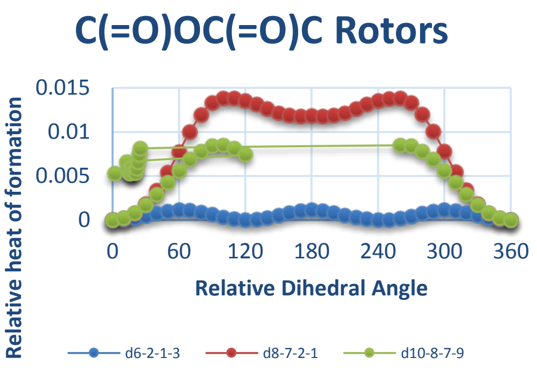
Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System (Continued)











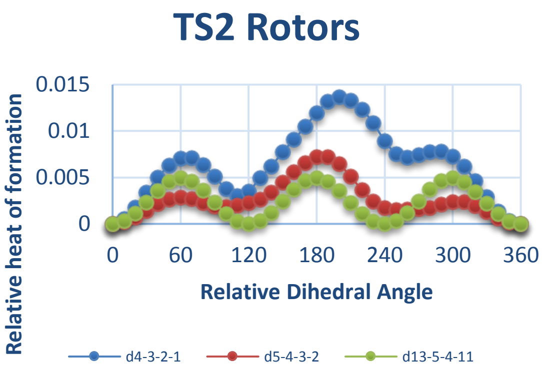


Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System (Continued)

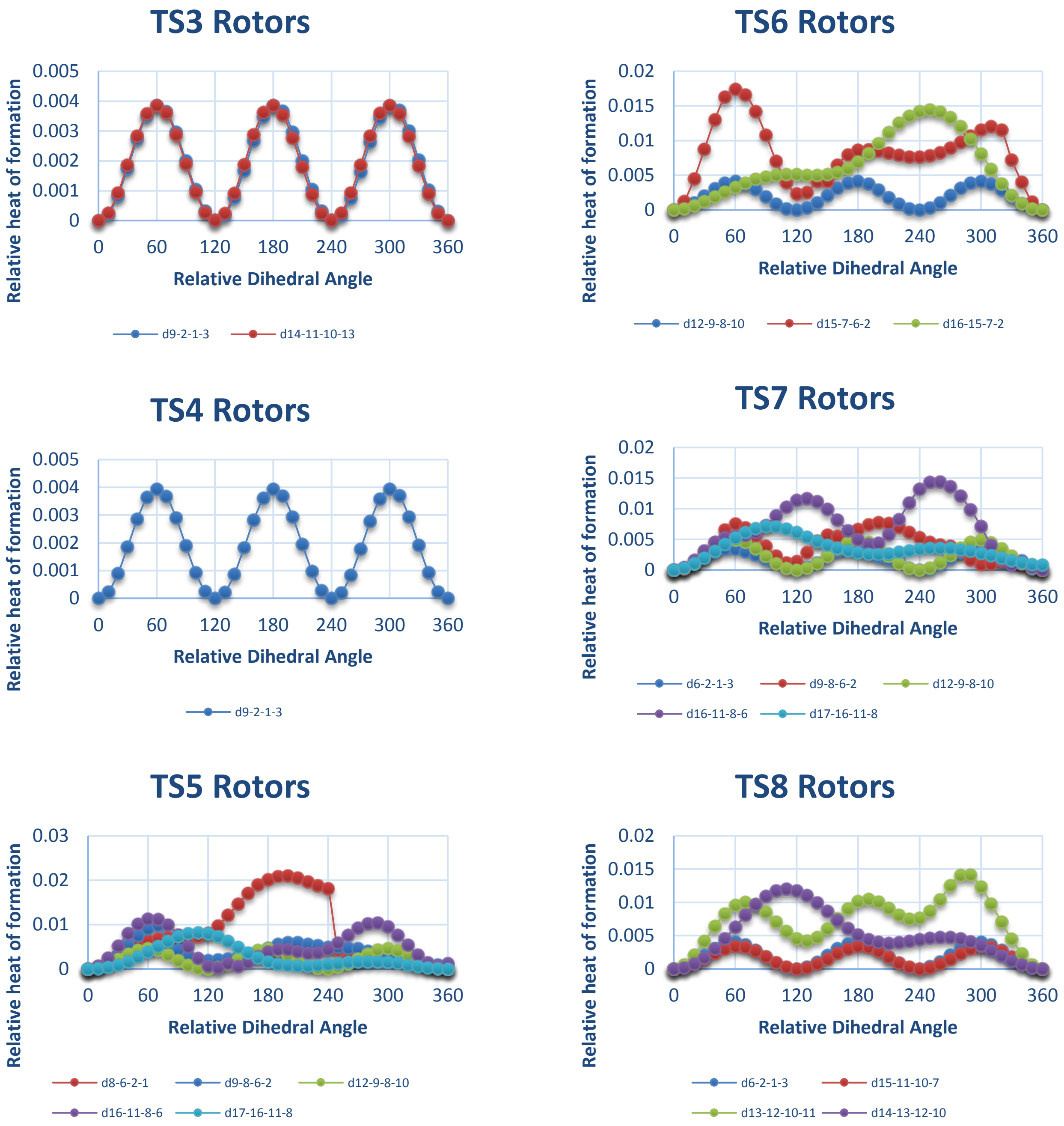


Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System (Continued)

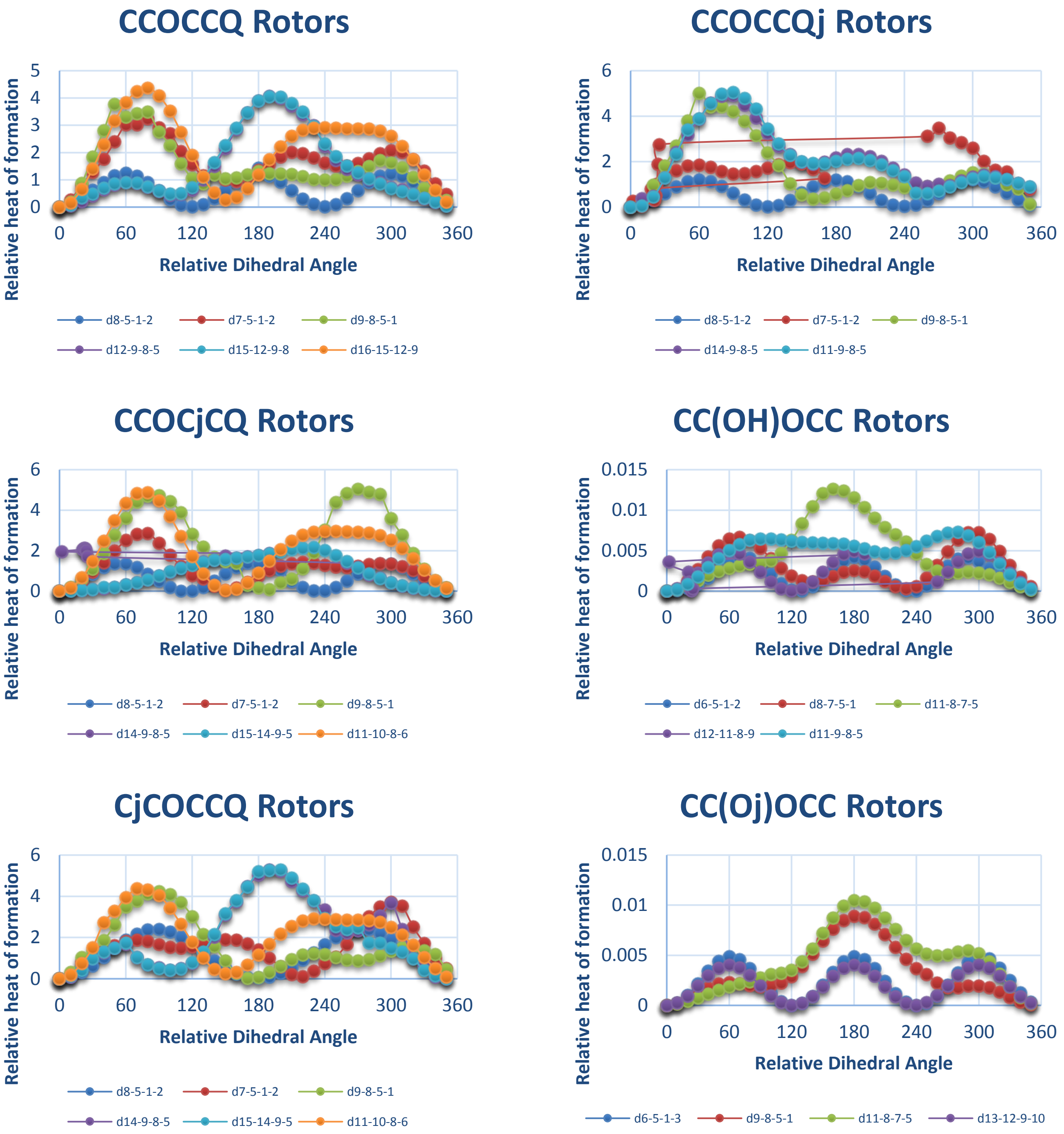


Figure F.1 Potential Energy Profiles of Species in Diethyl Ether Oxidation System (Continued)

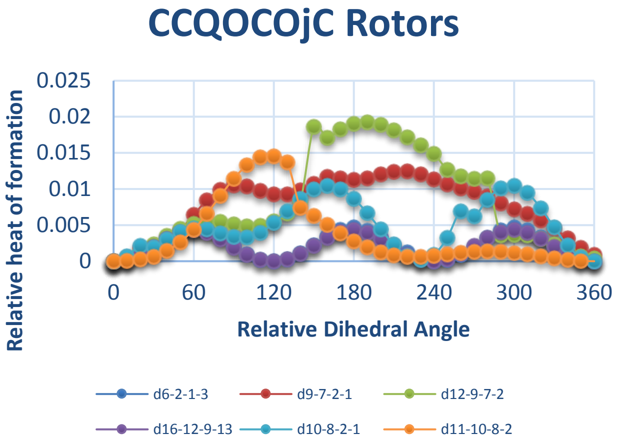


Table F.3 Isodesmic Reactions Calculations for Diethyl Ether Species in Systems

Isodesmic Work Reaction								$\Delta H^\circ_{f\,298}$ (kcal/mol)		
								M06-2x	WB97x	B2PLYP
CCOCC	+	C	=	CCOC	+	CC		-60.7	-60.8	-61.0
CCOCC	+	CC	=	CCOC	+	CCC		-61.3	-61.4	-61.8
CCOCC	+	CCOH	=	CCOC	+	C2COH		-61.2	-61.7	-62.1
CCOCC	+	COC	=	CCOC	+	CCOC		-62.3	-62.5	-62.8
CCOCC	+	C2COC	=	CCOC	+	C3COC		-60.7	-61.7	-63.0
CCOCC	+	CCOC	=	CCOC	+	C2COC		-60.3	-60.8	-61.1
							average	-61.1	-61.5	-62.0
							st. dev.	0.7	0.6	0.8
CC•OCC	+	CCOH	=	CCOCC	+	CC•OH		-17.2	-17.0	-17.4
CC•OCC	+	CCOH	=	CCOCC	+	C•COH		-16.9	-17.4	-17.0
CC•OCC	+	CCOH	=	CCOCC	+	CCC•OH		-17.3	-17.2	-17.4
CC•OCC	+	CCOC	=	CCOCC	+	C•COC		-16.2	-16.8	-16.6
CC•OCC	+	COC	=	CCOCC	+	C•OC		-16.2	-16.9	-16.6
CC•OCC	+	CCOC	=	CCOCC	+	CC•OC		-17.4	-17.3	-17.2
							average	-16.8	-17.1	-17.0
							st. dev.	0.5	0.2	0.4
C•COCC	+	C	=	CCOCC	+	CH_3		-9.8	-10.2	-9.3
C•COCC	+	CC	=	CCOCC	+	C•C		-10.0	-9.8	-9.5
C•COCC	+	COC	=	CCOCC	+	C•OC		-9.8	-9.1	-8.9
C•COCC	+	CCOC	=	CCOCC	+	C•COC		-8.7	-8.6	-8.3
C•COCC	+	CCOH	=	CCOCC	+	C•COH		-9.3	-9.1	-8.8
C•COCC	+	CCCOH	=	CCOCC	+	C•CCOH		-8.9	-9.0	-8.7
							average	-9.4	-9.3	-8.9
							st. dev.	0.6	0.6	0.4

Table F.3 Isodesmic Reactions Calculations for Diethyl Ether Species in Systems (Continued)

Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
CCQOC•C	+	CCOH	=	CCQOCC	+	CC•OH		-46.6	-46.2	-46.5
CCQOC•C	+	CCOC	=	CCQOCC	+	CC•OC		-47.2	-46.9	-47.1
CCQOC•C	+	CCOH	=	CCQOCC	+	C•COH		-46.3	-46.5	-46.1
CCQOC•C	+	CCCOH	=	CCQOCC	+	CCC•OH		-46.8	-46.3	-46.5
CCQOC•C	+	CCOC	=	CCQOCC	+	CCOC•		-45.6	-46.0	-45.7
CCQOC•C	+	COC	=	CCQOCC	+	C•OC		-46.8	-46.5	-46.3
							average	-46.5	-46.4	-46.4
							st. dev.	0.6	0.3	0.5
CCQOCC•	+	CCOH	=	CCQOCC	+	C•COH		-39.6	-38.8	-38.5
CCQOCC•	+	CCOC	=	CCQOCC	+	C•COC		-38.9	-38.2	-38.1
CCQOCC•	+	CCOCOH	=	CCQOCC	+	C•COCOH		-44.0	-43.4	-43.2
CCQOCC•	+	COC	=	CCQOCC	+	C•OC		-40.1	-38.7	-38.7
CCQOCC•	+	CCCOH	=	CCQOCC	+	C•CCOH		-39.2	-38.6	-38.5
							average	-40.4	-39.5	-39.4
							st. dev.	1.9	2.0	1.9
CCQ•OCC	+	CQ	=	CCQOCC	+	CQ•		-52.2	-52.3	-52.5
CCQ•OCC	+	CCQ	=	CCQOCC	+	CCQ•		-52.6	-52.8	-52.9
CCQ•OCC	+	CCCQ	=	CCQOCC	+	CCCQ•		-53.5	-53.6	-53.7
							average	-52.8	-52.9	-53.0
							st. dev.	0.7	0.6	0.6
CCOC(=O)C	+	C	=	CCOCC	+	C(=O)		-106.9	-107.5	-106.5
CCOC(=O)C	+	CC	=	CCOCC	+	CC(=O)		-106.7	-106.9	-106.1
CCOC(=O)C	+	CCC	=	CCOCC	+	CCC(=O)		-107.7	-107.7	-107.2
							average	-107.1	-107.4	-106.6
							st. dev.	0.6	0.4	0.6

Table F.3 Isodesmic Reactions Calculations for Diethyl Ether Species in Systems (Continued)

Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
CCQOCQC	+	C	=	CCQOCC	+	CQ		-122.1	-120.7	-119.5
CCQOCQC	+	CC	=	CCQOCC	+	CCQ		-122.1	-120.7	-121.1
CCQOCQC	+	C3C	=	CCQOCC	+	C3CQ		-122.6	-122.1	-121.1
CCQOCQC	+	COC	=	CCQOCC	+	COCQ		-122.7	-121.3	-120.5
							Average	-122.4	-121.2	-120.2
							st. dev.	0.3	0.7	0.7
CCQ•OCQC	+	CQ	=	CCQOCQC	+	CQ•		-84.7	-84.9	-85.4
CCQ•OCQC	+	CCQ	=	CCQOCQC	+	CCQ•		-85.1	-85.4	-85.8
CCQ•OCQC	+	CCCQ	=	CCQOCQC	+	CCCQ•		-85.9	-86.2	-86.6
							average	-85.2	-85.5	-85.9
							st. dev.	0.65	0.63	0.59
CCQOCQC•	+	CCOH	=	CCQOCQC	+	C•COH		-70.7	-70.5	-70.4
CCQOCQC•	+	CCOC	=	CCQOCQC	+	C•COC		-70.1	-70.0	-70.0
CCQOCQC•	+	CCOH	=	CCQOCQC	+	CC•OH		-71.0	-70.1	-70.7
CCQOCQC•	+	COC	=	CCQOCQC	+	C•OC		-71.2	-70.4	-70.6
CCQOCQC•	+	CCCOH	=	CCQOCQC	+	C•CCOH		-70.3	-70.3	-70.4
							average	-70.7	-70.3	-70.4
							st. dev.	0.5	0.2	0.3
CC(=O)OCQC	+	COC	=	CCOC(=O)C	+	COCQ		-133.9	-133.0	-132.4
CC(=O)OCQC	+	C3C	=	CCOC(=O)C	+	C3CQ		-133.8	-133.9	-133.0
CC(=O)OCQC	+	CC	=	CCOC(=O)C	+	CCQ		-133.4	-132.5	-131.7
CC(=O)OCQC	+	CCC	=	CCOC(=O)C	+	CCCQ		-132.8	-132.3	-131.4
							average	-133.5	-132.9	-132.1
							st. dev.	0.5	0.7	0.7

Table F.3 Isodesmic Reactions Calculations for Diethyl Ether Species in Systems (Continued)

Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
C=COCQC	+	C	=	C=COCC	+	CQ		-62.9	-62.2	-61.8
C=COCQC	+	CC	=	C=COCC	+	CCQ		-62.9	-62.2	-62.0
C=COCQC	+	CCC	=	C=COCC	+	CCCQ		-62.3	-62.0	-61.7
C=COCQC	+	C3C	=	C=COCC	+	C3CQ		-63.4	-63.6	-63.3
C=COCQC	+	COC	=	C=COCC	+	COCQ		-63.5	-62.7	-62.7
							average	-63.0	-62.6	-62.3
							st. dev.	0.5	0.7	0.7
Y(COC)OCQC	+	C	=	Y(COC)OCC	+	CQ		-102.6	-102.0	-101.2
Y(COC)OCQC	+	CC	=	Y(COC)OCC	+	CCQ		-102.6	-102.0	-101.4
Y(COC)OCQC	+	C3C	=	Y(COC)OCC	+	C3CQ		-103.1	-103.4	-102.7
Y(COC)OCQC	+	COC	=	Y(COC)OCC	+	COCQ		-103.2	-102.5	-102.1
							average	-102.9	-102.5	-101.8
							st. dev	0.3	0.7	0.7
CC(OH)OCC	+	CCC	=	CCOCC	+	CC(OH)C		-106.7	-106.4	-105.9
CC(OH)OCC	+	CCCC	=	CCOCC	+	CC(OH)CC		-106.6	-106.2	-105.8
CC(OH)OCC	+	Y(CCC)	=	CCOCC	+	Y(CCC)OH		-106.5	-105.7	-105.5
CC(OH)OCC	+	CCQ	=	CCOCC	+	C(OH)CQ		-106.3	-105.7	-105.7
							average	-106.5	-106.0	-105.7
							st. dev	0.2	0.4	0.2
CC(O•)OCC	+	CCOH	=	CC(OH)OCC	+	CCO•		-52.5	-52.7	-52.3
CC(O•)OCC	+	CCCOH	=	CC(OH)OCC	+	CCCO•		-52.7	-52.9	-52.5
CC(O•)OCC	+	C(OH)C(OH)	=	CC(OH)OCC	+	C(OH)C(O•)		-52.3	-52.5	-52.7
CC(O•)OCC	+	CC(OH)C	=	CC(OH)OCC	+	CC(O•)C		-52.4	-52.7	-52.8
							average	-52.5	-52.7	-52.6
							st. dev	0.2	0.2	0.2

Table F.3 Isodesmic Reactions Calculations for Diethyl Ether Species in Systems (Continued)

Isodesmic Work Reaction								M06-2x	WB97x	B2PLYP
CCOCCQ	+	C	=	CCOCC	+	CQ		-78.5	-78.2	-78.1
CCOCCQ	+	CC	=	CCOCC	+	CCQ		-78.5	-78.3	-78.3
CCOCCQ	+	CCC	=	CCOCC	+	CCCQ		-77.9	-78.1	-78.0
CCOCCQ	+	COC	=	CCOCC	+	COCQ		-79.1	-78.8	-79.0
							average	-78.5	-78.3	-78.4
							st. dev	0.5	0.3	0.5
CCOCCQ•	+	CQ	=	CCOCCQ	+	CQ•		-45.5	-45.3	-45.0
CCOCCQ•	+	CCQ	=	CCOCCQ	+	CCQ•		-45.8	-45.6	-45.3
CCOCCQ•	+	CCCQ	=	CCOCCQ	+	CCCQ•		-46.4	-46.1	-45.8
							average	-45.9	-45.7	-45.4
							st. dev	0.5	0.4	0.4
CCQOC(OH)C	+	CCC	=	CCQOCC	+	CC(OH)C		-137.5	-137.7	-137.4
CCQOC(OH)C	+	CQ	=	CCQOCC	+	CQOH		-137.1	-137.0	-137.2
CCQOC(OH)C	+	CC	=	CCQOCC	+	CCOH		-138.0	-137.8	-137.5
CCQOC(OH)C	+	CCC	=	CCQOCC	+	C2COH		-137.9	-138.1	-137.9
							average	-137.6	-137.6	-137.5
							st. dev	0.4	0.5	0.23
CCQOC(O•)C	+	CCOH	=	CCQOC(OH)C	+	CCO•		-82.4	-82.6	-82.1
CCQOC(O•)C	+	CCCOH	=	CCQOC(OH)C	+	CCCO•		-82.7	-82.8	-82.3
CCQOC(O•)C	+	C(OH)C(OH)	=	CCQOC(OH)C	+	C(OH)C(O•)		-82.3	-82.3	-82.5
CCQOC(O•)C	+	CC(OH)C	=	CCQOC(OH)C	+	CC(O•)C		-82.3	-82.6	-82.6
							average	-82.4	-82.6	-82.4
							st. dev	0.2	0.2	0.2

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